WRI-06-R025R

# FINAL REPORT

# DEVELOPMENT OF A NOVEL OXYGEN SUPPLY PROCESS AND ITS INTEGRATION WITH AN OXY-FUEL COAL-FIRED BOILER

**Jointly Sponsored Research Proposal**
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**For**
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**Murray Hill, NJ 07974**

**And**
**U.S. Department of Energy**
**National Energy Technology Laboratory**
**Morgantown, West Virginia**

**By**
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## DISCLAIMER

# ABSTRACT

BOC, the world's second largest industrial gas company, has developed a novel high temperature sorption based technology referred to as CAR (Cyclic Autothermal Recovery) for oxygen production and supply to oxy-fuel boilers with flue gas recycle. This technology is based on sorption and storage of oxygen in a fixed bed containing mixed ionic and electronic conductor materials.

The objective of the proposed work was to construct a CAR PDU that was capable of producing 10-scfm of oxygen, using steam or recycled flue gas as the sweep gas, and install it in the Combustion Test Facility. The unit was designed and fabricated at BOC/The Linde Group, Murray Hill, New Jersey. The unit was then shipped to WRI where the site had been prepared for the unit by installation of air, carbon dioxide, natural gas, nitrogen, computer, electrical and infrastructure systems.

Initial experiments with the PDU consisted of flowing air into both sides of the absorption systems and using the air heaters to ramp up the bed temperatures. The two beds were tested individually to operational temperatures up to 900°C in air. The cycling process was tested where gases are flowed alternatively from the top then bottom of the beds. The PDU unit behaved properly with respect to flow, pressure and heat during tests. The PDU was advanced to the point where oxygen production testing could begin and integration to the combustion test facility could occur.

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# EXECUTIVE SUMMARY


BOC, the world's second largest industrial gas company, has developed a novel high temperature sorption based technology referred to as CAR (Cyclic Autothermal Recovery) for oxygen production and supply to oxy-fuel boilers with flue gas recycle. This technology is based on sorption and storage of oxygen in a fixed bed containing mixed ionic and electronic conductor materials.

The objective of the proposed work was to construct a CAR PDU that was capable of producing 10-scfm of oxygen, using steam or recycled flue gas as the sweep gas, and install it in the Combustion Test Facility. The unit was designed and fabricated at BOC/The Linde Group, Murray Hill, New Jersey. The unit was then shipped to WRI where the site had been prepared for the unit by installation of air, carbon dioxide, natural gas, nitrogen, computer, electrical and infrastructure systems.

Staff from BOC came to WRI to assist in the installation and shakedown of the PDU unit. The ceramic material for the absorption beds was reinstalled. All heaters, flow controllers, pressure control and safety systems were tested for safe operation. The logic control system (PLC) was turned on and communications between the control computer and the PLC were checked. Initial tests included beginning flow of air and carbon dioxide through the flow control systems and the absorption vessels. When flow was established the heaters were slowly brought up in temperature and the thermocouple systems checked for data collection. Within a short time, and after minor alterations and hardware adjustments, all systems were found to be within operational parameters.

Initial experiments with the PDU consisted of flowing air into both sides of the absorption systems and using the air heaters to ramp up the bed temperatures. The two beds were tested individually to operational temperatures up to 900°C in air. The cycling process was tested where gases are flowed alternatively from the top then bottom of the beds. The PDU unit behaved properly with respect to flow, pressure and heat during tests. The PDU was advanced to the point where oxygen production testing could begin and integration to the combustion test facility could occur. Oxy-combustion tests were conducted with the combustion test facility to measure the performance of the unit under a carbon dioxide/oxygen flow at 21% and 27% oxygen. The team received additional funding to continue development of the CAR process under DE-FC26-06NT42478, so the continuation of the JSR project was not pursued and the scope of the JSR project limited.

# INTRODUCTION

Coal-fired power plants of the future will need to incorporate processes that can cost-effectively capture and sequester their $CO_2$ emissions.  One of the more promising options is oxy-combustion with flue gas recycle.  This technique uses oxygen rather than air to combust a fuel, producing a $CO_2$-rich flue gas that can subsequently be sequestered. In this process, the recycled flue gas serves to moderate temperatures, allowing the use of conventional or existing equipment.  The biggest barrier to implementation of oxy-combustion is the cost of producing the oxygen.  The standard method for large-scale oxygen production is the cryogenic air separation process.  Since this process is very capital and energy intensive, there is a need to develop alternate, lower-cost oxygen production technologies.

BOC, the world's second largest industrial gas company, has developed a novel high temperature sorption based technology referred to as CAR (Cyclic Autothermal Recovery) for oxygen production and supply to oxy-fuel boilers with flue gas recycle. This technology is based on sorption and storage of oxygen in a fixed bed containing mixed ionic and electronic conductor materials.

The stored oxygen is then released for use in the boiler by partial pressure reduction using a sweep gas such as hot recycled flue gas or steam.  The process operation is made continuous by operating two beds in a cyclic process; air is passed through one bed to allow sorption and storage of oxygen and steam or hot flue gas is passed through the other to release the stored oxygen and using it in the boiler. One of the key requirements for next stage technology validation is a process development unit (PDU) design, integration with a coal fired boiler and operating the integrated unit to identify and resolve issues.

WRI proposed to use the Combustion Test Facility (CTF) for integrated pilot-scale testing of a CAR process development unit.

## OBJECTIVES

The objectives of the proposed work were to:

- Construct a CAR PDU that is capable of producing 10 scfm oxygen, using steam or recycled flue gas as the sweep gas, and install it in the Combustion Test Facility
- Integrate this pilot-scale CAR unit with the CTF
- Determine operability of the CAR system, when fully integrated with the CTF
- Determine combustion and heat transfer characteristics of the CTF when operated with the CAR system

## FABRICATION

The CAR process development unit (PDU) was designed as a skid mounted system with two additional vertical vessels and associated support equipment located off the skid. The skid contains the programmable logic control (PLC) system, the piping, valves, flow controls, pressure controls, and heater systems. The inlets consist of individual lines for carbon dioxide or flue gas, air, natural gas, steam and nitrogen. Each inlet line has pressure regulators and flow controllers, each operated by the PLC. The nitrogen system is used as a purge gas incase of emergency shutdown. The steam system was added as an alternative sweep gas to carbon dioxide and to act as a rinse cycle between oxygen absorption and emission steps. The inlets link together before entering the electrical gas heaters used to bring the beds up to operational temperatures. Thermocouples are placed at multiple locations after the heaters to monitor heat production and flow. Hot gases flow into the ceramic beds in the vertical vessels that operate as the oxygen absorption hardware. High temperature valves allow the direction of flow through the beds to switch during the absorption/desorption cycle. Gases exiting from the beds pass through heat exchangers and flow measurement devices. An on line gas analyzer is used to monitor composition of gases in the product and waste outlets.

The fabrication of the vessels was contracted out as they were designed as pressure vessels. BOC/The Linde Group in Murray Hill, New Jersey conducted the majority of purchasing and acquisition. The compressors, blowers, air-heating unit, carbon dioxide heating unit and perovskite filled pressure vessels were installed and plumbed. Natural gas was brought to the unit and exit lines attached for nitrogen and the carbon dioxide/oxygen product stream. Electrical power connections were made and heat exchangers assembled. The devices were assembled on skids for relocation. Principal systems were tested to confirm flow and control.

## INSTALLATION AND OPERATION

PDU Installation

The PDU unit of the CAR system was delivered to WRI. The unit was moved into place and all attachments were made for power, computer control, internet access, carbon dioxide, air, nitrogen, natural gas, and vent lines. Initial shakedown showed that additional airflow was required so a second compressor was installed.

PDU Shakedown

Staff from BOC came to WRI to assist in the installation and shakedown of the PDU unit. The ceramic material for the absorption beds was reinstalled. All heaters, flow controllers, pressure control and safety systems were tested for safe operation. The logic control system (PLC) was turned on and communications between the control computer and the PLC were checked. Initial tests included beginning flow of air and carbon dioxide through the flow control systems and the absorption vessels. When flow was established the heaters were slowly brought up in temperature and the thermocouple systems checked for data collection. Within a short time, and after minor alterations and hardware adjustments, all systems were found to be within operational parameters. Eventually computer access on line was established so that BOC staff could monitor the unit remotely.

PDU Testing

The oxygen is separated from the air stream using a perovskite ceramic material at high temperature (800-900 $^{o}$C). The unit contains two separate beds that are cycled to deliver the oxygen flow (one bed is adsorbing the oxygen while the other is desorbing). The oxygen is desorbed from the catalyst by a partial pressure swing where a gas containing no oxygen is introduced to the bed; $CO_2$ is currently being used for this purpose. Cycle times are being varied to determine the most efficient operational parameters, but will likely fall in the 30-second to 1-minute range. During a typical operation, the process parameters are as follows:

**Table 1. Typical Process Parameters**

| **Process Parameter** | **Typical Range** |
|---|---|
| Inlet Air Flow | 45-70 SCFM |
| Inlet $CO_2$ Flow | 40-50 SCFM |
| Air Heater Outlet Temperature | 700 $^{o}$C |
| $CO_2$ Heater Outlet Temperature | 575 $^{o}$C |
| Methane Flow for Warm-Up | 1.5 SCFM per bed |
| Methane Flow to Maintain Temperature | 0.5 SCFM per bed |
| Cycle Time | 30-60 seconds per side |

Multiple temperatures are monitored in the catalytic bed. These are spatially placed to give an accurate representation of the bulk temperatures in the ceramic bed. The thermocouple locations are as follows (these locations will be used to show the temperature profiles during normal operation).

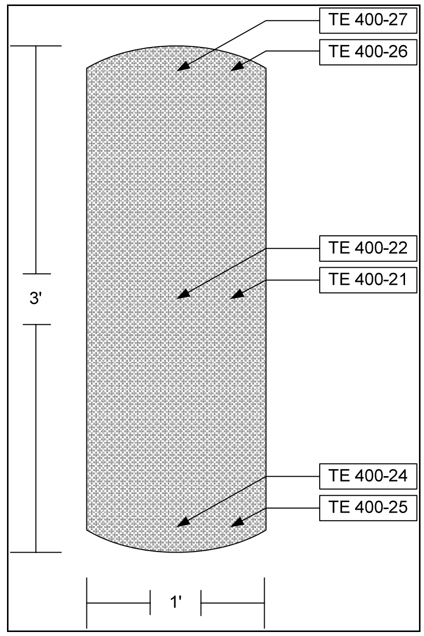



**Figure 1. Ceramic Bed Thermocouple Location**

The initial phase of startup involves heating the ceramic bed to an adequate temperature, to burn a mixture of sub-LEL methane in air. This is achieved using an electric flow-through air heater. A bulk temperature of about 400 $^{o}$C must be reached in the beds to meet this requirement. Figure 2 shows a typical time-temperature profile for this phase of startup.

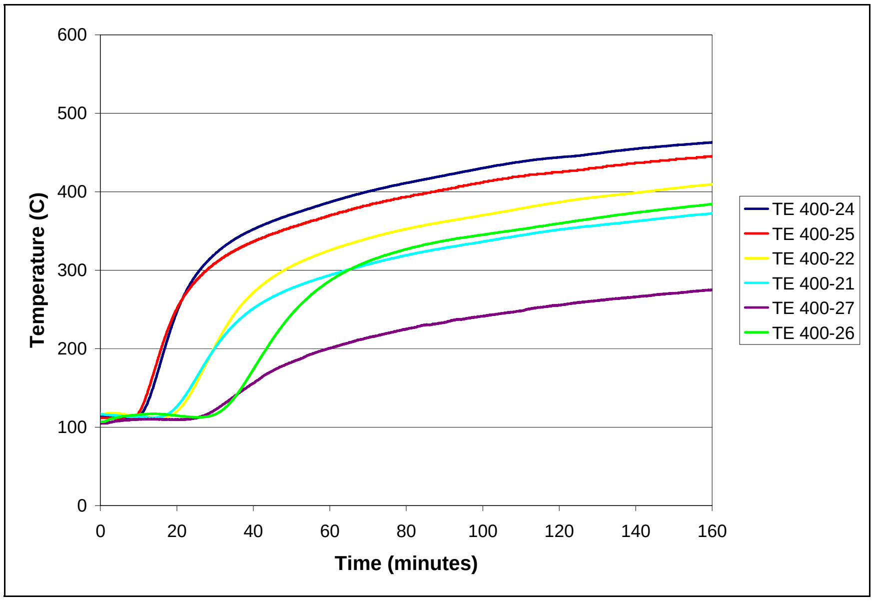



**Figure 2. Pre-Methane Warm up Temperature Profile**

Once the ceramic bed reaches adequate temperatures, methane is introduced at low concentration (2-3% by volume) to heat the bed up to operational temperatures. Although this concentration of methane is less than that required for normal combustion, the bed material has some catalytic ability for combustion. Temperatures of 800-900 $^{o}$C must be reached in the bed to maintain proper temperatures when cycling is started. Figure 3 shows a typical time-temperature profile for the ceramic bed under methane heating.

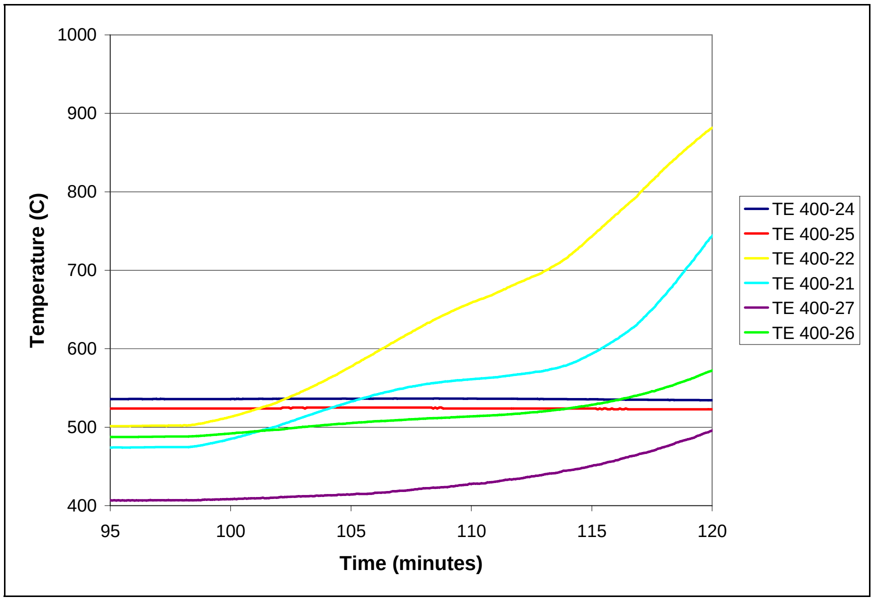



**Figure 3. Methane Warm up Temperature Profile**

After the ceramic bed reaches the proper temperatures, cycling is initiated. Air is introduced to one bed flowing from bottom-to-top, while $CO_2$ is introduced to the other flowing top-to-bottom. This pattern is cycled between the beds at a rate of 30 to 60 seconds. Methane flow is maintained, but the concentration is adjusted to hold the average bed temperature steady. Figure 4 shows a typical temperature profile for a cycling bed, while Figure 5 shows the system oxygen output.

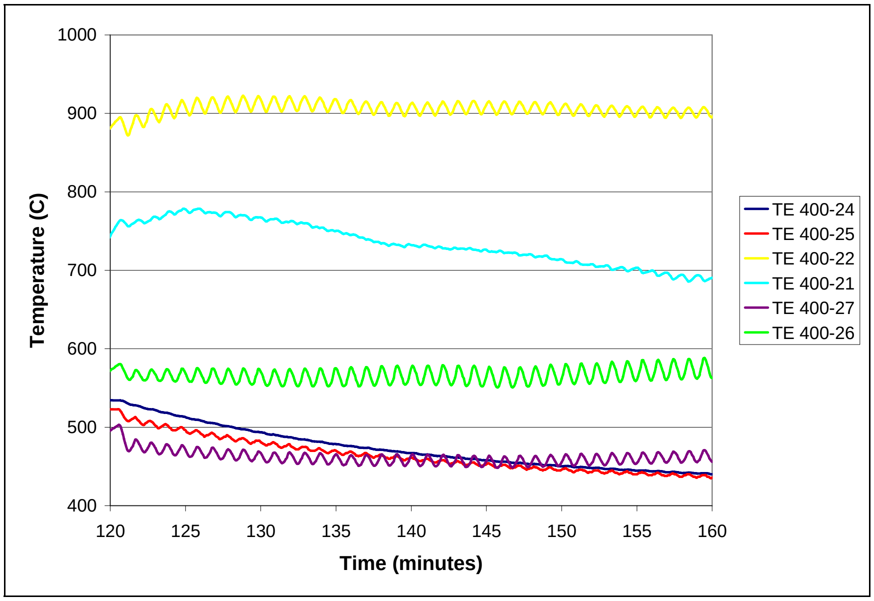



**Figure 4. Cycling Bed Temperature Profile**

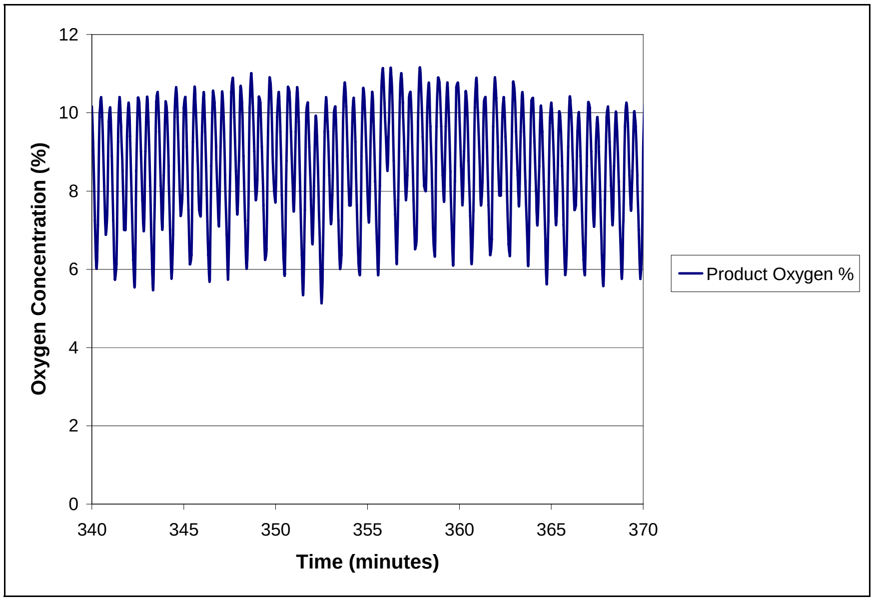



**Figure 5. Cycling Bed Oxygen Production**

In preliminary tests, the system has produced about 11% oxygen in a 40-50 SCFM $CO_2$ stream. Average production of about 8.5% corresponds to approximately 5 cfm of oxygen. This concentration is affected by a number of conditions, many of which have yet to be optimized. Merely decreasing the carbon dioxide flow will increase oxygen concentration, although the net oxygen production by weight would remain the same. Conditions remaining to optimize include carbon dioxide flow rate, bed temperature, bed temperature uniformity, ceramic volume, ceramic material absorption capability, cycle times, and methane concentration. The CAR PDU will be used to test all of these performance variables before moving to the commercial scale unit.

The PDU was advanced to the point where integration to the combustion test facility could occur.

Oxy-combustion Testing

Oxy-combustion tests were conducted with the combustion test facility to measure performance of the unit under a carbon dioxide/oxygen flow at 21% and 27% oxygen. Flow rates were adjusted during these tests to keep the total mass flow constant regardless of the coal or air/oxy condition. Those tests were very successful and gave heating and combustion data that will be used during the CAR PDU/CTF integration. Three different coals were used for this testing on the combustion test facility, a bituminous coal, a sub-bituminous coal and a, lignite. Carbon dioxide and oxygen for these tests came from dewars simulating eventual operation during integration with the CAR PDU. The data from these tests can be found in Appendix D. The conclusions drawn from these preliminary tests are as follows:

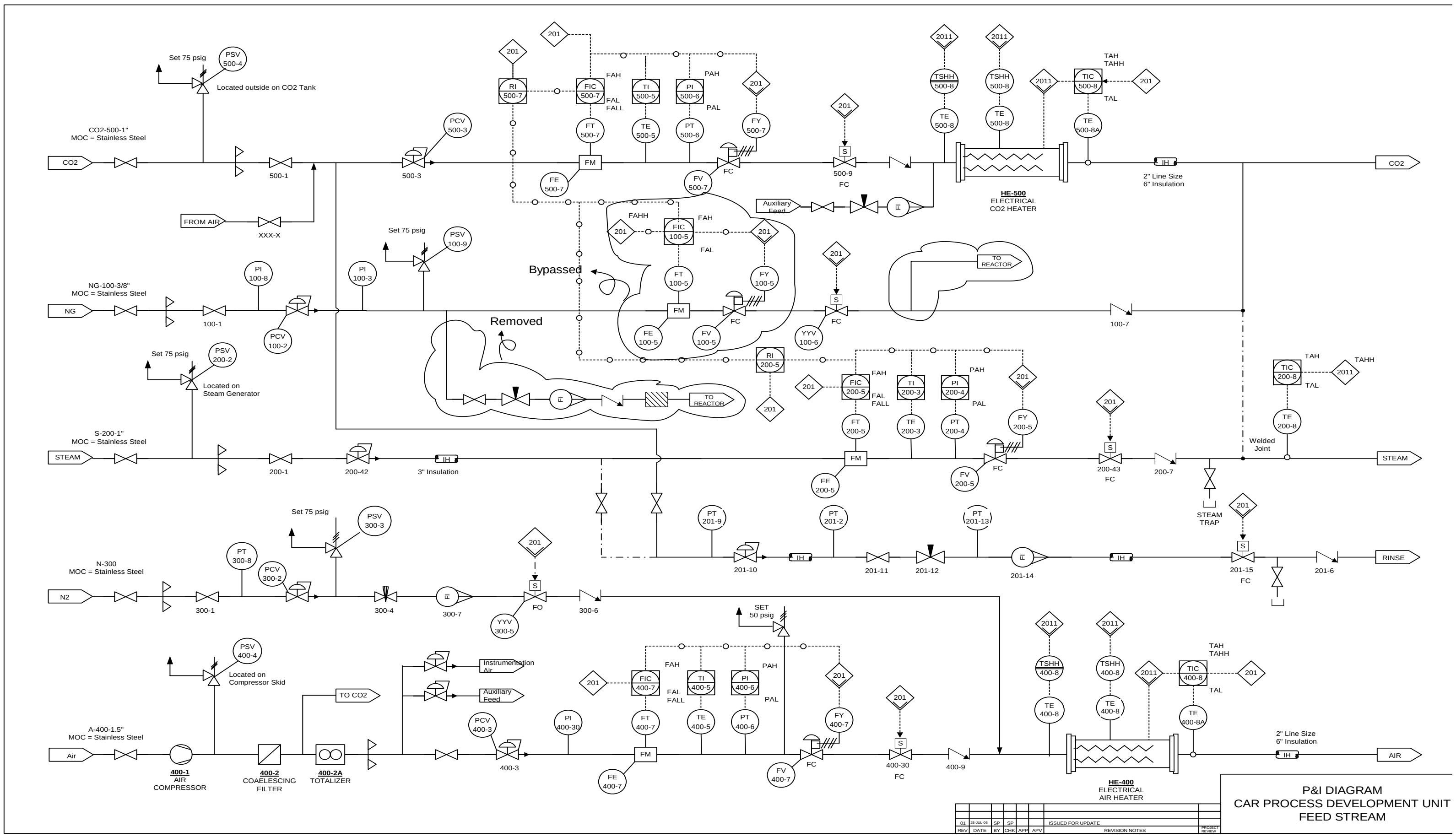
- The 21% oxygen/carbon dioxide mixture did not match the thermal performance of air-blown operation leading to lower overall temperatures throughout the furnace. The 27% oxygen/carbon dioxide mixture did very closely match the thermal properties of the furnace during operation during tests and as predicted by modeling.

- Most pollutant levels were reduced during oxy-combustion operation under 27% oxygen including $SO_2$, $NO_x$ and mercury species.

# CONCLUSIONS

- The CAR PDU was designed and fabricated at the BOC/The Linde Group facilities in New Jersey.
- Preliminary tests were conducted to confirm proper performance of flow, pressure and control equipment.
- The CAR PDU was shipped to WRI site in Laramie, Wyoming.
- The PDU was installed at the site with all inlet, outlet, electrical and computer connections.
- Experiments were conducted to shake down the unit to confirm the operational conditions.
- A design was produced to integrate the CAR PDU with the combustion test facility for demonstration of the oxy-combustion benefit for coal utilization.
- It is always the goal of any JSR project to further demonstration under other funding. The team received additional funding to continue development of the CAR process under DE-FC26-06NT42478, so the continuation of the JSR project was not pursued and the scope of the JSR project limited.

**APPENDIX A**
**PHOTOGRAPHS**


P&I DIAGRAM
CAR PROCESS DEVELOPMENT UNIT
FEED STREAM
HE-500
ELECTRICAL
CO2 HEATER
HE-400
ELECTRICAL
AIR HEATER
400-1
AIR
COMPRESSOR
400-2
COAELESCING
FILTER
400-2A
TOTALIZER
Bypassed
Removed

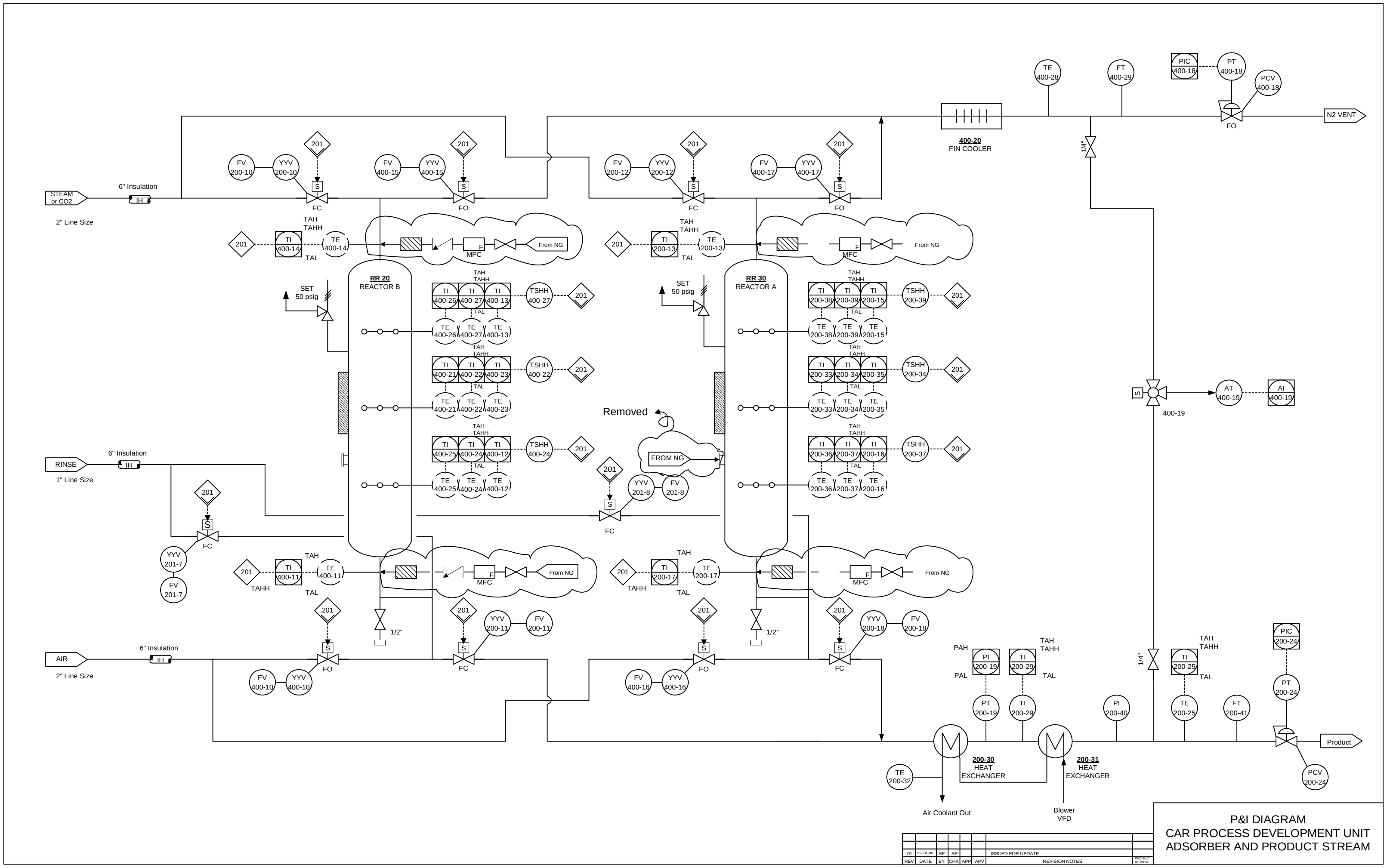



**Figure 6. P and ID Design Diagram for the CAR PDU**

**Figure 7. CAR Heat Exchangers Under Construction at BOC**

**Figure 8. CAR Vent Piping Under Construction at BOC**

**Figure 9. CAR PLC Controls Under Construction at BOC**

**Figure 10. CAR High Temperature Valving Under Construction at BOC**


**Figure 11. CAR Vessels in Place at BOC**

**Figure 12. CAR PDU Vessels Crated for Shipment to WRI**

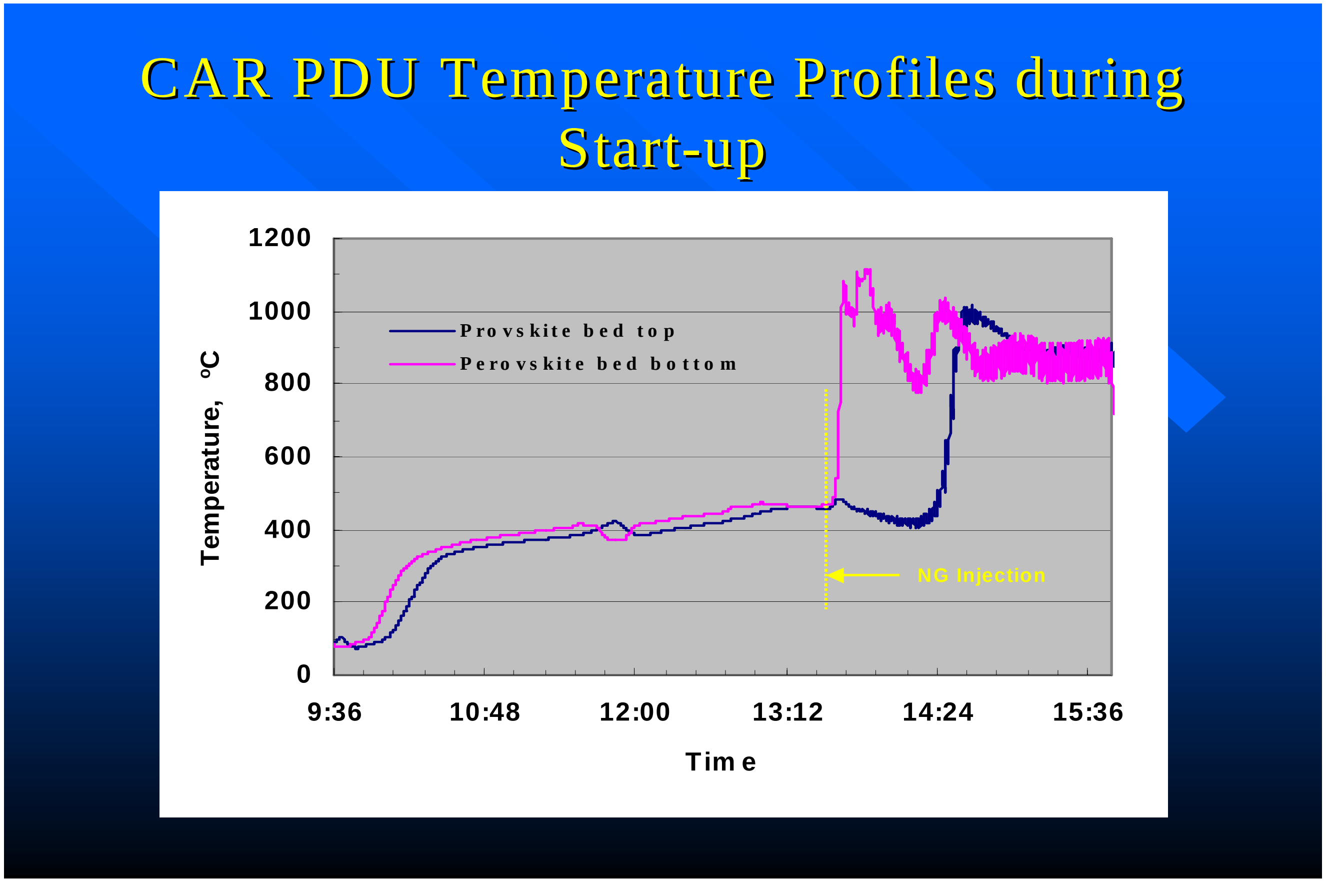
**Figure 13. Installation of Carbon Dioxide Unit at WRI**


**Figure 14. CAR PDU in Place at WRI**


**Figure 15. Compressors and Carbon Dioxide Unit at WRI**

**APPENDIX B**
**DATA**

**Table 2. CAR PDU Temperature Profiles During Start-up**



**APPENDIX C**
**PUBLICATION**

## DEVELOPMENT OF A HIGH TEMPERATURE OXYGEN GENERATION PROCESS AND ITS APPLICATION TO OXYCOMBUSTION POWER PLANTS WITH CARBON DIOXIDE CAPTURE

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### *Abstract*

Oxycombustion is one of the promising options for power generation with carbon dioxide capture. In the oxy-combustion based power plant, oxygen rather than air is used to combust a fuel, producing a $CO_2$-rich flue gas that can subsequently be captured at relatively low-cost and sequestered. The purpose of flue gas recycle is to dilute the oxygen, moderating temperatures and allowing the use of conventional or existing equipment. One of the key barriers to implementation of oxy- combustion, however, is the cost of producing the oxygen. Significant reduction in the cost of oxygen compared to current best cryogenic technology is a key requirement to making the oxy-combustion power plant a viable future option when carbon dioxide capture becomes a requirement. In this paper, we present recent progress made in the development of a high temperature oxygen sorption based technology termed CAR (Ceramic Autothermal Recovery) and its application in an oxyfuel based power plant.

The CAR technology is based on sorption and storage of oxygen at high temperatures (~ 600-800ºC) in a fixed bed containing mixed ionic and electronic conductor materials. The stored oxygen is then released for use in the boiler by partial pressure reduction using a sweep gas such as hot recycled flue gas, steam or an admixture of the two. The process operation is made continuous by operating two (or multiple) beds in a cyclic process; air is passed through one bed to allow sorption and storage of oxygen and steam or hot flue gas is passed through the other to release the stored oxygen and using it in the boiler.

In this paper, we present a design, engineering and economic evaluation of the CAR technology and its integration in a 700 MW pulverized coal oxyfuel power plant. The key process parameters affecting the economics and a parametric sensitivity analysis are presented. Design of a CAR process development unit and planned testing in conjunction with a pilot-scale pulverized coal oxyfuel combustion unit is also discussed.

## 1. Introduction

It is widely accepted that global climate change is due, in large part, to the emissions of greenhouse gases such as $CO_2$. Since fossil fuel will remain the primary energy source for some time, coal-fired power plants of the future will need to incorporate processes that can cost-effectively capture and sequester their $CO_2$ emissions.

The three leading $CO_2$ capture options for coal-fired power plants include: (1) post-combustion $CO_2$ scrubbing, (2) oxycombustion, and (3) gasification with pre-combustion de-carbonization. In post-combustion $CO_2$ scrubbing, a sorbent is used to remove $CO_2$ from the flue gas. The low partial pressure of $CO_2$ in the flue gas necessitates the use of chemical sorbents such as methyl ethyl amine (MEA), which has to be regenerated. In oxycombustion, the combustion air is replaced with a mixture of oxygen and recycled flue gas to produce a $CO_2$-rich flue gas. The recirculated flue gas serves to moderate temperatures in the boiler and maintain heat transfer characteristics. In gasification with pre-combustion de-carbonization, coal is first gasified to produce synthesis gas. This synthesis gas is then converted to a $H_2/CO_2$ mixture in one or more water-gas shift reactors. $CO_2$ is removed from this mixture and the hydrogen is used to generate power in a fuel cell and/or gas turbine system.

In terms of compliance to the Kyoto protocol and regulatory requirements on $CO_2$ emissions going forward, Europe has been leading the charge. Vattenfall, a leading European utility expects that European targets to reduce greenhouse gas emissions will become “quite ambitious” in the coming years and that the price of carbon trading certificates will rise significantly. For coal power to have a future under such circumstances, power companies must invest in $CO_2$ emissions reduction technologies. Vattenfall has announced its plans to build a low carbon coal-fired power plant incorporating the oxy-combustion process at Schwarze Pumpe, Germany. Construction of this 40 Million Euro plant is expected to begin in 2006, and the plant could become operational in 2008.

Simbeck [1] compared the above three $CO_2$ capture technologies when applied to an existing 292 MW pulverized coal-fired power plant. He concluded that oxycombustion and gasification are more economically favorable than post-combustion $CO_2$ scrubbing. Nsakala et al. [2] also examined the technical and economic feasibility of $CO_2$ capture on an existing US coal-fired power plant, and evaluated AEP’s 450 MW Conesville, OH plant. This study also found that oxyfuel combustion with flue gas recycle was more economically favorable than $CO_2$ scrubbing. Although pre-combustion de-carbonization is an attractive option, it is primarily only suited for new plants. On the other hand, oxy-combustion is an ideal retrofit option for existing coal-fired power plants.

In each of the aforementioned studies, the oxygen source was assumed to be a cryogenic Air Separation Unit (ASU). Cryogenic air separation is a highly energy- and capital-intensive process. For oxy-combustion to be economically attractive, the cost of oxygen needs to be reduced substantially from current levels. However, cryogenic air separation is a mature technology and only limited improvements can be expected in the coming years. Oxygen Transport Membranes (OTMs) have been studied in great depth over the past decade and have been conceived as potentially a step-change technology in oxygen production. However, significant technical challenges remain, preventing this technology from becoming a commercially viable solution for economical oxygen production, at least in the near future. Hence there is a need for alternate, low-cost oxygen production technologies.

## 2. The BOC CAR Process

The technology being discussed here is BOC's CAR oxygen production process. BOC, the world's second largest industrial gas company, has developed a novel high-temperature sorption-based technology referred to as CAR (Ceramic Autothermal Recovery) for oxygen production and supply to oxyfuel boilers with flue gas recycle. The process utilizes the oxygen storage capacity of Perovskite materials at high temperatures, and involves cyclic operation with traditional fixed bed vessels containing the material in the form of extrudates [3]. This process consists of two main steps: (1) oxygen sorption and (2) oxygen release. In the air step , air is passed through one bed to allow sorption and storage of oxygen, while in the oxygen purge step, a sweep gas such as flue gas or steam is passed through the other bed to release the stored oxygen. The process operation is made continuous by operating two beds in a cyclic process. The two steps are carried out counter-currently in order to achieve higher oxygen concentrations in the product mixture as well as to effectively recover the heat in the gas streams leaving the bed. Since oxygen sorption on Perovskite is exothermic while oxygen release is endothermic, once initiated the process operates autothermally with little or no heat input. Another process parameter is the rinse step. This is required to remove nitrogen present in the bed voids at the end of the oxygen sorption step. During this step, steam is passed through the bed to flush out nitrogen prior to the injection of the sweep gas for the oxygen release step. To prevent an interruption in oxygen flow, a buffer tank may be installed between the CAR unit and the point of use.

An important feature of the CAR process, which makes it ideally suited for oxycombustion with flue gas recycle, is that it can be tailored to produce low-pressure oxygen at the concentration required for combustion by using recycled flue gas as the sweep gas. Figure 1 shows the specific case of how a CAR unit would be integrated with a pulverized coal-fired utility boiler to produce a $CO_2$-rich flue gas.

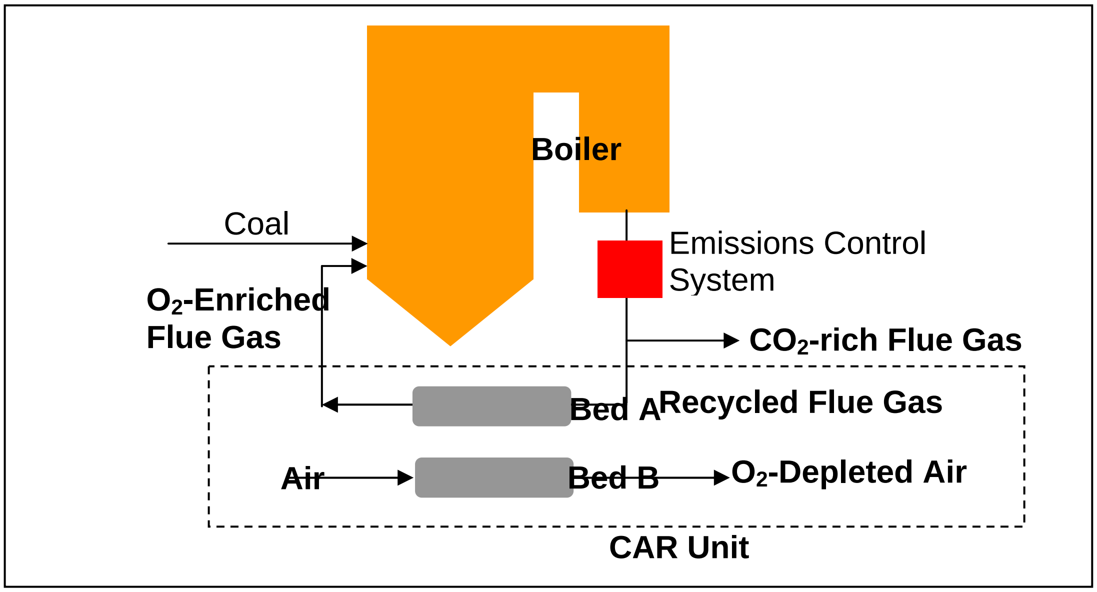


***Figure 1. Schematic of CAR unit integrated with coal-fired boiler***

An alternative oxygen production technology is the aforementioned Oxygen Transport Membrane (OTM) concept. This technology is elegant in principle, but faces major challenges with respect to the manufacture and stability of the membranes, and the scale-up and design of large plants. Specifically, very specialized fabrication and assembly techniques are required to maintain integrity and sealing, and to prevent the formation of pinholes and cracks. Also, the pressure differential across the membrane results in stresses and mechanical instability.

The CAR process, on the other hand, utilizes conventional sorbent and reactor configurations that are easy to fabricate and readily available. Because the CAR sorbent is alternately regenerated to restore oxidation state, there are no continuous stress related issues. The CAR process utilizes internal heat-recovery elements, enabling the use of stainless steel heat exchangers, while special metallurgy is required for the external OTM heat recovery elements. In addition, scale-up is challenging for OTM modules, while conventional scale-up methods can be applied to the CAR process. Also, there is very limited industrial experience with high-temperature membrane modules, but significant industrial experience in operating large cyclic systems such as Pressure Swing Adsorption (PSA) units.

## 3. Design and Engineering Study of CAR Process

The goal of this study was to determine the technical and economical feasibility of using the CAR technology for oxygen supply to a oxy-combustion based lignite fired powerplant. The specific objectives were to determine the net plant efficiency, the capital investment costs and the cost of electricity of the overall plant. In this study, the 700MW Lippendorf power plant near Leipzig, Germany was used as a basis. This power plant had also been used in a previous study of oxy-combustion with oxygen supply from a cryogenic air separation unit [4,5].

A simulation of the Lippendorf plant with oxy-combustion based on cryogenic air separation was used as the reference case [6] for the process simulations of the oxyfuel cycle with the CAR process. Data for this reference case are given in Table 1.

***Table 1. Data for Lippendorf Reference Case [6]***

| | |
|---|---|
| Fuel flow [kg/s] | 196.8 |
| Thermal input [$MW_{th}$] | 2065.6 |
| Gross power output [MW] | 876.8 |
| $O_2$ flow [kg/s] | 180.0 |
| Air compression for cryogenic ASU [MW] | -148.9 |
| $CO_2$ compression [MW] | -66.2 |
| Net power Gate Cycle [MW] | 662.6 |
| Feedwater preheating [MW] | 16.3 |
| Air fans [MW] | 2.9 |
| Steam turbine driven $CO_2$/Air compressors [MW] | 5.2 |
| Total net power [MW] | 687.0 |
| | |
| | |
| Net efficiency [%] | 33.3 |

**3.1 CAR process options**

Operation of the CAR process is based on swings in the oxygen partial pressure. The partial pressure of oxygen is lowered during the purge step compared to that in the air step and this provides the necessary driving force for oxygen desorption. Therefore, a purge gas containing little or no oxygen is required. Two basic options for oxy-combustion are available depending on the purge gas used. For integration with power plants, the purge gas could be either recycled flue gas or low pressure superheated steam. In terms of the overall performance of the CAR system, either purge gas can give high O2 recoveries and comparable O2 enrichment levels. The process operating conditions in the two cases are also reasonably similar in terms of the air to purge ratio and the pressure differential between the air and purge steps. The selection of the purge medium must therefore be made on the basis of availability, cost and other benefits, which may be associated with the integrated scheme.

**3.2 Process flow diagram (PFD) and pressure balance**

A generic process flow diagram of the CAR system is shown in Figure 2. The system mainly consists of the adsorber vessels, valve and piping module, buffer tank for product to smooth out flow/concentration fluctuations, heat exchangers and an air compressor. While there may be multiple modules depending on the required production rate, the PFD shown in Figure 2 is useful to establish pressure levels at various locations in the CAR system and these form a basis for the material and heat balance calculations.

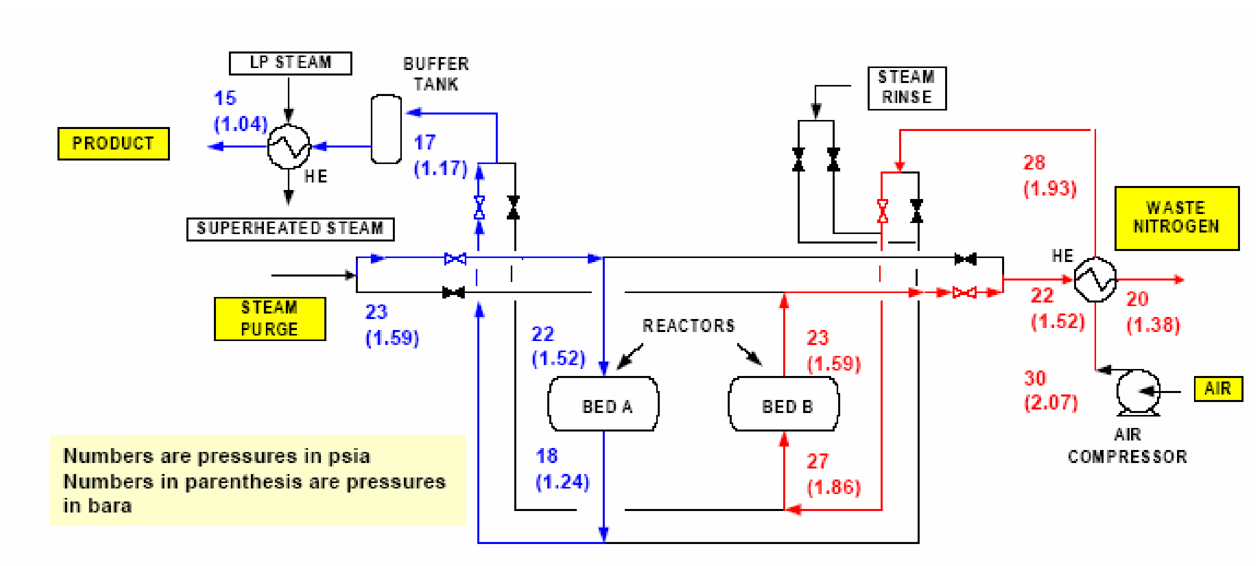


***Figure 2. CAR system process flow diagram with pressure balance***

Figure 2 shows Bed B on the air step (red line) and Bed A on the purge step (blue line). Air flows from the bottom of the bed to the top while the steam flows from top of the bed to the bottom of the bed in counter-current fashion.

### *3.3 CAR System Design Philosophy*

The CAR system design philosophy is based on providing efficient heat recovery and minimizing impact of high temperatures on equipment metallurgy and reliability. In general it is thought prudent to retain the bulk of the heat inside the CAR beds. This is achieved by placing the sorption material layer between inert layers filled with ceramic material. This not only enables efficient regenerative heat exchange but also helps in minimizing bed voids and hence the steam rinse requirement. Based on input from valve vendors, a general guideline was developed that the streams entering or leaving the CAR beds in a large scale plant should not be greater than 250-300$^{o}$ C. The reliability of switch over valves is critical for a cyclic process like CAR in which valves control the flow directions and are required to move from open to closed positions or vice versa approximately every 30 sec. It is also a requirement of the process that the valves move fairly quickly with target time being ~2 sec to move from fully open to fully close position. It was therefore decided to restrict the valve size and line size to 24”.

### *3.4 Cycle Selection*

Selection of CAR cycle is also based on the cyclic nature of this process. Since an additional step of steam rinse is necessary to remove void nitrogen, it becomes necessary to interrupt either the air flow or the steam purge flow. While interrupting steam purge flow means that the airflow can be continuous, such a cycle would interrupt production time for 5 sec. A buffer tank would then be necessary for the product to enable supply of the product during non-production time. A simple calculation showed that it would require an excessively large volume of buffer to store the product for 5 sec. It was therefore decided to adopt a continuous purge cycle so that the product can be produced continuously and thus eliminate the need for large buffer volume. The penalty for such a cycle is that the airflow is now interrupted and some compressed air will be lost during this period. In a multiple train system, we have investigated and identified options to minimize or eliminate air flow fluctuations and compressor energy loss.

### *3.5 Process Scale-up*

A 10-bed CAR cycle was proposed to provide 180 kg/sec of oxygen. The adsorber beds are horizontal with 2.5m ID and 25.6m Tan-Tan (?) length. A sketch of the vessel cross section is shown in Figure 3. At any given time 5 out of 10 beds are on air step, while the other 5 are on steam purge step. As can be seen in Figure 4, the steam purge is continuous while the air step has an idle time of 5 sec during which the steam rinse step is carried out.

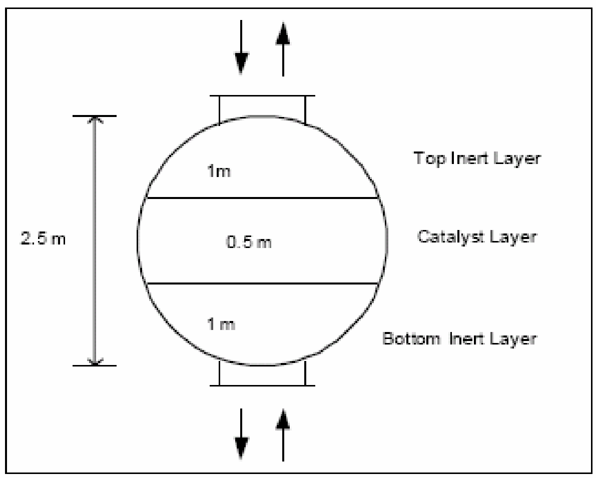


**Figure 3. Adsorber cross-section**

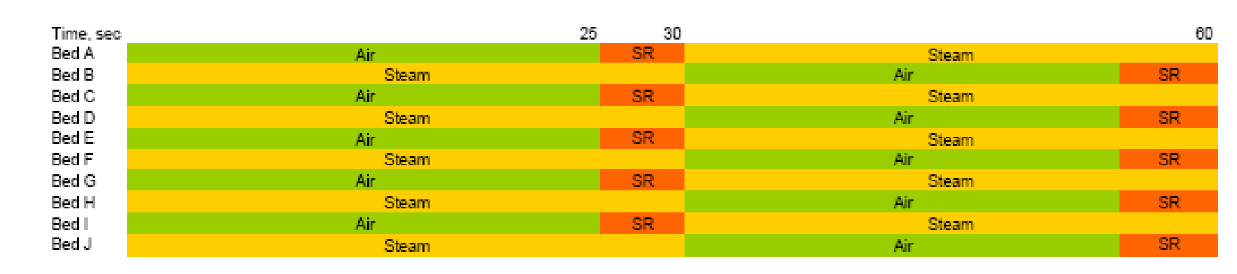


**Figure 4. CAR process cycle**

The cycle shown in Figure 4 is considered the basic cycle. A number of variations are possible to make it semi-continuous to minimize the impact of the 5 sec idle time. Since the valve and line sizes here are large (24"), and anticipated valve moving time from fully closed to fully open is about 2 sec, a control strategy based on pre-opening and pre-closing the valves may minimize the air loss during the idle period. It is also possible to design the cycle for continuous operation of all three steps, for example, 4 beds on air step, 1 bed on steam rinse and 5 beds on steam purge steps. Such cycles, while increasing the capital cost, will completely eliminate the idle step.

A simplified CAR system PFD with 10 beds is shown in Figure 5.

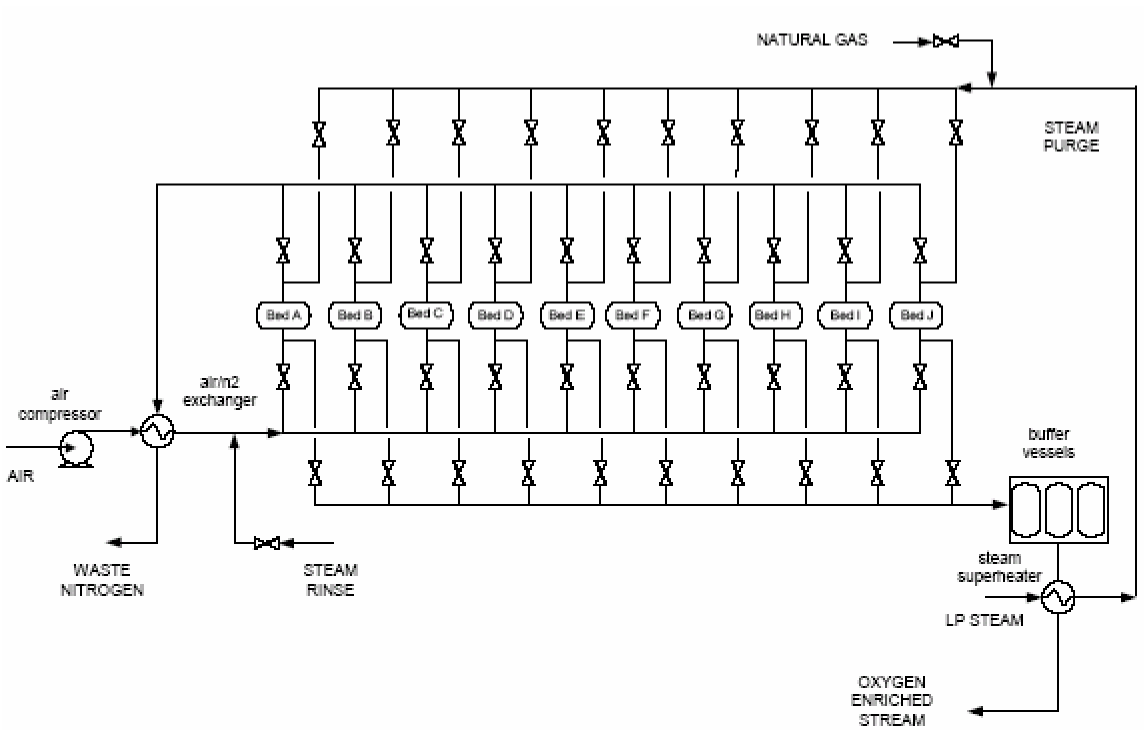


***Figure 5. 10-bed CAR system***

Figure 5 shows buffer vessels for the product stream. As discussed earlier, the product flow is continuous. However, as with any adsorption/desorption system, there may be some variation in the product composition and flow. The main purpose of the buffer vessels is to smooth out any fluctuations in product flow and/or composition during the cycle.

3.6 Equipment Selection

The above 10-bed system was further modularized into 5 identical trains. Each train consists of 2 adsorber vessels with one on air step and the other on steam purge step, one air compressor and the heat exchangers. Based on a quote received from the heat exchanger vendor, both exchangers i.e. the air/nitrogen exchanger and the steam superheater would actually consist of 3 parallel units.

A schematic of 1 train is shown in Figure 6.

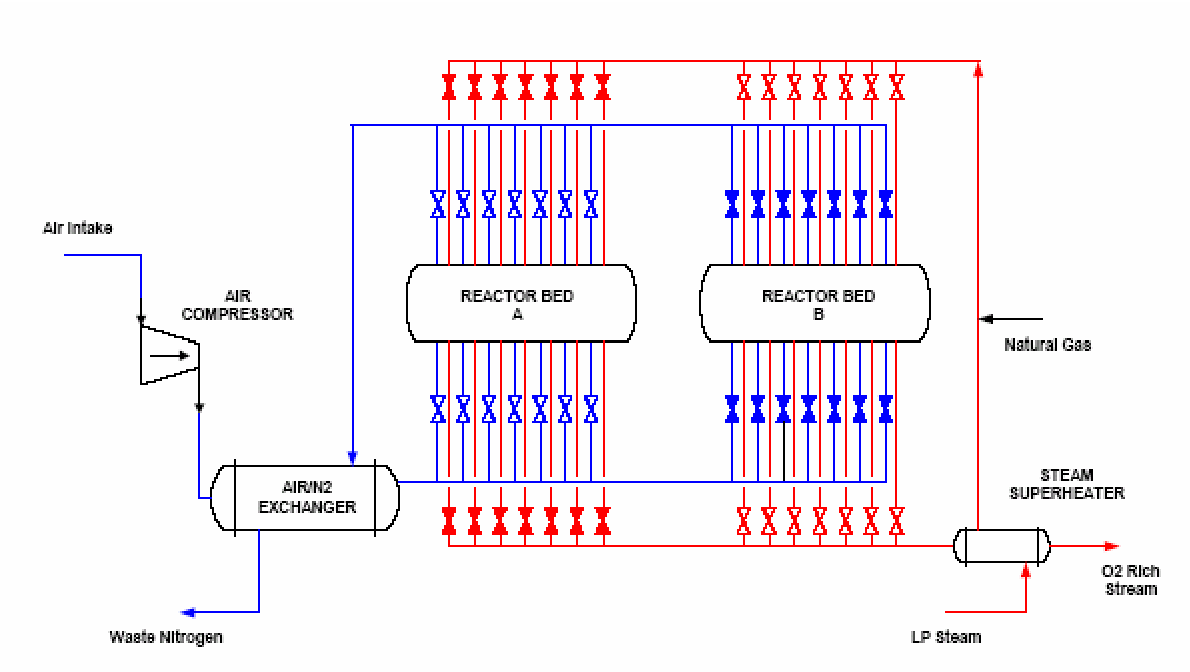


***Figure 6. CAR schematic showing 1 of 5 trains***

### *3.7 Integration of CAR with Power Plant*

In the study, purge steam was extracted at 1.6 bar from the Low Pressure (LP) steam turbine. In practice, this will require one of the Lippendorf LP turbines being rebuilt as a back-pressure turbine and a reduction in the size of the vacuum condenser. Extracted at 1.6 bar, the steam is slightly superheated, and final superheating to 210°C takes place in a superheater that is integrated with the CAR process. A simplified sketch of the process is shown in Figure 7 and some performance data are given in Table 2.

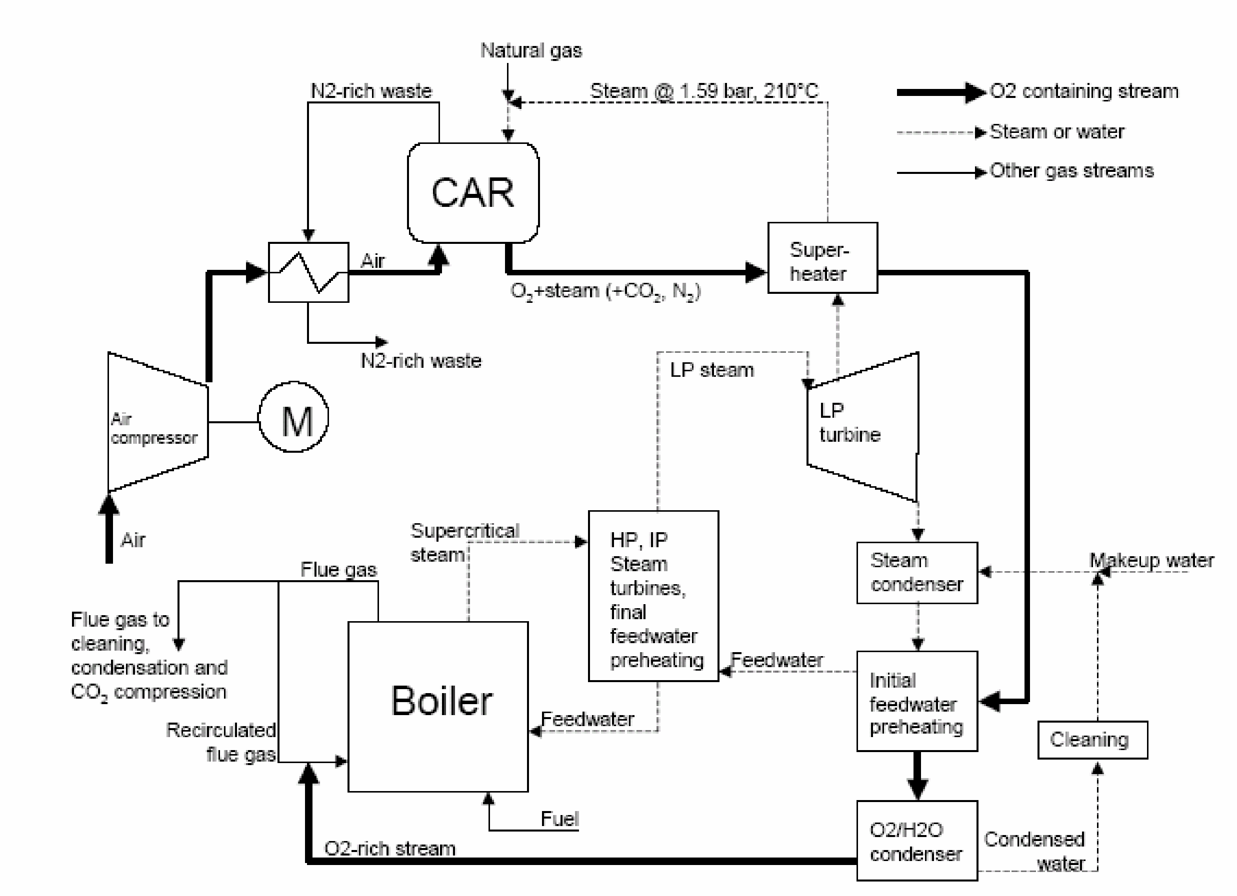


***Figure 7. Schematic showing integration of CAR with power plant***

***Table 2. CAR integration with Lippendorf power plant***

| | |
|---|---|
| CAR steam extraction pressure | 1.6 bar |
| CAR steam extraction temperature | 163.1°C |
| $O_2$/$H_2O$ stream temperature after CAR superheater | 208.2°C |
| $O_2$/$H_2O$ stream temperature after feedwater preheater | 92.2°C |
| Additional water cooling requirement | 502.8 MW |
| Condenser cooling requirement | 613.2 MW |
| Makeup water | 12.3 kg/s[1] |
| HP steam mass flow | 692.1 kg/s |
| Air compression power | 67.6 MW |
| $CO_2$compression power | 63.4 MW |
| Net power output[2] | 726.0 MW |
| Natural gas fuel | 65.3 $MW_{th}$ |
| Lignite fuel | 2064.7 $MW_{th}$ |
| Plant efficiency | 34.0 % |

The steam/oxygen molar ratio used in the study was 1.74. It became clear from the results of the study that this leads to significant steam consumption. A parameter variation was made in the simulations to illustrate the impact of the air/steam ratio on cycle performance. The results are shown in Table 3.

***Table 3. Effect of steam consumption on plant efficiency***

| Air/steam molar ratio | Steam to CAR [kg/s] | Plant Efficiency [% of Reference] |
|---|---|---|
| **1.74** | **297.08** | **100** |
| 2.11 | 250 | 103.1 |
| 2.66 | 200 | 106.2 |
| 3.60 | 150 | 109.7 |

Table 3 shows that for this power cycle, every 50 kg/s (15%) reduction in steam consumption corresponds to a 3% increase in plant efficiency, which is about one percentage point in efficiency improvement.

**4. Economic Analysis Relative**

A comparative cost assessment was made between an oxy-combustion plant with a cryogenic ASU and a CAR plant for oxygen production. Since the CAR process produces an argon free stream, the cryogenic ASU is assumed to be a high-purity oxygen production plant (99% purity).

In this evaluation, preliminary capital cost estimates were generated for all of the equipment components as well as for engineering and installation.

Figure 8a shows a comparison of the power consumption and capital costs of the CAR-based oxy-combustion plant with a cryogenic ASU based oxy-fuel plant. For the cryogenic ASU case, the primary power consumption goes to the ASU air compressors. The power required by the CAR process consists of power required for the air blowers and power required to generate the low pressure steam. The total power consumption of the CAR plant is about 74% of that of the cryogenic air separation plant. Our current assessment of capital costs indicate a capital cost reduction for the CAR process of over 50% compared to the cryogenic ASU. However, some additional capital is required in the oxy-fuel plant to support the steam integration. Overall, the capital cost savings potential is still very significant

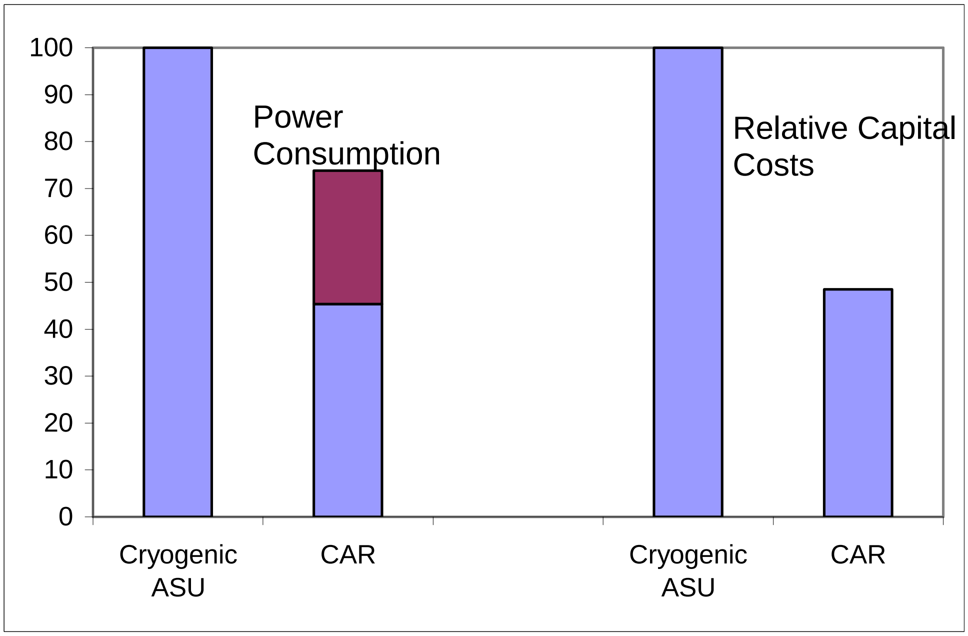


**Figure 8a. Power consumption and capital costs of CAR plant relative to cryogenic ASU**

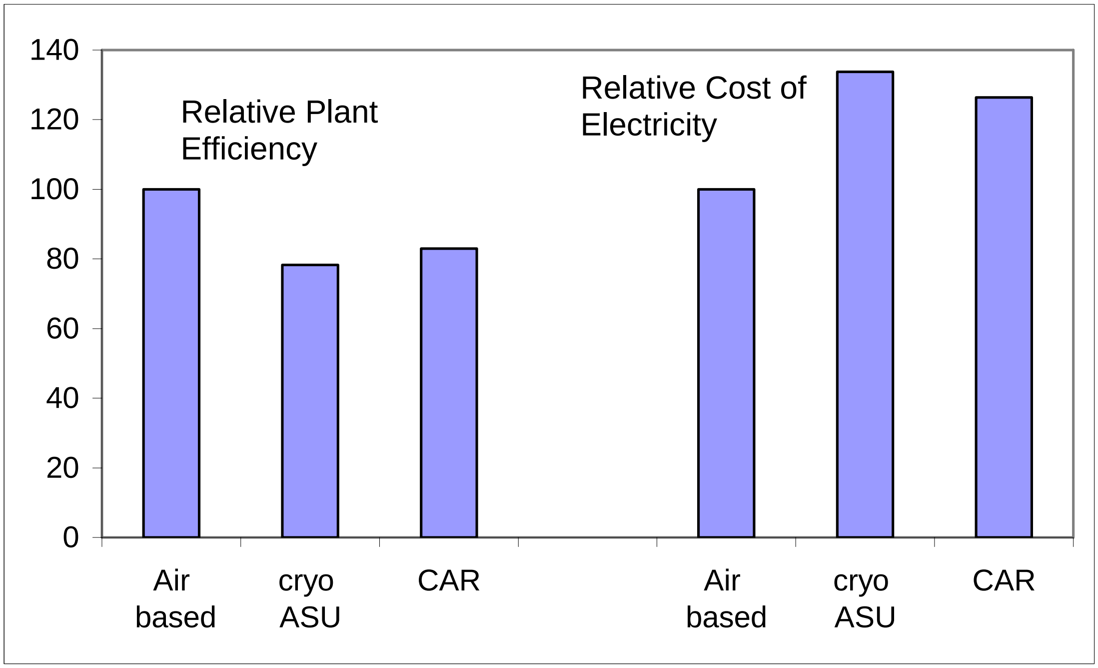


**Figure 8b. shows a comparison of the net power generated by the cryogenic ASU based oxy-fuel plant and the CAR based oxy-fuel plant with the air fired power plant as a reference (100%)**. The net power generated in the cryogenic ASU based oxy-fuel plant is 78.3% of the reference air-fired plant. While the net power of the CAR- based oxy-fuel plant is 83% of the air fired plant. Also shown in Figure 8b

is the cost of electricity for the cryogenic ASU and CAR-based oxy-combustion plants, with the air based plant as a reference. The incremental increase in cost of electricity for oxy-combustion plants using cryogenic air separation is 33.7% while the increase in cost-of-electricity for CAR based oxy-combustion plants is 26.3%.

Figure 8b Power generation efficiency and cost-of-electricity of CAR-based and cryogenic ASU-based oxy-combustion plants, relative to air-fired plant

**5. PDU Testing and Integration with a Coal-fired Combustor**

Significant laboratory-scale testing has been performed to validate the CAR process concept [3]. In these prior efforts, BOC carried out bench-scale experiments in a 38-mm diameter packed-bed CAR apparatus. This vessel was placed in a tubular furnace to maintain temperature, and about 300 $cm^3$ of extruded Perovskite pellets were sandwiched between two layers of alumina beads. Air and sweep gas were alternately fed into the vessel in a counter current fashion, with a step time of 30 seconds. The main process parameters investigated were the air-to-sweep ratio, differential pressure between the air and sweep steps, and sweep gas compositions. The parameters were optimized for a given sweep gas composition to give optimum oxygen enrichment and recovery. Figure 9 shows results of bench-scale tests in which $CO_2$ was used as the sweep gas. During the 30-sec sweep step (between dashed lines), the average $O_2$ concentration was 27%.

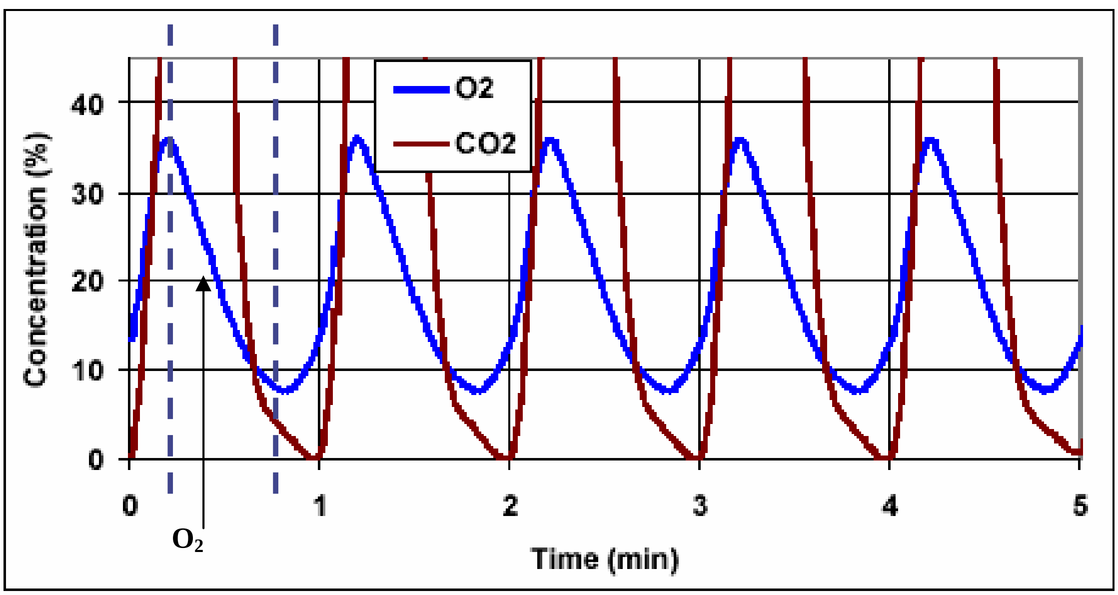


**Figure 9. CAR Bench-scale Tests: Oxygen and Carbon Dioxide Concentration Profiles**

In addition to the demonstration of CAR process concept as shown by small scale testing, it is important to demonstrate the following at a process development scale.

(i) Validate the heat management concept during operation. The internal regenerative thermal mass material should be demonstrated to handle the heat transfer between the exothermic (oxygen sorption) and endothermic (oxygen release) steps in the cyclic process.
(ii) Characterization of heat losses in a practical size internally insulated reactor vessel and the validation of the method to compensate for any heat losses.
(iii) Characterization of the performance of the perovskite material at larger scale and the validation of targeted purity, recovery and bed capacities.

Construction of a 0.7-1.0 ton/day O2 capacity CAR process development unit (PDU) is currently in progress under a DOE co-funded Jointly Sponsored Research (JSR) project at Western Research Institute (WRI)- (DE-FC26-98FT40323). A simplified process flow diagram of the CAR PDU is shown in Figure 9.

Initial testing of the PDU at WRI will use blends of $CO_2$ and steam to simulate the sweep gas. The validation of the internal heat management system and the methods to handle start-up to address heat losses during steady operation would be done during this phase. The characterization of the perovskite material and the performance validation would also be achieved during this phase. Following this the CAR process development unit will be integrated with WRI's combustion test facility (CTF) shown in Figure 10. The CTF is a 250,000 Btu/hr balanced-draft system designed to closely replicate a pulverized coal-fired utility boiler. In its present configuration, the unit has been set up to simulate a tangential-fired boiler, but it may be easily adapted to wall-fired or other configurations. The fuel feed system consists of screw-based feeders and pneumatic transport to four burners inserted in the corners of a refractory-lined firebox. The unit is equipped with appropriately sized heat-recovery surfaces such that the time/temperature profile of a utility boiler can be replicated. These comprise a water-cooled waterwall section, and air-cooled superheater, reheater, and economizer simulators. The CTF also includes provisions for preheating the combustion air to mimic an air preheater, and over-fire air injection ports for combustion staging. The unit is equipped with a bag filter and solids and gas sampling. The gas analysis system includes on-line analyzers for the monitoring of $O_2$, NOx, $SO_2$, CO, $CO_2$, and speciated vapor-phase mercury.

Once integrated with the CTF, the system will undergo shakedown testing to optimize the start-up procedure, control of the fluegas recycle stream, and operation of the CAR temperature control system. The integrated CTF/CAR system will be operated under various conditions to assess the long term performance of the CAR unit, and to determine the effects on CTF emissions ($NO_X$, $SO_2$, CO, unburnt carbon) and heat transfer characteristics.

## 6. Conclusions and Future Activities

Oxy-combustion has been identified as a leading option for coal-based power generation with carbon dioxide capture. BOC's CAR process technology involving high temperature oxygen generation has been shown to be an attractive option for reducing the cost of $CO_2$ capture when compared to cryogenic ASU based oxy-combustion plants. A techno-economic assessment of the CAR technology, when applied to a 700 MW lignite-fired oxy-combustion power plant has shown that the power consumption of a CAR unit will be 74% of that of a cryogenic ASU, while the capital costs will be approximately half those of a cryogenic ASU. As a result the cost of electricity from a CAR-based oxy-combustion plant will increase by 26%, compared to 34% from a cryogenic ASU-based plant.

BOC has validated the CAR concept at laboratory scale and is collaborating with Western Research Institute (WRI) to construct a CAR process development unit that will be tested and integrated with WRI's 250,000 Btu/hr coal combustion test facility.

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# APPENDIX D
# OXY-COMBUSTION
# TEST RESULTS

**Table 1. Mass Balance**

| Coal Type | | Flow Rates Per Burner (total 4 Burners) Coal Feed Rate lbs/hr | Primary Gas lbs/hr | Secondary Gas lbs/hr | OFA Gas SCFM | Flue gas mass flow rate lbs/hr | Heating Value Btu/lbs | Heat Load Btu/hr |
|---|---|---|---|---|---|---|---|---|
| Wyodak | Air Blown | 6.1 | 8.1 | 20.8 | 5 | 237 | 9862 | 240633 |
| Wyodak | Oxygen Blown (27% $O_2$ / 73% $CO_2$) | 5.7 | 8.1 | 20.8 | 4.2 | 235 | 9862 | 224854 |
| Lignite | Air Blown | 5.6 | 8 | 20.8 | 5 | 235 | 9188 | 205811 |
| Lignite | Oxygen Blown (27% $O_2$ / 73% $CO_2$) | 5.3 | 8 | 20.8 | 4.2 | 233 | 9188 | 194786 |
| Bituminous | Air Blown | 4.5 | 8.1 | 22.5 | 5 | 237 | 12985 | 233730 |
| Bituminous | Oxygen Blown (21% $O_2$ / 79% $CO_2$) | 3.4 | 8.1 | 22.5 | 3.5 | 216 | 12885 | 175236 |
| Bituminous | Oxygen Blown (27% $O_2$ / 73% $CO_2$) | 4.6 | 8.2 | 22.5 | 3.5 | 222 | 12808 | 235667 |

**Table 2. Energy Balance**

| Coal Type | | Water Wall Btu/hr | Superheater Btu/hr | Upper Economizer Btu/hr | Lower Econ. Btu/hr | Total Heat Rejected, Btu/hr | Heat Rejected % of Total |
|---|---|---|---|---|---|---|---|
| Wyodak | Air Blown | 105885 | 12014 | 23991 | 24083 | 165973 | 0.69 |
| Wyodak | Oxygen Blown (27% $O_2$ / 73% $CO_2$) | 110297 | 12749 | 27493 | 24090 | 174629 | 0.78 |
| Lignite | Air Blown | 105134 | 10556 | 24081 | 20376 | 160147 | 0.78 |
| Lignite | Oxygen Blown (27% $O_2$ / 73% $CO_2$) | 103745 | 10903 | 25942 | 22231 | 162821 | 0.84 |
| Bituminous | Air Blown | 121919 | 15775 | 27912 | 19975 | 185581 | 0.79 |
| Bituminous | Oxygen Blown (21% $O_2$ / 79% $CO_2$) | 95655 | 10876 | 17054 | 17450 | 141035 | 0.80 |
| Bituminous | Oxygen Blown (27% $O_2$ / 73% $CO_2$) | 125537 | 13222 | 24189 | 23747 | 186695 | 0.79 |

**Table 3. Emission Data**

| Coal Type | | $SO_2$ @ 3% $O_2$ Exp. ppm | $SO_2$ lb/MMBtu | $N_2$ Exp % mole | $CO_2$ Exp. % mole | $O_2$ Exp. % mole | NOx @ 3% $O_2$ Exp. ppm | NOx lb/MMBtu | CO @ 3% $O_2$ Exp. ppm | Hg Total Exp. ug/$m^3$ |
|---|---|---|---|---|---|---|---|---|---|---|
| Wyodak | Air Blown | 377 | 0.73 | 78.77 | 17.4 | 3.81 | 182 | 0.17 | 15 | 1.6 |
| Wyodak | Oxygen Blown (27% $O_2$ / 73% $CO_2$) | 380 | 0.56 | 0.49 | 96.65 | 2.85 | 206 | 0.14 | 5 | 0.9 |
| Lignite | Air Blown | 1522 | 3.46 | 78.1 | 18.5 | 3.34 | 227 | 0.24 | 13 | 3.3 |
| Lignite | Oxygen Blown (27% $O_2$ / 73% $CO_2$) | 2095 | 3.56 | 0.27 | 94.75 | 4.96 | 241 | 0.19 | 15 | 3.3 |
| Bituminous | Air Blown | 653 | 1.34 | 79.5 | 15.52 | 4.98 | 466 | 0.45 | 0 | 2.9 |
| Bituminous | Oxygen Blown (21% $O_2$ / 79% $CO_2$) | 674 | 1.19 | 0.96 | 95.59 | 3.45 | 123 | 0.10 | 284 | 0.0 |
| Bituminous | Oxygen Blown (27% $O_2$ / 73% $CO_2$) | 950 | 1.28 | 0.76 | 95.56 | 3.68 | 397 | 0.25 | 70 | 0.0 |

Notes:

1) Combustion test with bituminous coal will be repeated to close the mercury mass balance

2) Reduction of SO2 emission using wyodak coal in the oxy-combustion mode is been confirmed based on the trend a similar test conducted earlier as similar conditions

3) Noticeable reduction in total mercury emission during oxy-combustion test with wyodak coal

4) No change in mercury emission between oxy-combustion and air blown combustion modes with lignite coal. The high SO2 believed to be a big factor toward that trend.

**Table 4. Percentage of Unburned Carbon in Fly Ash**

| Coal Type | | Sample 1 | Sample 2 | Sample 3 | Sample 4 |
|---|---|---|---|---|---|
| Bituminous | Air Blown | 5.2% | 4.6% | NA | NA |
| Bituminous | Oxygen Blown (21% $O_2$ / 79% $N_2$) | 35.7% | 30.48% | NA | NA |
| Bituminous | Oxygen Blown (27% $O_2$ / 73% $N_2$) | 5.3% | 5.9% | 8.8% | 3.3% |

Analysis of isokinitic fly ash samples for both wyodak and Lignite will be determined