OLD DOMINION UNIVERSITY
MARS OXYGEN PRODUCTION SYSTEM DESIGN

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Abstract

This report summarizes the design and construction phase of the Mars oxygen demonstration project. The basic hardware required to produce oxygen from simulated Mars atmosphere has been assembled and tested. Some design problems still remain with the sample collection and storage system. In addition, design and development of computer compatible data acquisition and control instrumentation is ongoing.

Introduction

The combination of a stronger gravitational field and greater distance from the Earth makes round trip missions to the surface of Mars more difficult than to the lunar surface. Using conventional propulsion approaches, the ascent vehicle required for Mars liftoff and Earth return is a large part of the payload at Earth launch. Furthermore, propellant mass accounts for as much as ninety percent of the Mars ascent vehicle mass. When liquid propellants are used, liquid oxygen accounts typically for eighty percent of the propellant mass and oxygen can be produced at Mars (Ref. 1). While oxygen production from Mars atmosphere is straightforward, acceptance of oxygen production as an option for early round trip missions to Mars is lacking. The research goal of Old Dominion University's Mars oxygen demonstration (MOD) project is to build and operate an oxygen production system for the purpose of establishing its viability for near term Mars missions.

Mars oxygen production is an ideal candidate for extraterrestrial resource utilization because:

(1) The carbon dioxide feedstock is certain;
(2) The feedstock is not landing site dependent; and
(3) Collection of a gaseous feedstock is simple
and requires little equipment; (4) Electrochemical extraction of oxygen from the feedstock is simple, requiring no moving parts; and (5) Oxygen is a vital resource for human survival and an enabling resource for a variety of propulsive applications. The ability to produce oxygen on the Martian surface reliably and autonomously for long periods of time and in large quantities is an important goal for future space missions.

Mars atmosphere is 95.32 percent carbon dioxide (Ref. 2). A variety of devices can be used to collect Mars atmosphere, and since dissociation of carbon dioxide is not affected by pressure, it is only necessary to pressurize the atmosphere mildly to move it through the system and keep the volume of the oxygen separation system small. Oxygen separation is accomplished by heating Mars atmosphere to temperatures on the order of 1000 K where measurable dissociation of carbon dioxide into carbon monoxide and oxygen occurs. Stabilized zirconia can conduct oxygen ions (O2-) at elevated temperatures. (Ionized oxygen is produced at the cathode of the electrolyte and pumped across the membrane to the anode where it is converted to O2.) Hence, oxygen can be removed and separated from a heated Mars atmosphere stream by applying a voltage across a sealed zirconia membrane. The oxygen thus collected can be pressurized and liquefied for storage using a variety of machines (Ref. 3).

The MOD system has been designed to operate a zirconia cell at temperatures and pressures similar to those that would be used on Mars. The design assumes that Mars atmosphere is provided at pressures between 50 and 100 mb and at temperatures on the order of 300 K. The supply temperature will be at least 300 K if any kind of compressor is used to pump the feed gas and will exceed 300 K if thermal absorption devices are used for compression (Ref. 3). The zirconia cell environment is controlled by the oven temperature, and the supply and collection pressures. Both the supply and oxygen collection pressures will be varied as part of this study. In addition, the oven temperature will be varied. The MOD system terminates at the point where oxygen is supplied for liquefaction and storage. The spent exhaust gas is returned to the surroundings.

Overall System Design

The Mars oxygen processor is shown schematically in Figure 1. Simulated Mars atmosphere is provided from pressurized bottles of custom mixed specialty gas. The composition of the simulant and of Mars atmosphere are compared in Table 1. It is noted that trace elements and water vapor (which is variable) are omitted for economic reasons. In addition, rather than increase the carbon dioxide content to achieve a proportional approximation of Mars atmosphere, the argon content was increased. Additional argon was used since it is inert and will act as a buffer gas, degrading dissociation of carbon dioxide, rather than increasing performance artificially.

A two-bottle, manifold system (Union Carbide System SG 9150) is used to provide a continuous supply of feed gas for endurance testing. The bottles are switched automatically and can be replaced when they are empty. The feed gas, which is supplied at a pressure of 55 atmospheres (800 psi), is throttled to a pressure of approximately four atmospheres before it is introduced into the flow network. The supply line upstream from the flow controller is of sufficient length to resublimate any dry ice that might form through the throttling process.
A mass flow controller (Omega Engineering, Model FMA-663-0-V) is used to control the flow of simulated Mars atmosphere. Flow rates between 0 and 370 standard cubic centimeters per minute (SCCM) can be maintained. The feedgas pressure is monitored using a Datametrics, Barocell Type 600 pressure transducer which has a useful range of 0 to 100 torr absolute. The controlled feed gas flow is then introduced into the zirconia cell and oven where it is heated to temperatures on the order of 1500 K. The yttria stabilized zirconia cell was manufactured by Ceramatec Corporation and a schematic of the cell assembly is shown schematically in Figure 2. The cell assembly consists of an outer ceramic alumina housing, a thermocouple well, a tubular zirconia cell and seal, stainless steel electrical leads and connections, and a end plate with plumbing for the carbon dioxide, oxygen, and exhaust gas flows. The zirconia tube is open only at the oxygen outlet end (at the top of the assembly). Both sides of the zirconia tube are coated with a porous platinum paste which formed the anode and cathode. Voltage and current are controlled and supplied through a d.c., high current power supply. The oven used presently was also manufactured by Ceramatec Corporation and has a useful upper temperature limit of approximately 1500 K. It is capable of maintaining constant temperatures to within ±2 °C of its set point.

The oven exhaust gas flow is monitored using an Omega Engineering Model FMA-566-5-V, mass flow meter which measures a maximum flow rate of 500 SCCM. The oxygen production rate is monitored using an Omega Engineering Model FMA-663-0-V mass flow meter with a full scale range of 50 SCCM. Line pressures are measured with silicon-diaphragm, piezo-resistive differential pressure transducers (Omega Engineering, Model 241PC15G).

System pressure is maintained through a 45.3 liter ballast tank which is connected to a Gast, Model 5BA-1 vacuum pump. The vacuum pump is capable of removing 0.1 l/s at 0.01 torr and its volume flow characteristics are shown in Figure 3 over the pressure range of interest. Both the oxygen and exhaust gas lines are connected to the ballast tank, where the two streams are combined and pumped back to the atmosphere. Hence the vacuum pump controls the system throughput.

Because of the low flow rates, additional heat exchangers are not required. Rather, using thermal analyses, the tube runs have been made long enough between the oven and the pressure and flow transducers to ensure that the fluid temperatures are approximately at ambient conditions.

Temperatures will be measured throughout the system using thermocouples. The thermal instrumentation has not been installed fully at this time due to problems with the computer interface. Copper-constantan, iron-constantan, chromel-alumel and nickel-al-constantan (Type N) thermocouples are being evaluated for various measurements throughout the system. A concern in thermocouple selection has been the reported degradation of chromel-alumel thermocouples during prolonged, cyclic use at 1000°C (Ref. 4). Presently, type N thermocouples are being considered because they have been shown to be more stable (Ref. 4).

A Keithley 500 data acquisition and control system (DAC) has been used during the year for data acquisition and control studies. The DAC was connected to an IBM PC AT Computer which served as the data acquisition host as well as the control system manager. The DAC employed Soft 500 operating software which was compatible with BASIC to facilitate data acquisition and control programming. Different circuit boards are installed in the data acquisition and control box for thermocouple measurements, voltage measurements and analog outputs. However, a major system or software failure occurred during the semester, requiring the DAC and one circuit board to be shipped back to the manufacturer. Presently, a Keithley 570 system is being used which has similar features to the original system but which is not capable of supporting the number of data channels and output channels that will be required for the autonomous system. The data acquisition and control aspects of this project are still in the development phase.

Computer based data acquisition and control system design has become the primary focus of the project at this time. In order for autonomous oxygen production to be demonstrated, a network of sensors must be integrated into the system which provide sufficient digital information to enable a computer to monitor the health of the oxygen production system. The initial focus has been to identify and install sensors which measure temperature, pressure, mass flow rate, voltage and current and which provide signals to the data acquisition system. Presently, the following measurements have been identified as necessary for autonomous operation:

1. Cell voltage, current and temperature
2. Supply gas bottle pressures
3. Supply mass flow rate
4. Supply gas temperature and pressure
5. Oven temperature distribution and power consumption
6. Oxygen temperature, pressure and mass flow rate
7. Exhaust gas temperature, pressure and mass flow rate
8. Ballast tank pressure
9. Power consumed by the vacuum pump
10. Availability of external electrical power

These measurements represent approximately 20 channels of data which must be monitored and evaluated by the computer.

At this time, the only quantities which will be controlled actively by the computer are: (1) The supply gas flow rate; (2) Power to the zirconia cell; and (3) Power to the oven. The mass flow is controlled via the computer because its design facilitates computer control. Cell voltage and power must be controlled actively to avoid cell destruction during a system upset. In addition, even though the oven has its own very primitive (but reliable), "bang-bang" temperature control, it is necessary only to cut off the oven power in the
event that certain types of system failures or upsets occur. Tests have shown that the oven cools down gradually when power is removed, thereby protecting the cell from destruction due to thermal stresses.

The long range plans for the system are to implement more computer based control elements and ultimately employ a symbolic, expert system controller which can identify and avoid certain types of system failures as well as enable extended, autonomous operation. That activity will require significant graduate student involvement (Ref. 5).

The present, Ceramatec cell design does not address two key Mars design questions--long-life, high temperature, seal designs and the relative ratio of thermal to electrical energy requirements. The Ceramatec cell has been designed so that all of the seals and virtually all of the electrical connectors are in a thermal environment near ambient conditions. While Figure 2 does not show the oven directly, it does indicate that the upper assembly extends outside of the oven. That part of the system is air cooled with a small electric fan, mounted on the oven controller. The thermal aspects of the seal design problem are thus avoided, but the heat losses for a Mars system would be excessive using this approach. Furthermore, since Mars lacks an electric power generation facility, the magnitude of any extra electric power requirement translates directly into additional system mass (Ref. 1). Hence, the actual Mars oxygen production system should be designed to utilize either solar or radioisotope thermal energy supplies wherever possible, since electric power translates into a fourfold or larger corresponding thermal energy requirement (than do direct thermal needs). The present design wastes a good deal of electrical energy for unnecessary heat generation.

A Mars design requires that the cell system, which may employ a network of more than 1000 cells (Ref. 6), minimize heat losses to the Mars environment. That energy can be managed properly only if the majority of the cells and their seals are maintained within the same 1000 K thermal environment. Hence, the seals and connections must be designed differently than the present design. Furthermore, Richter (Ref. 7) has shown that the energy required for dissociation of the carbon dioxide can be supplied at least partially by thermal means. It is anticipated that the work at Clemson University, which is part of the USRA program as well as research at Stanford University, Jet Propulsion Laboratory, and Ceramatec Corporation will address cell optimization in terms of seal design, geometry and energy management.

Single cell tests using the Ceramatec design will demonstrate the stability of the electrochemical process for Mars applications. The tests will not address seal and geometry issues which require more sophisticated (and expensive) design talent than a team of undergraduate students can realistically produce. The endurance tests, which still represent the ultimate goal of this program, will occur intermittently to accommodate a variety of other tests which have been delineated during this study. The following tests have been identified: (1) Nominal cell performance tests; (2) MOD system certification and failure tests; and (3) Cell deterioration and repair tests. Each of these test programs are described briefly in the following paragraphs.

(1) Nominal Cell Performance Tests

Starting with pure carbon dioxide, or during Phase A tests, the cell(s) will be evaluated over a range of cell voltages, operating temperatures, pressures and mass flow rates. Those tests will establish conversion efficiency and cell power requirements as a function of the control parameters. In addition, the system will be monitored carefully to make sure that the various flows obey the known physical laws (i.e. no leaks or other system anomalies).

Subsequently, in Phase B, the simulated Mars atmosphere will be used over a somewhat narrower parametric range to establish the overall performance of the cell when the feed gas is no longer a single species. Those measurements should be the first tests which measure oxygen yield under Mars-like conditions.

(2) MOD Certification and Failure Tests

During the carbon dioxide tests, where the yields and cell performance are predictable, the system will be monitored as closely as the cell performance. The goal of the system evaluation will be to certify that all of the instrumentation and gas streams are consistent. Those tests will be carried out in parallel with the Phase A cell study. Both studies require the ability to take accurate samples from the various system lines. The sampling system has been given special attention and will be described at the end of this section.

Some types of system failures (such as deliberate leaks and instrument malfunctions) will be introduced during this study in order to verify that the instrumentation will record the upset and permit its identification. Those studies will be especially helpful to the graduate students assisting in this study.

(3) Cell Deterioration and Repair Tests

Depending on the operating conditions, the stability of zirconia in conducting oxygen ions becomes critical. Since oxygen is already contained in the zirconia cell lattice, albeit stabilized with yttria, some migration or oxygen depletion may occur over time. That depletion will be observable through changes in cell resistance and electrical current for fixed voltage operation. Tests will be conducted to determine deterioration rate as a function of operating conditions. Interestingly, Gur and Huggins (Ref. 8) have observed that depletion of oxygen near the cathode surface of a zirconia membrane enhances or catalyzes the production of oxygen from a nitric acid supply and this may also be true for carbon dioxide. However, regardless of deliberate or accidental oxygen depletion, cell life must be studied under those conditions.
Simple cell repair may also be possible by briefly reversing the cell polarity and conducting oxygen back into the feed gas stream. That process is known to clear or even open new oxygen paths through the porous platinum electrodes. In addition, it may be possible to replace depleted oxygen atoms in the cell matrix under the proper set of applied voltage and controlled thermal conditions. Those tests will be conducted as part of this study.

Sampling System

Because most of the MOD system is operated at pressures below one atmosphere, sample collection and prevention of sample contamination during handling are major concerns. As shown in Figure 1, a sample collection flow network (including sample bottles for Mars Gas, Oxygen and Exhaust) has been designed into the MOD system. That system can be evacuated below operating conditions using an independent vacuum pump. The sampling system, including sample bottles, can be pumped down to pressure as low as 0.1 torr to minimize residual gas contamination.

By properly operating the valve system on the MOD network, a sample can be taken of the feed gas, exhaust gas or oxygen. The feed gas can be collected at a pressure in excess of four atmospheres and therefore sample leaks only reduce the sample size. However, the oxygen and exhaust gases must be collected at pressures between 50 and 100 mb and can be contaminated by leaks. In order to preserve subatmospheric samples, the exhaust and oxygen sample bottles will be pressurized above one atmosphere, using helium gas before they are removed from the MOD system. Since helium is used as the carrier gas for gas chromatograph analytical systems, it will not influence gas chromatograph analyses. That part of the sample collection system has not been added to the MOD system at this time.

Summary and Conclusions

To date, the MOD system has been operated with a carbon dioxide feed gas to produce oxygen. Tests will be started during the summer which will begin to define the optimal operating regime. A significant amount of instrumentation and control work will be needed before autonomous, endurance tests can be demonstrated.

Acknowledgement

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References


Table 1

<table>
<thead>
<tr>
<th>Component</th>
<th>Percent by Volume</th>
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<tr>
<td>CO2</td>
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<tr>
<td>Ar</td>
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<td>CO</td>
<td>0.07</td>
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<tr>
<td>Trace†</td>
<td>Balance</td>
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</table>

† Reference 2

| Nominal atmosphere compositions: CO2, 0.03%; N2, 2.5 ppm; Ar, 0.3 ppm; O2, 0.08 ppm; CO, 0.03 ppm.
Figure 1. Schematic Diagram of Mars Oxygen Production System
Fig. 2 Ceramatec Oxygen Separation Cell Assembly Showing Zirconia Cell on Central Axis.

Fig. 3 Combined oxygen and exhaust gas flow rate as a function of ballast tank pressure.