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Oxygen Production on Mars and the Moon

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## Abstract

Significant progress has been made in the area of in-situ oxygen production in the last year. In order to reduce sealing problems due to thermal expansion mismatch in the disk configuration, several all-Zirconia cells have been constructed and are being tested. Two of these cells have been run successfully for extended periods of time. One was run for over 200 hours and the other for over 800 hours. These extended runs, along with gas sample analysis, have shown that the oxygen being produced is definitely from CO_2 and not from air leaks or from the disk material. A new tube system is being constructed that is more rugged, portable, durable and energy efficient. The important operating parameters of this system will be better controlled compared to previous systems. An electrochemical compressor will also be constructed with a similar configuration. The electrochemical compressor will use less energy since the feedstock is already heated in the separation unit. In addition, it does not have moving parts.

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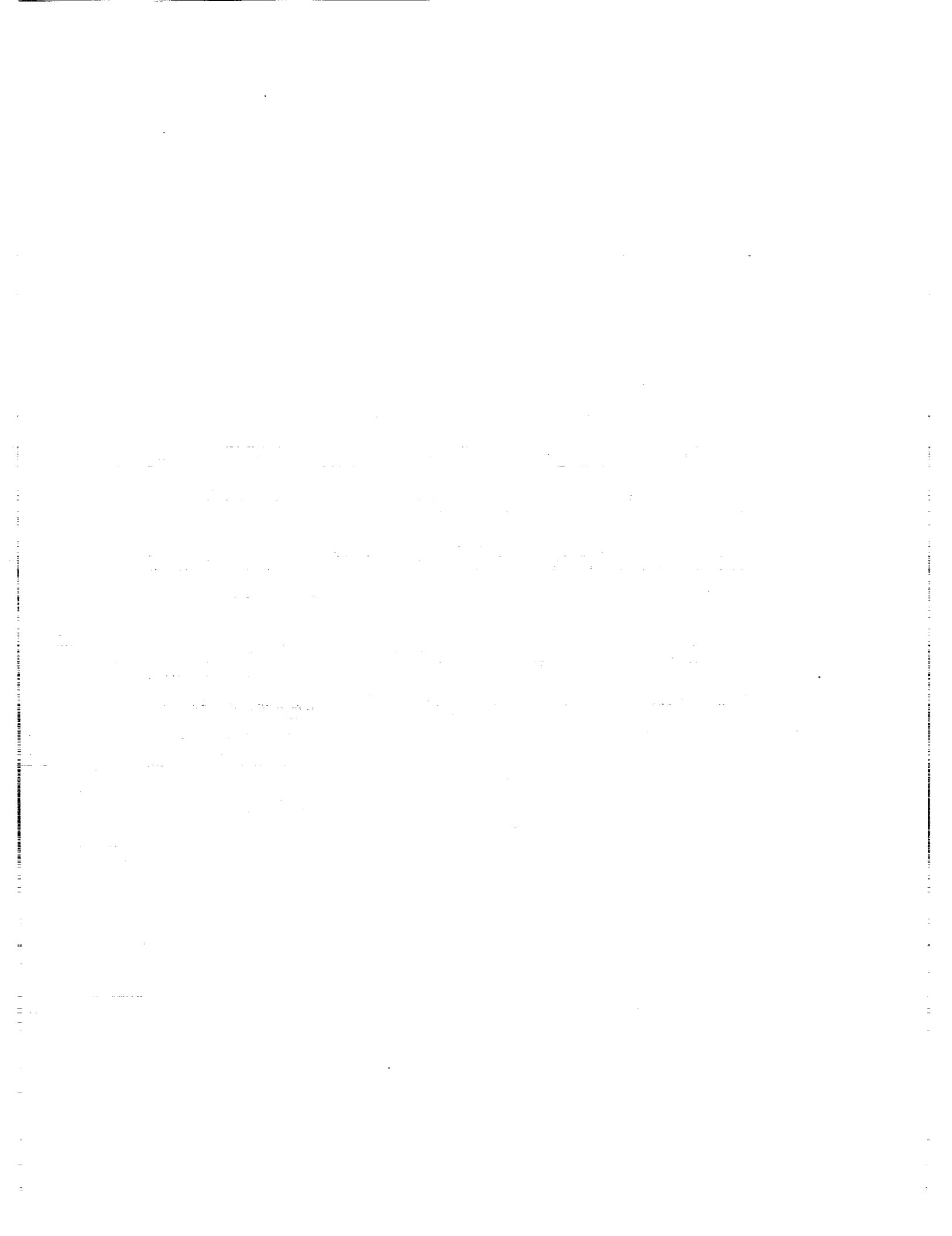
Introduction

With the forthcoming missions to Mars and the Moon, one way of reducing launch costs is in-situ production of propellant. Since oxygen represents most of the propellant mass, in-situ production of oxygen could provide a dramatic savings in launch mass and therefore launch costs. Thus the motivation for development of a production plant is very strong from an economic point of view. There are many components to consider for such an oxygen production plant, but the main focus of this study is the separation of oxygen from carbon dioxide. The first part of this report will focus on the electrochemical issues of oxygen separation using a disk configuration. The second part will describe the work being conducted in designing a device using tubular cells to separate oxygen and compress it. Basically, the CO_2 is heated to high temperatures where it dissociates into CO and O_2. The oxygen is then separated from the CO using an electrochemical separation cell. The details of this process are described in [1]. The separation cell, shown in *Figure 1*, consists of a solid Zirconia electrolyte with a precious metal electrode on either side. There are several properties of the electrolyte and the electrode which determine the performance of the cell. One example is that the electrode must be porous enough to allow the oxygen to pass through it but solid enough to be a good electrical conductor. The selection of the optimal electrode and electrolyte materials and understanding the long duration performance of the cell is the objective of the tests conducted on the disk system. This is described in Part A of the report. Tubular electrochemical cells have been used to build proof-of-concept and scale-up testbeds for oxygen production. Details on the design and performance of these systems can be found in [1]. The experience and knowledge gained in operating these systems have been incorporated into developing a new electrochemical cell cluster that has four tubular cells. This new cluster eliminates the problem elements of previous systems. In addition, the design is more robust, easily repairable and more energy efficient. The same cluster can also be used to compress oxygen to higher pressures for liquification and storage. The progress in these areas is described in Part B.
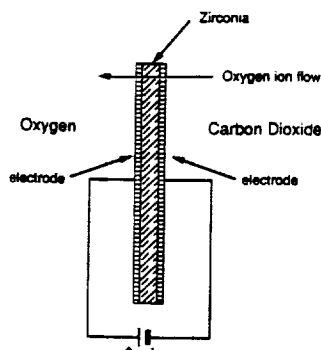

Figure 1 - Electrochemical Separation Cell, Disk Geometry

Part A: Electrochemical Separation of Oxygen From Carbon Dioxide – Disk Geometry
Graduate Student: Brian Vaniman

The progress that has been made to date on the disk geometry for the electrochemical cells is discussed here.

Electrolyte and Electrode
The electrolyte used in this study is Yttria stabilized Zirconia (ZrO_2-Y_2O_3 8% mole). The precious metals Silver and Platinum as well as the perovskite Lanthanum Strontium Manganate (LSM) have been selected as electrode material. The details concerning the choice of these materials are outlined in [1].

Electrolyte Fabrication
There are two techniques being used to fabricate the electrolyte, cold pressing and tape casting. Cold pressing involves mixing the ceramic powder with a dry, powdered binder which is poured into a metal die and uniaxially pressed under 12 to 14 tons of force. The tape casting process is somewhat more complicated. The ceramic powder is mixed with an acrylic binder and ball milled to produce a smooth slurry. This slurry is then poured onto a sheet of glass and a blade is drawn over it to produce a uniform thickness layer of material. After drying, the disk shape can be cut out of the tape. At this point, disks produced by either method must be sintered to evaporate the binder and leave a solid Zirconia disk. The sintering process consists of ramping and holding the temperature at several different levels until the maximum sintering temperature is reached, and then ramping back down. The cold pressed disks are sintered to 1650 °C and the tape cast disks are sintered to 1340 °C. The disks are placed in a Zirconia firing plate and covered with Zirconia powder to keep them from warping during the sintering process. The disks that were cold pressed resulted in flat disks 2.9 cm in diameter and .064 cm thick. The disks from the tape casting could not be fired flat and came out wavy around the edge. These disks were made very thin (~13 mm) and were vary brittle. The furnace used to sinter these disks had the capability to ramp at intervals of 1 °C/min. The firing schedule called for a ramp rate of .24 °C/min at some points. Future tape cast disks will be sintered in a furnace with higher resolution ramp rate in an attempt to remove the waviness.

Electrode Application

The electrode material is commercially available in paste form. Hereaus Products Silver and Platinum pastes thinned with ethanol were used. Also used was a LSM paste consisting of LSM in an organic binder thinned with Toluene. The paste is applied to the disk with a swab in a thin layer. Then a connecting wire is dabbed with the paste and laid on the electrode. The disks, with electrode, are then fired to set the paste.

System Testbed

A schematic drawing of the system testbed is shown in *Figure 2*. The CO_2 is supplied by a bottle and is fed into the system through a flowmeter which is used to control the flow rate. The CO + CO_2 exhaust is vented to the air or connected to an oxygen meter to check for air leaks. The O_2 produced flows out through a very sensitive flowmeter and is then either vented to the air or connected to the oxygen meter. There is also a system for collecting the CO + CO_2 exhaust and the O_2 produced in gas sampling bottles which can then be taken to a gas chromatograph or mass spectrometer for analysis. The ZrO_2 cell is raised to temperatures of 800 - 1000 °C using a ceramic clam-shell heater. The heater is controlled by a QuickBasic program running on a PC which reads the temperature of the cell from a thermocouple. The program controls ramping the system up to temperature and holding at temperature. The cell voltage is supplied by an Acopian power supply and two meters measure the voltage across and the current through the disk. The heater and Zirconia cell are surrounded in Kaowool insulation to reduce heat loss.

A schematic drawing of the ZrO_2 cell is shown in *Figure 3*. The disk with electrodes and connecting wires is sandwiched between two Coors Ceramics Zirconia manifolds and cemented together with Aremco's Ceramabond 569 ceramic cement. Prior to this the manifolds have holes drilled in them for the CO_2 feed tube, the CO + CO_2 exhaust tube and the O_2 production tube as well as smaller holes for the connecting wires. The tubes, which are made of alumina (Al_2O_3), and wires are also cemented to the manifolds. The cell is then fired to set the cement. Previously, aluminum silicate had been used for the manifolding material, but there were sealing problems due to thermal expansion differences between the Zirconia disk and the manifold. With the Zirconia manifolds, this aspect of the sealing problem has been eliminated. It should be noted that thermal expansion mismatches still occur due to geometric differences, however this mismatch is not as severe.
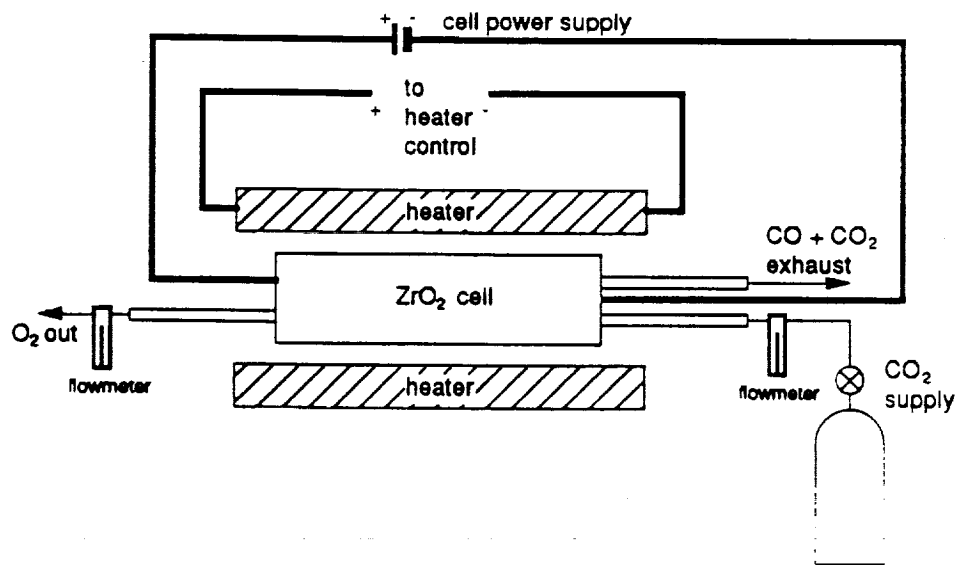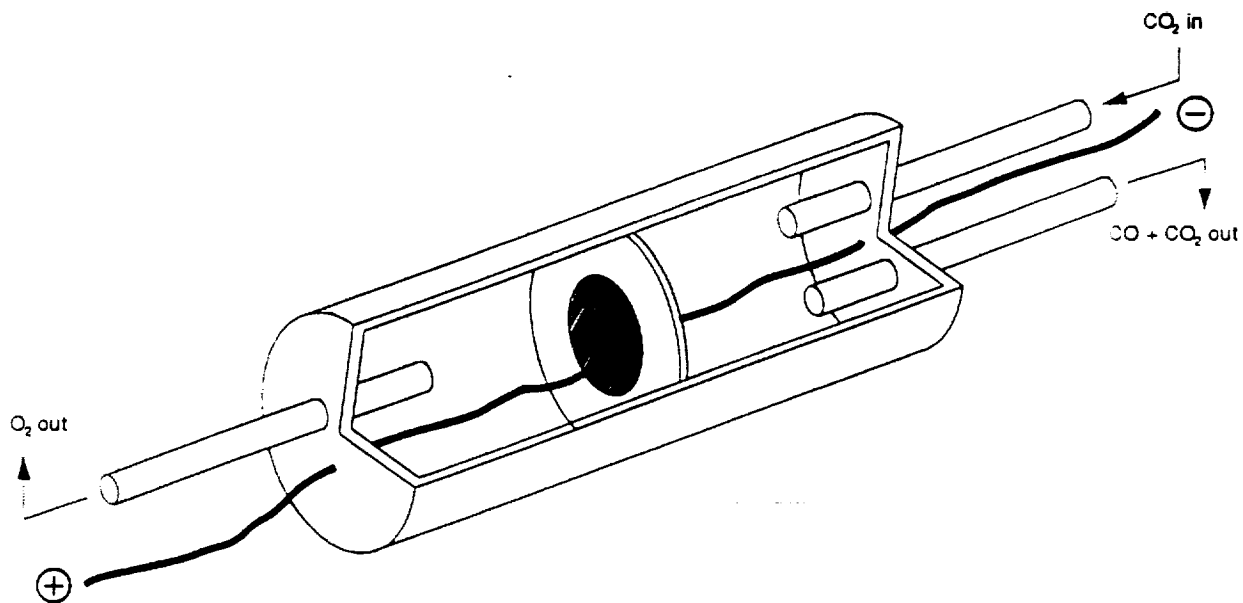
Figure 2 - System Testbed For Disk Geometry

Figure 3 - Cutaway Of ZrO$_2$ Cell

Results and Discussion

In the last two months, two extended cell runs have been made. The first cell consisted of a cold pressed disk with a Platinum electrode and platinum connecting wires. The potential across the cell was between 1.71 and 1.78 Volts and the cell was at a temperature of 950 °C. This cell was run for over 200 hours and produced oxygen very consistently at approximately .4 cc/min. The oxygen production over time is shown in *Figure 4*. Mass spectrometer analysis of the CO + CO_2 exhaust and the O_2 production gave the gas percentages shown in Table 1.

	Nitrogen	Oxygen	Carbon Monoxide	Carbon Dioxide
CO + CO_2 exhaust	13.9	0.1	3.6	82.3
O_2 production	65.0	31.0	not detected	3.0

Table 1 -- Gas percentages for first cell

The large amounts of nitrogen on both sides of the cell would indicate an air leak in the cell. When the cell was examined after the run, a crack was found on the CO_2 side of the manifold. This would explain the presence of nitrogen on that side. The nitrogen on the O_2 side could be from diffusion of air into the sample bottle since the flow rate of oxygen is very small (~ .4 cc/min).

The second cell is identical in construction to the first and at the writing of this report is still running. It has been running for over 800 hours and is still producing oxygen consistently at approximately .35 cc/min. The cell potential is between 1.68 and 1.75 Volts. The oxygen production over time for this cell is shown if *Figure 5*. Mass spectrometer analysis of the CO + CO_2 exhaust and the O_2 production gave the gas percentages shown in Table 2.

	Nitrogen	Oxygen	Carbon Monoxide	Carbon Dioxide
CO + CO_2 exhaust	4.5	0.3	13.7	81.6
O_2 production	35.3	64.3	not detected	0.4

Table 2 -- Gas percentages for second cell

The low amounts of nitrogen and oxygen on the CO_2 side of the cell indicate that there was probably no air leak on that side. Additional proof of this was given by connecting the oxygen meter to the CO + CO_2 exhaust and measuring a value of 0.0% oxygen. This goes to show that the
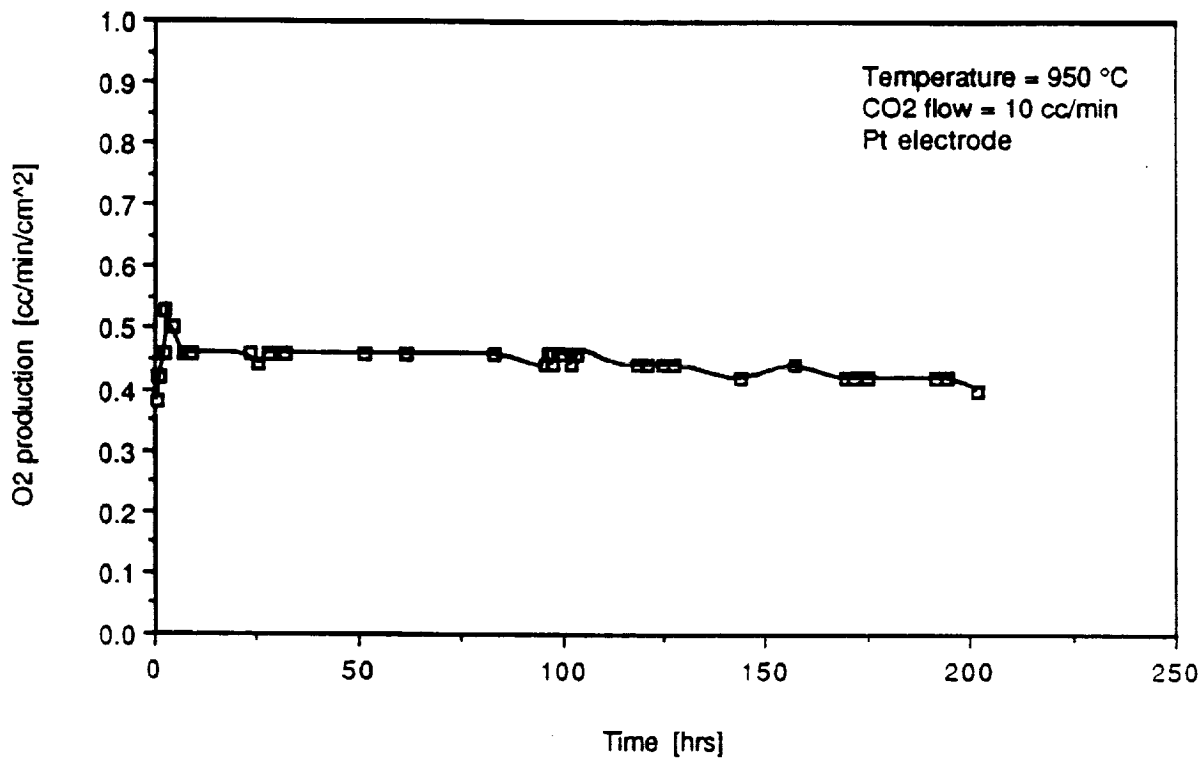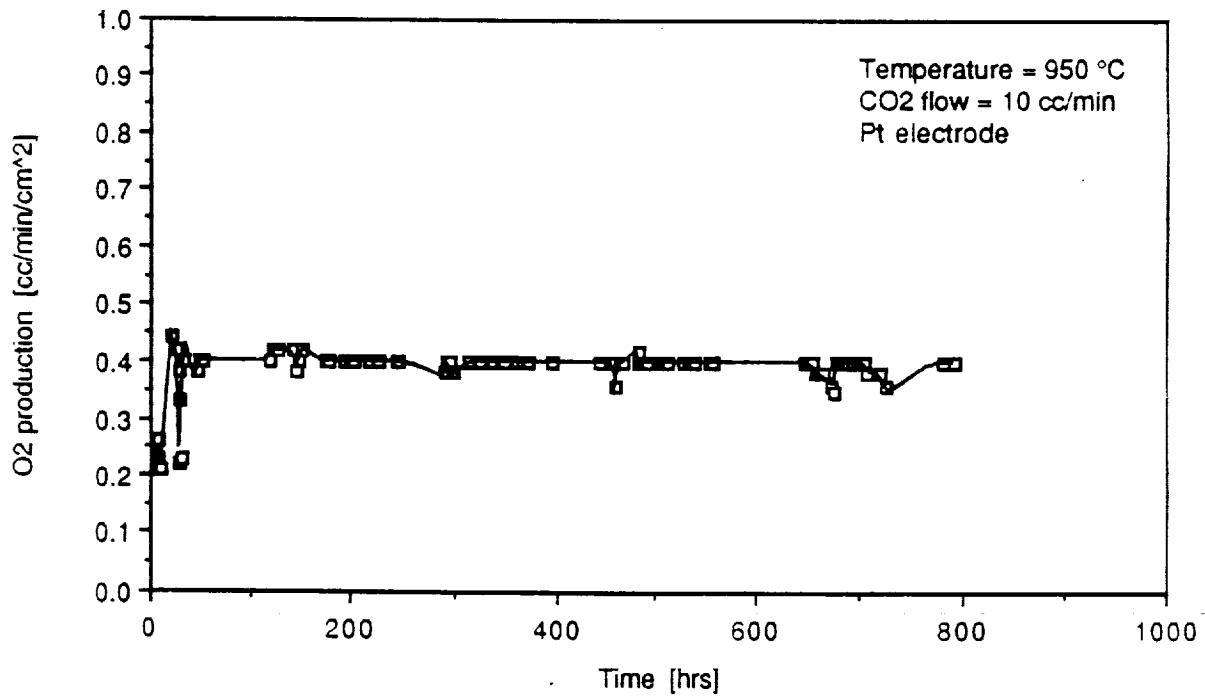
Figure 4 - Cell #1 Performance

Figure 5 - Cell #2 Performance

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oxygen being produced is from the CO_2 and not from air. More proof of this is that .35 cc/min of O_2 produced should show up as .7 cc/min of CO on the exhaust side. Knowing the exhaust flow rate of 10 cc/min, the percentage of CO should be about 7%. Since the percentage measured in the gas analysis is at least this much, it can be said that the oxygen is being produced from CO_2, not air. The nitrogen on the O_2 side could again be from diffusion of air into the sample bottle.

There is also speculation that the oxygen is coming from the disk itself, and not CO_2, since it does contain oxygen. However, a very simple calculation will show that the amount of oxygen in the disk would only last for approximately 24 hours at a flow rate of .4 cc/min. Due to their extended run times, both of these runs show that this is not the source of the oxygen produced.

An additional test was performed on the second cell. This was to see how the CO_2 flow rate effected the O_2 production. The results of this test are shown in *Figure 6*. It can be seen that at a CO_2 flow rate of 3 cc/min and higher, the oxygen production is independent of CO_2 flow rate. Below 3 cc/min, the production of oxygen decreases with decreasing CO_2 flow rate. The utilization of CO_2 is approximately 36% at 2 cc/min of CO_2 flow and approximately 26% at 3 cc/min.

In comparison with the tube system, whose *best* results gave a .214 cc/min/cm^2 O_2 production, the non-optimized disk system is approximately 63% more productive at .35 - .4 cc/min/cm^2. In comparison with an *average* tube system which gave .132 cc/min/cm^2 O_2 production, the disk system is approximately 166% more productive. The disk system also has the capacity to be more compact and less massive than the tube system.

Future Plans for the Disk System

Immediate plans call for extensive testing to study the effects of various electrodes, electrode application techniques and disk thicknesses on oxygen production. The next phase of testing for the 2.9 cm diameter disk system is to run it in a vacuum furnace, with the chamber filled with CO_2 at Martian atmospheric pressure. This will show how the system performs at the lower pressure on Mars. The next step is to build cells of larger diameter in order to produce more oxygen. Plans are to build a system based on a 3.5 inch diameter disk. These disks will most likely be made by tape casting, dependant on the acquisition or construction of a tape casting machine.
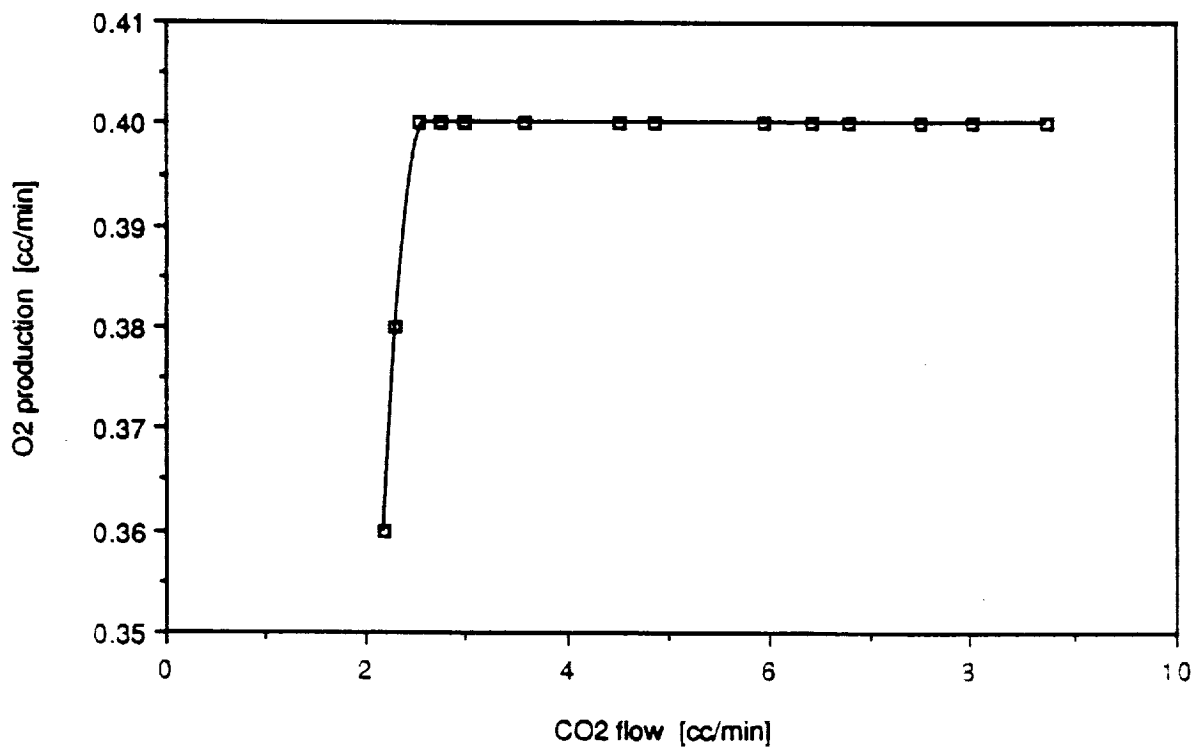
Figure 6 - O2 Production vs. CO2 Flow

Part B: Oxygen Production Plant and Compressor
Using Tube Geometry
Graduate Student: Scott Miller

Oxygen Production Plant

The electrochemical cells for the oxygen separation are available in tubular form. This shape offers an alternative to the disk geometry described above and can also function as a compressor for the separated oxygen. The tubes were custom made for UA/NASA SERC by Ceramatec, Inc. of Salt Lake City, Utah. The tubular device and the design motivation will be described here.

The design of the oxygen production plant was made with two main objectives in mind. The development of an operational portable system capable of remote operation, and its use as an oxygen compressor. The motivation behind the design of this device has been to develop a system that is at a higher Technology Readiness Level than the previous devices described in [1]. Some criteria important in the development of a complete system are: ease of use, high efficiency, reliability, repairability, and intelligent control. The compactness and modularity of the process cluster is illustrated in *Figure 7* and 8. Each subsystem can be removed/replaced without a significant pause in operations. The system can be serviced - replacing of the Zirconia cells for example - by one person with one electric wrench in a matter of seconds. This would be an important consideration on the Moon or Mars. In order to make the device more reliable, all the problems encountered in the development of the 16-cell breadboard were addressed and systematically eliminated in the current design. A few of these issues are discussed below.

Previously, the oxygen plant was fragile because it had alumina feed tubes. This required the complete disassembly of the system and the refitting of the Zirconia tubes with a new alumina feed tube when one broke. The new design employs an Inconel feed tube which does not protrude from the system housing. Another problem in the previous experimental set up was the less than desirable electrical connections to the Zirconia tubes. Improper contacts caused a loss of d.c. potential across the tube, resulting in a lower O_2 production. At elevated temperatures, the sealing of electrical contacts through the system causes gas leaks, compromising the data obtained. This problem was solved in the new system by using Conax type electric feed through fittings for the
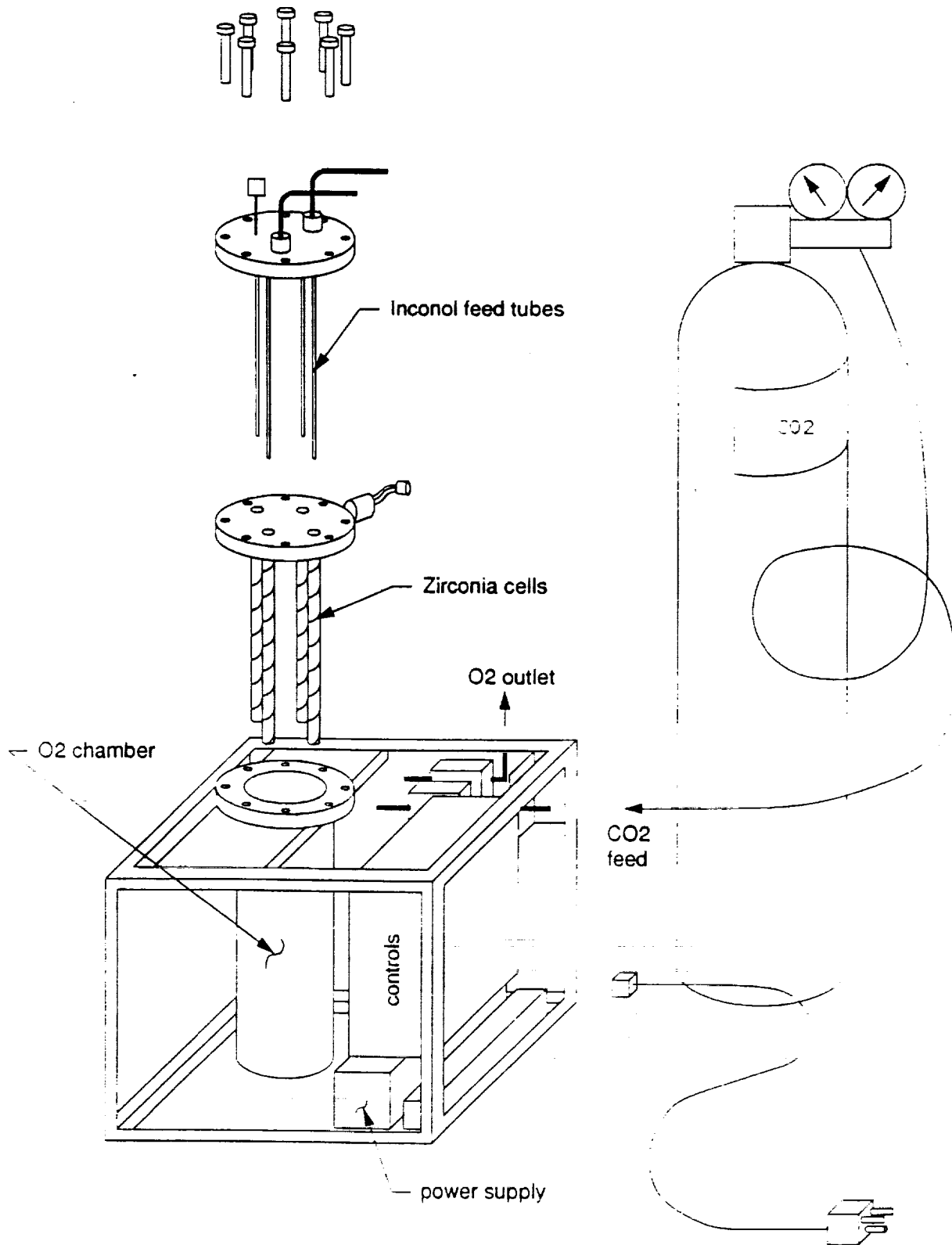
Inconol feed tubes

Zirconia cells

O2 outlet

O2 chamber

CO2

CO2 feed

controls

power supply

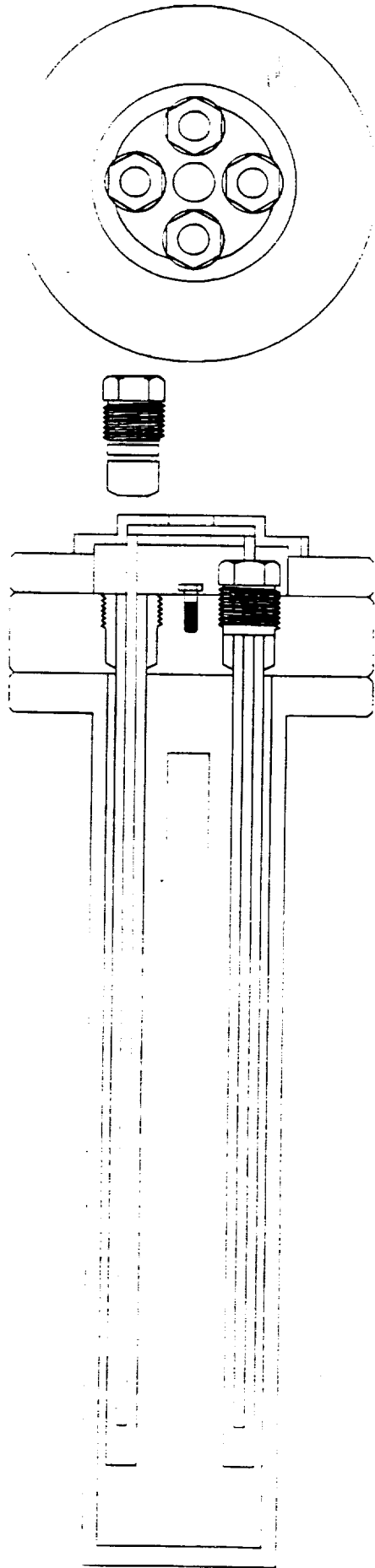Figure 7 - Design of Oxygen Production Plant and Compressor.

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Figure 8 - Cross Section of Oxygen Separation Process Cluster

positive leads and thermocouple. These and other design modifications provide for a robust design.

The 16-cell unit has cold Teflon seals that were water cooled. The new design has Conax type fittings with Lava seals that can withstand the high temperature of operation. With this design, the complete length of the tubular cell can be effectively utilized and the heater power can be drastically reduced. Reliable gas flow monitoring, good electrical contacts, the availability of temperature data at various points in the cluster, and a hot seal provides us with a system in which meaningful control experiments can be run and high confidence level data can be collected. At the time of writing this report, a system has been built and is in the process of being tested. Data on the experiments will be reported in the near future.

Oxygen Compressor

The electrochemical cell can be used as an oxygen compressor. If sufficient d. c. potential is applied to the cell, the partial pressure of oxygen that is pumped can be significantly increased. *Figure 9* is an illustration of a 4-cell unit that has been described in [1]. This unit was used to compress pure oxygen. Oxygen entered the unit at atmospheric pressure and was compressed to 366 psig with this device. The results of this test are shown in *Figure 10*. The cold Teflon seals prevented further pressurization of the chamber. A new design with the hot seals is presently being developed. The results will be reported in the near future.

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Reference

1. Sridhar, K.R. and P. Kaloupis, "Electrochemical Separation of Oxygen from Carbon Dioxide", NASA Space Engineering Research Center Annual Progress Report 1991, APR-91/F, University of Arizona, 1991, pp. IB-1 -- IB-22.
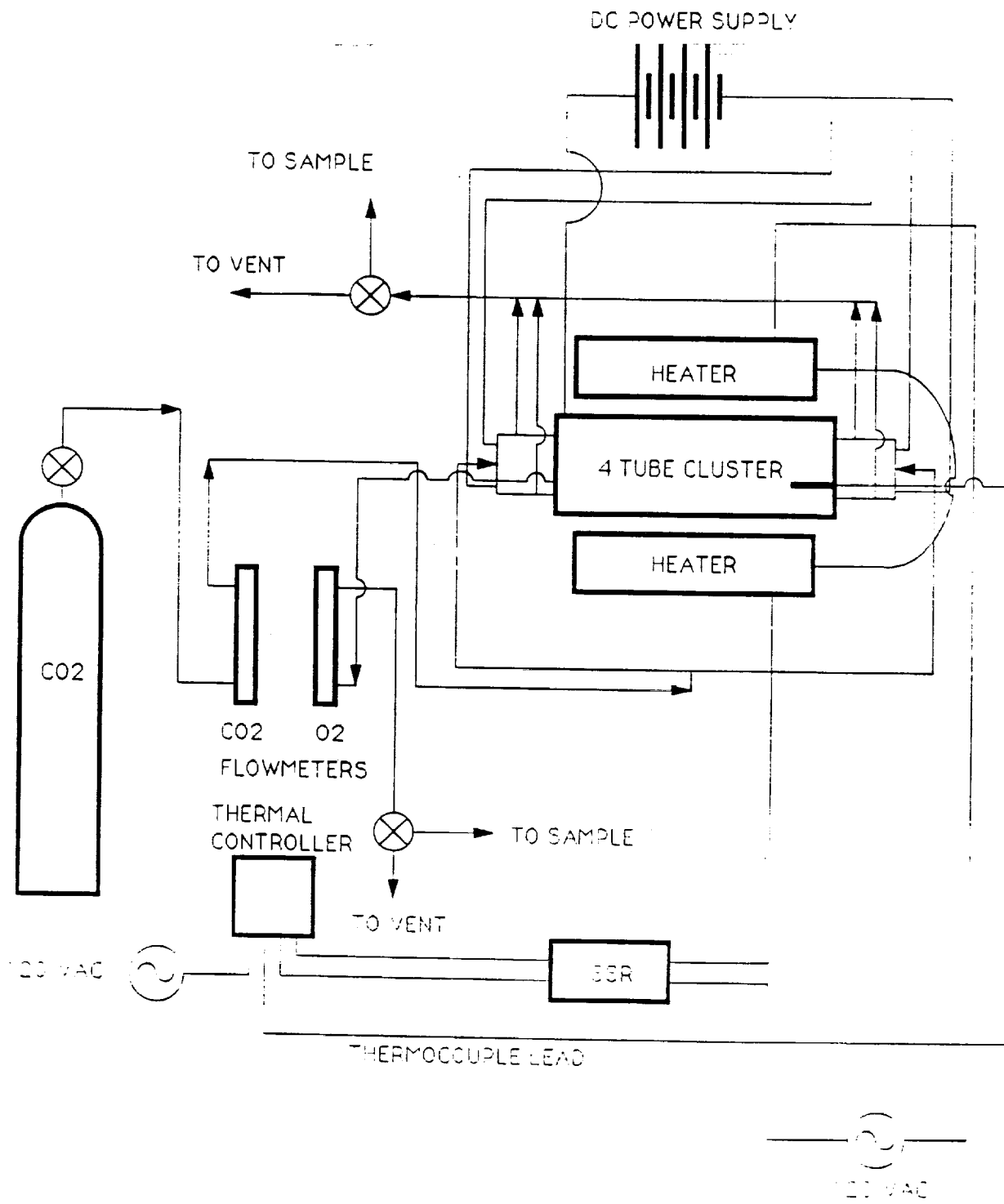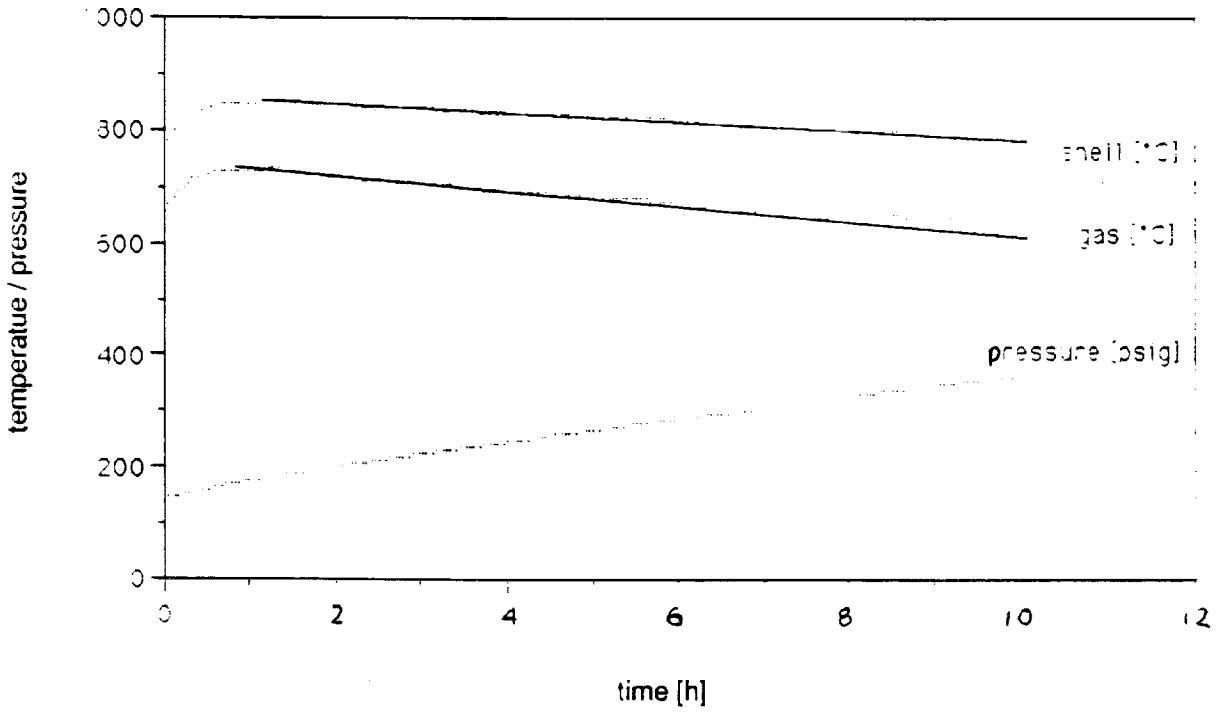
Figure 9 - Block Diagram of Oxygen Production Plant

Figure 10 - Temperate / Pressure vs. Time for the Oxygen Compressor