

Mars Atmospheric In Situ Resource Utilization Projects at the Kennedy Space Center

A. C. Muscatello¹, P. E. Hintze², A. J. Caraccio³, J. A. Bayliss⁴, L. J. Karr⁵, M. S. Paley⁶, M. J. Marone⁷, T. L. Gibson⁸, J. M. Surma⁹, J. M. Mansell¹⁰, G. M. Lunn¹¹, R. W. Devor¹², J. G. Captain¹³ and M. Berggren¹⁴

¹Applied Chemistry Laboratory, Applied Science Branch, UB-R3-A, National Aeronautics and Space Administration, Kennedy Space Center, FL 32899; Ph (321) 867-3498; email: anthony.c.muscatello@nasa.gov

²Applied Chemistry Laboratory, Applied Science Branch, UB-R3-A, National Aeronautics and Space Administration, Kennedy Space Center, FL 32899; Ph (321) 867-3751; email: paul.e.hintze@nasa.gov

³Chemical Analysis Laboratory, Analytical Laboratories Branch, NE-L3, National Aeronautics and Space Administration, Kennedy Space Center, FL 32899; Ph (321) 861-9315; email: anne.caraccio@nasa.gov

⁴Testing and Design Branch, Engineering Directorate, NE-L1, National Aeronautics and Space Administration, Kennedy Space Center, FL 32899; Ph (321) 861-8954; email: jon.a.bayliss@nasa.gov

⁵NASA Engineering, EM10, National Aeronautics and Space Administration, George C. Marshall Space Flight Center, Huntsville, AL 35812; Ph (256) 544-7817; email: laurel.j.karr@nasa.gov

⁶AZ Technology, 7047 Old Madison Pike, Suite 300, Huntsville, AL 35806; Ph (256) 544-7775; email: mark.s.paley@nasa.gov

⁷Department of Physics, Mercer University, 1400 Coleman Ave., Macon, GA 31207; Ph (478) 301-2597; email: MARONE_MJ@mercer.edu

⁸Chemical and Biological Sciences, ESC-870, VENCORE, Kennedy Space Center, FL 32899; Ph (321) 867-7572; email: tracy.l.gibson@nasa.gov

⁹Chemical and Biological Sciences, ESC-870, Sierra Lobo, Kennedy Space Center, FL 32899; Ph (321) 867-6928; email: jan.m.surma@nasa.gov

¹⁰NASA Engineering, ECLSS Development Branch, ES62, National Aeronautics and Space Administration, George C. Marshall Space Flight Center, Huntsville, AL 35812; Ph (256) 544-8297; email: matt.mansell@nasa.gov

¹¹Chemical and Biological Sciences, ESC-870, SGT, Kennedy Space Center, FL 32899; Ph (321) 867-2680; email: griffin.m.lunn@nasa.gov

¹²Chemical and Biological Sciences, ESC-870, VENCORE, Kennedy Space Center, FL 32899; Ph (321) 867-4985; email: robert.w.devor@nasa.gov

¹³Chemical and Biological Sciences, ESC-870, VENCORE, Kennedy Space Center, FL 32899; Ph (321) 867-8185; email: james.g.captain@nasa.gov

¹⁴Pioneer Astronautics, 11111 W. 8th Ave., Unit A, Lakewood, CO 80215; Ph (303) 980-0231; email: mberggren@pioneerastro.com

ABSTRACT

The atmosphere of Mars, which is ~95% carbon dioxide (CO₂), is a rich resource for the human exploration of the red planet, primarily by the production of rocket

propellants and oxygen for life support. Three recent projects led by NASA's Kennedy Space Center have been investigating the processing of CO₂. The first project successfully demonstrated the Mars Atmospheric Processing Module (APM), which freezes CO₂ with cryocoolers and combines sublimated CO₂ with hydrogen to make methane and water. The second project absorbs CO₂ with Ionic Liquids and electrolyzes it with water to make methane and oxygen, but with limited success so far. A third project plans to recover up to 100% of the oxygen in spacecraft respiratory CO₂. A combination of the Reverse Water Gas Shift reaction and the Boudouard reaction eventually fill the reactor up with carbon, stopping the process. A system to continuously remove and collect carbon is under construction.

MARS ATMOSPHERIC PROCESSING MODULE

The multi-NASA center Mars Atmosphere and Regolith Collector/Processor for Lander Operations (MARCO POLO) project was established to build and demonstrate a methane (CH₄) and oxygen (O₂) propellant production system in a Mars analog environment. Work at the Kennedy Space Center (KSC) has focused on the Atmospheric Processing Module (APM). The APM first freezes CO₂ from a simulated Mars atmosphere at Mars pressures (~1 kPa) by using dual cryocoolers. The resulting pressurized CO₂ plus hydrogen (H₂) are fed to a Sabatier reactor on the APM to make CH₄ and water (H₂O) vapor. The CH₄ is sent to the Liquefaction Module. The H₂O vapor is condensed and is sent to the Water Cleanup Module (KSC) followed by the Water Processing Module (WPM), built by the Johnson Space Center (JSC), where it is electrolyzed. The resulting O₂ is liquefied and stored and the H₂ is sent back to the Sabatier subsystem to make more CH₄. We previously reported the progress on the APM at Earth & Space 2014 in Muscatello et al. (2014). The MARCO POLO project was described in detail by Interbartolo et al. (2012).

Recently, the operation of the two CO₂ freezers has been verified to meet the required 88 g CO₂/h collection/supply rate and the CH₄ production rate by a new Sabatier reactor was verified to meet the 32 g/h design goal. The H₂O produced by the Sabatier reactor approaches its design requirement of 72 g/h. Combined with an additional 72 g of H₂O/h expected from the Soil Processing Module (SPM), which extracts H₂O from simulated Mars regolith and is under development at JSC, the Sabatier H₂O would be processed by the WPM to make a total of 128 g O₂/h. These hourly rates of CH₄ and O₂ production are suitable for fueling a Mars Ascent Vehicle (MAV) for a small Mars Sample Return mission.

The major tasks that preceded the verification of these production rates were to complete setup and testing of the Sabatier subsystem including a new Sabatier reactor, verify the operation of the CO₂ pump and the associated storage tanks, and operate them with the CO₂ freezers to ready the APM for a potential analog demonstration with the other components of MARCO POLO, i.e. regolith mining, H₂O recovery from regolith, H₂O purification, and H₂O electrolysis, e.g. the MASTER (Mars Atmosphere & Soil Testbed for Extraction of Resources) project at JSC and KSC. The APM can also be used to test alternative CO₂ collection and CO₂ conversion technologies as they become available by replacing the freezers or Sabatier reactor. Further details of the recent work follow below.

Sabatier Subsystem

As mentioned in our 2014 report, we designed and built a new Sabatier reactor because of the overheating we encountered with a previous reactor design. The reactor design was based on one developed at Pioneer Astronautics, as reported by Berggren et al. (2014), which has a novel heat exchanger designed to control the exothermic Sabatier reaction. Figure 1 shows the initial design for the new Sabatier reactor. The reactor is a stainless steel tube that is 30 cm long with an O.D. of 2.54 cm and a wall thickness of 0.21 cm.

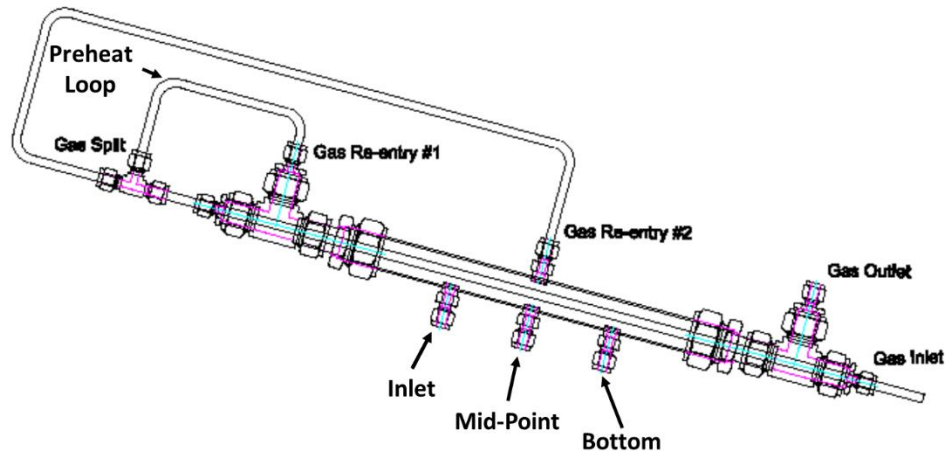


Figure 1. Design of KSC Sabatier Reactor.

The reactor was designed to contain the same amount of ruthenium on alumina catalyst as that in the previous design, but with the ability to shed controllable amounts of heat to the environment from the gases heated by passing through the center of the catalyst bed instead of a shell surrounding the bed. During testing of the new reactor, we determined that the large outer heat exchanger (“Gas Re-Entry #2) was not needed at our operating conditions due to heat loss from the long, narrow reactor, so it was removed to simplify operations.

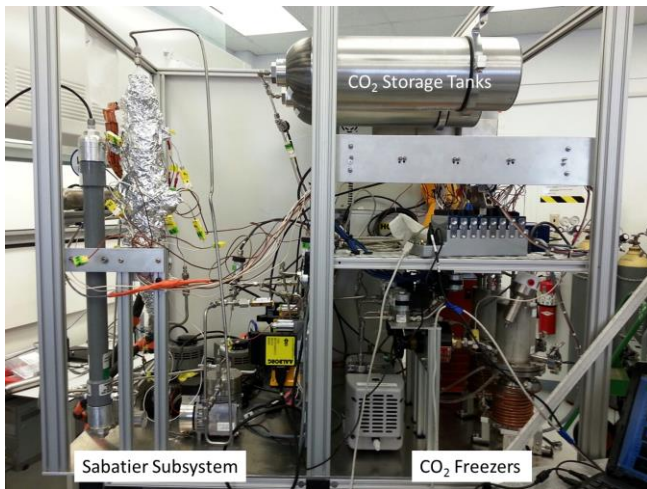


Figure 2. Mars Atmospheric Processing Module.

Figure 2 is a photo of the current setup of the Sabatier Subsystem on the left after installation of the recycling system and a heat exchanger from Exergy (Model 00540-03) that is chilled to 3 °C using a standard recirculating chiller bath. The H₂O from the condenser is collected in a 300 ml stainless steel vessel from Swagelok that is drained periodically during operations to measure the volume of H₂O

produced. The vessel is currently below and to the left of the aluminum floor plate (and is not visible in Figure 2). The two CO₂ Freezers are on the lower right side of Figure 2 while the two CO₂ Storage Tanks are at the top right.

Testing of the Sabatier reactor with pure CO₂ and H₂ from compressed gas bottles showed >90% conversion of 88 g CO₂/h to CH₄ in a single pass as determined by gas chromatography with no overheating issues (>600 °C), so we had confirmed that we had a functional reactor. The original JSC design for the Sabatier subsystem used an electrochemical H₂/CH₄ separator which was not available to us. Instead, we installed a separation membrane module-based system (see Muscatello et al. (2014) for details). The combination of the recycling system and the Sabatier reactor was successful, with pure CH₄ and H₂O products being produced with near 100% conversion of the CO₂ feed as long as the pressure differential between the membrane retentate (CH₄) and the permeate (H₂/CH₄/CO₂) was ~200 kPa.

CO₂ Freezer Subsystem

With the Sabatier Subsystem operating properly, we turned our attention to the CO₂ Freezer Subsystem to ensure it could supply CO₂ for methanation. Prior testing had verified that the cryocoolers were capable of freezing an average of 99 g CO₂/h from simulated Mars atmosphere (95.4 % CO₂, 3% nitrogen (N₂), and 1.6% argon (Ar)) and supplying an average of 94 g CO₂/h, both during 1.4-hour cycle times. The system has a compromised design that requires a pump to compress the CO₂ into two 10-liter storage tanks at up to 700 kPa to avoid pressurizing the cryocooler cold fingers, the connecting flange, and the freezing tanks. As noted in our prior work, the cryocooler and its flange are designed only for vacuum systems, not for the ~5.5 MPa that would result from sublimating and liquefying the CO₂ product. The initial project budget did not support stamped and certified ASME code tanks required by NASA safety and the large copper cold head needed to freeze for the anticipated 14-h daily operating time was not meeting requirements. So the 1.4-h cycle time and a smaller copper cold head was chosen. A KNF NPK 09 DC rocking piston pump was selected to compress the CO₂. Unfortunately, the piston pump contaminates the CO₂ with air leaks if the inlet pressure is below ambient room conditions. A solenoid pump was procured and tested as a replacement, but, in addition to being rather loud, it failed after only a short time. The solenoid pump was repaired by the vendor, but failed quickly again during testing.

An alternate method was implemented that uses a 25-liter Tedlar[®] gas sampling bag to provide a volume into which the sublimating CO₂ can expand while not pressurizing the freezing chamber. Periodically, the CO₂ was pumped into the storage tanks by the piston pump, taking care not to completely evacuate the Tedlar[®] bag. This process resulted in pure CO₂ being stored at up to 700 kPa in two 10-liter aluminum tanks to provide sufficient feed to the Sabatier reactor for 1.4 h while a new batch of dry ice is collected for the next 1.4 h interval. The process can be automated by installing flow meters at the outlet of the freezer tanks and at the inlet of the piston pump. By knowing how much CO₂ has been sent to the bag and how much has been sent to the storage tanks, the amount left in the bag can be calculated and the pump can be stopped before the bag is empty. Testing of the CO₂ freezers using the bag as interim storage showed they could collect at the expected rate and that alternating them could produce adequate CO₂ to run the Sabatier subsystem at the desired CH₄ production

rate. Additional funding is being sought to upgrade the cryocoolers and the freezing tanks to make the subsystem more flight-like.

Integrated Testing

With the CO₂ Freezer Subsystem ready, it was used to supply the Sabatier Subsystem during a ~1.5 h test. Figure 3 shows the gas composition for that test, measured with a gas chromatograph. The Sabatier Subsystem was operated starting at minute 250 and turned off at minute 340. The CH₄ from the membrane retentate was pure. The CO₂ concentrations increased after minute 340 as the H₂ flow to the Sabatier reactor was stopped. An integrating flow meter showed that the CH₄ production rate was 32 g/h and 67 g H₂O/h were collected. All the other components operated as planned so we were ready to pursue our goal of running the integrated module for three days with 7 h of pure CH₄ production each day at the desired rate of 32 g/h. The 7-h duration is based on 5 cycles of operation of the CO₂ Freezers while fitting into a normal work day.

The CH₄ production rate was 32 g/h and 67 g H₂O/h were collected. All the other components operated as planned so we were ready to pursue our goal of running the integrated module for three days with 7 h of pure CH₄ production each day at the desired rate of 32 g/h. The 7-h duration is based on 5 cycles of operation of the CO₂ Freezers while fitting into a normal work day.

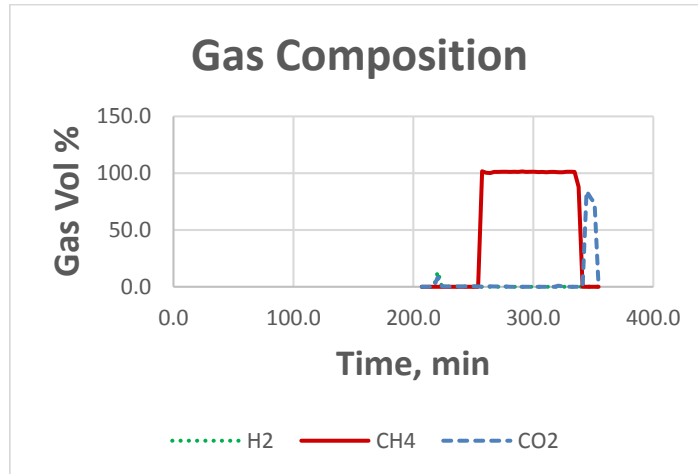


Figure 3. Integrated Atmospheric Processing Module CH₄ Purity.

We were successful in operating the APM for the three non-consecutive days with the desired CH₄ production rates for 7 h each day as planned. Table 1 summarizes the results of the three long-duration runs. The Sabatier subsystem performed as desired with no overheating. The CH₄ production rate and gas chromatography indicate ~100% conversion of the 88 g CO₂/h fed by the CO₂ Freezers and the storage tanks. During the first run, there was a minor issue with the loss of some CO₂ through a malfunctioning magnetic latch solenoid valve, which was replaced before the next run. The lost CO₂ was replaced with a Tedlar[®] bag filled from a gas supply bottle. Otherwise, the first run was nominal. The second and third runs were also nominal, with no interruptions or failures. Pure CO₂ was fed to the freezers during the first and second runs while the third run was fed simulated Mars atmosphere. The freezers were slightly less efficient (72% CO₂ capture vs. 79% and 76% for the first and second runs) when using simulated Mars gas during the long duration run, as expected because of the presence of N₂ and Ar. Prior to the start of the third run, two additional freeze cycles using Mars gas were performed to prefill the CO₂ storage tanks for the run. The results from these two freeze cycles were included in the data reported in Table 1. When operated with either Mars gas or pure CO₂ the freezer performance varied between cycles for unknown reasons. We plan more testing with Mars simulant to verify the

freezer performance using Mars gas simulant. The freezers have been operated many times with pure CO₂ and the average CO₂ capture efficiency was 78%.

Table 1. Results of the Long-Duration APM Tests.

<i>Run No.</i>	<i>1</i>	<i>2</i>	<i>3</i>
Sabatier Run Duration	7.0 h	7.0 h	7.0 h
Gas Composition	CO ₂	CO ₂	Mars Gas
Average CO ₂ Freezing Rate	102 g/h	100 g/h	102 g/h
Average Fraction of CO ₂ Frozen	79%	76%	72%
Average Cryocooler Power	139 W	150 W	158 W
Average energy needed to Freeze CO ₂	4917 J/g	5051 J/g	5655 J/g
Average CO ₂ Supply Rate to Freezers	128 g/h	142 g/h	146 g CO ₂ /h
Average CH ₄ Production Rate	32 g/h	32 g/h	32 g/h
Average CH ₄ Purity	~99.9%	~99.9%	~99.9%
Average H ₂ O Produced	67 g/h	69 g/h	64 g/h

To illustrate the results of the three runs in more detail, Figure 4 shows the CO₂ Freezer cold head temperatures and cryocooler power consumption during the third run while Figure 5 shows the temperatures of the Sabatier reactor during the second run.

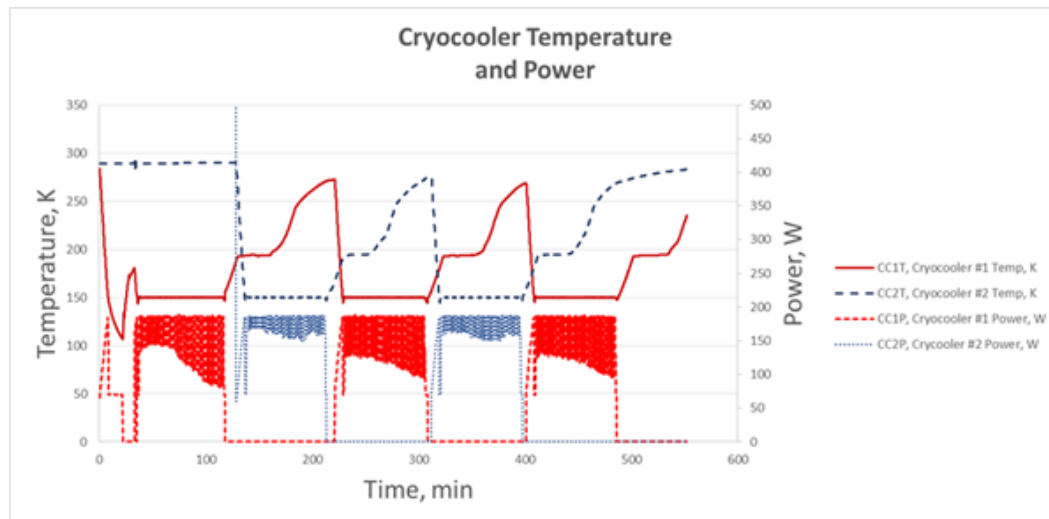


Figure 4. CO₂ Freezer Cold Head Temperatures and Cryocooler Power Consumption during the Third Run of the 7-h Integrated Test Series.

The cryocooler power values are particularly important for future, large-scale CO₂ freezer designs. For example, one can estimate the mass, power, hardware, and thermal output for a freezer capable of supplying 3.1 kg of CO₂/h to a Solid Oxide Electrolyzer producing 1.0 kg O₂/h, which can be combined with duplicate modules to produce sufficient for O₂ for a Mars Ascent Vehicle for a human Mars mission. The theoretical value to freeze 102 g CO₂/h in the laboratory starting at 293 K is 20.6 W or

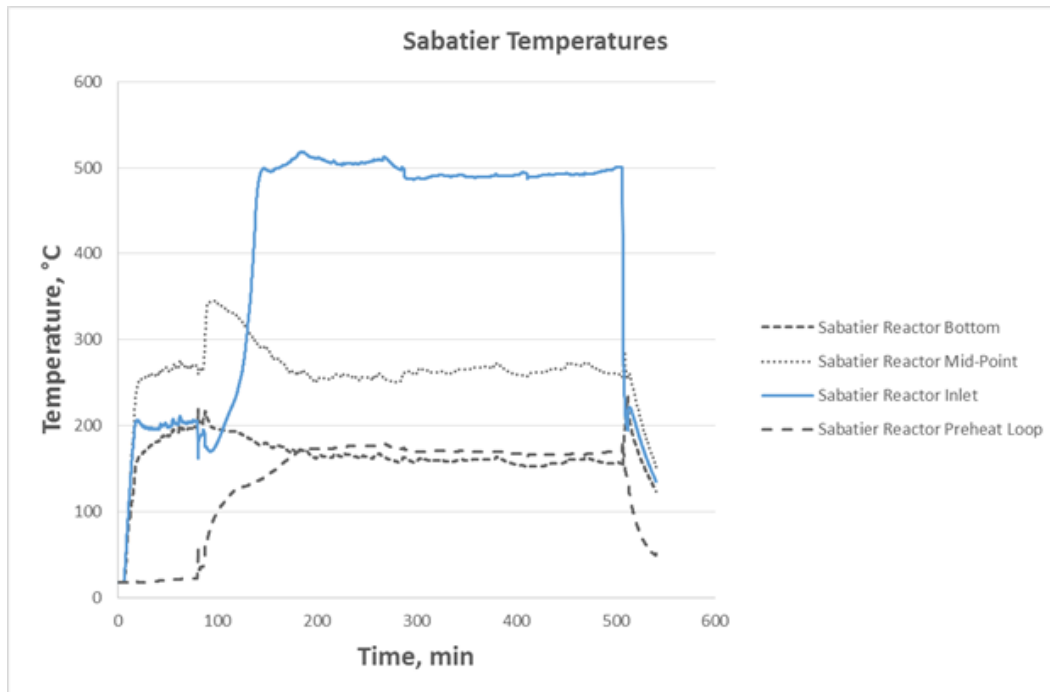


Figure 5. Sabatier Reactor Temperatures during the Second Run of the 7-Hour Integrated Test Series. (See Figure 1 for locations.)

0.202 W/g CO₂/h, including chilling unfrozen CO₂, N₂, and Ar, but not including heat leak or chilling the copper cold head. The actual power consumed while freezing 102 g CO₂/h averages 158 W out of a total capacity of 240 W for the Cryotel GT cryocooler. The GT model has a maximum cooling power (“lift”) of 34 W at 150 K so the actual lift used is 22.4 W, leading to a lift requirement of 0.219 W/g CO₂/h, which is only 8.4% more than the theoretical value. The measured value can then be used to estimate that the lift needed for the large-scale system is 680 W, which is 18% higher than the theoretical power of 576 W needed to chill the Mars atmosphere from 210 K and freeze 3.1 kg CO₂/h. The higher than theoretical value is caused by a higher starting temperature for the gases (293 K vs. 210 K) and by heat leakage from the environment, which should be less on Mars than in our lab. A Qdrive 2S241K-FAR cryocooler has a lift of 750 W at 150 K, which would be sufficient for freezing 3.1 kg CO₂/h. This cryocooler requires an electrical input power of 4,500 W to provide 750 W of lift so the calculated electrical power for the large-scale system would be ~4,100 W. Our prior electrical power estimates had used the full Cryotel GT lift of 34 W since we had no measurement of the heat leak from the lab environment, which turns out to be small, greatly reducing the predicted power requirement on Mars.

Future work will focus on automating the LabVIEW data acquisition/operating system to simplify testing, followed by integrating and operating the APM with other MARCO POLO hardware at KSC, which includes the RASSOR (Regolith Advanced Surface Systems Operations Robot) excavator, the dust tolerant umbilical connector, the regolith feed system, and the lander mockup. Some reconfiguration of the APM is needed to fit properly on the lander. If funded by JSC, the APM will be integrated and tested at JSC with the KSC Water Cleanup Module, the JSC Soil reactor, and the JSC

Water Processing Module (Electrolyzer). Overall, we are very pleased with our progress on this project.

MARS PROPELLANT PRODUCTION WITH IONIC LIQUIDS

In 2014, KSC initiated a project titled “Mars Propellant Production with Ionic Liquids”. The purpose of the project was to investigate and demonstrate the simultaneous production of CH₄ and O₂ via the electrolysis of CO₂ and H₂O in one or more ionic liquids (ILs). Ionic Liquids are salts with large, bulky organic cations and/or anions that melt at or near room temperatures. The project included the following tasks: 1) evaluation of process development; 2) process selection; 3) development of system requirements and experimental techniques; 4) system design, fabrication; applied research; and 5) preparation of documentation. As part of this project, KSC partnered with NASA Marshall Space Flight Center (MSFC) and Mercer University. MSFC was tasked to develop novel task-specific ionic liquids (TSILs) with high CO₂ solubility through a contract with AZ Technology and Mercer University was tasked with evaluation of the properties of the developed ionic liquids, including measurement of their electrochemical windows and conductivity as well as CO₂ solubility as a function of temperature. The major accomplishments of the project are as follows.

(1) CH₄ production was observed during the electrolysis of CO₂ dissolved in an IL. Carbon monoxide (CO) and possible CH₄ production was observed during electrolysis of CO₂ in AZ Technology-synthesized TSILs in a one-compartment electrochemical cell. (2) Five commercial and three MSFC synthesized ionic liquids were screened for feasibility by measuring CO₂ uptake, electrochemical window, conductivity, and compatibility with the electrode material. The AZ Technology-synthesized ILs were demonstrated to be capable of absorbing 70 - 90 mol% CO₂. (3) Electrolysis experiments were performed on ILs that met feasibility requirements during screening. (4) Four different electrolysis cells and multiple electrode configurations were investigated in an attempt to produce CH₄.

A detailed literature review of research literature and the internet was conducted regarding the use of ILs for conversion of CO₂ and H₂O to CH₄ and O₂. A great deal of literature exists describing the use of ionic liquids in the electrochemical reduction of CO₂. Based on the literature review, initial research was focused on using the commercially available [EMIM] and [BMIM] ionic liquids with either tetrafluoroborate [BF₄] or hexafluorophosphate [PF₆] anions. Also, based on the literature review, a copper cathode and a platinum anode were chosen for the initial electrochemical cell design. Figure 6 shows a schematic of the electrochemical cell design and the desired reactions needed to make CH₄ and O₂.

During this project, eight ILs were evaluated for use in the electrochemical production of CH₄ from CO₂ and H₂O. CO₂ capture capability was evaluated for all eight ILs, as well as determination of their electrochemical properties both with and without the presence of CO₂. Additionally, the compatibility of the ionic liquids with copper was evaluated to ensure that the ionic liquids could be used with the chosen electrochemical cell design. The ILs that performed best overall in these evaluations were tested first in the electrolysis experiments.

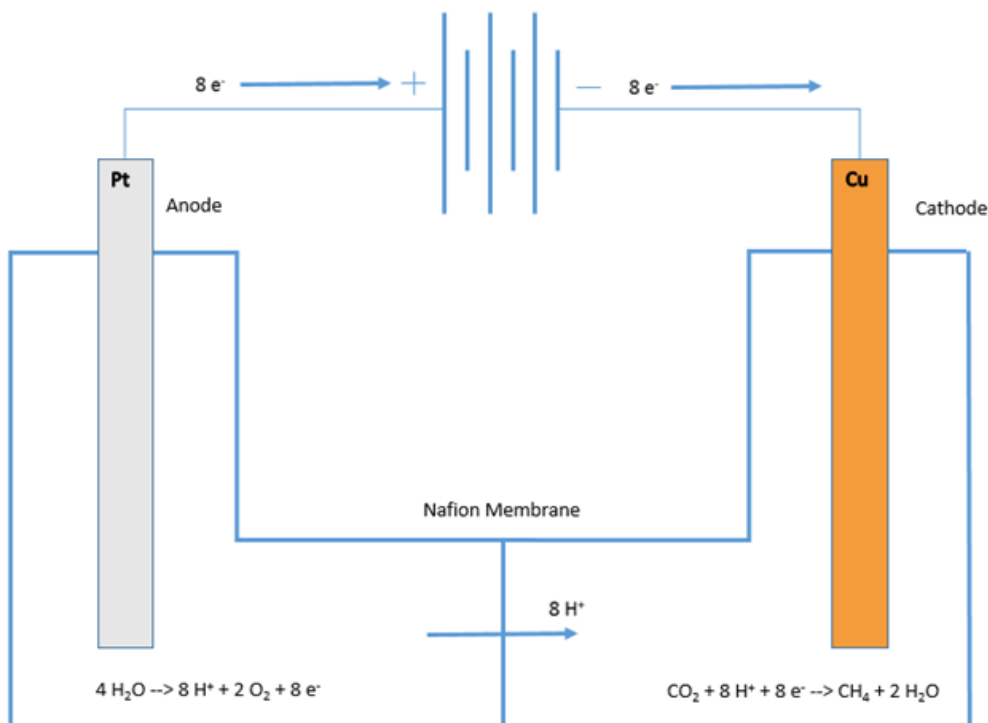


Figure 6. Schematic of an Electrochemical System for Conversion of CO₂ to CH₄. (Water is in the left cell and an IL is in the right cell.)

Measurements of the electrical conductivity of TSILs were performed at Mercer University. The conductivity of the AZ Technology-synthesized ILs show a strong temperature dependence with and without the presence of CO₂. Typical results show an order of magnitude increase in conductivity between room temperature and 80 °C. CO₂ reduces the conductivity of the IL's while the presence of H₂O, at the level of a few percent, partially offsets the reduction.

Multiple electrolysis experiments were conducted in an effort to prove the feasibility of the simultaneous production of CH₄ and O₂ from the electrolysis of CO₂ and H₂O. Initial CH₄ production experiments utilized polycarbonate electrochemical cells equipped with copper mesh working electrodes (cathode) and a platinum mesh counter electrodes (anode). All cells used at KSC had two chambers, separated by a proton-exchange membrane. The first test cells were fabricated from polycarbonate, and initial experiments were carried out with a cell holding 10 ml of each electrolyte with a membrane area of 11 cm². Test results obtained from electrolysis experiments performed using this cell were unexpected; the copper working electrode was poisoned and the presence of calcium and carbonate were detected on the surface of the electrode. Further investigation led to the conclusion that the source of the calcium and carbonate was the polycarbonate used for cell fabrication. To eliminate the presence of calcium and carbonate, an exact replica of the 10 ml cell was fabricated from high density polyethylene (HDPE).

CO, H₂, and formate ion were produced with the HDPE cell, but no CH₄ was identified. Therefore, a different cell design was tested. The next cell was a commercially available, two-chamber glass electrochemical cell purchased from Pine

Research Instrumentation. The Pine electrochemical cell holds a total volume of approximately 25 – 30 ml of each electrolyte and is designed to allow a 5 cm² proton-exchange membrane to be used to separate the two halves of the cell. Small quantities of CH₄ were produced during electrolysis using this cell, but in all experiments, CO and H₂ were also produced. In total, six electrochemical cell designs were evaluated during this project.

Various ionic liquids were utilized in the electrochemical experiments. Half of the ionic liquids initially selected were found to be incompatible with copper and were not subjected to further testing. Overall, the results of these experiments were somewhat inconclusive. Bubbles were routinely observed on both the anode and cathode. However, the amount of gas produced was very near the detection limit of the gas chromatograph used for analysis and could therefore not be quantified. Although CH₄ was identified in multiple experiments, it was always produced with CO and H₂ indicating the electrochemical system was not very selective towards CH₄. In addition, formate ion was identified in the cathode electrolyte. Experiments conducted using glass electrochemical cells were more successful, with the Pine Research Instrumentation glass cell having the best results. The results for experiments conducted using the 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM] [TfB]) ionic liquid were the most promising; the production of CH₄ was observed, but the production rate was determined to be very low. A darkening of the copper cathode was also observed in these experiments. Various tests were performed using a cathode with increased surface area (5x) to try to improve the CH₄ production rate. To date, however, increasing the surface area of the cathode has not resulted in increased CH₄ production rates.

Experiments were also performed at Mercer University using a single compartment cell. This cell consisted of a titanium dioxide working electrode and a platinum counter electrode. The TSIL was saturated with CO₂ and 2% (by volume) H₂O was added. Preliminary results show that small quantities of CH₄ and CO were produced.

There were a number of challenges identified during the project that remain unsolved. (1) CH₄ production occurred with very low faradaic efficiency, and always with the co-production of the unwanted byproducts, H₂ and CO, even though the literature suggested that the chosen electrode material and cell design should have high efficiency and minimize byproducts. (2) Even when initial screening indicated that the copper electrode was compatible with the IL, the electrode was always altered during electrolysis experiments. This indicates that electrode stability is an extremely complex issue that needs to be addressed. (3) The nature of the electrode material is important. The literature review indicated that copper electrodes were most successful in producing CH₄. However, copper can have different forms and this was often not reported in the literature. In experiments performed at KSC, a sputtered copper electrode performed better than a copper mesh electrode. It is unknown why this difference exists. Future evaluations of this process should pay close attention to the electrode material, whether it is copper or something else.

We plan to propose further activities in this area in the future after careful consideration of the issues encountered and we develop approaches to resolve them.

SELF-CLEANING BOUDOUARD REACTOR

Oxygen recovery from respiratory CO₂ is an important aspect of human spaceflight and Mars exploration. Methods exist to capture the CO₂, but production of O₂ needs further development. The current ISS Carbon Dioxide Reduction System (CRS) uses the Sabatier reaction to produce H₂O (and ultimately O₂ for breathing air). O₂ recovery is limited to 50% because half of the H₂ used is lost as CH₄, which is vented overboard, and supplemental H₂ availability is limited. The Bosch reaction ($\text{CO}_2 + \text{H}_2 \rightarrow \text{C} + \text{H}_2\text{O}$) is a promising alternative to the Sabatier reaction that does not consume H₂. The Bosch reaction can be considered to be the combination of the Reverse Water Gas Shift reaction and the Boudouard reaction, as shown in Figure 7. However, during the Boudouard reaction step the resulting carbon buildup will eventually foul the nickel or iron catalyst, reducing reactor life and increasing the use of consumables. Abney et al. (2014) at MSFC have demonstrated full conversion of CO₂ into O₂ and carbon using the Bosch reaction with a steel wool Boudouard catalyst using only 0.0019 g of catalyst/g O₂ recovered. Nevertheless, the catalyst bed is eventually clogged with carbon and the catalyst is not recoverable.

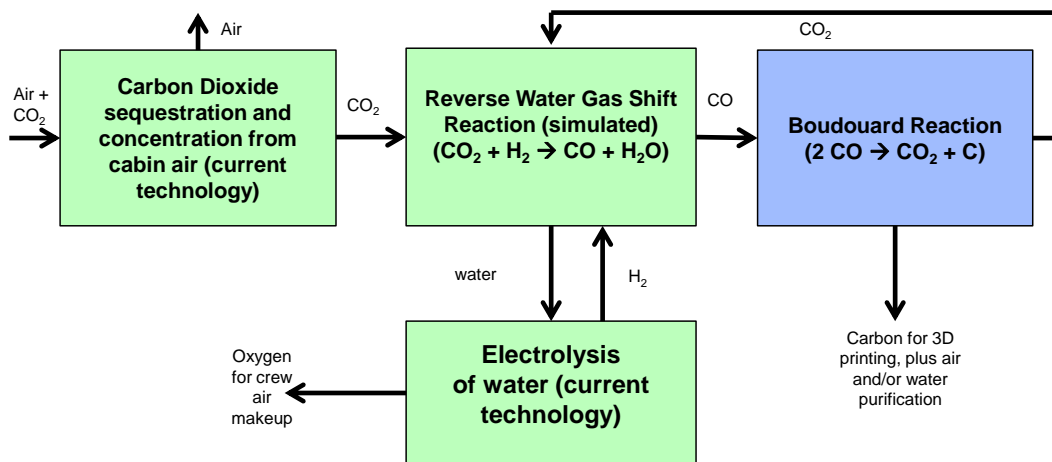


Figure 7. Schematic Representation of the Bosch Reaction by a Combination of the RWGS Reaction and the Boudouard Reaction Followed by Electrolysis of Water to Recover Oxygen from Carbon Dioxide.

To minimize this fouling, find a use for this waste product, and increase efficiency, we have designed various self-cleaning catalysts and selected a few which we deem the most reliable for conversion and lack of fouling. Criteria that we considered include the estimated mechanical reliability of the cleaning method and its ability to maintain high conversion efficiency. The above chemical reactions are well understood, but reusable self-cleaning Boudouard catalysts have not been investigated before.

As noted above, the current ISS O₂ recovery method utilizes the Sabatier process which is only 50% efficient due to limits on H₂ availability. This means that for a full crew over 3 kg of H₂O/day are used in making O₂ that is not recovered from CO₂. At cargo launch prices of \$10,000-\$40,000/kg, this costs \$30,000-\$120,000/day, depending on the supplier. For deep space exploration missions, in-space resupply is

virtually impossible so nearly 100% recovery is essential to reduce launch mass. The carbon product could be used as air or H₂O purification filters, which we will test, as a filler for 3D printing, as a dry lubricant suitable for low-pressure applications, or as a reactant in other processes, such as carbothermal reduction or as consumable electrodes for metal production. By producing a self-cleaning Boudouard reactor the single greatest challenge of the Bosch process is resolved and full O₂ recovery can be realized. The decrease in consumable requirements will be significant for the ISS and enabling for deep space exploration missions. In addition, O₂ production is a limiting factor in ISS population and a system such as this can help improve that situation.

Using our experience with similar chemical reactions in ISRU and the Boudouard reaction expertise of team member Pioneer Astronautics, e.g. Berggren et al. (2009), we are building a few Boudouard reactors with different cleaning methods for testing on a MSFC test stand that simulates upstream conversion of CO₂ to CO from a Reverse Water Gas Shift (RWGS) reactor. The synthetic CO stream, which may contain H₂ to enhance the reaction, will be fed to the Boudouard reactor, which will convert it to CO₂ and carbon fines. The gases will be analyzed with gas chromatography (GC) and mass flow meters. Peak performance, as well as continuous performance after multiple regenerations, will be documented to determine reactor performance. The goal is to arrive at a reactor and catalyst design which reduces or eliminates consumables with this reaction by 80% or greater. We have designed our first reactor which is under construction for shakedown tests at KSC before shipment to MSFC for testing in their system. Calculations based on work at MSFC indicate the surface area of our reusable catalyst should be comparable to that of their steel wool catalyst, but with the potential for removal of the carbon deposits as they form. Exact designs will remain proprietary until determinations are made on their patentability.

References.

- Abney, M. B., Mansell, J. M., Rabenberg, E., Stanley, C. M., Edmunson, J., Alleman, J. E., Chen, K. and Dumez, S. (2014). "Series-Bosch Technology For Oxygen Recovery During Lunar or Martian Surface Missions." *44th International Conference on Environmental Systems*.
- Berggren, M., Zubrin, R., Carrera, S., and Jonscher, P. (2014). "Lunar Organic Waste Reformer," *Space Resources Roundtable and Planetary & Terrestrial Mining Sciences Symposium*, Colorado School of Mines.
- Berggren, M., Zubrin, R., Carrera, S., Rose, H., Kilgore, J., Jameson, N., and Wilson, C. (2009). "Carbon Monoxide Silicate Reduction System." NASA JSC SBIR Phase II Final Report, Contract NNJ06JE51C, Pioneer Astronautics.
- Interbartolo III, M. A., Sanders, G. B., Oryshchyn, L., Lee, K., Vaccaro, H., Santiago-Maldonado, E., and Muscatello, A. C. (2012). "Prototype Development of an Integrated Mars Atmosphere and Soil-Processing System." *Journal of Aerospace Engineering*, 26(1), 57-66.
- Muscatello, A., Devor, R., and Captain, J. (2015) "Atmospheric Processing Module for Mars Propellant Production." *Earth and Space 2014*: pp. 444-454.