Carbon Dioxide Capture for Storage in Deep Geologic Formations – Results from the CO₂ 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



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 Phone: +44 1865 84 3682
Kidlington, Oxford Fax: +44 1865 84 3931
OX5 1GB, UK 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

© 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.



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

ELSEVIER

BOOK AID International

Sabre Foundation

Chapter 30

REVAMPING HEATERS AND BOILERS TO OXYFIRING—PRODUCING OXYGEN BY ITM TECHNOLOGY

Rodney Allam¹, Vince White¹, VanEric Stein², Colin McDonald¹, Neil Ivens¹ and Mark Simmonds³

¹Air Products PLC, Hersham, Surrey, UK ²Air Products and Chemicals, Inc., Allentown, PA, USA ³BP, Sunbury, UK

ABSTRACT

The work reported in Chapter 30 considered the issues involved in modifying the process heaters and boilers for oxyfuel combustion and locating two world scale air separation plants totalling up to 7400 tonnes/day of oxygen plus a CO_2 compression and purification system on a congested site. In addition we presented the scheme 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 (EOR). In this Chapter, we will look at an alternative oxygen generation technology that would replace the two cryogenic air separation units (ASUs). This technology utilises ion transport membranes (ITMs) to produce the oxygen.

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.

The base case, Case 1, is presented and costed and 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 (HRSG) 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 to 3828 tonnes/day. Case 3 uses one Siemens V94.3 gas turbine plus a HRSG, but in this case the fuel is hydrogen produced from an oxygen autothermal reformer (ATR) with product steam generation and CO2 removed using an methyl diethanolamine (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 minimising export power and decreasing capital cost. In each of these three cases the total quantity of CO2 emission avoided and the quantity of CO2 available for pipeline delivery is calculated, costed and presented in Table 1.

Abbreviations: ASU, air separation unit; ATR, autothermal reformer; EOR, enhanced oil recovery; GTCC, gas turbine combined cycle; HRSG, heat recovery steam generator; ITM, ion transport membrane; MDEA, methyl diethanolamine; MLC, multi-layer ceramic capacitors.

Case	Oxygen flow (tonnes/day)	CO ₂ captured (×10 ⁶ tonnes/year)	CO_2 avoided $(\times 10^6$ tonnes/year)	Export power (MW)	Power consumption (MW)	Cost CO ₂ captured (\$/tonne)	Cost CO ₂ avoided (\$/tonne)
1	6626	1.89	1.71	446.2	54.7	33.5	37.0
2	3828	1.09	1.43	289.9	26.4	25.1	20.0
3	6051 ^a	2.62	2.06	121.4	71.3	28.5	38.1

TABLE 1 SUMMARY OF STUDY RESULTS

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 CO₂ 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 shown in Figure 1.

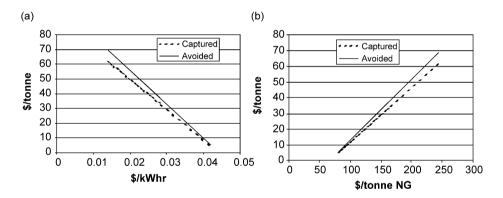


Figure 1: Effect of natural gas price and export power price on cost of CO₂ removal.

INTRODUCTION

The work reported in Chapter 30 considered the issues involved in modifying the process heaters and boilers for oxyfuel combustion and locating two world scale air separation plants totalling up to 7400 tonnes/day of oxygen plus a CO₂ compression and purification system on a congested site—the Grangemouth refinery and petrochemical complex of BP, located in Scotland between Edinburgh and Glasgow. In addition, we presented the scheme for distributing the oxygen around the site and collecting the CO₂-rich effluent from the combustion processes for purification, final compression, and delivery into a pipeline for enhanced oil recovery (EOR). In this Chapter, we will look at an alternative oxygen generation technology, which would replace the two cryogenic air separation units (ASUs). This technology utilises ion transport membranes (ITMs), integrated with one or two gas turbines, to produce the oxygen. The gas turbine duty and selection are fixed by the oxygen demand—the large excess power production will be exported.

^a Includes 1620 tonnes/day oxygen for ATR.

The oxyfuel conversion study includes the provision of all additional site services required for this area including cooling water and power production. Power is required for the CO₂ compressors. This power will be provided by the gas turbine integrated with the ITM oxygen system. Three cases are examined:

Case 1. Two Siemens V94.2 gas turbine combined cycle (GTCC) systems are used to generate power and supply feed air to the ITM oxygen plant. There is no integration between the steam system associated with the GTCC unit and the refinery system. All steam generated in the heat recovery steam generators (HRSGs) associated with the gas turbines is used for power production.

Case 2. The steam production from gas turbine waste heat recovery is primarily at the 127 bar level and is used to replace part of the boiler steam, thus saving oxygen flow to the boilers. Some additional 13.7 bara steam is also produced. Two Siemens V94.2 gas turbines are required for feed air supply to the ITM, but since steam produced in the HRSG is backing out steam production from the boilers, no steam turbines are required. This option also saves on cooling water requirements since none is required for condenser duty in the power generation system. The ITM oxygen plant is smaller due to the reduction in firing of the boilers allowed by the generation of steam in the gas turbine HRSG.

Case 3. The gas turbine is fuelled with hydrogen with part of the oxygen being used for hydrogen production in an autothermal reformer (ATR) with shift conversion and CO₂ removal using a methyl diethanolamine (MDEA) system. For this case, we have assumed that excess steam production from both the ATR waste heat boiler and the gas turbine HRSG, is sent to the refinery steam system. One Siemens V94.3 gas turbine is required for feed air supply to the ITM oxygen plant.

STUDY METHODOLOGY

Process Description

In Chapter 26 we examined the practicalities and costs of a site wide conversion of several units from air firing to oxyfuel firing. The oxygen required was produced in a cryogenic ASU. In this Chapter, the option to use an ITM in place of the ASU is investigated. The list of units to be converted is as reported in Chapter 26. The conversion of these units is affected very little by the change from cryogenically produced oxygen to ITM oxygen. There will be a small efficiency gain since the oxygen will be hot $(200-250 \,^{\circ}\text{C})$ after highlevel heat recovery, and the CO_2 purification will be more efficient since the oxygen purity is higher $(99\% \,^{\circ}O_2, 1\% \,^{\circ}N_2)$ by nature of the ITM oxygen system. The overall process is described below.

Oxygen generation

The maximum total oxygen demand of 7300 tonnes/day, which includes a 10% flow margin, is provided by an ITM unit. Oxygen is delivered at 99% purity and 0.7 barg for transmission in a pipeline system which runs to each of the oxyfuel use points. The plant utilises a ceramic membrane system operating at high temperature to preferentially separate oxygen from a high-pressure heated air stream. In addition to oxygen, some nitrogen (<1 mol%) may also enter the product stream through small leaks in the membranes and/or their ceramic-to-metal seals. The oxygen product stream is available at 281 °C after high-level heat recovery.

Oxygen distribution

The units to be converted and the area of the site which could locate the extra equipment cover an area of around $600 \text{ m} \times 700 \text{ m}$. The oxygen must be distributed around this site to each unit. An economic study has shown that oxygen distribution at low pressure (0.7 barg feed pressure) is most favourable. In this work, since the oxygen is to be delivered hot, stainless steal piping must be used. In Chapter 26 the oxygen piping distribution network was designed in order not to exceed a maximum velocity in the carbon steel piping for oxygen safety reasons. Since we are now using stainless steel piping we no longer have the same impingement concerns. However, the piping layout was not modified to reflect this. Therefore, although long radius bends were used in Chapter 26, this is not compulsory and more use could be made of T-junctions.

Heater and boiler conversion

The list of units which will be converted for oxyfuel firing is shown in Chapter 26 and is summarised as follows: five Simon Carves boilers each supplying 300,000 lb/h steam with a typical fuel mix of 40% gas, 60% oil by weight, linked to two stacks; two Babcock steam boilers each supplying 500,000 lb/h steam with an average fuel mix of 40% gas, 60% oil by weight, linked to a single stack; 12 process heaters of various types—box, cabin or vertical cylindrical—with duties varying from 10.3–112.3 MW, fuelled either by gas alone or by a combination of gas and fuel oil; and a hydrogen producing steam/natural gas reformer furnace fired by fuel gas.

Each heater and boiler considered within the study must be converted to fire on oxygen rather than air, with air firing maintained as a backup. Foster Wheeler have considered the conversion of the heaters and Mitsui Babcock the boilers. Each unit produces a hot wet CO₂ stream that must be cooled, dried, purified and compressed.

Summary details of the heater and boiler conversions are given in Table 2. The table shows the CO_2 emissions with air firing, the CO_2 delivered to the pipeline when operating in the oxyfuel mode, and the total oxygen consumptions for both the cryogenic air separation case of Chapter 26 and the ITM oxygen results. With cryogenic air separation the reduction in fuel due to oxyfuel firing was 6.2%. Using the ITM oxygen system this reduction increases to 7.8% because of the higher oxygen delivery temperature. Although the fuel requirement has decreased in the ITM oxygen case, more CO_2 is captured than for the cryogenic air separation case since the lower inert content of the oxygen increases the overall CO_2 recovery from 92.3 to 94.3%.

Local CO₂ collection and drying

Due to the widely scattered location of the boilers and heaters in the refinery, it is necessary to collect the CO_2 rich flue gas and pipe it to a central location for final purification and compression. The units to be converted are considered to be within one of five zones. These zones are numbered and the association between the boilers and heaters and the zones are given in Table 3. Each of these zones takes the hot, wet CO_2 from the converted heaters or boilers, cools this stream and removes water by direct contact with cooling water. The crude CO_2 gas is then compressed and further dried to a dew point of $-60\,^{\circ}C$. A summary of the performance of this system is shown in Table 4. See Chapter 26 for more details on the CO_2 collection and drying process.

CO2 collection

The compressed, dry, impure CO₂ is transported at a pressure of 30 barg by a carbon steel piping network from each of the five local zones to a central zone for further purification and compression. The layout of this pipeline was also considered and where possible routed with the oxygen piping.

CO₂ purification and compression

The central CO_2 purification and compression system takes the dried CO_2 from the distribution pipeline and removes inerts from this stream by cooling close to the triple point of CO_2 and separating out the uncondensed inerts. The purified gas is then further compressed to the delivery CO_2 pressure of 220 barg and transported by pipeline to the EOR site for disposal.

Oxygen Production and Distribution

ITM oxygen

Boilers and heaters normally firing on air are converted to oxyfuel firing by replacing the air feed with oxygen and recycling part of the hot flue gases. In order to generate this oxygen, an ITM oxygen plant may be used in place of cryogenic ASUs. ITM oxygen technology is based on a special class of mixed-conducting ceramic materials that have both electronic and oxygen ionic conductivity when operated at high temperatures, typically $800-900\,^{\circ}$ C. The mixed conductors are complex formulations of inorganic mixed-metal oxides (e.g. perovskites such as (La,Sr)(Fe,Co,Cu)O_{3- δ}) that are stoichiometrically deficient of oxygen, causing a distribution of oxygen vacancies in their lattice. Oxygen molecules adsorb onto the surface of the membrane, where they dissociate and ionise by electron transfer from the membrane. Under a gradient in oxygen activity, applied by maintaining a difference in oxygen partial pressure on opposite sides of the membrane, oxygen ions can move from vacancy to vacancy within the lattice, giving rise to a net flux

TABLE 2 GRANGEMOUTH HEATERS AND BOILERS

	Air f	iring	0	xyfuel firing-AS	SU	Oxyfuel firing-ITM			
	Total fuel consumption (kg/h)	Total CO ₂ emitted (kg/h)	Total fuel consumption (kg/h)	Total O ₂ consumption (kg/h)	Total CO ₂ captured (kg/h)	Total fuel consumption (kg/h)	Total O ₂ consumption (kg/h)	Total CO ₂ captured (kg/h)	
Boilers B1-B7	54,810	164,270	52,520	179,835	145,290	51,600	176,688	145,873	
Heaters H1-H12	26,511	73,827	24,303	90,339	62,676	23,959	89,029	63,193	
Reformer H13	3600	9791	2813	10,494	7080	2774	10,348	7127	
Totals	84,921 kg/h	2.17 million tonnes/year	79,636 kg/h	6736 tonnes/day	1.88 million tonnes/year	78,333 kg/h	6626 tonnes/day	1.89 million tonnes/year	

TABLE 3
DISTRIBUTED CO₂ TREATMENT ZONES

Zone 1				2			3				4	5								
Unit	В1	В2	В3	В4	В5	В6	В7	Н9	H10	H11	H12	H13	H4	Н5	Н6	Н7	Н8	H2	НЗ	H1

TABLE 4 PERFORMANCE SUMMARY FOR THE CO_2 TREATMENT SYSTEM

	Cooling water (tonnes/h)	CO_2 compressor (MW)	Turbo expander (MW)
Zone 1	3981	13.53	_
Zone 2	1061	2.54	_
Zone 3	512	1.37	_
Zone 4	754	2.01	_
Zone 5	173	0.52	_
Central zone	1710	8.44	3.18
Total	8192	25.23	

of oxygen ions. Electrons must move counter to the oxygen ion motion to maintain charge balance in the material. At the permeate surface of the membrane, the oxygen ions release their electrons, recombine, and desorb from the surface as molecules. Since no mechanism exists for transport of other species, the separation is 100% selective for oxygen, in the absence of leaks, cracks, or flaws in the membrane. The process is represented schematically in Figure 2. ITM oxygen materials are so-called "mixed conductors", in that both oxygen ions and electrons both are highly mobile within the solid. Detailed descriptions of the materials and electrochemical processes can be found in Refs. [1–3].

In contrast to conventional membrane processes in which flux of the permeating species varies according to a partial pressure difference across the membrane, the electrochemical process driving the oxygen flux in ITM oxygen depends on the natural log of oxygen partial pressure ratio to a good approximation. As a practical matter the partial pressure ratio can be varied over a much wider range than a partial pressure difference. Thus, in general, electrolytic membranes may sustain much higher fluxes than their conventional counterparts.

To achieve a desirable partial pressure ratio driving force, compression of a feed stream having a relatively low concentration of oxygen, such as air, is advantageous. Accordingly, some of the most attractive processes for producing oxygen with ITM oxygen technology make available a high-temperature, high-pressure oxygen-containing gas as an ITM process feed. An excellent example is an air stream extracted from a gas turbine set prior to the power combustor, as is shown in Figure 3. The ITM oxygen vessel that contains the membranes for oxygen separation is preceded by a pre-combustor unit, since the operating temperature of the ceramic membrane is above the compressor discharge temperature, but below the firing temperature of most large gas turbine engines. The pre-combustor heats the incoming stream to the ITM vessel by direct combustion of an added fuel, consuming a portion of the incoming oxygen. After extraction of oxygen by the ITMs, the rejected stream is further heated by direct combustion in the gas turbine's power combustor and passed through to the expansion side of the turbine set for power generation. Further downstream processing in a HRSG can result in an overall product mix of oxygen, power, and steam. The hot, low-pressure oxygen permeate stream is cooled and compressed, if necessary, to the required pressure.

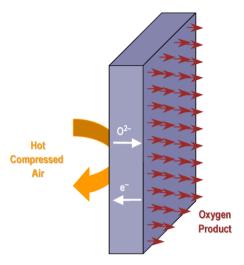


Figure 2: Mixed-conducting ion transport membrane. Oxygen anions move counter to electrons at high temperature in the same material under an oxygen activity gradient.

Thermodynamic and process economic analyses indicate that the ITM oxygen process produces oxygen at a significantly lower cost than conventional, cryogenic processes.

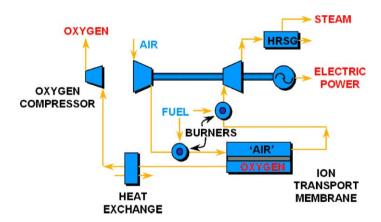


Figure 3: Basic scheme for integration of an ITM oxygen air separation unit into a gas turbine power cycle. Process outputs are oxygen, power, and steam.

The ITM device geometry influences several important design factors such as ease of manufacture; mechanical integrity during operation and installation; the geometry and cost of the temperature and pressure boundaries in which the device is placed during operation; and the ultimate flux performance of the membrane. After detailed consideration of each of these factors, the Air Products team chose a planar supported-membrane structure.

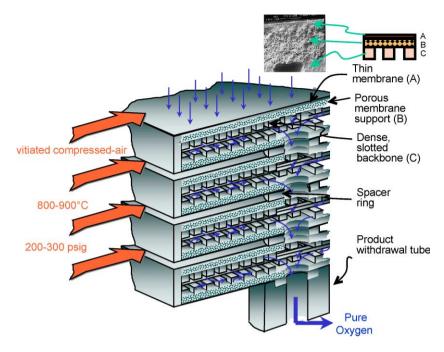


Figure 4: Schematic of ITM oxygen planar supported-membrane device. Four double-sided wafers are shown, separated by spacer rings and attached to a product withdrawal tube.

The planar supported-membrane device shown schematically in Figure 4 consists of laminated planar supported-membrane wafers, spacer rings between each wafer, and an oxygen withdrawal tube. All components are fabricated from the novel ceramic compounds described above. Each wafer is comprised of three types of layers, one laminated upon another. An outer, thin dense membrane layer (A) is supported by a (slightly) thicker porous layer (B). The porous layer is supported by a slotted, dense backbone layer (C) that provides most of the structural integrity of the wafer as well as an open gas path for the oxygen to reach the central collection tube. Each wafer is doubled-sided, i.e. the laminated composite consisting of the three types of layers is repeated on both sides of the wafer. Adjacent wafers are separated by a spacer ring located at the centre of the wafer, which allows the feed gas to flow between the wafers. As multiple wafers and spacer rings are stacked alternately upon each other, a "membrane module" is formed. All of the purified oxygen flowing from each wafer in the module is collected in the central column created by the stacked spacer rings. Finally, the module is connected to a withdrawal tube from which the product oxygen is collected. With an appropriate driving force, oxygen is transported to the membrane surface from the bulk feed gas flowing in the gaps between wafers. The oxygen is ionised on the outer membrane surface, diffuses through the thin separating layer on the outer surface of the wafer, and forms oxygen molecules on the interior surface of the separating layer. After passing through the porous layer, oxygen flows into the slotted region where it travels to the central column and into the oxygen withdrawal tube from which it is removed as product gas.

Some of the ITM literature suggests the use of a sweep gas to lower the permeate partial pressure of oxygen and increase the driving force for oxygen flux. In most applications, though, it is preferable to avoid the use of permeate sweep and instead recover a pure oxygen product. That is also true of this application. Because of the low product pressure requirement, there is little or no potential capital cost savings in product compression by sweeping with gas at greater than product pressure. Thus, the only potential capital cost

savings arise from a decrease in membrane area requirements by improving the oxygen partial pressure driving force across the ITM. To achieve a reasonable improvement in driving force, the sweep gas molar flow rate needs to be at least five times greater than the oxygen product flow rate. Assuming that steam is the only reasonable choice of sweep gas for this application, this flow ratio would require generation, distribution, and condensation of an enormous quantity of steam. Although the sweep scenario was not rigorously analysed for this study it is readily apparent that the additional capital costs of the required steam circuit would outweigh any savings in ITM costs. Normally, flue gas might be a viable choice of sweep gas; however, because of the high-sulphur fuels, the SO₂ content of the flue gas is above the maximum tolerable SO₂ concentration for the ITM unit. In addition, the flue gas recycle loops are all local to the various individual boilers, while the oxygen production is centralised. Thus, flue gas sweep, too, is completely impractical for this application, excepting perhaps the possibility that it might be economically attractive for other reasons to consider distributed oxygen generation by ITM. Furthermore, use of sweep gas precludes recovery of a pure oxygen product. Although that shortcoming may not be relevant in this application, it might impact, for example, a suggested value improvement to Case 2, that being production of excess oxygen for use elsewhere in the refinery or export off-site at low incremental cost.

Stacking the planar supported-membrane wafers on a common withdrawal tube allows the construction of compact oxygen separation modules. The space-filling efficiency of the planar approach is evident when compared with other device geometries. For example, by analogy with finned heat exchanger tubes, planar membrane modules pack several times more surface area into an equivalent volume of unfinned tubes [4]. The effect is illustrated conceptually in Figure 5. The space efficiency can be further appreciated by comparisons of the volumes of conceptual ITM oxygen vessels with those of typical conventional cryogenic distillation columns (Figure 6). In general, for equivalent oxygen production, the ITM oxygen vessel requires less than one-quarter of the volume of the conventional ASU distillation column. (This comparison also sheds light on the cost advantages of the ITM technology over conventional distillation technology.) Additionally, the compact ITM oxygen separation modules require dramatically fewer ceramic-to-metal seals per unit active area than would a purely tubular approach. Fewer seals imply lowered performance requirements of each individual seal and lowered overall costs.

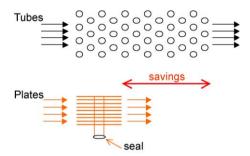


Figure 5: Space filling characteristics of planar device geometry compared with a tubular device geometry. Planar devices pack more surface area into the same volume, reducing the cost of vessels and seals.

Another advantage of the planar system is its simple hydrodynamics which facilitate rapid, uniform gas phase mass transfer. The flow of oxygen-containing gas between planar membranes is well described by the classical hydrodynamics problem of turbulent flow between parallel plates. Text book correlations for mass transfer coefficient to describe this situation provide accurate estimates of mass transfer resistance in the gas phase, which must be added to the mass transfer resistance in the membrane module to arrive at an overall mass transfer resistance for an operating device. Because, to a good approximation, the mass transfer resistance is uniform across the wafer surface, the analysis is simplified. In contrast, as shown in Figure 7, a non-rectilinear geometry, such as a tube, will promote the formation of eddies on the trailing edge

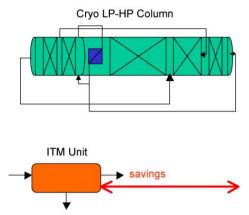


Figure 6: Illustration of effect of using highly compact ITM oxygen devices. ITM oxygen ASU requires $< \frac{1}{4}$ the volume of a cryogenic distillation double column.

of the device. The local mass transfer resistance at the surface of the tube varies considerably as a result. Furthermore, the gas phase velocity profile is strongly affected by the presence of these eddies. As a practical matter, tube banks in heat exchangers often require elaborate baffling fixtures, which attempt to correct for the uneven gas distribution across the bank. The chosen planar wafer geometry avoids these difficulties.

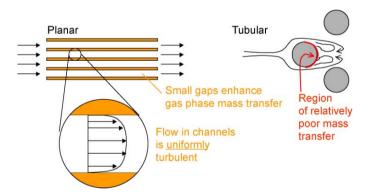


Figure 7: Illustration of influence on gas phase mass transfer by device geometry. Planar devices create more uniformly turbulent flow, without gross eddy formation as seen in non-planar devices such as tubes.

A further advantage of planar systems is their inherent stability under mechanical load. This is largely a result of the simple symmetry of the planar system. For example, because the compressive hydrostatic forces present in a typical application with an ITM oxygen membrane wafer tend to counteract each other from opposite sides of the wafer, there is no net force to cause deformation. In general, the opposite is true with structures of lesser symmetry. An example is illustrated in Figure 8, showing the results from finite element stress analysis on a representative portion of a membrane structure. The imposed forces on the wafer are caused by the vortex shedding from the thin trailing edge of the wafer, producing "flow-induced vibration" in the structure. Deflections from planarity must be exaggerated by 10⁶ times to be visible.

The wafer strength is such that these vibrations are survivable with high probability. In contrast, calculations of creep deformation of tubes, also illustrated in Figure 8, show that given a small variation in wall thickness around the circumference of the tube, the tube will collapse in a relatively short time. For the conditions shown, the collapse time is less than 10,000 h. This behaviour has been observed experimentally.

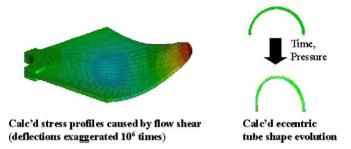


Figure 8: Simulations of planar and tubular geometries under anticipated stresses. Planar: stresses caused by flow-induced vibration (magnified 10^6 times; one-quarter of wafer shown). Tubular: stresses caused by slight eccentricity between inside and outside diameter of tube during manufacture (no magnification; half a tube is shown). Timescale for tube deformation is < 10,000 h.

Finally, planar-supported membrane structures are attractive because of their inherent ease of manufacture. Because the wafer structure is built up from separate, laminated layers of ceramic, gravitational forces that would otherwise act to distort a non-rectilinear structure, such as a tube, work to ensure layer uniformity in a planar structure. In addition, standard ceramic processing techniques, such as those used commercially in the fabrication of thin, multi-layer ceramic capacitors (MLCs), can be used in the production of planar membrane wafers. Accordingly, standard slip tapecasting is the basis for the technology. The tape is cast, cut, and laminated. Laminated green wafers are fired in temperature-programmed furnaces, and the fired wafers are joined with other components to make finished modules. The conventional approach to wafer fabrication eliminates a more costly development effort.

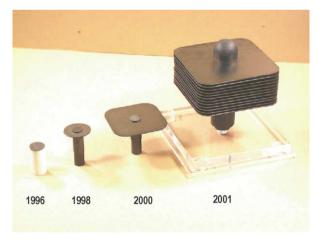


Figure 9: Progression of ITM oxygen planar supported-membrane wafer modules. 1996: laminate, half-wafers; 1998: subscale; 2000: intermediate scale; 2001: full size wafers in a 12-wafer stack.

Figure 9 illustrates the notable improvements made recently in both wafer membrane size and wafer module construction. ITM oxygen wafers are shown in four evolutionary stages labelled by year of first manufacture. In 1996, the first planar laminate structures were created. These consisted of only half a wafer, i.e. a thin, dense membrane supported by porous and slotted layers below. The half wafers were attached to alumna tubes and were used in material-screening experiments. In 1998 a new material was developed, and the first two-sided wafer modules were constructed from it. These circular "subscale" modules have been extensively tested for flux and material lifetime. An "intermediate" scale wafer was developed in 2000 as a test of the appropriate scaling rules in the transition to larger, square wafers. The square wafers fill space better than circular wafers, and present a more uniform flow path to the feed gas when contained in a module. Finally, in 2001, the first full-size wafers were developed. Progress toward building multi-wafer stacks of full-size wafers was rapid: a 12-wafer Subscale Module ("Submodule") was achieved during the same year, as shown.

Achieving the 12-wafer Submodule is significant, in that it represents the fundamental building block for larger ITM oxygen modules. Multiple Submodules can be stacked one upon another to build commercial scale ITM oxygen modules capable of producing a nominal 1 tonnes/day of oxygen. Multiple commercial scale modules located in an appropriate pressure and temperature envelope will produce the thousands of tonnes of oxygen per day needed for many world scale process applications.

A variety of experiments has guided the ITM oxygen development work and proven the feasibility of the technology. Bench-scale apparatus have demonstrated the thermodynamic stability of the high-flux materials subjected to various contaminants over thousands of hours. Stable operating performance in a pilot-scale unit has proven the robustness of the full-size parts under steady and transient operating conditions at high oxygen flux. Perhaps the most striking illustration of meaningful progress toward performance verification appears in Figure 10. The relative flux measured in subscale modules is shown increasing as various improvements were made to the membrane materials and module construction. The flux reached the commercial target in October 2000, and significantly exceeded it less than a year later, in April 2001. All experiments were conducted at the appropriate driving force for oxygen flux approximating commercial operating conditions of 800–900 °C and 200–300 psig feed gas pressure. The current flux achieved exceeds the minimum commercial flux target by over 30%.



Figure 10: Relative oxygen flux progression as measured with subscale ITM oxygen wafers. The commercial flux target is consistent with the goal for producing oxygen at one-third lower cost than conventional processes.

In module life testing at high flux conditions, several subscale and full-size ITM oxygen modules have performed steadily for hundreds to thousands of hours. For example, a subscale module has operated steadily at the minimum flux target for over 5000 h. Inspection of samples following extended operating campaigns have revealed no significant changes to the membrane material or wafer structure.

Based on the exciting progress made in establishing the feasibility of the technology and substantiating its expected benefit, the ITM oxygen team is continuing with further scale-up and demonstration of the technology at 1–5 tonnes/day oxygen production. Sufficient scaling information will be collected during this phase to enable a 25–50 tonnes/day pre-commercial demonstration, in which the ITM oxygen membranes will be subject to the full range of dynamics of a gas turbine-integrated process. That pre-commercial demonstration is expected to conclude, with subsequent commercialisation beginning, toward the end of this decade.

Considerations for gas turbine/ITM oxygen integration

Air to the ITM oxygen plant is supplied by either two V94.2 gas turbines or one V94.3 gas turbine. Since these gas turbines allow for external combustion of the air in large silo combustors, they are ideally suited for the sizeable air extraction requirements of ITM oxygen technology. In addition, the large silo combustors are more easily modified for operation in the oxygen-depleted air environment that will occur downstream of the ITM oxygen plant. While newer, more advanced turbines generally have higher compression ratios, which would increase the driving force for oxygen flux and reduce the size and cost of the membranes, they also generally have numerous, more tightly integrated can-annular combustors. This type of configuration is less conducive to substantial air extraction and likely to involve a more extensive development effort. Other gas turbine models also feature external combustion in large silo combustors, but the V94.2 was chosen for this study based on best fit to the air requirements of the base case.

The performance of the V94.2 gas turbine was simulated using information from GT Pro Release 11.0, which is a commercial software program. Because of the external combustion feature, it was assumed that all of the compressor discharge air could be extracted, except for the 10% estimated by GT Pro for turbine cooling requirements. Given this air flow rate, it was determined that two V94.2 machines would be required to provide the air requirements for Case 1.

ITM oxygen case specifics

This section gives the specifics of the ITM oxygen systems for each of the cases being studied.

Case 1—the base case (two gas turbines, combined cycle). The maximum total oxygen demand of 7300 tonnes/day, which includes a 10% flow margin, is provided by an ITM unit. The oxygen is delivered at 99% purity and 0.7 barg for transmission in a pipeline system which runs to each of the oxyfuel use points. The plant utilises a ceramic membrane operating at high temperature to preferentially separate oxygen from a high-pressure hot air stream. In addition to oxygen, some nitrogen (<1 mol%) and trace argon also enter the product stream through small leaks in the membranes and/or their ceramic-to-metal seals. The oxygen product stream is available at 281 °C after high-level heat recovery. This higher oxygen supply temperature reduces the fuel requirements of the boilers and heaters and hence the oxygen requirements are reduced to 6626 tonnes/day. A summary of Case 1 is given in Table 5.

TABLE 5 CASE 1 SUMMARY

Oxygen flow	6626 tonnes/day
Fuel flow	2028 tonnes/day
127 barg Steam flow	0 tonnes/day
13.7 barg Steam flow	0 tonnes/day
Boiler feed water flow	0 tonnes/day
Cooling water flow	42248 tonnes/h
ITM auxiliaries power requirement	20.9 MW
Steam turbine power	213 MW
GT power	288 MW

ITM oxygen technology is ideally suited for use in this study where a large oxygen flow is required and no utilities are available. The plant consists of: gas turbine system, an ITM unit and associated auxiliaries,

a HRSG and a steam turbine system. This process offers the benefits of compactness, high reliability, low maintenance cost, and it is simple to install and operate. An isometric drawing of the gas turbine and ITM module installation is shown in Figure 11.

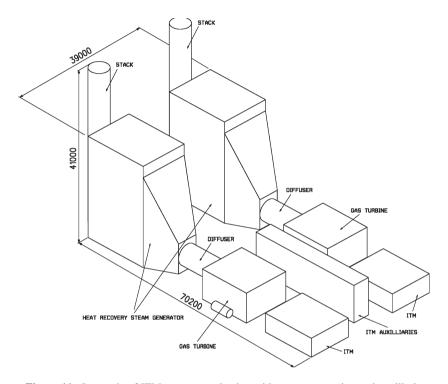


Figure 11: Isometric of ITM oxygen production with steam generation and auxiliaries.

Case 2—two gas turbines, steam generation. In this case the power generation system is integrated with the existing boilers and steam turbines. Steam is produced in the HRSG of the gas turbine primarily at the 127 barg level and is used to replace part of the boiler steam, thus saving oxygen flow to the boilers. Because of the reduced oxygen requirements, the two Siemens V94.2 gas turbines provide more than enough air to the ITM oxygen plant. However, the ITM oxygen plant still takes all of the available air to minimize oxygen recovery and, hence, minimise membrane area requirements. Any attempt to downsize the gas turbines to save capital would cause a corresponding decrease in the steam available from the HRSG. This would force an increase in the oxygen requirement for the boilers and a corresponding increase in air requirement from the gas turbines. Thus, the Case 2 gas turbine configuration was left identical to Case 1 for direct comparison.

Since the steam produced in the HRSG is backing out steam production from the boilers, no steam turbines are required. This option also saves on cooling water requirements since none is needed for the power generation system. Another potential advantage of Case 2 is that additional oxygen capacity could be generated for other parts of the refinery or other nearby applications, if necessary or desired, for a relatively minor incremental increase in capital cost of the ITM system. If such an additional demand is not present, it may be possible to use one or more alternative gas turbines to better suit the oxygen requirements. One such possibility is the Siemens V94.3 gas turbine, which like the Siemens V94.2, allows external combustion of

the air in large silo combustors. In addition, the Siemens V94.3 has a higher compression ratio, which would increase the driving force for oxygen flux and reduce the size and cost of the membranes.

A summary of Case 2 is given in Table 6. Due to the production of 127 barg steam, boilers B1, B2, B3, B5 and B7 can be shut down.

TABLE 6 CASE 2 SUMMARY

Oxygen flow	3828 tonnes/day
Fuel flow	1683 tonnes/day
127 barg Steam flow	12581 tonnes/day
13.7 barg Steam flow	1438 tonnes/day
Boiler feed water flow	16090 tonnes/day
Cooling water flow	4759 tonnes/h
ITM auxiliaries power requirement	25.4 MW
Steam turbine power	0 MW
GT power	283.0 MW
Boilers to be shut down	B1, B2, B3, B5, B7

Case 3—single gas turbine, pre-combustion de-carbonisation. In this case a single Siemens V94.3 gas turbine is operated in pre-combustion decarbonisation mode with part of the oxygen from the ITM being used for hydrogen production in an ATR with shift conversion and CO₂ removal using an MDEA system. The Siemens V94.3 has a 20% higher air flow than the Siemens V94.2 gas turbine. The gas turbine combustor is fired with hydrogen, which can undergo stable combustion with a much lower oxygen concentration than natural gas. As a result, the maximum achievable oxygen production is limited by the driving force across the ITM, rather than the minimum oxygen concentration in the non-permeate to support stable combustion, as is the case with natural gas-fired integrations. Because of these factors, a hydrogen-fired configuration allows for increased oxygen production from a given air flow rate, i.e. the Siemens V94.3 can support a higher maximum oxygen production.

As in Case 2, the oxygen demand is lower because the production of 127 barg steam enables the boiler duty to be reduced. However, due to the oxygen requirement of the ATR coupled with the 4 barg steam requirement of the MDEA system, less 127 barg steam can be produced than in Case 2, and therefore the oxygen demand is higher at 5870 tonnes/day for maximum flows.

Initially, it appeared that one Siemens V94.3 gas turbine would suffice for the oxygen demands on the system. However, as the case was further refined, it became apparent that the demand is higher than the capabilities of one Siemens V94.3 gas turbine to produce, and therefore boilers B1 and B5 will remain air fired. The additional CO_2 loss this represents is compensated by the capture of CO_2 from the ATR process, which allows the gas turbine to operate with virtually no CO_2 in the flue gas. It may be possible to supply the full demand with either one or more alternative gas turbines. A summary of Case 3 is given in Table 7.

Site Layout

One of the main challenges of this project was locating all of the new equipment required for the project on the site at Grangemouth. Figure 12 shows the layout of the whole system in the refinery with the relative location of the oxyfuel systems, the ITM train and the cooling towers, together with the CO₂ and oxygen piping runs superimposed on a grid to show typical spacings and piping runs required.

TABLE 7 CASE 3 SUMMARY

Total avvigan flow	6051 tonnac/day
Total oxygen flow	6051 tonnes/day
ATR oxygen demand	1620 tonnes/day
Oxygen flow to boilers/Heaters	4431 tonnes/day
Max required oxygen flow	4396 tonnes/day
Fuel flow	1504.6 tonnes/day
ATR hydrogen production	458 tonnes/day
ATR CO ₂ production	3724 tonnes/day
127 barg Steam flow	8566 tonnes/day
30 bara Steam flow	2898 tonnes/day
4 barg Steam flow	3437 tonnes/day
Boiler feed water flow	8572 tonnes/day
Cooling water flow	53986 tonnes/h
ITM auxiliaries power requirement	37.3 MW
Steam turbine power	$0 \mathrm{MW}$
GT power	192.7 MW
Boilers to be shut down	B2, B3, B4
Boilers to remain air fed	B1, B5

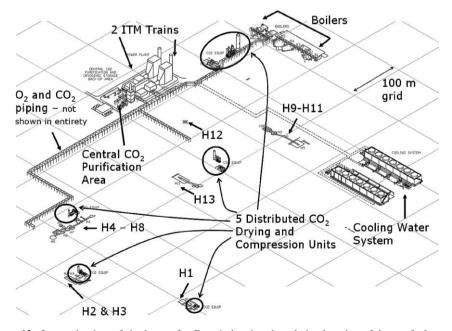


Figure 12: Isometric view of site layout for Case 1 showing the relative location of the oxyfuel systems, the ITM unit and the cooling towers, together with the CO₂ and oxygen piping runs.

RESULTS AND DISCUSSION

Performance Summary

The overall performance of the complete system for these options is given in Table 8 based on isothermal CO₂ compression in an intercooled compressor. Table 9 gives the extra natural gas requirements and total equivalent fuel gas and fuel oil requirements for the system. Table 10 summarises the overall performance of these three cases, where Case 0 is air firing. For terminology clarifications see Chapter 26.

Cost Estimates and Overall Cost of CO2 Removed

This section summarises the estimate basis for initial capital investment and long-term operating costs required to implement the base case scheme (Case 1) for CO_2 sequestration. The section is divided into three main parts: capital costs, operating costs (including operating savings derived from oxyfuel operation of fired units) and an estimate of the cost per tonne of CO_2 captured on a gross and net basis, for comparison with alternative methods of CO_2 capture. A final section aims to give the indicative cost impact for the alternative technology scope described in Case 2 and Case 3 elsewhere, in order to quantify whether these alternatives would lead to an even lower cost of CO_2 capture.

The financial figures presented in this section and elsewhere in this report are presented as budgetary estimates for information only and do not constitute a commercial offer on behalf of Air Products, Mitsui Babcock, Foster Wheeler Energy, Siemens Westinghouse or any other potential suppliers of the scope of the study.

Capital estimate basis

The capital cost is provided on the same basis as described in Chapter 26 and is summarised for Case 1 in Table 11.

Operating cost estimate

An estimate of the operating costs for Case 1 is given in Table 12. It should be noted that both the fuel cost and export power credit are very large components of the overall cost of CO_2 capture and make the CO_2 capture cost sensitive to variations in natural gas price and power price, as is shown in Figure 1a and b. However, these two prices will be linked in most countries that derive a large part of their power from natural gas fired generation, as in UK. This will tend to cancel out the sensitivity effect.

Cost of CO2 capture

One of the key measures for comparison with alternative methods of CO_2 capture is "cost per tonne of CO_2 captured or avoided". This is a simple calculation, dividing the total annual costs by the tonnes per year of CO_2 captured (or avoided).

To get a time-averaged annual cost for the significant capital investment, which must be made at the beginning of the project, it is normal to derive a "capital multiplier" or "capital factor". This takes into account: the operating or accounting life of the equipment, the cost of investment capital, tax rates in the country of investment and required return on investment criteria of the owner/operator. For this study a value of 0.1 or 10% has been used:

```
Annual capital charge = \$535,398,000 \times 0.1 = \$53,540,000 per year Therefore total annual costs = \$53,540,000 + \$9,735,000 = \$63,275,000
```

Cost of CO_2 captured. The CO_2 captured and available for sequestration for the base case, Case 1, is 1,890,000 tonnes/year. Therefore the cost per tonne of CO_2 captured is:

```
$63,275,000/1,890,000 = $33.49 \text{ per tonne CO}_2 \text{ captured}
```

Cost of CO_2 avoided (net reduction in CO_2 emissions). The net CO_2 removed from potential emissions to the atmosphere for Case 1 is 1,650,000 tonnes/year. Therefore the cost per tonne of CO_2 avoided is:

```
$63,275,000/1,710,000 = $37.00 \text{ per tonne CO}_2 \text{ avoided}
```

TABLE 8 COMPARISON OF DIFFERENT POWER GENERATION OPTIONS

Case	GT	Power (MW)		Fuel to power F system (MW)	Reduction in fuel to	Reduction in fuel to	CO ₂ from GT exhaust	Boiler steam, ($\times 10^3$ lb/h)		Additional steam	
		GT	ST	system (MW)	boilers (MW)	heaters ^a (MW)	(×10 ⁶ tonnes/year)	From boilers	From GT HRSG	tonnes/h	MW
1	2 × V94.2	288	213	1032.7	27.75	22.75	1.876	1771	0	0.0	0.0
2	$2 \times V94.2$	283	0	913.1	459.78	22.75	1.661	615	1156	185.0	33.3
3	1 × V94.3	193	0	789.2	323.98	22.75	0.070	983	787	209.0	37.7
Case	Total power generated (MW)	O ₂ produced (tonnes/day)	O ₂ to boilers (tonnes/day)	Total power requirement (MW)	Export power (MW)	IGCC cooling water (tonnes/h)	Total cooling water (tonnes/h)	${ m CO_2}$ captured $(\times 10^6$ tonnes/year)	${ m CO_2}$ avoided $(\times 10^6$ tonnes/year)		
1	501	6626	4316	54.7	446.2	34,057	42,248	1.89	1.71		
2	316	3828	1499	26.4	289.9	27	4759	1.09	1.43		
3	193	6051 ^b	2397	71.3	121.4	46,506	53,986	2.62	2.06		

^a Corrected for air pre-heating stream gain and steam generation steam loss. ^b Includes 1620 tonnes/day oxygen for ATR.

TABLE 9 FUEL REQUIREMENT SUMMARY

	Fuel gas/oil reduction (MW)	Fuel to GTCC (MW)	Natural gas CV (MJ/kg)	Fuel to GTCC (tonnes/h)	Natural gas equivalent fuel gas/oil reduction (tonnes/h)	Net equivalent natural gas requirement (tonnes/h)
Case 1	50.50	1032.69	46.89	79.29	3.88	75.41
Case 2	482.52	913.11	46.89	70.10	37.05	33.06
Case 3	346.73	789.15	46.89	60.59	26.62	33.97

TABLE 10 FUEL AND POWER SUMMARY

Case	GT type	Total power generated (MW)	Export power (MW)	Total fuel (MW)	O ₂ produced (tonnes/day)	Total cooling water (tonnes/h)	$\begin{array}{c} \rm CO_2 \\ captured \\ (\times 10^6 \\ tonnes/ \\ year) \end{array}$	CO_2 avoided $(\times 10^6$ tonnes/ year)
0	n/a	n/a	0	1045.8	0	0	0	0
1	$2 \times V94.2$	501	446.2	2028.0	6626	42,248	1.89	1.71
2	$2 \times V94.2$	316	289.9	1476.4	3828	4759	1.09	1.43
3	$1 \times V94.3$	193	121.4	1488.3	6051 ^a	53,986	2.62	2.06

^a Includes 1620 tonnes/day oxygen for ATR.

 ${\it TABLE~11} \\ {\it SUMMARY~OF~CAPITAL~COST~ESTIMATE~(ALL~COSTS~IN~000~USD)}$

Description	Materials	Sub-contracts	Total	Comments
Air separation units (ITM units + auxilliaries)	34,294	14,603	48,897	
O ₂ distribution and CO ₂ gathering pipework	1386	5114	6500	
CO ₂ drying, compression and purification	45,802	23,718	69,520	Distributed and centralised
Cogeneration system			190,000	2 × V94.2 package
Cooling water system			18,000	Constructed package
Boiler modifications	9030	8960	17,990	Mitsui Babcock estimate

(continued)

TABLE 11 CONTINUED

Description	Materials	Sub-contracts	Total	Comments
Fired heater modifications			12,039	AP/FWE estimate
Total direct field costs	90,512	52,395	362,946	
Construction management			3800	
Pre-commissioning/ commissioning support			1891	
Temporary facilities Vendor reps Heavy lift				Included in sub-contracts Included in construction management/ commissioning support Included in sub-contracts/
Freight (10% of matl.) 2-Year operating spares (2% of matl.)			9051 1810	freight
Commissioning spares (0.5% of matl.)			453	
Total indirect field costs			17,005	
Project management, engineering and procurement			22,000	
Total home office costs			22,000	
Total field and office costs			401,951	
Escalation Reserve/contingency (20%)			0 80,390	Excluded
Total capital cost			482,341	
Other costs License fees Owners costs (10%) C.A.R insurance (1%)			48,234 4823	None
Overall total			535,398	

TABLE 12 SUMMARY OF ANNUAL OPERATING COSTS

Description	Annual cost (\$000)	Comments	
Gas turbine fuel cost	112,840	Natural gas at UK rate	
Export power credit	-109,444	Exported to grid	
Fired unit fuel reduction	-5365	Natural gas equivalent value	
Make-up water	4400	Possible to use condensed water from flue gases	
Operator manpower	1450		
Maintenance	5354		
Consumables	500		
Total operating costs	9735	per year	

TABLE 13 COST DIFFERENCE FOR CASE 2

Item	Difference to base case costs	
	Case 2	Comments
		Steam integration of combined cycle plant with fired units
Capital cost	- 20%	Less O ₂ required by turned down boilers. Smaller ITM units and CO ₂ system. Simple cycle cogeneration system with HRSG but no ST
Operating cost	- 284%	Higher fuel to cogen, but large amount of fuel saved in turned down boilers, by more efficient production of steam duty by Cogen. Export power maintained at a high level. Net positive cashflow in this option from exported power and lower overall fuel flow.
Total annual costs	- 57%	
CO ₂ captured Cost/tonne CO ₂ captured	- 42% - 25%	Boilers turned down
CO ₂ avoided	-20%	Large amount of CO ₂ avoided by more efficient steam generation
Cost/tonne CO ₂ avoided	-46%	more emercial steam generation

TABLE 14 COST DIFFERENCE FOR CASE 3

Item	Difference to base case costs		
	Case 3	Comments	
Capital cost	- 15%	O ₂ autothermal reformer (ATR) for hydrogen fuel More O ₂ required for ATR, ATR capital itself and enlarged CO ₂ system. Single GT instead of two GTs.	
Operating cost	+225%	Higher fuel to cogen, reduced export power, larger fuel saving in fired units.	
Total annual costs	+18%		
CO ₂ captured Cost/tonne CO ₂ captured	+39% -15%		
CO ₂ avoided Cost/tonne CO ₂ avoided	+15% +3%		

It is likely that further development, integration and optimisation of the base case process will lead to a reduction in the CO_2 still emitted to atmosphere and therefore a further reduction in the cost of CO_2 avoided. For instance, methods of recovering the large quantity of additional CO_2 from the gas turbine exhaust have not been covered in this report.

Alternatives to Base Case

Indicative changes in the base case costing for the two alternative power generation schemes, Case 2 and Case 3, are presented in Table 13 and Table 14. As can be seen, Case 2 will lead to a significant further reduction in cost per tonne of CO_2 capture. With this option there is a net operating cost improvement by the more efficient generation of the fixed duty of steam, whilst maintaining significant export power credits. However the amount of CO_2 captured for sequestration would be lower than the 2 million tonnes/year target. Case 3 would give a significant increase in the amount of CO_2 captured for sequestration, in excess of the 2 million tonnes/year target. The costs of all three cases are summarised in Table 1.

CONCLUSIONS

The work presented in Chapter 26 showed that it is feasible to apply Oxyfuel technology to a complete refinery system with multiple CO₂ emissions points spread out over a large area. This involves a centralised oxygen supply system and a CO₂ recovery, purification and compression facility. The work presented in this Chapter has further shown the compatibility of ITM oxygen technology with this process.

ITMs have been shown to be ideally suited for integration with gas turbines, allowing for high purity oxygen production alongside power production. This is of importance in this instance where all utilities must be provided. In particular, Siemens Westinghouse V94.2 and V94.3 gas turbines have been shown to tie in well with the ITM oxygen units as these particular gas turbines allow for external combustion and hence oxygen separation from the whole gas turbine compressed air flow, along with ease of modification for operation of the gas turbine combustor in oxygen-depleted air.

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 waste heat boiler can produce steam at refinery conditions with resulting lower levels of steam production in the existing boilers and lower oxygen requirement for oxyfuel combustion. The cases chosen use either two V94.2 or one V94.3 gas turbine to illustrate the effect of having a wide variation in export power production.

It is further possible to generate hydrogen for gas turbine fuel from natural gas in an ATR fired with pure oxygen and using an MDEA system for CO₂ removal. This is the case considered for the application of a single V94.3.

Including the costs of the power generation equipment, capital costs of the ITM system are about the same as the cryogenic system: \$430 to 510 million for cryogenic oxygen compared to \$428 to 535 million for the ITM system. However, separating the cost of the power generation equipment, assuming 550\$/kW of export power, reduces the capital cost allocated to CO₂ capture in ITM Case 1 to \$178–285 million.

A key factor in the selection of the optimum configuration is the cost of the natural gas fuel for the gas turbine and the price achieved for excess power production as shown in Figure 1. Operating costs and overall cost of CO_2 avoided are heavily dependent on these figures. The avoided cost for the three cases considered varied from 20.0–38.1 \$/tonne. The lower number is where the GTCC system used to produce the hot air stream for the ITM unit is integrated with the boiler system such that the HRSG produces steam at the boiler steam condition and four of the boilers are shut down. Capital cost is reduced since less oxygen is required by the boilers and so the ITM units and the CO_2 treatment system are smaller, and no steam turbines are required for the GTCC since the current boiler turbines are used instead. A large amount of fuel is saved due to more efficient production of steam in the GTCC compared to the current boilers.

The 20.0-38.1 \$/tonne range for ITM can be compared with the costs for cryogenic oxygen cases which varied from 38.9-43.2 \$/tonne. Clearly the cost of avoided CO_2 is significantly reduced by the use of ITM oxygen technology. This result gives a significant incentive to reach a successful conclusion to the current development program for this important future application.

RECOMMENDATIONS

In addition to the recommendations presented in Chapter 26, is recommended that the ITM oxygen production technology continues to be developed and progressed to the demonstration phase in which a prototype ITM module producing 25–50 tonnes/day oxygen is integrated with a gas turbine and properly demonstrated.

REFERENCES

- D. Wright, R.J. Copeland, Report No. TDA-GRI-90/0303 prepared for the Gas Research Institute, September 1990.
- 2. B.C.H. Steele, C. R. Acad. Sci. Paris **t.1** (Serie II) (1998) 533.
- 3. P.N. Dyer, R.E. Richards, S.L. Russek, D.M. Taylor, Ion transport membrane technology for oxygen separation and syngas production, *Solid State Ionics* **134** (2000) 21–33.
- 4. R.H. Perry, D.W. Green, J.O. Maloney (Eds.), *Perry's Chemical Engineers Handbook*, sixth ed., vol. 11, McGraw-Hill, New York, 1984, p. 11.