## CONTROLLING POWER PLANT CO<sub>2</sub> EMISSIONS: A LONG RANGE VIEW

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## ABSTRACT

ALSTOM Power (ALSTOM) is an international supplier of power generation with concern for the environment. We are aware of the present scientific concerns regarding greenhouse gas emissions and the role of fossil fuel use for power generation. Although the scientific and policy dialogue on global climate change is far from conclusive, ALSTOM continues to invest in R&D to develop:

- high efficiency power generation equipment with the most modern technologies to utilize fossil fuels with the lowest possible emissions (short, medium and long term) term), and
- technologies to remove and sequester carbon dioxide created in power plants in an environmentally and economically favorable manner (long term).

This paper is an overview of activities to study and develop controls for carbon dioxide ( $CO_2$ ) emissions from power generation. First, energy efficiency improvements for both new and existing fossil fuel power plants are briefly reviewed for both coal and natural gas fuels. Greater depth is then given to options for  $CO_2$  capture and sequestration. These studies are looking at current and novel power generation technologies.

### CARBON DIOXIDE EMISSIONS FROM FOSSIL FUELS

When greenhouse gas emissions are under discussion,  $CO_2$  is generally the gas which receives the most attention for its greenhouse effect. Although the radiative forcing of  $CO_2$  is much less than other greenhouse gases (CH<sub>4</sub>, N<sub>2</sub>O, CFCs, etc.), CO<sub>2</sub> is emitted in large amounts into the atmosphere and has a rather long atmospheric lifetime. When all these parameters are modelled, with our current state of knowledge, to evaluate the global warming potential, CO<sub>2</sub> is estimated to contribute approximately 60% of the enhanced greenhouse gas effect [1]. The exponential growth of the global economy since 1860 has been based on fossil fuel consumption. During this period, mankind has collectively released approximately 950 billion tons of carbon dioxide (260 Gt of carbon) from the burning of oil, coal and natural gas [2]. These fossil fuel emissions have been increasing at an average rate of 2% a year to a 1997 annual global output of around 23 billion tons of carbon dioxide (6.3 Gt of carbon) (Figure 1a). Roughly half of these emissions (3.5 Gt of carbon) remain in the atmosphere, the rest being adsorbed by natural processes [3]. CO<sub>2</sub> concentrations have increased by 35% from the pre-industrial 280 parts per million by volume (ppmv) to the current 370 ppmv (Figure 2). Coincident with these changes, the global average temperatures have increased by almost 1°C at the surface of the earth.



Figures 1a and 1b: CO<sub>2</sub> emissions from (fossil) fuel combustion

Climate scientists argue that in order to stabilize these rising concentrations and temperatures, reduction in  $CO_2$  emissions of 60 to 80% may be required [5].





Figure 2b: CO<sub>2</sub> concentration over the last 150 years [7, 8]



The 1997  $CO_2$  emissions picture for the four principal sector sources by fuel used are shown in Figure 1b. Since fossil fuel-fired power plants exist at fixed locations, they are easier to

regulate than are other major sources of  $CO_2$  (transportation, space heating, and industrial processing). Should  $CO_2$  reductions be deemed necessary, it is likely that the electricity and heat generation sector would be required to make significant contributions to reduce  $CO_2$  emissions. (Other greenhouse gases are not discussed here.)

Such actions will have a profound impact on the use of fossil fuels and, in particular, on ALSTOM's businesses. We are keenly aware of this issue and committed to working with our customers to identify and deliver solutions. A variety of technical options are being evaluated which could reduce such emissions. These include improved energy efficiency, fuel switching, renewable energy sources and nuclear power. Alternatively, greenhouse gases, in particular  $CO_2$  from fossil fuel use, may be captured and stored. New capture and sequestration technologies will be needed if  $CO_2$  concentrations in the atmosphere need to be stabilized to avoid the potential consequences of global warming. Some technology responses are available today, while others require further development. ALSTOM is focusing on the development of new and cost effective solutions aimed at both improved efficiency and emissions control. This paper discusses the following two approaches:

- reduction of energy consumption, e.g. by increasing the efficiency of energy conversion and utilization of all fossil fuels, and
- capture and sequestration of CO<sub>2</sub> from fossil fuel combustion

# **OPPORTUNITIES TO INCREASE EFFICIENCY OF ENERGY CONVERSION AND UTILIZATION**

There are large variations in CO<sub>2</sub> emissions per MWh of electricity generated by fossil fuels due to differences in generation efficiency, fuel selection, and plant age. However, there has been a steady decline in average emissions per MWh due to both a gradual switch from carbon-intensive fuels like coal, to low-carbon fuels such as natural gas (Figure 3a) and improvements in energy conversion efficiency (Figure 3b). As illustrated in Figure 3a, in 1997, the Annex II countries emitted 920 kg of CO2/MWh for coal, 583 kg/MWh for oil and 452 kg/MWh for gas.



Figure 3a: CO<sub>2</sub> emissions from Electricity and Heat Generation sector in Annex II countries [2]



Figure 3b: CO<sub>2</sub> emissions rates from various fossil fuel technologies [9]



Fossil fuel power stations traditionally have been designed around steam turbines to convert heat into electricity. Conversion efficiencies of new steam power stations can exceed 40% (on LHV). New supercritical steam boiler designs, involving new materials, allow higher steam temperatures and pressures, enabling efficiencies of close to 50% (LHV). In the long run, further improvements might be expected. The past decade or so has also significant advancements in combined cycle gas turbines (CCGTs). A gas turbine can withstand much higher inlet temperatures than a steam turbine. This factor produces considerable increases in overall efficiency. The latest designs currently under construction can achieve efficiencies of over 60% LHV. All these efficiency improvements correspondingly translate into a reduction of the specific emissions on a per MWh basis. Hence, there is a potential for up to 30% reduction in  $CO_2$  emissions by raising overall efficiency from the 40% level to the 60% level [10].

## **CO<sub>2</sub> CAPTURE AND SEQUESTRATION**

Although substantial reductions in emissions of  $CO_2$  could be achieved by increases in efficiency of energy conversion and utilization, these reductions alone may not be sufficient to achieve atmospheric  $CO_2$  stabilization, should that prove necessary. Efforts are also directed towards the capture and sequestration of  $CO_2$  that comes out of fossil fuel-fired power plants (typically in  $CO_2$  concentrations of 3 to 15% by volume). Sequestration of  $CO_2$ entails the storage or utilization of  $CO_2$  in such a way that it is kept out of the atmosphere. While a long-range strategy for decreasing dependence on fossil fuels is theoretically attractive, short-term major disruptions in our energy infrastructure have major economic consequences. Carbon capture and sequestration may be an effective transitional strategy. ALSTOM is actively evaluating the three main possibilities for  $CO_2$  capture:

- pre-combustion methods (fuel decarbonization)
- combustion in O<sub>2</sub>/CO<sub>2</sub> atmospheres (oxy-fuel firing)
- post-combustion capture methods

#### **Fuel decarbonization**

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 while the latter is subsequently combusted. Different methods exist, i.e., steam reforming, gasification, partial oxidation, etc. The removal of  $CO_2$  in such a gas stream prior to the combustion is often much easier than after combustion due to higher concentration, lower volumetric flow rates and higher pressures. However, both a syngas manufacturing plant and a  $CO_2$  removal and transport infrastructure are required, significantly adding to the total plant capital cost. Further, the utilization of synthesis gas for fuel requires either modifications to currently available gas turbines or the development of new machines or technology for power generation. One of the key issues for this technology is the availability of an economical hydrogen-fired system.

### **Oxy-fuel firing**

The combustion in  $O_2$ /recycled flue gas includes different power generation cycles using pure or enriched oxygen as the oxidant instead of air. A separate  $CO_2$  removal process is avoided and/or minimized with this approach. A substantial energy penalty is incurred with this process due to the large power requirements of producing pure oxygen. This power requirement is in the same range as that for fuel decarbonization.

#### **Post Combustion Capture**

Several different methods to remove  $CO_2$  from a gas stream exist, including absorption by use of amines, different adsorption techniques, use of membranes, etc. These  $CO_2$  capture processes have significant energy requirements, which reduce the power generation plant's efficiency by up to 40% (relative), and net power output up to 40%. Using  $CO_2$  separation methods based on chemical absorption, physical absorption or adsorption, it is possible to recover 85 to 95% of  $CO_2$  in the fuel.  $CO_2$  can also be captured by utilizing solid chemicals that react with the gas in solid form. These chemicals can be removed from the gas stream more easily and with less energy intensity than traditional solution scrubbing techniques. The solids can be regenerated producing a relatively pure  $CO_2$  stream for utilization or sequestration.

### Sequestration

Having captured the  $CO_2$ , it would be necessary to sequester it or put it to use. Utilization of  $CO_2$  to make chemicals would use only a small proportion of the amount that could be captured. Utilization of  $CO_2$  for enhancing oil and natural gas production is promising due to the large quantities of gas required and the potential to create value from the captured  $CO_2$ . Storage of  $CO_2$  could be accomplished in a number of ways including underground storage or in ocean sequestration. In principle,  $CO_2$  can be stored in any gas-tight underground structure that has space or that contains a substance such as water that can be removed. If  $CO_2$  is injected underground, some will dissolve in water and some will form a gaseous phase, which is trapped in the formation. Storage of  $CO_2$  in deep saline reservoirs (estimates range from 400 to 10,000 Gt of  $CO_2$ ) or in the ocean has the greatest potential capacity. However, there are still environmental issues with ocean storage, in particular, that are the subject of considerable study and debate.

Enhanced oil recovery (EOR) is an established use for  $CO_2$ , whereby the gas is injected underground to assist in the recovery of oil. Much of the  $CO_2$  will remain stored in the reservoir. About 33 Mt per year of  $CO_2$  are already used at 74 EOR projects in the USA (most of this  $CO_2$  is extracted from natural reservoirs, but some is captured from natural gas treatment plants and ammonia production). A further 6 Mt per year of  $CO_2$  has been injected as part of a large  $CO_2$ -EOR project in Turkey [11]. A similar approach is used for enhanced gas recovery (EGR). The  $CO_2$  storage capacity of depleted oil and gas fields has been estimated to be up to 920 Gt of  $CO_2$ . Another potential storage medium is unmineable coal.  $CO_2$  can be injected into suitable coal beds where it will be adsorbed onto the coal, locking it up permanently, provided the coal is never mined. Moreover, the gas preferentially displaces methane that exists along with the coal. This methane can be recovered for commercial use, thus increasing world energy supplies, reducing carbon intensity, and reducing the cost of carbon sequestration. So far, there is only one experimental  $CO_2$  have been injected over a three-year period [12].

## CO2 MITIGATION OPTIONS PRESENTLY UNDER STUDY AND DEVELOPMENT

As an industry leader in providing high-efficiency power generation equipment with the most modern technology to utilize fossil fuels with the lowest possible emissions, ALSTOM has recently begun the evaluation and the development of technologies to remove and dispose of carbon dioxide created in power plants. If these options can be found to be technically and economically feasible, they could play a substantial role in limiting greenhouse gas emissions and allow for the continued use of the established fossil fuel infrastructure in an environmentally acceptable manner.

### Gas Turbine Combined Cycle Efficiency

ALSTOM gas turbine combined cycle plants have improved significantly for all areas of performance in the recent years as indicated in Figure 4a. High levels of efficiency are achieved today, both when fully and partially loaded, with a high degree of flexibility during operation. At the same time emissions are substantially reduced and overall levels of investment costs are low.



Figure 4a: Evolution of ALSTOM Power CCGT environmental and efficiency performance



Figure 4b: ALSTOM Power Komoti project in northern Greece (Net Ouptut: 476 MW (2xCCGT13E2), Efficiency: 52.5%)

#### Figures 4a and 4b: Combined cycle gas turbines

Currently about 18% of the world generating capacity is over 30 years old. Much of this capacity is in the form of older, low efficient power plants. Over the next few years, some of this plant capacity will be replaced. To the extent that these power plants will be based on gas, there will be a net reduction of  $CO_2$  emissions in many of the OECD countries. However, recent increases in the price of natural gas in some areas have highlighted the importance of considering all economic aspects of this problem. Of course, as fuel prices increase, the driver for efficiency is stronger. Thus for economical and environmental reasons, the developmental of high efficiency and highly reliability GTCC power systems remains a key.

#### Zero Emission Power Concept for Gas Turbines

Also under investigation is the possibility of developing a gas turbine with oxygen combustion, resulting in a "zero emissions" system. By combusting it in oxygen, methane is transformed into pure  $H_2O$  and  $CO_2$ , without any nitrogen dilution. The water can then be recovered simply by condensation, greatly reducing separation costs, leaving pure  $CO_2$  in the remaining stream. Part of the  $CO_2$  is recycled to the turbine inlet as a diluent for combustion. The rest is compressed for storage.

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). Should such oxygen procurement methods be utilized for the supply of pure oxygen to combustion processes within gas turbine cycles, the net power output and hence the thermal efficiency, will be reduced 20% and 10% respectively. Oxygen production via cryogenic means will also substantially increase the price of electric power, perhaps as much as 50%.

A less energy intensive (and thus more cost effective) proposition being followed is the use of oxygen production membranes to produce pure oxygen from air. These membranes consist of complex crystalline structures, which incorporate oxygen ion vacancies (5 to 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 the 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. 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 selectivity of the membranes is infinite as long as the membrane surface is perfect (i.e., no cracks or pores are present).

Integration of this technology into a power plant can be achieved by various means. A number of such solutions, each of which represents a different cycle characterized by distinct cycle efficiencies (as well as technical challenges), have been studied and compared with existing best available technologies. Preliminary findings indicate that the most efficient and cost effective methodology for deploying the membrane process is to integrate it in a conventional gas turbine. Essentially, this new reactor would combine oxygen-separation, combustion and heat transfer processes to replace the conventional burner in a standard gas turbine power plant, as indicated in Figure 5.

Preliminary evaluations show that the proposed process could potentially:

- achieve 100% reduction of CO<sub>2</sub>
- reduce NO<sub>x</sub> emissions to below 1 ppm
- reduce the cost of  $CO_2$  separation (compared to tail-end capture) by 25-35% within 6 years
- separate CO<sub>2</sub> with only a 2% loss of power plant efficiency, compared with up to a 10% loss when conventional, tail-end methods of CO<sub>2</sub> capture are used



Figure 5: Zero emissions gas turbine-based power generation concept (including an integrated membrane for production of oxygen)

The gas turbine and its auxiliary systems consist of standard equipment. This proposed solution dictates that the major research and development efforts be focused on the new components in the membrane reactor. This approach limits the need for the development of an entirely new cycle - and its associated new equipment - substantially reducing technical and commercial risks.

### **Boiler Steam Power Plant Efficiency**

Since the 1950's, the technology of coal-fired steam power plants has experienced meaningful development driven by market needs for lower cost, more reliable power and improved efficiency. Efficiency improvements have been achieved by operation at higher temperature and pressure steam conditions, and employing improved materials and plant designs. ALSTOM has been at the forefront of developing and deploying advanced steam plants over its history and today is actively engaged in material technology advancement and steam plant design efforts to allow for coal power plants with greater than 50% (LHV) net plant efficiency [13].



Figure 6a: Efficiency Trend of ALSTOM Power steam plants



Figure 6b: ALSTOM Power Elsam project in Denmark (Nordjyllansværket #3) (Net Ouptut: 385 MW, Efficiency (LHV): 47%)

#### Figures 6a and 6b: Steam cycle plants

## Boiler Steam Power Plant with CO2 Capture

ALSTOM has been looking at a number of technologies concerning  $CO_2$  mitigation from boilers steam power plants and has recently teamed with American Electric Power (AEP), ABB Lummus Global Inc., the US DOE NETL, and the Ohio Coal Development Office to conduct a comprehensive study evaluating the technical feasibility and economics of alternate  $CO_2$  capture and sequestration technologies applied to an existing US coal-fired electric generation power plant. This study looked at:

- coal combustion in air, followed by CO<sub>2</sub> separation with Kerr-McGee/ABB Lummus Global's commercial MEA-based absorption/stripping process
- coal combustion with O<sub>2</sub> firing and flue gas recycle
- coal combustion in air with oxygen removal and CO<sub>2</sub> separation by a mixture of primary and tertiary amines

Each of these technologies was evaluated against a baseline case and  $CO_2$  tax options from the standpoints of performance and impacts on power generating cost.

A similar study was conducted for one of TransAlta Ltd.'s pulverized coal boilers in Canada. In this study, ALSTOM teamed also with ABB Lummus Global Inc. to study the technical and economic feasibility of retrofitting one of TransAlta's tangentially coal-fired boilers to operate under  $O_2$ /recycled flue gas for  $CO_2$  sequestration or use in enhanced oil recovery or enhanced gas recovery [15].

In both studies, the oxy-fuel firing approach was similar for the AEP, Conesville, Ohio, and No. 5, plants (Figure 7). The basic concept of the overall system is to replace air with oxygen for combustion in the furnace. In addition, a stream of re-circulated flue gas back to the furnace is required to maintain thermal balance in the existing boiler between the lower furnace region where evaporation takes place and the convective heat transfer surfaces where steam is superheated and reheated to the required temperature level. This arrangement

produces a high carbon dioxide content flue gas which, after leaving the boiler system, is processed to provide high-pressure carbon dioxide liquid product, suitable for use or sequestration.

Based on the current state-of-the-art, the cryogenic method of air separation is deemed to be the most cost effective, commercially available method, in producing the large quantities of oxygen required for a power plant retrofit application. Hence, this method of oxygen production was assumed in the two previous studies. However, multiple trains of an air separation unit would have to be used to produce the oxygen, because these quantities (e.g., 8'100 tons of oxygen a day for the OCDO/DOE/AEP study) are approximately three times larger than the largest operating air separation unit today. Furthermore, these and other studies found that the production of oxygen by cryogenic method is very energy-intensive, requiring approximately 20% of the generator output in auxiliary power. Therefore, ALSTOM has also evaluated membrane-based technologies of producing oxygen, which are being developed by major industrial gas companies [16]. The relative performance and cost benefits of this promising advanced oxygen production technology for  $CO_2$  capture are discussed below.

Another approach to capture  $CO_2$  from a steam power plant is a post combustion furnace amine-based absorption/stripping process (Figure 8). The Kerr-McGee/ABB Lummus Global's MEA-based technology has been proven commercially at various installations. The treated gas from the desulfurization system, after cooling and water removal, is sent to an absorber where it is scrubbed with MEA to recover most of the  $CO_2$ . The scrubbed flue gases are vented to the atmosphere after water washing to minimize MEA losses. Rich amine solution from the absorber is preheated in the solution exchanger against the lean amine solution and then sent to a flash tank. The flashed liquid solution is sent to the stripper and the flashed vapors are combined with the stripper overhead vapors and sent to a stream stripper for regeration. The flash vapors are combined with the stripper overhead vapors and sent to the condenser where water vapor is condensed. Water condensed from the stripper overhead is returned to the system. The lean amine solution leaving the solution exchanger is filtered, cooled and returned to the absorber. This process has been described elsewhere [17].



Figure 7: Simplified gas side process flow diagram for CO<sub>2</sub> separation with oxygen firing



Figure 8: Simplified gas side process flow diagram for CO<sub>2</sub> separation by MEA absorption

### Summary of Boiler Steam Plant CO<sub>2</sub> Capture Performance and Costs

Figures 9 and 10 compare net plant heat rates and  $CO_2$  emissions for several studies. The OCDO/DOE/AEP study shows a significantly greater impact on net plant heat rate for the MEA process than shown elsewhere [18]. A partial explanation for this difference is the higher  $CO_2$  removal (as can be seen in Figure 10). These results show a number of things with respect to the AEP study, particularly:

- Energy requirements and power consumption are high, resulting in significant decrease in overall power plant efficiencies, yielding only 22 to 24% efficiency as compared to 37% for the base case, LHV basis;
- Specific carbon dioxide emissions were reduced from about 0.91 kg/kWh for the base case to 0.05-0.12 kg/kWh for the study cases.



Figure 9: Comparative coal power net plant heat rate results



Figure 10: Comparative coal-fired power plant CO<sub>2</sub> emissions

With respect to oxy-fuel firing, it is seen that producing the oxygen in a ceramic membrane system leads to an improvement in net plant heat rate of more than 20% over the case whereby the cryogenic method is used to produce oxygen (10,501 vs. 13,796 Btu/kWh). Investment costs, currently being developed, will be significant. Previous studies indicate investment costs falling in the 900-1,200  $\$ /kW range for CO<sub>2</sub> capture with the MEA or through oxy-fuel firing, while using the cryogenic method of producing the oxygen. When oxygen is produced via a ceramic membrane, the total investment costs are estimated to range from about 600 to 800  $\$ /kW. These results indicate that considerable costs and energy consumption are involved in retrofitting existing plants for CO<sub>2</sub> capture. Such costs would be economically unsustainable. Additional R&D work is necessary to not only reduce costs and energy consumption of these technologies, but also to develop more economical alternatives.

### THE CHALLENGE AHEAD

There is no single, all-encompassing, technological option for greenhouse gas mitigation; rather, there will be a variety of actions that will be needed. These actions encompass a range of technologies with technical and economic barriers for industrial implementation. These technologies will require field demonstration to confirm practical considerations such as performance, reliability, robustness, environmental impact and economics. Collaborative efforts, with governmental assistance to facilitate the process, are required. Simultaneously, basic R&D is needed leading to the discovery of completely new and innovative methods for dealing with CO<sub>2</sub>.

ALSTOM continues to focus its major R&D investments in the demonstration of cost effective and practical power generation systems aimed at both improved efficiency and emissions control (including capture). Through these principles, ALSTOM is committed to

the continuous improvement of its technology portfolio in order to meet the present and future needs of its customers.

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