Second Nordic Minisymposium on Carbon Dioxide Capture and Storage, Göteborg, October 26, 2001. available at http://www.entek.chalmers.se/~anly/symp/symp2001.html

## AZEP - Development of an Integrated Air Separation Membrane -Gas Turbine

Sven Gunnar Sundkvist, ALSTOM Power Sweden AB Timothy Griffin, ALSTOM Power Technology Ltd, Switzerland Niels Peter Thorshaug, Norsk Hydro ASA, Norway

### Abstract

AZEP ('Advanced Zero Emissions Power Plant') addresses the development of a specific, zero emissions, gas turbine-based, power generation process to reduce local and global emissions in a cost-effective way. In this innovative cycle 100% reduction of  $CO_2$  emission is made possible, with NOx << 1 ppm. Cost of  $CO_2$  separation (compared to tail-end capture) is reduced by 25-35% in < 6 years, and by 35-50% in < 10 years. Conventional, air-based, gas turbine equipment is utilised, allowing retrofitting. Loss in power plant efficiency is less than 2 percentage points, compared with up to a 10 point loss of efficiency when conventional tail-end  $CO_2$  capture methods are employed.

The key to achieving these targets is the development of an integrated reactor, in which  $O_2$  is separated from air, such that combustion occurs in an  $N_2$ -free environment. To this effect, the following objectives have been set for Phase 1 of the development project: establish the economic/environmental advantages of the proposed process, reflecting emerging  $CO_2$  disposal strategies, develop a mixed conducting membrane (MCM) for cost-effective supply of  $O_2$ , and integrate the components (membrane, combustor, heat exchanger) into a single unit MCM-Reactor, and perform functionality tests. The key deliverables of Phase 1 are test results from the individual and integrated test programme to validate key components and an implementation plan to allow the full-scale demonstration of the AZEP concept in the following Phase 2. It is estimated that AZEP will be available for exploitation some 5-7 years after completion of the first project phase.

### Introduction

Man-made  $CO_2$  emissions originate from many different sources. Despite power generation not being the largest source of  $CO_2$  emissions, it is likely that it will have to bear the main share of initial reductions, as power plants are large, individual units and thus more feasible to target than other sources, from both technical and political perspectives.

Based on agreements in the Kyoto protocol, the emissions of greenhouse gases should decrease by 8% for the period 2008-2012, compared to 1990 emission levels. According to the European Commission Green Paper "Towards a European Strategy for the Security of Energy Supply" (November 2000) the  $CO_2$  emission will increase 5% in this period even when taking the shift from coal to natural gas into account. This requires, then, a reduction of approximately 13% compared to 1990.

The AZEP concept ('Advanced Zero Emissions Power Plant') offers a zero emissions gas turbine based power production cycle which potentially reduces the costs of CO<sub>2</sub>-removal by at least 50% compared to other, existing CO<sub>2</sub>-removal technologies. Additionally, the investment costs of this technology are significantly lower (< 400  $\notin$ kW in the short term, <250  $\notin$ kW in the long term) than current, tail-end CO<sub>2</sub> removal methods (costing ca. 550  $\notin$ kW).

### State of the art

Fossil fuel-based power plants produce flue gas streams with  $CO_2$  concentrations of 3 to 15%. The remainder of the exhaust gas is nitrogen, some excess oxygen, water and trace impurities such as  $NO_x$ . The major challenge in  $CO_2$  removal is to develop a technology for its efficient separation from nitrogen. Once separated, it is assumed that emerging technologies will be available to allow near infinite disposal of  $CO_2$  in onshore or offshore underground reservoirs.

The three main possibilities for CO<sub>2</sub> reduction/removal from power generation flue gases are:

- 1. Tail-end capture solutions: e.g. amine scrubbing, various adsorption techniques, membranes, etc.
- 2. Fuel de-carbonisation: Prior to combustion, several methods can be adopted to extract  $H_2$  from hydrocarbon fuels. These processes result in the production of  $CO_2$  and  $H_2$ ; the former is recovered whilst the latter is subsequently combusted.
- 3. Combustion in  $O_2$  /  $CO_2$  atmospheres: Various power generation cycles are based upon the utilisation of pure  $O_2$  or oxygen-enriched environments instead of normal air.

Technology	Efficiency Loss (percentage points)	CO <sub>2</sub> Capture	NO <sub>x</sub> Level
Tail-end CO <sub>2</sub> capture	up to 10	85 – 95%	25 ppm (standard gas turbine combustion)
Fuel de-carbonisation	8 to 10	85 - 95%	> 25  ppm (H <sub>2</sub> combustion)
CO <sub>2</sub> cycles with cryogenic air separation	up to 10	100%	< 1 ppm
ÂŻEP	2	100%	<< 1 ppm

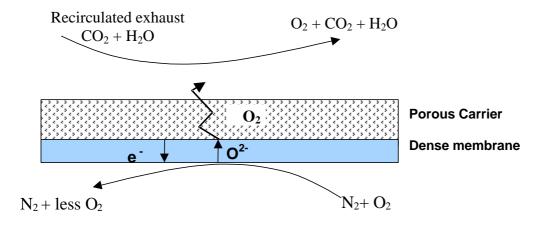
The performance characteristics of these  $CO_2$  reduction techniques are summarised in Table 1.

### Table 1. Summary of performance for various zero emissions gas turbine power plant concepts.

Existing  $CO_2$  capture processes (including the aforementioned methods) have significant energy requirements which reduce the power plant's efficiency and net power output by up to 10% and 20%, respectively. Methods 1 and 2 permit the recovery of 85% to 95% of  $CO_2$ , but emitted NO<sub>x</sub> levels are similar to those in conventional power generation processes. Subsequent reduction of  $NO_X$  requires the implementation of further processes such as SCR (Selective Catalytic Reduction). Additionally, in method 2, both a syngas manufacturing plant and  $CO_2$  removal infrastructure is required, significantly adding to the total plant capital cost. Combustion in O<sub>2</sub>/CO<sub>2</sub> atmospheres (method 3) enables 100% CO2 recovery as well as NOX levels to be reduced below 1 ppm. However, the weakness of this method is the need for expensive (and energy-consuming) oxygen supplies, as well as the development of new (and costly) turbomachinery equipment (e.g. a gas turbine cycle using  $CO_2$  as the working fluid). Commercial air separation methods for the production of pure oxygen (e.g. cryogenic separation or pressure swing absorption (PSA)) require 250 to 300 kWh/tonne oxygen produced. Should such oxygen procurement methods be utilised for the supply of pure oxygen to combustion processes within gas turbine cycles, the net power output, and hence the thermal efficiency, will be diminished by at least 20%, and some 10%, respectively. Oxygen production via cryogenic air separation will also substantially increase the cost of electric power; it may even amount to 50% of this cost.

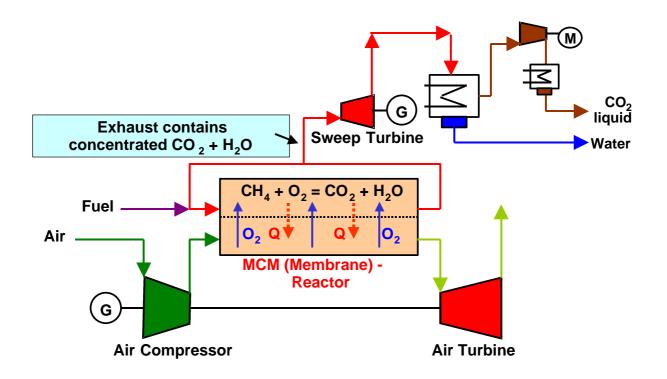
### The AZEP concept

The AZEP concept proposes a less energy-intensive (and hence more cost-effective) proposition for zero emissions power. The key to this is the Mixed Conducting Membrane (MCM), which produces pure oxygen from air. Research in dense, oxygen-selective membranes has increased substantially during recent years (evidenced by more than 50 patents filed in this field in the period 1993-2001, compared with fewer than 10 such filings prior to 1993). These materials consist of complex crystalline structures, which incorporate oxygen ion vacancies (5 - 15%). The transport principle for oxygen through the membranes is adsorption on the surface followed by decomposition into ions, which are transported through the membrane by sequentially occupying oxygen ion vacancies. The ion transport is counterbalanced by a flow of electrons in the opposite direction. The driving force is a difference in oxygen partial pressure between the permeate and retentate sides of the membrane, see Figure 1. The transport process also requires high temperatures, i.e. > 700 °C. Since this transport process is based on ion diffusion and not molecular sieving, the selective of the membranes is infinite as long as the membrane surface is perfect, i.e. no cracks or pores are present.



# Figure 1. Schematic drawing of the MCM-membrane, with oxygen swept from the permeate side of the membrane by recirculated exhaust gas.

Integration of this MCM technology into a power plant can be achieved by various means. A number of such solutions, each of which represents a different cycle characterised by distinct cycle efficiencies (as well as technical challenges), has been studied and compared with existing best available technologies. Our findings and knowledge pool indicate that the most efficient, cost effective and promising utilisation of the MCM-Reactor is its integration in a conventional gas turbine. Essentially, the MCM-Reactor, which combines oxygen-separation, combustion and heat transfer processes, replaces the conventional burner in a standard gas turbine power plant, as indicated in Figure 2, thereby creating the AZEP. The gas turbine set and its auxiliary systems consist of standard equipment. This proposed solution dictates that the major research and development efforts be concentrated upon the new components within the MCM-Reactor, thereby limiting the need for the development of an entirely new cycle - and its associated new equipment - and substantially reducing technical and commercial risks.



## Figure 2. Conventional gas turbine with an MCM-Reactor, including an integrated membrane for production of oxygen.

### **AZEP** development project

After a successful feasibility study jointly performed previously by ALSTOM Power and Norsk Hydro, it was agreed that the estimated performance characteristics of AZEP are extremely promising. A logical progression was to develop this technology in a consortium, bringing in other partners with complementing skills and involving academia and supporting SMEs. The trans-European consortium draws its partners (ALSTOM, Norsk Hydro, Borsig, FCT, EniTecnologie, Paul Scherrer Institut, Univ. of Ulster, KTH, LTH) from six European nations: Sweden, Norway, Germany, Italy, the UK and Switzerland. There is a complementary combination of expertise covering all the necessary skills, including:

- Material development,
- Ceramic manufacturing,
- High temperature heat-exchanger development,
- Gas turbine and power plant development,
- Techno-economic and environmental analysis.

The vertically integrated industrial involvement in this proposal is significant and covers expertise in the design, manufacture, supply and operation of state-of-the-art power systems. The academic partners are well established and respected experts in their fields which are all essential for this novel and important development. Total project cost is  $M \in 9.3$  with funding by EC ( $M \in 3.4$ ) and the Swiss government.

The AZEP development project will be phased in two phases. The first phase (3 years) will primarily focus the research and development of the MCM-Reactor upon its constituent units, the combination of these components into an integrated reactor, and its subsequent scale-up for future integration in a gas turbine. The second phase (3 years) will focus on the MCM-Reactor integration in the gas turbine and

the demonstration of the total concept in a pilot plant. It is estimated that AZEP will be available for exploitation some 5-7 years after completion of the first project phase.

The work in Phase 1 is divided into the following main areas:

- Process optimisation, economic evaluation, and environmental impact in order to develop the optimum gas turbine/MCM-Reactor combination, and determine its future market potential.
- Development of MCM materials with respect to:
  - Oxygen flux
  - Long-term stability
  - Thermo-mechanical properties
  - Fabrication methods
  - Suitability for the operating environment within the MCM-Reactor
- Development of a high-temperature heat exchanger, whose purpose is to generate the conditions necessary for MCM functionality and for optimal gas turbine operation.
- Combustion methodology, in order to develop the optimum combustion method to be used in the MCM-Reactor.
- Reactor design to optimally combine the MCM-Reactor components into a single unit.
- Lab-scale testing of the MCM-Reactor to evaluate performance and functionality of both individual components and the integrated unit as a whole.
- Scaling up of the MCM-Reactor for integration in a gas turbine, followed by functional, technical and economic assessment of this new technology.

Technical risks evident in the main research and development areas have been identified as:

- Fabrication of supported membranes, which allow for sufficient oxygen flux and stability during application in the MCM.
- Membrane structural design and sealing will be critical; it is necessary to reduce the impact of process instabilities.
- The MCM-Reactor will be operated at temperatures between 450 and 1250 °C. Material stability and integration issues require particular consideration regarding the design of the high-temperature heat exchanger, MCM (membrane) and the combustor units.
- Combustion stability within the MCM-Reactor. Stable combustion must be maintained in spite of the necessary high level of exhaust gas dilution (with H<sub>2</sub>O and/or CO<sub>2</sub>) and moderate combustion temperatures (< 1200 °C)

The MCM-Reactor will be split up into three separate functional units (MCM, combustor and high temperature heat exchanger). By doing so, the total risk can be distributed among the separate components, thereby lowering overall risk. Since the MCM-Reactor itself is relatively easy to scale due to its modular nature, lab-scale test is sufficient for evaluating the performance of the entire process. This will reduce the overall development costs whilst allowing the major technical risks of the design to be quantitatively evaluated.

### Summary and concluding remarks

Goals for the first project phase are to identify, test and verify a commercially viable, power generation concept without emissions of  $CO_2$ , at state-of-the-art efficiency. The commercial application of this technology would enable Europe to increase its utilisation of European natural gas reserves while reducing  $CO_2$  emissions. Conventional power generation equipment will be utilised. Retrofitting of existing natural gas-fired, combined cycle power plants, therefore, represents a new market opportunity, the possibilities of which will be fully exploited.

The AZEP technology will provide production of power on a modular basis, hence it will be equally well suited for small or large scale power generation, both offshore and onshore. Offshore application is very attractive compared to alternative technologies due to the compactness of the AZEP process.  $CO_2$  may be injected directly into an aquifer or used for enhanced oil recovery in the field. If applied on a large scale in the North Sea, it would improve the use of the European natural gas sources. Offshore power plant sizes will range from 10 to 60 MW.

Onshore applications are foreseen to be the largest market for the AZEP technology. Both large scale (400 MW) and distributed scale (below 50 MW) are of interest. Additionally, since the AZEP process produces highly concentrated  $CO_2$  in the exhaust gas (compared to conventional processes) which is virtually free of  $NO_x$ , small power plants (100 kW to 3 MW) may be attractive for use in populated areas. As in the offshore case,  $CO_2$  may be injected underground. A 1996 Joule study estimated that this type of storage capacity allows for the disposal of more than 800 billion tonnes of  $CO_2$  within Europe. In contrast, the annual  $CO_2$  production from European power stations is only 1000 Mtonnes.

## **List of References**

- 1. Appel, C. Mantzaras, I., Scharen, R., Bombach, R., Inauen, A., Catalytic combustion of H<sub>2</sub>/air mixtures over platinum, *accepted Sixth International Conference on Technologies and Combustion for a Clean Environment*, 9-12 July 2001, Porto, Portugal.
- 2. Berroth, K., Bittner, H.-G., Weber, H., Complex shaped silicon carbide ceramic heat exchanger for application in high-temperature recuperative burner, *W.Liere-Netheler, Industrial Ceramics 215 3*, 1995.
- Bill, A., Span, R., Griffin, T., Kelsall, G., Sundkvist, S G., Technology options for 'Zero Emissions' gas turbine power generation, *International Conference Power Generation and Sustainable Development*, Liège, Belgium, 8 – 9 October 2001.
- 4. Campbell, P.E., Brennan, S.E., McCahey, S., McMullan, J.T., Williams, B.C., Process Simulation of High Temperature Fuel Cells, *Proc 2nd Int Conf on Combustion and Emissions Control*, InstE, London, pp 353-363, 1995.
- 5. Griffin, T., Bill, A., Marion, J. L., Nsakala ya Nsakala, Controlling Power Plant CO2 Emissons: A Long Range View, *PowerGen Europe 2001*, Brussels, Belgium, May 2001.
- 6. Griffin, T. and Scherer, V., Katalytisch unterstützte Verbrennung in Gasturbinen: Potentiale und Grenzen, *VGB Kraftwerkstechnik*, 75, Heft 5, 421-426, 1995.
- 7. Hellberg, A., et al., Zero Emission Power Plant Process Selection, *Internal Report ABB ALSTOM Power*, RT T10 57/99, July 1999.
- 8. Howard, P.J., Pyke, S.H., and Wood, A., High Temperature Sealing of Zirconia Ceramics using Glass-Ceramic Bond Materials, *Materials Technology*, 15 (1) pp 6-8, March 2000.
- 9. McCahey, S., McMullan, J.T., Williams, B.C. (1996) The Integration of Solid Oxide Fuel Cells into Power Generation Systems, *Proceedings of the 2nd European Solid Oxide Fuel Cell Forum*, Publisher, Dr. Ulf Bossel, Switz, Vol 1, ISBN 3-922 148-19-0, pp79-88.
- 10. Selimovicz, A., Solide oxide fuel cell modelling for SOFC/gas turbine combined cycle simulations, *Thesis for degreee Licentiate in Engineering*, Lund Institute of Technology, Sweden, 2000.
- 11. Svenssson, F., Torisson, T., Carbon dioxide reduced processes, *Fifth Int Conf on Greenhouse Gas Control technologies (GHGT-5)*, Australia, 2000.
- 12. Williams, B.C., The Development of the ECLIPSE Process Simulator and its Application to the Techno-Economic Assessment of Fossil Fuel Based Power Generation Technologies. *DPhil Thesis*, University of Ulster, 202 pp, 1994.
- 13. Zwinkels, M., Haussner, O., Menon, G. and Järås, S., Preparation and Characterization of LaCrO<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub> Methane Combustion Catalysts Supported on LaAl<sub>11</sub>O<sub>18</sub>-and Al<sub>2</sub>O<sub>3</sub>-coated Monoliths, *Catalysis Today*, 47:73-82, 1999.