

# OXYFUEL CONVERSION OF REFINERY PROCESS EQUIPMENT UTILISING FLUE GAS RECYCLE FOR CO<sub>2</sub> CAPTURE

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## ABSTRACT

The CO<sub>2</sub> Capture Project (CCP) is a major joint initiative by eight leading energy companies to address problems of CO<sub>2</sub> emissions that have the potential to cause climate change. Its objective is to provide significant reductions in CO<sub>2</sub> capture and storage costs compared to existing technologies, by developing a range of technology options applied to several real world scenarios.

The CCP sponsored feasibility study reported in this paper involves the application of Oxyfuel technology on a refinery-wide basis at a typical European refinery. A total of seven boilers and thirteen process heaters of various types, burning a mixture of refinery fuel gas and fuel oil and emitting approximately 2.0 million tonnes per annum of CO<sub>2</sub>, form the basis of this study. This paper highlights the technical challenges and costs involved in converting process heaters and boilers to oxyfuel operation using today's commercially proven cryogenic oxygen generation technology and will go on to identify the cost reduction opportunities available from using the next generation of oxygen separation technology: Ion Transport Membranes (ITMs). This new technology, which is integrated with gas turbines, results in a reduction of avoided CO<sub>2</sub> cost of from 15% to 50% depending upon the level of integration with the current steam generation within the refinery site.

## INTRODUCTION

The work reported previously [1] considered the issues involved in modifying the process heaters and boilers for oxyfuel combustion and locating two world scale cryogenic air separation plants totalling up to 7400 tonne/day of oxygen, plus a CO<sub>2</sub> compression and purification system, on a congested refinery site. In addition, a scheme for distributing the oxygen around the site and collecting the CO<sub>2</sub>-rich effluent from the combustion processes for purification, final compression, and delivery into a pipeline, was presented. In this paper we will look at an alternative oxygen generation technology which would replace the two cryogenic air separation units. 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 excess power production will be exported. The study includes the provision of all additional site services required.

## ITM OXYGEN

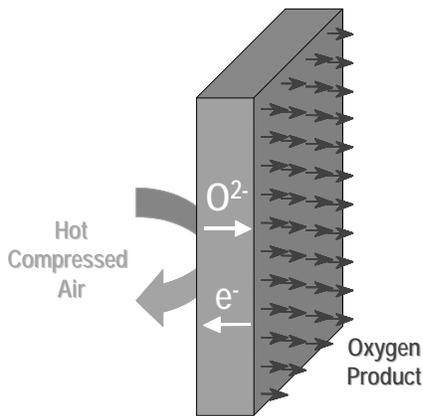
Boilers and heaters normally firing on air are converted to oxyfuel firing by replacing the air feed with oxygen and recycling part of the hot flue gases. In order to generate this oxygen, an ITM Oxygen plant may be used in place of cryogenic air separation units. ITM Oxygen technology is based on a special class of mixed-conducting ceramic materials that have both electronic and oxygen ionic conductivity when operated at high temperatures, typically 800 to 900°C. The mixed conductors are complex formulations of inorganic mixed-metal oxides (e.g. perovskites such as (La,Sr)(Fe,Co,Cu)O<sub>3-δ</sub>) whose crystal lattice structures are deficient in oxygen to achieve charge neutrality, causing a distribution of oxygen vacancies in their lattices. 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 of oxygen ions. Electrons

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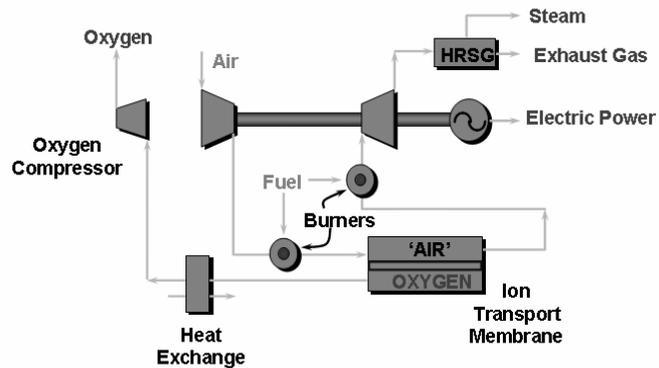
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must move counter to the oxygen ion motion to maintain charge balance in the material. At the permeate surface of the membrane, the oxygen ions release their electrons, recombine, and desorb from the surface as molecules. Since no mechanism exists 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 1. ITM Oxygen materials are so-called “mixed conductors”, in that both oxygen ions and electrons are highly mobile within the solid. Detailed descriptions of the materials and electrochemical processes can be found elsewhere [2,3,4].

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 sustain much higher fluxes than their conventional counterparts.



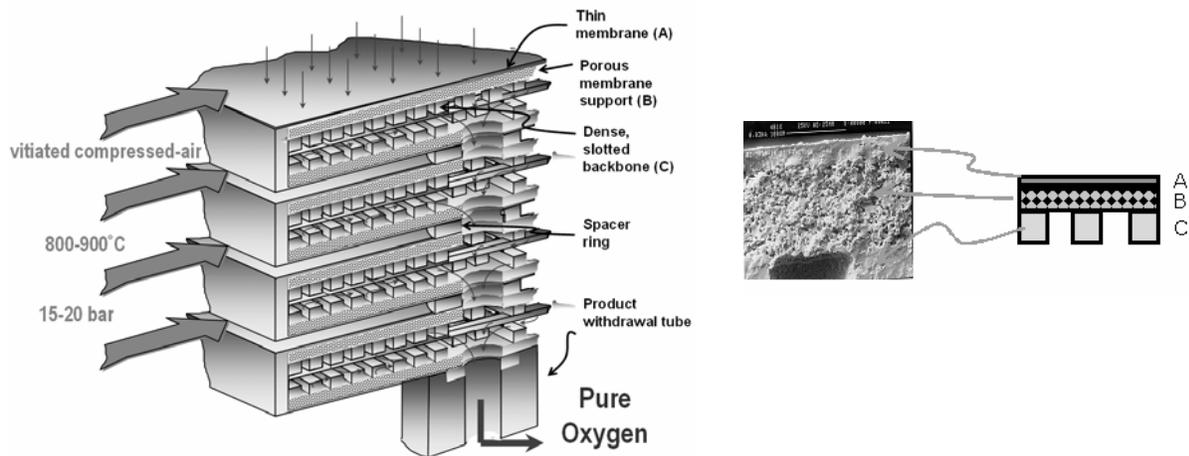
**Figure 1:** Mixed-conducting ITM.  $O^{2-}$  anions move counter to electrons at high temperature in the same material under an oxygen activity gradient.



**Figure 2:** Basic scheme for integration of an ITM Oxygen air separation unit into a gas turbine power cycle. Process outputs are oxygen, power, and steam.

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 2. 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 to the required pressure. Thermodynamic and process economic analyses indicate that the ITM Oxygen process produces oxygen at a significantly lower cost than conventional, cryogenic processes [5].

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 3:** 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 3, 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.

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 commercial flux target for over 5000 hours. Inspection of samples following extended operating campaigns have revealed no significant changes to the membrane material or wafer structure.

### Considerations for Gas Turbine/ITM Oxygen Integration

Air to the ITM Oxygen plant is supplied by either two Siemens 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 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 and for combustion of hydrogen rich gases which require a diffusion burner. 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. For these reasons, gas turbines with silo combustors are attractive as an earlier-entry platform for ITM Oxygen technology, though development efforts are underway to adapt more advanced machines for this purpose. 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 produced by Thermoflow INC. 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.

## PROCESS DESCRIPTION

### Oxygen Generation and Distribution

The maximum total oxygen demand for the base case is 7300 tonne/day, which includes a 10% flow margin. 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. In addition to oxygen, some nitrogen (<1 mole%) 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 about 280°C after high-level heat recovery. The units to be converted and the area of the site which could locate the extra equipment cover an area of around 600m by 700m. 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, insulated, stainless steel piping must be used. All oxygen systems for production and delivery have been designed using the highest standards for safe operation of oxygen systems.

### Heater and Boiler Conversion

TABLE 1: HEATERS AND BOILERS FOR OXYFUEL CONVERSION

	Air Firing		Oxyfuel Firing – Cryogenic			Oxyfuel Firing – ITM		
	Total Fuel Consumption kg/hr	Total CO <sub>2</sub> Emitted kg/hr	Total Fuel Consumption kg/hr	Total O <sub>2</sub> Consumption kg/hr	Total CO <sub>2</sub> Captured kg/hr	Total Fuel Consumption kg/hr	Total O <sub>2</sub> Consumption kg/hr	Total CO <sub>2</sub> Captured kg/hr
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	3,600	9,791	2,813	10,494	7,080	2,774	10,348	7,127
Totals (LHV)	84,921 kg/hr (1046 MW)	2.17 million tonnes/year	79,636 kg/hr (980 MW)	6,736 tonnes/day	1.88 million tonnes/year	78,333 kg/hr (964 MW)	6,626 tonnes/day	1.89 million tonnes/year

Each heater and boiler considered within the study must be converted to fire on oxygen with recycled flue gas 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 CO<sub>2</sub> stream that must be cooled, dried, purified and compressed.

The list of units which will be converted for oxyfuel firing is summarised as follows: five Simon Carves boilers each supplying 136.4 tonne/hr steam with a typical fuel mix of 40% gas, 60% oil by weight, linked to two stacks; two Babcock steam boilers each supplying 227.3 tonne/hr 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 10.3MW to 112.3MW, 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. Air leakage into the boilers and heaters were estimated at 1.5% for the heaters and 2.2 to 3.3% for the boilers.

Table 1 shows the CO<sub>2</sub> emissions with air firing, the CO<sub>2</sub> delivered to the pipeline when operating in the oxyfuel mode, and the total oxygen consumptions for both the cryogenic air separation case [1] and the ITM Oxygen results presented herein. With cryogenic air separation the reduction in fuel due to oxyfuel firing was 6.2%. This reduction occurs because of the recycle of hot flue gas. Using the ITM Oxygen system this reduction increases to 7.8%

because of the higher oxygen delivery temperature (200-250°C). Although the fuel requirement has decreased in the ITM Oxygen case, more CO<sub>2</sub> is captured than for the cryogenic air separation case since the lower inert content of the oxygen increases the overall CO<sub>2</sub> recovery from 92.3% to 94.3%.

### **Local CO<sub>2</sub> Collection and Drying**

Due to the widely scattered location of the boilers and heaters in the refinery, it is necessary to collect the CO<sub>2</sub> 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. Each of these zones takes the hot, wet CO<sub>2</sub> from the converted heaters or boilers, cools this stream and removes water by direct contact with cooling water in a venturi scrubber followed by a packed column. The crude CO<sub>2</sub> gas is then compressed to 30 barg and further dried in a dual bed desiccant drier to a dew point of -60°C [1].

### **CO<sub>2</sub> Collection, Purification and Compression**

The compressed, dry, impure CO<sub>2</sub> is transported 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. The central CO<sub>2</sub> purification and compression system takes the dried CO<sub>2</sub> from the distribution pipeline, removes inerts and compresses to the pipeline CO<sub>2</sub> delivery pressure of 220 barg. The inerts gas removal plant, using CO<sub>2</sub> refrigeration, separates the inert gases from the CO<sub>2</sub> at a temperature of about -55°C which is close to the CO<sub>2</sub> freezing temperature. At this point the CO<sub>2</sub> partial pressure in the vapour phase has been reduced to about 7 bar. The refrigeration is obtained by evaporating two streams of CO<sub>2</sub> at pressure levels of typically around 10 bar and 20 bar and recycling the CO<sub>2</sub> gas in the main CO<sub>2</sub> compressor. The separated inert gas at 29 bar can be heated and passed through a power recovery turbine. It is possible to reach a CO<sub>2</sub> purity in excess of 96% using this method at inlet CO<sub>2</sub> concentrations as low as 80% with a CO<sub>2</sub> recovery of better than 90%.

### **ITM Oxygen Case Specifics**

#### *Case 1 – The Base Case (Two Siemens V94.2 gas turbines, combined cycle, natural gas fuel)*

The maximum total oxygen demand of 7300 tonne/day, which includes a 10% flow margin, is provided by an ITM unit integrated with two Siemens V94.2 gas turbine combined cycle (GTCC) systems that are used to generate power and supply feed air to the ITM Oxygen plant.

#### *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 518°C level used in the refinery 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 turbine(s) 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 turbine(s). 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. Due to the production of 127 barg steam, boilers B1, B2, B3, B5 and B7 can be shut down which results in a reduction in the oxygen requirement from 6626 tonne/day to 3828 tonne/day.

### 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. Part of the oxygen from the ITM is used for hydrogen production in a natural gas fuelled autothermal reformer (ATR) with shift conversion and CO<sub>2</sub> removal using an MDEA system. The Siemens V94.3 has a 20% higher air flow than the Siemens V94.2 gas turbine and a higher pressure ratio. 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. The combustion of hydrogen in the gas turbine combustor must be tested and verified by the vendor.

As in Case 2, the oxygen demand is lower because the production of 127 barg 518°C 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 tonne/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<sub>2</sub> loss this represents is compensated by the capture of CO<sub>2</sub> from the ATR process, which allows the gas turbine to operate with virtually no CO<sub>2</sub> in the flue gas. It may be possible to supply the full demand with either one or more alternative gas turbines.

## RESULTS AND DISCUSSION

The overall performance of the complete system for these options is given in Table 2, where Case 0 is air firing. Excess steam production in Cases 2 and 3 is used to produce power.

TABLE 2: FUEL, POWER AND STEAM SUMMARY

Case	GT	Fuel to Power System MW	Total Fuel MW	Power Generation, MW		Export Power MW	Reduction in Fuel to Boilers MW	Reduction in Fuel to Heaters MW	Boiler Steam, tonne/hr			Additional Steam	
				GT	ST				From Boilers	From GT	HRSG	tonne/hr	MW
0	N/A	N/A	1045.8	0	0	0	0	0	803	N/A	0	0	
1	2 x V94.2	1032.7	2028	288	213	446.2	27.75	22.75	803	0	0	0	
2	2 x V94.2	913.1	1476.4	283	0	289.9	459.78	22.75	279	524	185	33.3	
3	1 x V94.3	789.2	1488.3	193	0	121.4	323.98	22.75	446	357	209	37.7	

The capital cost estimate is summarised for Case 1 in Table 3. An estimate of the operating costs for Case 1 are given in Table 4. It should be noted that both the fuel cost and export power credit are very large components of the overall cost of CO<sub>2</sub> capture and make the CO<sub>2</sub> capture cost sensitive to variations in natural gas price and power price, as is shown in Figure 4 a) 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 the UK. This will tend to cancel out the sensitivity effect.

One of the key measures for comparison with alternative methods of CO<sub>2</sub> capture is ‘cost per tonne of CO<sub>2</sub> captured or avoided’. This is a simple calculation, dividing the total annual costs, assuming a 10% capital charge, by the tonnes per year of CO<sub>2</sub> captured (or avoided). Results are given in Table 5.

Indicative changes in the base case costing for the two alternative power generation schemes, Case 2 and Case 3, are presented in Table 6. As can be seen, Case 2 will lead to a significant further reduction in cost per tonne of CO<sub>2</sub> 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<sub>2</sub> captured would be lower than the 2 million tonne/year target. Case 3 would give a significant increase in the amount of CO<sub>2</sub> captured, in excess of the 2 million tonne/year target.

TABLE 3: SUMMARY OF CAPITAL COST ESTIMATE FOR ITM CASE 1

Description	USD
Air Separation Units (ITM Units + auxiliaries)	54,200,000
O <sub>2</sub> Distribution & CO <sub>2</sub> Gathering Pipework	7,200,000
CO <sub>2</sub> Drying , Compression & Purification	77,000,000
Cogeneration System	210,400,000
Cooling Water System	19,900,000
Boiler Modifications	19,900,000
Fired Heater Modifications	13,300,000
<b>TOTAL INSTALLED COSTS</b>	<b>\$401,900,000</b>
20% Contingency	80,380,000
10% Owners Costs	48,230,000
1% CAR (Contractors All Risk) Insurance	4,823,000
<b>TOTAL CAPITAL COSTS</b>	<b>\$535,333,000</b>

TABLE 4: SUMMARY OF ANNUAL OPERATING COSTS FOR ITM CASE 1

Description	Annual Cost, USD	Comments
Gas Turbine Fuel Cost	112,840,000	Natural gas at UK rate
Export Power Credit	-109,444,000	Exported to grid
Fired Unit Fuel Reduction	-5,365,000	Natural gas equivalent value
Make-up water	4,400,000	Possible to use condensed water from flue gases
Operator manpower	1,450,000	
Maintenance	5,354,000	
Consumables	500,000	
<b>Total Operating Costs</b>	<b>\$9,735,000</b>	<b>per year</b>

TABLE 5: SUMMARY OF STUDY RESULTS

Case	Oxygen Flow tonne/day	CO <sub>2</sub> Captured 10 <sup>6</sup> tonne/yr	CO <sub>2</sub> Emitted, 10 <sup>6</sup> tonne/yr			Export Power CO <sub>2</sub> Credit 10 <sup>6</sup> tonne/yr	CO <sub>2</sub> Avoided <sup>1</sup> 10 <sup>6</sup> tonne/yr	Cost CO <sub>2</sub> Captured \$/tonne	Cost CO <sub>2</sub> Avoided \$/tonne
			GT Exhaust	Process	Steam Penalty <sup>2</sup>				
Cryo Case 1	6736	1.884	0.374	0.158	0.028	0.037	1.648	38.0	43.2
Cryo Case 2	6034	1.688	0.455	0.141	0.028	0.012	1.560	36.1	38.9
Cryo Case 3	6889 <sup>3</sup>	2.327 <sup>4</sup>	0.022	0.146	0.028	(0.001)	1.974	33.8	39.3
ITM Case 1	6626	1.895	1.876	0.113	0.028	1.557	1.710	33.5	37.0
ITM Case 2	3828	1.095	1.611	0.065	0.028	1.011	1.428	25.1	20.0
ITM Case 3	6051 <sup>5</sup>	2.622 <sup>6</sup>	0.070	0.433 <sup>7</sup>	0.028	0.424	2.064	28.5	38.1

<sup>1</sup> CO<sub>2</sub> emitted with air firing (Table 1) + CO<sub>2</sub> power credit – CO<sub>2</sub> emitted with Oxyfuel firing

<sup>2</sup> To compensate for reduced steam make in converted heaters

<sup>3</sup> Includes 629 tonne/day for H<sub>2</sub> plant

<sup>4</sup> Includes 0.576 million tonnes captured from H<sub>2</sub> plant with MDEA system (assumed 100% recovery) and compressed to 220 bar

<sup>5</sup> Includes 1620 tonne/day for H<sub>2</sub> plant

<sup>6</sup> Includes 1.359 million tonnes captured from H<sub>2</sub> plant with MDEA system (assumed 100% recovery) and compressed to 220 bar

<sup>7</sup> Includes CO<sub>2</sub> from unconverted boilers B1 and B5

TABLE 6: COST DIFFERENCE BREAKDOWN FOR ALTERNATIVES CASE 2 AND 3

	Case 2 - Steam Integration of Combined Cycle plant with fired units		Case 3 - O <sub>2</sub> Autothermal Reformer (ATR) for Hydrogen Fuel	
Capital Cost	-20%	Less O <sub>2</sub> required by turned down boilers. Smaller ITM units and CO <sub>2</sub> system. GT with HRSG but no ST	-15%	More O <sub>2</sub> required for ATR, ATR capital itself and enlarged CO <sub>2</sub> system. Single GT instead of two GTs.
Operating Cost	-284%	Fuel saved by more efficient production of steam. Net positive cashflow from exported power and lower overall fuel flow.	+225%	Higher fuel to GT, reduced export power, larger fuel saving in fired units.
Total Annual Costs	-57%		+18%	
CO <sub>2</sub> Captured	-42%	Boilers turned down	+39%	
Cost /tonne	-25%		-15%	
CO <sub>2</sub> Avoided	-20%	Large amount of CO <sub>2</sub> avoided by more efficient steam generation	+15%	more efficient steam generation
Cost/tonne CO <sub>2</sub>	-46%		+3%	

## CONCLUSIONS

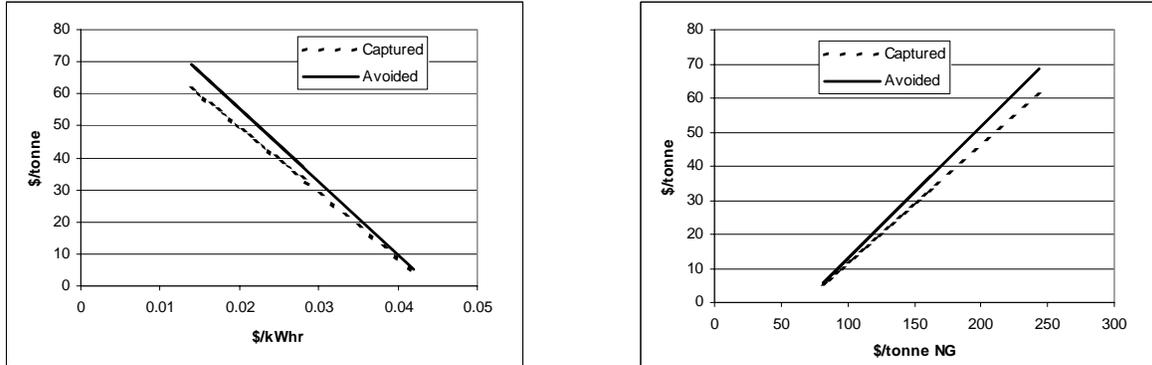
Ion transport membranes have been shown to be ideally suited for integration with gas turbines, allowing for high purity oxygen production alongside power production. This is of importance in this instance where all extra utilities for the oxyfuel CO<sub>2</sub> capture and compression system must be 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 autothermal reformer fired with natural gas and using pure oxygen plus shift and an MDEA system for CO<sub>2</sub> removal. This is the case considered for the application of a single V94.3.

In this study, Case 1 is presented in which the hot air for the ITM Oxygen process is provided by two Siemens V94.2 GTCCs and excess power is exported. Case 2 also uses two Siemens V94.2 gas turbines plus a HRSG producing steam at refinery conditions. The steam production from the existing boilers is reduced by a corresponding amount. The turndown of the steam boilers results in a reduction in the oxygen requirement from 6626 tonne/day to 3828 tonne/day. Case 3 uses one Siemens V94.3 gas turbine plus a HRSG, but in this case the fuel is hydrogen produced from an oxygen autothermal reformer with product steam generation and CO<sub>2</sub> removed using an MDEA system. The gas turbine HRSG 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 CO<sub>2</sub> emission avoided and the quantity of CO<sub>2</sub> available for pipeline delivery is calculated, costed and presented in Table 5.

In the previous study using oxygen produced by a cryogenic ASU, three cases were also presented [1]. In Case 1 the gas turbine and associated steam production was all used for power production. In Case 2 the steam production from the GT HRSG was used to replace part of the boiler steam, thus saving oxygen flow to the boilers. In Case 3 the gas turbine was run in the precombustion decarbonisation mode with part of the oxygen being used for hydrogen production in an autothermal reformer and with shift conversion and CO<sub>2</sub> removal using a MDEA system, with excess steam production sent to the refinery turbines. The results are summarized in Table 5.

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 CO<sub>2</sub> capture in ITM Case 1 to \$178 – 285 million.



a) Effect of export power price on cost of CO<sub>2</sub> removal – with fixed natural gas price      b) Effect of natural gas price on cost of CO<sub>2</sub> removal – with fixed electricity price

**Figure 4:** Effect of natural gas price and export power price on cost of CO<sub>2</sub> removal (ITM Case 1)

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 4. Operating costs and overall cost of CO<sub>2</sub> avoided are heavily dependent on these figures. The avoided cost for the three cases considered varied from 20.0 to 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<sub>2</sub> 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 to 38.1 \$/tonne range for ITM can be compared with the costs for cryogenic oxygen cases which varied from 38.9 to 43.2 \$/tonne. Clearly the cost of avoided CO<sub>2</sub> 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.

## REFERENCES

1. M.B. Wilkinson, M. Simmonds, R.J. Allam and V. White, "Oxyfuel conversion of heaters and boilers for CO<sub>2</sub> capture", Second National Conference on Carbon Sequestration, Alexandria, Virginia, May 5<sup>th</sup> -8<sup>th</sup> 2003.
2. D. Wright and R. J. Copeland, "Advanced Oxygen Separation Membranes", Report No. TDA-GRI-90/0303 prepared for the Gas Research Institute by TDA Research of Wheat Ridge, Colorado, September 1990
3. B. C. H. Steele, *C. R. Acad. Sci. Paris*, t.1, Serie II, 533 (1998).
4. P.N. Dyer, R.E. Richards, S.L. Russek, and D.M.Taylor, "Ion Transport Membrane Technology for Oxygen Separation and Syngas Production", *Solid State Ionics*, **134** (2000) 21-33.
5. R.J. Allam, E.P. Foster, V.E. Stein, "Improving Gasification Economics through ITM Oxygen Integration", proceedings of the Fifth (IChemE) European Gasification Conference, Noordwijk, The Netherlands, 8-10 Apr 2002.