Plasma Extraction of Oxygen from Martian Atmosphere

Richard R. Wheeler, Jr.[1], Neal M. Hadley,[2] Spencer R. Wambolt,[3] John T. Holtsnider,[4] Ross Dewberry,[5]
UMPQUA Research Company, Myrtle Creek, OR, 97457

and

Laurel J. Karr[6]
NASA Marshall Space Flight Center, Huntsville, AL, 35812

In support of NASA's In-Situ Resource Utilization (ISRU) objectives an SBIR Phase 1 effort has demonstrated conceptual feasibility of a novel Plasma Extraction of Oxygen from Martian Atmosphere (PEOMA) technology. Extraction of oxygen from the abundant carbon dioxide present on Mars (96% atmospheric composition) is an important goal in preparation for manned missions to the planet. Oxygen is not only a fundamental reactant with high specific energy chemical fuels such as hydrogen and methane, it, along with water, are clearly two of the most critical resources for life support. Using microwave plasma techniques to decompose CO_2 into CO and $\frac{1}{2}O_2$, coupled with subsequent O_2 separation, a PEOMA robotic processor located on the Martian surface would allow oxygen to be stockpiled for later use during manned exploration near this location. This investigative work has succeeded at validating effective molecular dissociation in a carbon dioxide plasma, with no solid carbon formation. Using innovative standing wave microwave plasma reactor designs, ubiquitous 2.45 GHz microwave technology was employed to demonstrate up to 86% single pass carbon dioxide decomposition.

Nomenclature

Al_2O_3	=	Alumina
AMU	=	Atomic Mass Unit
AR	=	Air Revitalization
C	=	Elemental Carbon
℃	=	Degrees Celsius
CO_2	=	Carbon dioxide
CO	=	Carbon monoxide
Co	=	Cobalt
CH_4	=	Methane
CM	=	Crew Member
DC	=	Direct Current
EM	=	Electromagnetic
Fe	=	Iron
GHz	=	Gigahertz
H_2	=	Molecular Hydrogen
H_2O	=	Water
ISRU	=	In-Situ Resource Utilization
ISS	=	International Space Station

[1] Senior Research Engineer, R&D Division, rwheeler@urcmail.net, 125 Volunteer Way /P.O. Box 609.
[2] Research Scientist, R&D Division, 125 Volunteer Way/P.O. Box 609.
[3] Design Engineer, R&D Division, 125 Volunteer Way/P.O. Box 609.
[4] Senior Chemist, R&D Division, 125 Volunteer Way/P.O. Box 609.
[5] Technician, R&D Division, 125 Volunteer Way/P.O. Box 609.
[6] Aerospace Engineer, ISRU Development, NASA-MSFC/ES62.

MSFC	=	Marshall Space Flight Center
mbar	=	millibar
NASA	=	National Aeronautics and Space Administration
Ni	=	Nickel
NO	=	Nitrous oxide
O_2	=	Molecular Oxygen
O	=	Atomic Oxygen
OGS	=	Oxygen Generation System
PEOMA	=	Plasma Extraction of Oxygen from Martian Atmosphere
PPA	=	Plasma Pyrolysis Assembly
q	=	electron charge ionization number on QMS molecular gas fragment
QMS	=	Quadrupole Mass Spectrometer
RGA	=	Residual Gas Analyzer
RF	=	Radio Frequency
Ru	=	Ruthenium
SBIR	=	Small Business Innovation Research
SOE	=	Solid Oxide Electrolysis
sccm	=	standard cubic centimeters per minute
TE_{10}	=	Transverse Electric (rectangular waveguide mode: m=1, n=0)
W	=	Watts
YSZ	=	Yttria-Stabilized Zirconia

I. Introduction

The extraction of oxygen from the Martian atmosphere may well be an enabling technology for future manned missions to the planet. Successful development of the Plasma Extraction of Oxygen from Martian Atmosphere (PEOMA) technology will result in enhanced capability during both robotic precursor and manned missions on Mars, where low power usage and high reliability are vital. This paper presents the results of an SBIR Phase 1 proof of concept effort for the development of plasma techniques to extract oxygen from the Martian atmosphere (96% CO_2) via the direct decomposition of carbon dioxide.

The thermally induced breakdown of a carbon dioxide molecule is depicted by the reaction pathway shown in Eq. (1):

$$CO_2 \xrightarrow{\text{+528 kJ/mole}} CO + O \xrightarrow{\text{-257 kJ/mole}} CO + \frac{1}{2}O_2 . \tag{1}$$
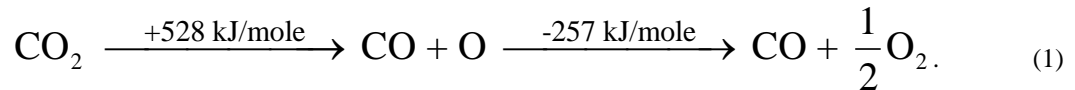
After initial decomposition, molecular oxygen (O_2) forms either by combination of one atomic oxygen (O) with another or by reaction of the O atom with a second CO_2 molecule. Regardless of the pathway, the overall reaction is endothermic and favorable (+271 kJ per mole of CO_2) for temperatures over 3,100°C at 1 bar pressure. Stable, efficient plasma environments that drive this reaction can be created over a wide range of process pressures including the nominal surface pressure on Mars (6 mbar) up to and above Earth's atmospheric pressure ($\geq$ 1 bar). A variety of methods to generate a reactive plasma exist, however microwave plasma techniques can be made to be particularly robust with a high single-pass conversion efficiency[1-7].

The ability to extract resources from regolith and soil on Mars, the Moon, and Asteroids/Phobos can completely change robotic and human mission architectures through the extraction of oxygen, metals, and volatiles (water, hydrogen, etc.) for propulsion, life support, and in-situ manufacturing. Also, materials and resources at the site of exploration can be used to protect crew and hardware, provide materials of construction, and generate energy to power systems brought from Earth. By using in-situ materials and resources, mission resupply logistics and risk can be mitigated.

Oxygen is not only an important reactant with high specific energy chemical fuels such as hydrogen and methane, it, along with water, are two of the most critical resources for life support. As such, robust, long lived methods for carbon dioxide electrolysis/dissociation into carbon monoxide and oxygen are needed to support future Mars exploration missions. Various techniques have been proposed and evaluated for application as primary oxygen extraction methods for Mars In-Situ Resource Utilization (ISRU). These include the reduction of Martian carbon dioxide to form methane and water vapor via the Sabatier reaction, shown in Eq. (2), which employs a fixed-bed catalytic reactor:

$$CO_2 + 4H_2 \xrightarrow{Ru/Al_2O_3} 2H_2O + CH_4 \text{.} \tag{2}$$
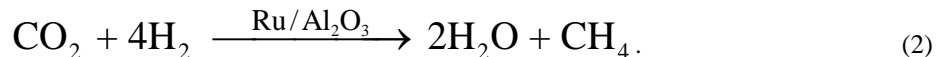
Using a variety of catalysts and reactor configurations, the Sabatier reaction has been studied extensively for the recovery of O_2 (as water via electrolysis) from CO_2 for employment aboard manned spacecraft[8,9]. The chief limitation to this approach for ISRU applications[10,11] is the requirement to supply the hydrogen reductant, which is ultimately locked up in the methane byproduct. Methane plasma pyrolysis techniques developed at UMPQUA, and embodied in NASA's Plasma Pyrolysis Assembly (PPA), can recovery up to 75% of the hydrogen that would otherwise be lost as methane. Nevertheless, even using the PPA, hydrogen is eventually lost to the process, albeit at a reduced rate. Hydrogen could potentially be supplied by electrolysis of indigenous water recovered via ISRU techniques with the added benefit of extra oxygen liberated from water during the process. This approach however, will arguably require a sophisticated overall system architecture which incorporates harvesting, transportation, extraction, electrolysis, storage and integration with a Sabatier reactor. As such, this level of complexity may be better suited for a mission scenario with a sustained human presence.

Like the Sabatier reaction, the Bosch reaction[12,13] is a well-known process allowing the recovery of oxygen from carbon dioxide by reacting it with hydrogen at elevated temperature in the presence of an appropriate catalyst forming water vapor and elemental carbon (C). Bosch is comprised of a multistep reaction pathway but is summarized by the net reaction shown in Eq. (3):

$$CO_2 + 2H_2 \xrightarrow{Fe/Co/Ni} 2H_2O + C(s) \text{.} \tag{3}$$

The advantage of the Bosch technology is that it potentially offers complete recovery of the oxygen and hydrogen resources. Like the Sabatier reaction, however, a supply of hydrogen is required even though it can theoretically be recovered and reused indefinitely via electrolysis of the product water. Catalysts used in the Bosch reaction are prone to carbon fouling and eventually define a limited operational life for a fixed bed reactor. In addition, while the products in Eq. (3) predominate, there are parasitic reactions that occur producing Sabatier methane, which effectively serve to remove hydrogen from the Bosch process. While research is on-going for this technology[14], significant advancements are still required to make it competitive with Sabatier.

One promising technique that has received much attention utilizes Solid Oxide Electrolysis (SOE) to simultaneously thermo-catalytically decompose CO_2 to CO and O while at the same time separating the oxygen product[15-19]. Here, CO_2 decomposition requires elevated temperatures between 750°C and 1000°C and occurs at cathodic platinum sites located on the surface of the nonporous solid electrolyte (e.g., yttria-stabilized zirconia (YSZ)). An applied electric field drives oxygen ion transport from one ion vacancy to the next across the solid electrolyte crystal lattice, thereby effecting oxygen separation. While recent advancements have improved oxygen transfer for these ceramic membranes[20,21], large surfaces areas are still required to support a significant oxygen flux.

Other techniques that have been investigated for oxygen extraction from the Martian atmosphere include both DC and RF induced glow discharge[22,23]. This work, while demonstrating the fundamental performance gains of a plasma process over SOE, nevertheless underscores the disadvantages of electrode and coil based reactor designs which, in general, are susceptible to electrode fouling or have restrictive geometric design limitations.

While the ISRU application of the PEOMA technology was the focus of the Phase 1 investigation, as described in this paper, the technology potentially lends itself to direct utilization within a habitat life support system. Acting as a first stage oxygen recovery process within the enclosure's Air Revitalization (AR) system, up to 50% of the oxygen contained in carbon dioxide from respiration can be converted by a PEOMA type processor, as indicated by the reaction in Eq. (1). The balance of the oxygen (in the form of water vapor) can be recovered downstream in a second stage reactor via a methanation reaction as shown in Eq. (4):

$$CO + 3H_2 \xrightarrow{Ru/Fe/Ni/Co} H_2O + CH_4 \text{.} \tag{4}$$
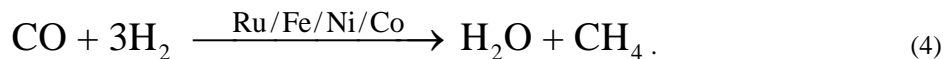
This reaction is completely analogous to the Sabatier reaction shown in Eq. (2), but acts directly on carbon monoxide instead of carbon dioxide to produce the same water and methane products. As a combined process, with a PEOMA type reactor and a methanation reactor working together, less hydrogen is required to recover the same amount of oxygen as in an AR system that uses a Sabatier reactor by itself. Clearly this benefit is a result of the direct recovery of oxygen from carbon dioxide without having to first be recovered in the form of water with subsequent electrolysis to oxygen. To be a competitive approach, however, the energetics of this combined PEOMA/methanation process must compare favorably to that of the Sabatier reactor acting alone. In addition, an effective way of separating the carbon monoxide and oxygen products leaving the PEOMA reactor must be employed before sending the carbon monoxide portion to the methanation reactor. Last but not least, since carbon monoxide is a poisonous gas, complete separation of carbon monoxide from the oxygen product must be assured in

addition to implementation of safe handling techniques that assure leak free operation. The fulfillment of these requirements must be thoroughly demonstrated prior to application within a habitat life support system.

Equilibria for the carbon-oxygen system are shown, contained in the plots in Figure 1, at the three distinct system pressures of 1 bar (Earth surface), 0.16 bar, and 0.006 bar (Mars surface) over a wide range of temperatures (0-10,000°C). Equilibria are seen to shift to the left (towards lower temperatures) as the system pressure decreases. In addition these plots show that a peak in O_2 production occurs at significantly elevated temperatures (~3,100°C at 1 bar dropping to ~2,300°C at 0.006 bar). In fact, regardless of the pressure, significant decomposition of CO_2 does not begin until the process temperature is raised above ~1,500°C. Since a thermodynamic analysis only describes the potential reaction under equilibrium conditions, a complete picture must include the process kinetics. Regardless, it is clear from equilibrium calculations that the temperature ranges commonly used in thermo-catalytic induced decomposition of CO_2 (such as used in the solid electrolysis approach described above) fall short of optimal values and necessitate the use of a catalyst. In contrast, plasma catalytic means for CO_2 decomposition offer reactive environments at much higher effective temperatures easily attaining the optimal equilibrium temperatures shown in these plots without the need of a vulnerable catalytic surface.

Microwave plasmas provide a useful means to produce an extreme thermal environment in a small, well-controlled region of space, resulting in very high energy density within the plasma. The free radicals, ions and highly energetic electrons contained in the plasma provide an extremely reactive environment promoting endothermic reactions which become thermodynamically favorable only at very high temperatures. Using microwave plasmas, high temperature reactions can be conducted using systems, which are smaller, lighter, and less complex than conventionally heated high temperature solid electrolyte, fixed bed or fluidized bed catalytic reactors.
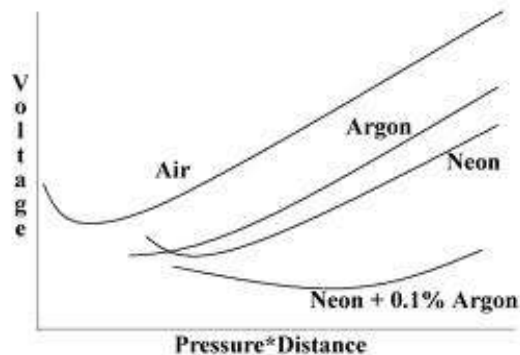
Plasma (a charge balanced ionized gas) is the fourth state of matter and, indeed, the most abundant form of matter in the universe. A plasma is produced when the rate of ionization within a gas exceeds the rate of recombination (known as avalanche or breakdown phenomena). It can be created by the heat produced in chemical reactions, such as is the flame in a fire, or by electromagnetic (EM) forces, such as in lightning. EM gas breakdown phenomena is driven by the electric field and is dependent not only on the field strength but also the frequency of the EM wave and the gas pressure (or molecular density). Due to the average spacing of gas molecules, breakdown occurs more
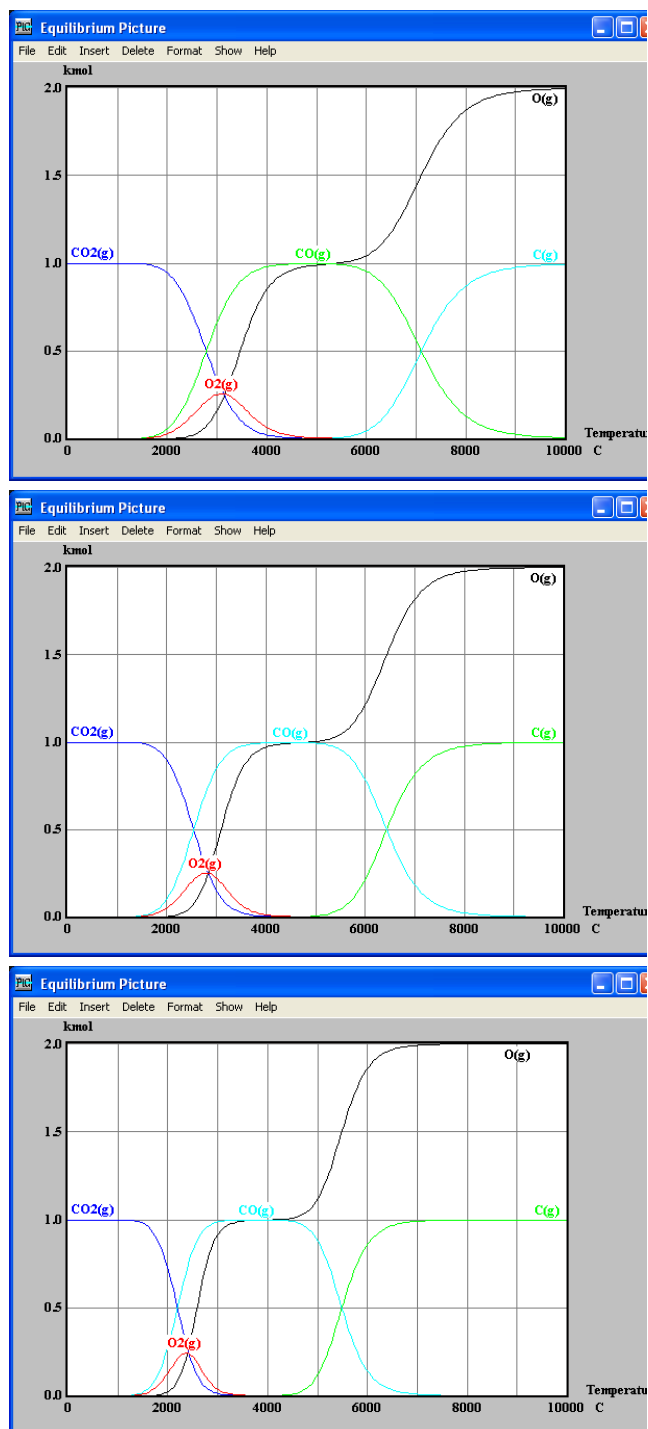
Figure 1.   Equilibria Plots, Produced by HSC 5.0 Software, for 1.0 kmol of Carbon Dioxide Decomposition at 1 bar.(top), 0.16 bar (center), and 0.006 bar (bottom.)

readily in the RF and microwave frequency bands of the EM spectrum with the optimal frequency dependent on the specific gas. Similarly, for a fixed EM frequency, as pressure is decreased the separation distance between molecules increases, permitting greater energy transfer to free electrons (which drive ionization) per EM wave cycle. As such, avalanche breakdown occurs more readily with decreasing pressure until the gas density becomes too diffuse and higher field strengths are required to induce breakdown. The net result is that a minimum in breakdown field strength occurs that is typically around 1 Torr for pure gases.

This phenomena is described for each gas at a given EM frequency by a Paschen curve (e.g., see curves in Figure 2), which is an empirical plot of the required electric field strength (or alternatively, the voltage) as a

Figure 2. Breakdown field as a function of pressure and gap distance.[24]

function of pressure (or alternatively, the pressure multiplied by gap distance). An interesting attribute of gas mixtures is the shift in this curve to higher pressures and a reduced breakdown minimum, as seen in Figure 2 for a mixture of Neon and Argon. For the present application, where the Martian atmosphere is not a pure CO_2 gas but rather has minor amounts of both nitrogen and (perhaps more importantly, because it breaks down more readily) argon, this is advantageous since it means that lower microwave power levels are needed to both trigger and sustain a plasma. In addition, the minimum breakdown pressure shifts towards the 4-6 Torr pressure typical of the Martian atmosphere. As such, a PEOMA processor located on the Martian surface will operate at minimum breakdown field strength at the local pressure without the need for either purification or compression of the atmospheric gas. Even if overall conversion efficiency of the PEOMA proves to be greater at slightly elevated pressures, above the breakdown minimum, then compression of Mars CO_2 can be accomplished using either conventional compressors or sorbent bed based systems.[25-28] The fundamental efficacy of CO_2 plasma generation and decomposition was first demonstrated in a prior Phase I.[29]

II. Planetary Protection Concerns

The production and subsequent release of CO on Mars by an ISRU process brings up potential concerns related to both planetary protection and potential fouling of the ISRU feedstock. Remediation of the CO may be achieved via chemical pathways. In theory, a CO product could be combined (at elevated temperature) with the Martian soil promoting the catalytic formation of CO_2 and solid carbon via the Boudouard reaction (2 CO → CO_2 + C) or, alternatively, to reduce iron oxide present in the soil (FeO + CO → Fe + CO_2). These mass and energy intensive measures, however, may not be warranted for a specific ISRU process. The Martian atmosphere has been measured by NASA's Curiosity rover's SAM instrument suite to contain up to 0.06% (mole basis) carbon monoxide, ranking CO as the fifth most abundant gas on the red planet following CO_2 (95.9%), Ar (2.0%), N_2 (1.9%) and O_2 (0.14%). While CO represents only a minor fraction of the Martian atmosphere composition, the fact that it is indigenous may circumvent planetary protection concerns pertaining to any ISRU process that merely adds more of an already existing gas (i.e., CO) to the Mars atmosphere. In addition, while it is conceivable that the local environment near the process intake could become overly rich in CO for efficient plasma extraction of oxygen, this concern can be addressed for a low throughput process (targeting 2.25 kg/hr CO_2, which equates to 3.2 cubic meters per minute at Mars' 6 mbar surface pressure) by appropriate separation of the intake and exhaust ports relative to one another coupled with adequate mixing/dilution of the product stream in the CO_2 rich atmosphere.
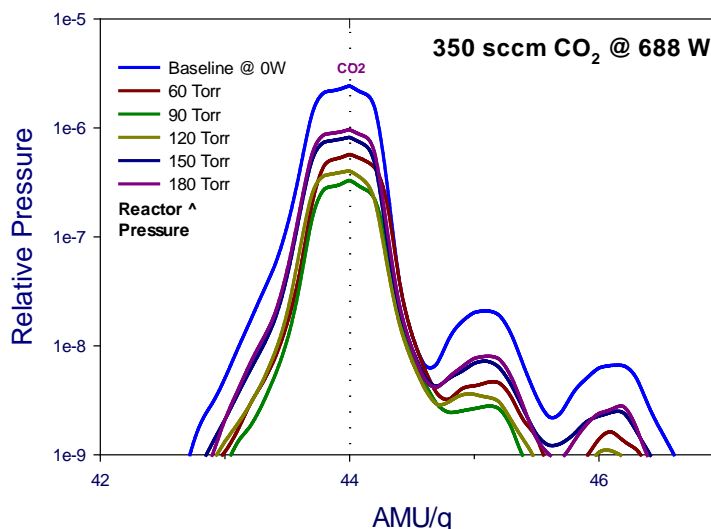
III. Demonstration of Plasma Decomposition of CO_2

Figure 3 contains plots of preliminary test data (CO_2 mass spectra at various operating pressures) generated in our laboratory, using a relatively crude microwave plasma apparatus. While rough, these data demonstrated that high conversion efficiencies were indeed possible for the proposed CO_2 plasma decomposition technique. As indicated by the one log reduction in relative pressure at 44 AMU/q (compare blue baseline curve to the green 90 Torr curve), a roughly 90% CO_2 conversion is possible at an optimal pressure of 90 Torr. Electrical to chemical energy conversion efficiency for this crude process equals 6.0% (where 90% CO_2 conversion and 65% electrical to microwave conversion efficiencies are assumed). While the energy efficiency is low for this non-optimal microwave plasma reactor, it is nevertheless nearly <u>three times greater than the 2.2% (=100% x 0.21W / 9.71W)</u>
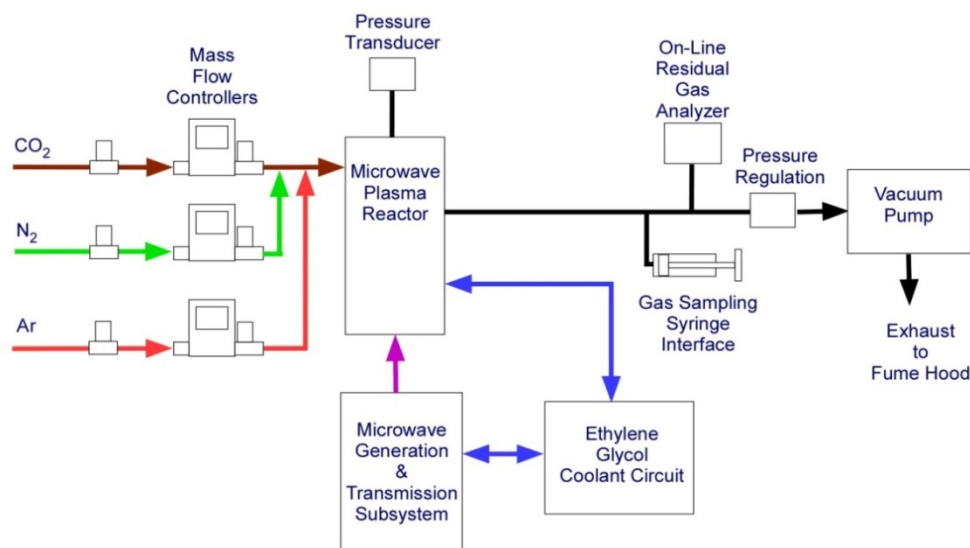
demonstrated by the SOE-based Oxygen Generation System (OGS) that was part of the ISRU hardware package built for the cancelled 2001 Mars Surveyor Lander mission[17]. The Mars OXygen In situ resource utilization Experiment (or MOXIE), which is currently baselined as an 'oxygen from carbon dioxide' ISRU experiment package on the next rover mission slated for launch in 2020[30-32], is also based on SOE. As such, it would likely have a similarly poor energy efficiency comparison with the PEOMA approach.

Proof of concept tests for the PEOMA technology included both independent and integrated testing. Independent testing evaluated the plasma decomposition and oxygen separation elements separately. Following these independent tests, the two system elements were to be combined for fully integrated demonstration testing.

A process flow diagram for the PEOMA test stand is shown in Figure 4. On-line, residual gas analysis is provided by a Stanford Research Systems QMS-200 quadrupole mass spectrometer. This

Figure 3. Preliminary CO_2 Plasma Decomposition Tests. X-Axis Units are AMUs Divided by the Absolute Value of the Electron Charge Ionization Number (i.e., 1, 2, 3,…).

device is capable of operation over a wide range of system pressures from 10 Torr to just above atmospheric pressure, using appropriate inlet capillaries. Reduced system pressure is maintained by an active pressure controller located just upstream from the vacuum pump. An ethylene glycol / water mixture is pumped from a flow through chiller, and cools both the microwave plasma reactor and the water load for the microwave subsystem. Reactor pressure is independently monitored using a pressure transducer located on the view port assembly. Three mass


Figure 4. PEOMA Process Flow Schematic.

flow controllers, one each for carbon dioxide, nitrogen, and argon, provide a combined gas stream to the reactor that approximates the composition of the Martian atmosphere (96% CO_2, 2% N_2 and 2% Ar).
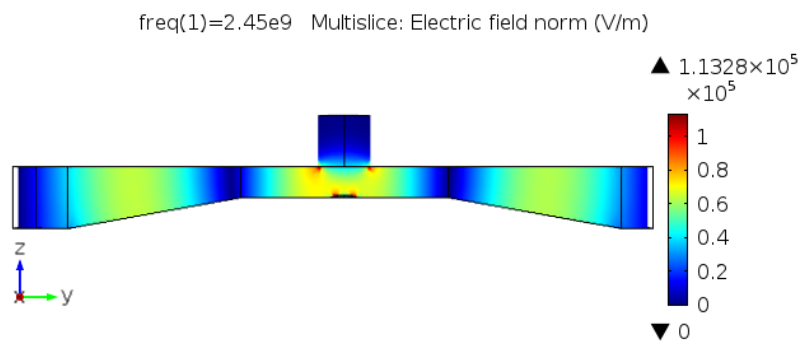
Plasma decomposition testing was performed in both cylindrical and rectangular PEOMA test reactors, each shown in Figure 5. Plasma can be seen located on the respective stubs for each reactor in the lower photos.
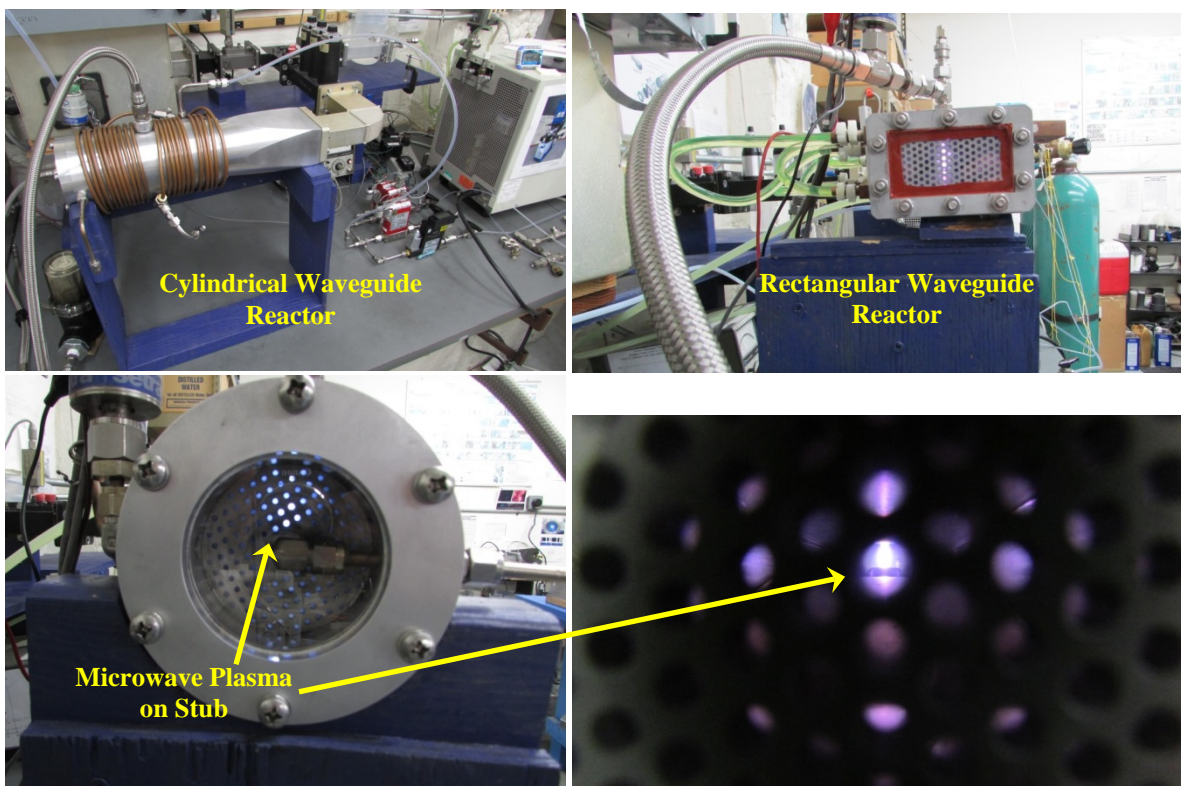
Figure 5. PEOMA Test Reactors: Cylindrical Reactor (Left Photos); Rectangular Reactor (Right Photos).

A plot of the electric field distribution for a Comsol multiphysics model of the as-built rectangular waveguide PEOMA is shown in Figure 6. In this model 2.45 GHz microwave power at 600 W is introduced from the right hand side of the device. The TE_{10} mode was intentionally excited, as would also be the case in the actual reactor. Located on the far left side of the reactor is the perforated plate viewport that also serves as a shorting (or reflection) plate for the microwaves. The effect of the reflection plate is to form a standing wave pattern in the reactor that, by geometric design, establishes a central standing wave maximum at the location of the plasma locating stub.

Accordingly, during operation an efficient microwave plasma will preferentially form where it is desired above the top of the stub. In this model, the stub tip is visible just inside the lower edge of the model geometry and bracketed by regions of high electric field strength (indicated by red coloring). The small, blue colored box centrally located above the reactor (and stub) represents just one possible exit port configuration that was considered. Due to operational limitations that could

Figure 6. Electromagnetic 2.45 GHz Model of PEOMA Rectangular Reactor.

not be overcome in the Phase 1 timeframe, test results for the actual rectangular reactor were inconclusive and will not be presented in this paper.

The cylindrical PEOMA reactor is cooled by coolant flow through copper tubing wrapped around the body of the reactor. During operation, the plasma is observed through an end view port. A polycarbonate window located in front of a perforated aluminum plate protects the operator by significantly attenuating any ultraviolet light produced by the plasma. This cylindrical reactor was originally designed and tested for application as a hydrogen recovery reactor in partial methane pyrolysis. A similar reactor of identical internal dimensions but having an external body

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that was box shaped, to facilitate in-wall cooling, was provided to the Air Revitalization group at NASA-MSFC in a 3rd Generation Plasma Pyrolysis Assembly. Cylindrical PEOMA tests used a 96% CO_2, 2% Ar, 2% N_2 feed stream that is representative of the Martian atmosphere. Initial reactor characterizations used the QMS-200 operating in mass spectra analog scan mode to identify all gaseous products produced in the plasma. Following these characterization tests, the PEOMA reactor was operated, as configured in Figure 5, over a range of microwave power levels and reactor pressures. The QMS-200 was set up to operate in continuous scan mode to permit direct comparison of reactor CO_2 decomposition performance from one set of power/pressure conditions to the next. In continuous scan mode the QMS-200 displays relative concentration traces as function of time for a predefined number of analyte mass fragments (up to ten AMU/q values).

Analog scans of both the influent (or "No Plasma", 0 W state) and effluent (or "Plasma On", 600 W state) gas streams at 95 Torr, acquired using the QMS-200, are shown in Figure 7. These analog scans contain the mass
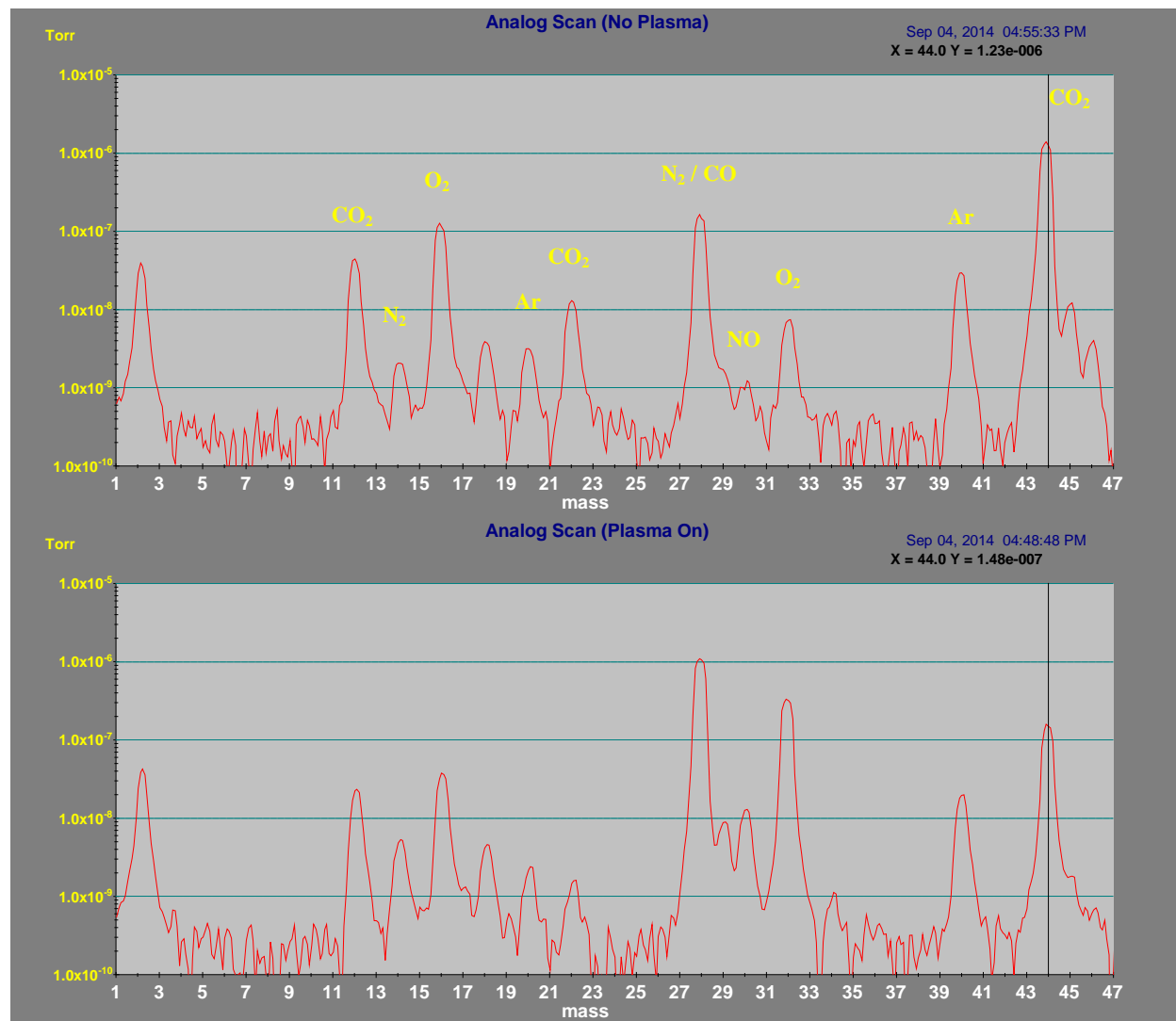
Figure 7. QMS Spectral Data for CO_2, CO, O_2, Ar and N_2 Acquired For Both the Influent (Top) and Plasma Effluent (Bottom) Gas Streams. Trace Hydrogen and Water Vapor Produces Background Peaks at 2 and 18 AMU/q, Respectively.
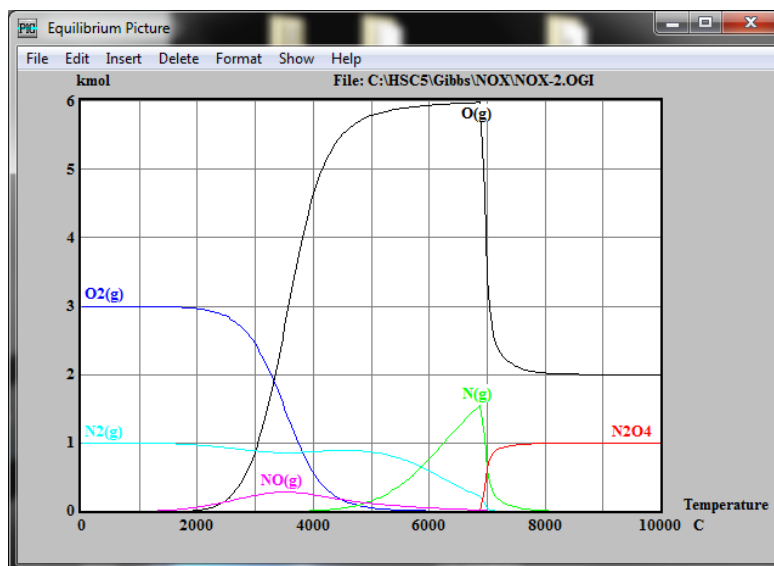
spectra data (or AMU/q peaks) for the component gases. Comparing the two scans, it is evident that no unexpected product peaks occur as a result of the energetic plasma. Spectra was acquired out to 65 AMU/q; however, only shown plotted to 47 AMU/q in Figure 7. Slightly elevated levels of Nitrous Oxide (NO) appear at 30 AMU/q. In contrast, there is clearly a significant reduction in CO_2 at 44 AMU/q, with a corresponding increase in CO and O_2 at 28 AMU/q and 32 AMU/q, respectively. This change corresponds to an 83% reduction in CO_2, as determined by

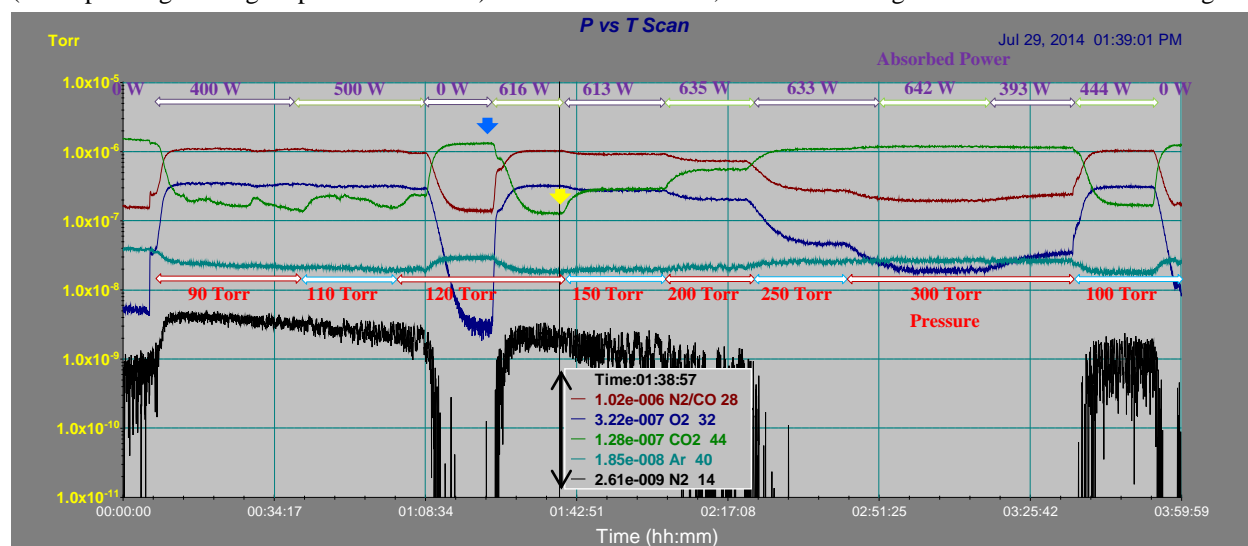International Conference on Environmental Systems

methods described below. The fact that the NO peak at 30 AMU/q, for the "Plasma On" case, is more than an order of magnitude smaller than the residual (~10%) CO_2 peak at 44 AMU/q, indicates that the NO concentration in the product stream is less than 1%. The minor amount of NO present in the plasma product, along with the apparent absence of the higher weight nitrogen/oxygen compounds (such as NO_2 or N_2O) is further supported by thermodynamic equilibrium data for nitrogen/oxygen mixtures representative of those expected in the PEOMA effluent, as demonstrated in Figure 8. In fact, this equilibrium data shows the relative absence of NO_2 and N_2O,

Figure 8. Thermodynamic Equilibrium for an Oxygen Nitrogen System.

with NO being the only nitrogen/oxygen compound of any significance that is favorable below ~6,900 °C, and it only appears as a minor component even at its optimal formation temperature of ~3,500 °C. Previous measurements made in our lab with hydrogen/methane plasmas at similar power levels have indicated neutral gas temperatures around 1,200 °C and effective excited species reaction temperatures (as indicated by products formed) of around 2,000 °C. By extension, if a similar thermal state exists in this CO_2 plasma, then a thermodynamics analysis predicts that only very minor amounts of NO can be formed.

A series of carbon dioxide plasma decomposition tests were performed at various microwave power levels and reactor pressure settings. Raw QMS data plotted as relative pressure (Torr) for primary mass to charge ratios peaks (corresponding to the gas species of interest) as a function of time, are shown in Figure 9. Both molecular nitrogen

Figure 9. QMS Peak Data for CO_2, CO, O_2, Ar and N_2 Acquired over Time, at Various Microwave Power Levels and Reactor Pressures, for a Gas Feed Mixture Containing 96% CO_2, 2% N_2 and 2% Ar. Blue Arrow – Plasma Off at 120 Torr; Yellow Arrow – Plasma On at 120 Torr and 616 W Absorbed Microwave Power Yields 86% Conversion of Carbon Dioxide.

and carbon monoxide contribute to the singly ionized 28 AMU/q peak. Similarly, the dominant peaks for molecular oxygen, carbon dioxide and argon are 32 AMU/q, 44 AMU/q and 40 AMU/q, respectively. Because nitrogen and carbon monoxide contribute to the same primary 28 AMU/q peak, a secondary nitrogen peak at 14 AMU/q,

corresponding to doubly electron ionized molecular nitrogen, is acquired as an independent measurement of nitrogen concentration. If QMS-200 gas sensitivity factors were known for each component gas, then this data could be used in a quantitative analysis to deconvolute nitrogen and carbon monoxide contributions yielding an accurate measure of the actual concentration of each gas in the product stream. However, the complexity of such an approach, with its inherently large experimental error, precludes its use. As such, only relative changes in concentration for individual gases, which do not have interfering peak contributions, can be accurately determined. Using this approach the relative change in carbon dioxide concentration from the "No Plasma" (0 W) state to the "Plasma On" state can be employed to estimate the degree of carbon dioxide decomposition produced within the plasma. This is possible because of the simple gas makeup of both the influent and effluent streams resulting from the straight forward stoichiometry of carbon dioxide plasma decomposition, as shown in Eq. (1).. As confirmed experimentally by the absence of significant levels of unwanted products (such as NOXs) observed in the analog scan. In addition, it is noteworthy that no solid carbon formation was observed in any of these experiments. As such, carbon fouling is not expected to be an issue for PEOMA technology. This a significant result which can only help promote a long useful life for a PEOMA reactor. This, in contrast to a gradual performance degradation resulting from carbon fouling of the catalyst in a Bosch reactor or, to a lesser extent, residual carbon buildup in the PPA reactor.

With the argon and nitrogen components remaining mostly unaltered, the known feed concentrations of all gases, coupled with the measured change in CO_2 concentration, can be used to calculate the concentrations of each component in the effluent gas stream. From this same analysis the percent conversion of CO_2 is also determined. The greatest degree of conversion observed with the cylindrical PEOMA reactor was achieved at 616 W of absorbed power (7 W reflected) at an operating pressure of 120 Torr and 380 sccm of carbon dioxide flow, resulting in 86% carbon dioxide conversion. This is significantly better than the ~40% achieved in previous work at similar power levels and flow rates. Electrical to chemical energy conversion efficiency for the demonstration reactor equals 7.0% for a 380 sccm CO_2 processing rate (with 85% decomposition) at 623 W of microwave power, and assuming a 65% electrical to microwave conversion efficiency. While this energy efficiency is low, as mentioned before it is significantly better than the 2.2% demonstrated by the SOE-based Oxygen Generation System (OGS) located within the ISRU hardware package built for the 2001 Mars Surveyor Lander.

IV. Oxygen Separation

A handful of ceramic oxygen separators were identified for evaluation in the PEOMA process. Both traditional yttria stabilized zirconia (YSZ) as well as more cutting-edge lanthanum strontium cobalt ferrite (LSCF) ceramics were acquired. Both of these are perovskite-type ceramics and require high temperatures to facilitate oxygen ion transport through the thin ceramic membrane from a high oxygen partial pressure side to a low oxygen partial pressure side. While the electronic circuit for a solid oxide electrolysis cell is completed (and potentially limited) by electron transfer from one side to the other, no attempt was made in this work to improve current flow by application of a voltage gradient across the membranes. Both tubular and flat ceramic forms of the YSZ membranes were acquired for evaluation, while only the raw LSCF ceramic powder was purchased and prepared as a flat disk membrane for evaluation. Independent testing with these ceramic membranes proved problematic and only limited integrated testing was performed which will not be presented in this paper. Due to our lack of success in applying these membranes, various experts in the field of ceramic oxygen separation were contacted in the course of this work as potential team members in future PEOMA development. In particular, Gordon Parkinson's research group at Curtin University (Perth Australia) showed interest in supporting such an advanced effort.

As an alternate approach for the Phase 1 effort, oxygen separation tests were performed at room temperature using a variety of sorbent materials including molecular sieves 3A, 4A, 5A and 13x, silica gel, alumina, and activated carbon. The goal here was to identify any
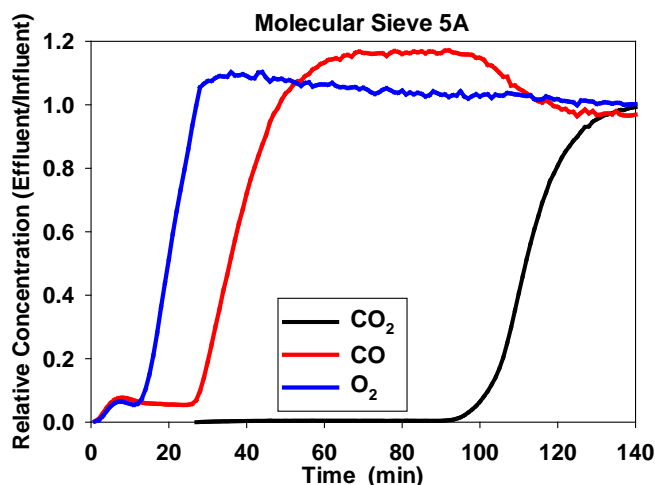
Figure 10. Sorption Breakthrough Curves Performed (at 20 ℃ and 1atm) for CO_2 Plasma Effluent Gases.

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materials that would preferentially adsorb carbon monoxide and carbon dioxide while passing pure oxygen. While many of the materials showed strong carbon dioxide removal, only molecular sieve 5A showed a slight amount of preferential separation between oxygen and carbon monoxide. Initially, each of the gases present in the plasma effluent stream were captured by the 5A, as seen by the relative concentration curves shown in Figure 10. Oxygen breakthrough started first with carbon monoxide breakthrough following immediately afterwards. In theory, this effect could be exploited for oxygen separation by opening a diverter valve at the appropriate time, thereby channeling liberated oxygen to a storage volume and closing the valve prior to carbon monoxide breakthrough. The degree of separation observed for molecular sieve 5A at room temperature may be improved upon by operation at subzero sorption temperatures (e.g., those commonly found on the Martian surface). In addition, by employing a carbon dioxide selective pre-adsorption bed (e.g., mole sieve 13x), oxygen and carbon monoxide separation may be further enhanced in the downstream 5A bed.

V. Conclusion

This paper summarizes work performed in an SBIR Phase 1 effort demonstrating conceptual feasibility of a novel Plasma Extraction of Oxygen from Martian Atmosphere (PEOMA) technology. Using microwave plasma techniques to decompose CO_2 coupled with an oxygen separation from the product gas, a PEOMA robotic processor located on the Martian surface would serve to stockpile oxygen for later use. Using innovative standing-wave microwave plasma reactor designs, inexpensive 2.45 GHz microwave oven technology is employed to provide 600 W of microwave power to drive CO_2 decomposition. This proof of concept work demonstrated operation of a cylindrical PEOMA reactor capable of converting over 85% of the CO_2, found in the abundant CO_2 available in the Martian atmosphere (96% CO_2, 2% N_2, 2% Ar, plus trace gases), to oxygen and carbon monoxide with no solid carbon formation. This level of conversion was achieved in a single pass through the PEOMA reactor at a flow rate of 380 sccm CO_2 and operating at pressures around 100 Torr, which represents a modest 20-fold compression of those found on Mars. This process rate corresponds to 0.038 kg/hr of CO_2 decomposition and 0.014 kg/hr of oxygen production. Scale-up of the PEOMA reactor processing rate is expected to be similar to scale-up of the PPA (another microwave plasma based technology), which progressed from a 0.5-CM scale device, embodied in a Phase 2 SBIR prototype, to a 5-CM scale system via a three year Phase 3 follow-on development effort with only moderate increases in system size and power. For product gas separation, either preferential sorption using molecular sieves or ceramic membrane oxygen separation technology are possible matches for the PEOMA plasma decomposition approach, but integrated operation remains to be shown.

Acknowledgments

References

[1]Fridman, A., Plasma Chemistry, Cambridge University Press, New York, New York, 2008.

[2]Atwater, J.E., Wheeler, R.R., Jr., Hadley, N.M., Dahl, R.W., and Carrasquillo, R.L., Hydrogen Recovery by Methane Decomposition in a Microwave Plasma Reactor, SAE Paper No, 2008-01-2099, presented at the 38th International Conference on Environmental Systems, San Francisco, June 29-July 2, 2008.

[3]Atwater, J.E., Wheeler, R.R., Jr., Hadley, N.M., Dahl, R.W., and Carrasquillo, R.L., Development and Testing of a Prototype Microwave Plasma Reactor for Hydrogen Recovery from Sabatier Waste Methane, SAE Paper No. 2009-01-2467, presented at the 39th International Conference on Environmental Systems, Atlanta, July 2009.

[4]Abney, M. B., Miller, L. A., and Williams, T., Sabatier Reactor System Integration with Microwave Plasma Methane Pyrolysis Post-Processor for Closed-Loop Hydrogen Recovery, AIAA Paper No. 2010-6274, presented at the 40th International Conference on Environmental Systems, Barcelona, July 2010.

[5]Mansell, J. M., Abney, M. B., and Miller, L. A., Influence of Oxygenated Compounds on Reaction Products in a Microwave Plasma Methane Pyrolysis Assembly for Post-Processing of Sabatier Methane, AIAA Paper No. 2011-5035, presented 41st International Conference on Environmental Systems, Portland, 2011.

[6]Wheeler, R.R., Jr., Hadley, N.M., Dahl, R.W., Abney, M.B., Greenwood, Z., Miller, L., and Medlen, A.., Advanced Plasma Pyrolysis Assembly (PPA) Reactor and Process Development, AIAA-2012-3553, presented 42nd International Conference on Environmental Systems, San Diego, July 16-19, 2012.

[7]Wheeler, R.R., Jr., Hadley, N.M., Wambolt, S.W., and Abney, M.B., Third Generation Advanced PPA Development, ICES-2014-034, presented 44th International Conference on Environmental Systems, Tucson, July, 2014.

[8]Zubrin, R. Price, S., Mason, L., Report on the Construction and Operation of a Mars In-Situ Propellant Plant., AIAA-94-2844, presented at the 30th AIAA/ASME Joint Propulsion Conference, Indianapolis, IN, June 1994.

[9]Nakata, A., Matsumoto, H., Hatano, S., Kita, Y., and Shimoda, T., Fundamental Study of Water Generation System on Mars, SAE 2001-01-2413, presented at the 31st International Conference on Environmental Systems, July 2001.

[10]Jeng, F.F., Lafuse, S., Smith, F.D., Lu, S.-D., Knox, J.C., Campbell, M.L., Scull, T.D., and Green, S., Analyses of the Integration of Carbon Dioxide Removal Assembly, Compressor, Accumulator and Sabatier Carbon Dioxide Reduction Assembly, SAE Paper No. 2004-01-2496, presented at the 34th International Conference on Environmental Systems, 2004.

[11]Murdoch, K.E., Scull, T.D., Carrasquillo, R.L., and Graf, J., Sabatier CO_2 Reduction System Design Status, SAE Paper No. 2002-01-2531, presented at the 32nd International Conference on Environmental Systems, 2002.

[12]Wagner, R.C., Carrasquillo, R., Edwards, J., and Holmes, R., Maturity of the Bosch CO_2 Reduction Technology for Space Station Application, SAE Paper No. 880995, presented at the 18st Intersociety Conference on Environmental Systems, July 1988.

[13]Bunnell, C.T., Boyda, R.B., and Lee, M.G., Optimization of the Bosch CO_2 Reduction Process, SAE Paper No. 911451, presented at the 21st International Conference on Environmental Systems, San Francisco, July 1991.

[14]Akse, J.R., Thompson, J.O., Regenerative Bosch Reactor, Phase I Final Report, NASA Contract NNX11CH43P, Marshal Space Flight Center, August 2011.

[15]Iacomini, C.S., Powers, A., and Durrant, T., Design of a Stand-alone Solid Oxide Electrolysis Stack with Embedded Sabatier Reactors for 100% Oxygen Regeneration, SAE Paper No. 2009-01-2440, presented at the 39th International Conference on Environmental Systems, Atlanta, July 2009.

[16]Sridhar K.R., Iacomini C.S., and Finn, J.E., Combined H_2O/CO_2 Solid Oxide Electrolysis for Mars In Situ Resource Utilization, *Journal Of Propulsion And Power*, Vol. 20, No. 5, September–October 2004.

[17]Sridhar, K.R., Gottmann, M., and Baird, R.S., 2001 Mars In-Situ Oxygen Production Flight Demonstration, AIAA Paper No. 99-2413, presented at the 35th Joint Propulsion Conference and Exhibit, 1999.

[18]Sridhar, K.R. and Vaniman, B.T., Oxygen Production on Mars Using Solid Oxide Electrolysis, SAE Paper No. 951737, presented at the 25th International Conference on Environmental Systems, 1995.

[19]Kelsey, L., Straus, J., and Zuniga, D., Contaminant Robust Water Extraction from Lunar and Martian Soil for In Situ Resource Utilization-System Architecture Development, AIAA-2012-3502, presented 42nd International Conference on Environmental Systems, San Diego, July 16-19, 2012.

[20]Hashim, S., Mohamed, A., and Bhatia, S., Current status of ceramic-based membranes for oxygen separation from air, *Advances in Colloid and Interface Science*, 160, 88–100, 2010.

[21]Xin Shao, Dehua Dong, Gordon Parkinson and Chun-Zhu Li, A Microchanneled Ceramic Membrane For Highly Efficient Oxygen Separation, *J. Mater. Chem. A*, 1, 9641-9644, 2013.

[22]Ash, R.L., Cotton, C.E., *et al.*, Mars Oxygen Production System Design, 4th Annual NASA/ USRA Design Review, University Advanced Design Program Conference, Kennedy Space Center, June 14-17, 1988.

[23]Vuskovic, L., Ash, R.L., Shi, Z., Popovic, S., and Dinh, T., Radio-Frequency-Discharge Reaction Cell for Oxygen Extraction from Martian Atmosphere, SAE 972499, 1997.

[24]Heald, J.R., "Paschen Breakdown in the Martian Atmosphere", NASA Kennedy Space Center [KSC Science Server], dated May 21, 2003, http://empl.ksc.nasa.gov/CurrentResearch/Breakdown/Breakdown.htm, Electrostatics and Surface Physics Laboratory, [cited 2 March 2015].

[25]Walton, K., and Le Van, M., A Novel Adsorption Cycle for CO_2 Recovery: Experimental and Theoretical Investigations of a Temperature Swing Compression Process, *Separation Science and Technology*, 41: 485-500, 2006.

[26]Johnson, K., Karlmann, P., Rapp, D., and Sharma, P., Sorbent Bed Acquisition and Compression of Carbon Dioxide from the Mars Atmosphere, SAE Paper No. 2000-01-2237, presented at the 30th International Conference on Environmental Systems, 2000.

[27]Mulloth, L., and Affleck, D., Development of a Temperature-Swing Adsorption Compressor for Carbon Dioxide, SAE Paper No. 2003-01-2627, presented at the 33th International Conference on Environmental Systems, 2003.

[28]Finn, J., Mulloth, L., and Borchers, B., Performance of Adsorption-Based CO_2 Acquisition Hardware for Mars ISRU, SAE Paper No. 2000-01-2238, presented at the 30th International Conference on Environmental Systems, 2000.

[29]Dahl, R.W., Hadley, N.M., and Wheeler, R.R., Jr., Plasma Catalytic Extraction of Oxygen from the Martian Atmosphere, Phase I Final Report, NASA Contract NNX11CF99P, Johnson Space Center, 2011.

[30]Weinstock, M., "Going to the Red Planet" - Mars Oxygen ISRU Experiment Instrument for Mars 2020 Rover is MOXIE, NASA Jet Propulsion Laboratory [online news article], dated 07.31.2014, http://mars.nasa.gov/mars2020/news/whatsnew/index.cfm?FuseAction=ShowNews&NewsID=1683, [cited 27 February 2015].

[31]Wall, M., "Oxygen-Generating Mars Rover to Bring Colonization Closer", Space.Com [online news article], dated Aug 01, 2014, http://www.space.com/26705-nasa-2020-rover-mars-colony-tech.html, [cited 27 February 2015].

[32]Weinstock, M., "Oxygen-creating instrument selected to fly on the upcoming Mars 2020 mission", Phys.Org [online news article], dated Aug 01, 2014, http://phys.org/news/2014-08-oxygen-creating-instrument-upcoming-mars-mission.html, [cited 27 February 2015].