Mars In Situ Resource Utilization Technology Evaluation

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We have examined the technologies required to enable Mars In-Situ Resource Utilization (ISRU) because our understanding of Mars resources has changed significantly in the last five years as a result of recent robotic missions to the red planet. Two major developments, (1) confirmation of the presence of near-surface water in the form of ice in very large amounts at high latitudes by the Phoenix Lander and (2) the likely existence of water at lower latitudes in the form of hydrates or ice in the top one meter of the regolith, have the potential to change ISRU technology selection. A brief technology assessment was performed for the most promising Mars atmospheric gas processing techniques: Reverse Water Gas Shift (RWGS) and Methanation (aka Sabatier), as well as an overview of soil processing technology to extract water from Martian soil.

Nomenclature

^{o}C	=	degrees Celsius
ISRU	=	In Situ Resource Utilization
I_{sp}	=	Specific Impulse
K	=	degrees Kelvin
OCT	=	NASA Office of the Chief Technologist
Psia	=	pounds per square inch absolute
TRL	=	Technical Readiness Level
v.p.	=	vapor pressure
W	=	Watts

I. Introduction

Recent national policy statements have established Mars as the ultimate destination of NASA's human exploration program. In Situ Resource Utilization (ISRU) is a key technology required to enable such missions and it is appropriate to review progress in this area and continue to advance the systems required to produce rocket propellant and other consumables on Mars using the carbon dioxide atmosphere and other potential resources. Our understanding of Mars resources have changed significantly in the last five years as a result of recent robotic missions to the red planet[1,2,3,4]. The indication of the presence of water in significant amounts at high latitudes, and possibly at lower latitudes, has a significant impact on ISRU technology and human exploration architectures. Prior to these robotic findings, the ISRU program has focused on the production of (1) methane from atmospheric CO_2 and hydrogen brought from Earth via the Sabatier reaction and (2) oxygen from a secondary atmospheric CO_2 processing unit in order to produce oxygen at the oxidizer-to-fuel mass ratio (3.4:1) required for propellant usage. The secondary atmospheric processing unit was focused on processes that do not consume Earth-supplied resources (i.e. hydrogen).

Smith and coworkers[4] reported a water ice table at the Phoenix landing site at depths of 5 to 18 centimeters. Also, a water vapor pressure in the atmosphere of 2 pascals, corresponding to the saturation vapor pressure of water at 210 K, was measured by Phoenix instruments. The utilization of water ice on Mars will require excavation techniques and soil processing technology to extract water. Although the lunar ISRU program was not investigating water ice mining technology, lunar regolith mining and processing are applicable to Mars ISRU. The technology needs for mining water from Mars will be further discussed in this paper.

II. Mars Atmospheric Gas Processing

The production of propellant and life support consumables in-situ on Mars is an enabling technology required for sustainable and affordable human exploration of Mars. Mars offers useful resources in the form of carbon dioxide

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from the atmosphere and water adsorbed on the soil and subsurface water ice. These resources can be processed to produce useful consumables, such as oxygen, methane, and water, among others. Leading technologies for processing CO_2 are solid oxide electrolysis (SOE), reverse water gas shift (RWGS), and the Sabatier reaction. The SOE process dissociates Martian CO_2 into O_2 and CO via a high temperature (~1000°C) electrochemical process through a thin-zirconia membrane. The Sabatier and RWGS processes use a catalyst to react CO_2 with H_2 to produce CH_4 and H_2O, and CO and H_2O, respectively. These chemical equations are summarized below:

$$SOE: \quad 2\,CO_2 \rightarrow 2\,CO + O_2 \qquad (1)$$
$$Sabatier: \quad CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \qquad (2)$$
$$RWGS: \quad CO_2 + H_2 \rightarrow CO + H_2O. \qquad (3)$$

A. Solid Oxide Electrolysis Process

The SOE process was developed to the point of a small ISRU demonstrator that was to fly on the 2001 Mars Surveyor Lander mission[5], but the mission was cancelled after the failure of the Mars Polar Lander in 1999. There was some further development of the process after that,[6,7] but the focus on lunar missions by NASA after 2005 led to a emphasis on lunar ISRU over Mars ISRU and little development work occurred since then. On the other hand, Sridhar reversed the technology and developed the Bloom Energy fuel cell, which uses steam-reformed natural gas as the fuel to generate electricity at high efficiency (www.bloomenergy.com). Several companies, including Google and Walmart have installed Bloom Energy generators as power supplies for buildings. The development of the Bloom Energy system may have addressed a key issue of the SOE process, which is the fragility of the ceramic membrane that acts as the electrolyte in the electrolysis of carbon dioxide.

Another limitation of the SOE process is that it provides only oxygen and carbon monoxide products. CO is a low I_{sp} fuel (290 s) for use as propellant, but work in this area shows that it is feasible to use it.[8] This work also shows the CO/O_2 mixture is difficult to ignite and maintain ignition, needing a H_2/O_2 ignitor or 0.3 wt% H_2 added to the CO. Alternatively, the SOE process may be used to supply the supplemental oxygen needed to combust all the methane produced by the Sabatier process as described below.

Figure 1. Methanation (Sabatier) Process Flow Diagram.

B. Sabatier Process

Combined with water electrolysis, the Sabatier process and the RWGS process produce oxygen for propellant use and breathing gas and hydrogen, which is recycled into the reactors. The Sabatier process is a well-known terrestrial process, and is shown in Figure 1.

The Sabatier (aka methanation) reaction is commercially carried out to remove carbon oxides from synthesis gas and from reagent streams prior to ammonia synthesis. Transition metal catalysts (e.g. nickel, ruthenium) used to catalyze the methanation reaction can provide >99% CO_2 conversion. Methanation reactors have typically been designed as packed bed reactors; however, recent improvement in manufacturing techniques has allowed the design of microchannel reactors, where the catalyst is deposited onto the microchannel walls. The microchannel reactors offer better temperature control of the catalyst bed (i.e. reducing temperature gradients and localized "hot spots" that could sinter and deactivate a packed bed catalyst[9]) and large mass savings over the traditional packed bed reactor design, with the penalty of increased pressure drop and increased probability of complete catalyst deactivation. The latter (catalyst deactivation) is believed to be the greatest disadvantage of the microchannel design because the total amount of catalyst present in the reactor is very small compared to the traditional packed bed, making the microchannel reactor design extremely sensitive to impurities in the gas stream, introducing new and more stringent requirements to gas separation processes to provide high purity gas to the reactor. Quantitative comparisons of the

masses, power, volume, and advantages of packed-bed reactors and microchannel reactors as well as ways to prevent catalyst deactivation and regenerate catalysts are needed.

Methanation catalysts are available commercially from BASF, Sud-Chemie, Haldor Topsoe, and others. The catalyst is available in the nickel and ruthenium form for high and low temperature application, respectively. Inquiries have been made to industry with respect to catalyst performance and lifecycle at an industrial level, but no response has been received so far.

Catalyst materials are typically sensitive to impurities and contaminants that would poison and deactivate the catalytic material. In the case of methanation catalyst, the catalytic materials (nickel or ruthenium) are sensitive to sulfur compounds, and slightly sensitive to water and oxygen. Sulfur compounds tend to poison and passivate the catalyst; whereas oxygen and water tend to oxidize the catalyst, deactivating it. As seen from Viking data summarized in Table 1, sulfur is not present in the Martian atmosphere, and oxygen and water are present in small amounts that do not present any immediate concern on the life of the catalyst, since typical methanation reactions are carried out in a fuel rich environment. However, sulfates and perchlorates do occur in the Martian regolith and dust, requiring high efficiency removal of fines from the gas stream fed to the methanation reactor.

Table 1. Composition of the Atmosphere of Mars

Viking atmospheric measurements		
Composition	95.32%	carbon dioxide
	2.7%	nitrogen
	1.6%	argon
	0.13%	oxygen
	0.07%	carbon monoxide
	0.03%	water vapor
	trace	neon, krypton, xenon, ozone, methane
Surface pressure	1-9 millibars, depending on altitude; average 7 mb	

Pioneer Astronautics successfully ran a combined Sabatier and RWGS process continuously for approximately 120 hours using a simulated Mars atmosphere gas mixture (95% CO_2, 2% Ar, and 3% N_2) with no detectable degradation of the process.[10] Combining the exothermic Sabatier reaction and the endothermic RWGS reaction reduces the amount of heat generated by 37%, decreasing concerns about catalyst sintering noted above, but at the cost of a methane-carbon monoxide cryodistillation step. However, the combined reaction also produces oxygen in the proper ratio for combusting all the methane generated, eliminating a separate process to make supplemental oxygen. This advantage is eliminated if Martian water sources are available.

These Martian atmosphere trace gases do not affect the processes' efficiency since they are not playing any role in the CO_2 reaction (i.e. not changing enthalpy or entropy); hence separation of CO_2 from Martian atmosphere may not be critical. These gases slightly decrease the partial pressure of CO_2 in the stream, but this small dilution, and 5% reduction in efficiency, would be off-set by the extra hardware, complexity, and reliability associated with an additional unit operation to perform the CO_2/trace gases separation. However, the power and mass of a pump required to pressurize the Martian atmosphere for processing relative to that required by a freezing process (see below) should be taken into consideration.

Martian trace gases are a useful resource for use as a buffer gas for life support systems, and would eventually require separation and capture. However, separation and capture of the buffer gases (i.e. N_2 and Ar) from CO_2 reduction product gas stream may prove to be simpler than the initial CO_2 separation.

The Sabatier process offers the most straightforward buffer gas separation scheme. The state-of-the-art Sabatier process has a high conversion of reactants into product, and could be considered to be 100% efficient. As shown previously, the CO_2 reduction via Sabatier process yields methane and water. In this process, water and methane can be easily condensed (below 373 K for water and below 112 K for methane) leaving the buffer gases in the gas phase. This separation technique would have to be evaluated to estimate the methane purity required for propulsion, and the solubility of the buffer gases in methane at the condensation temperature and pressure. However, liquid methane could be cryodistilled to remove any impurities that could be present as a result of the process.

C. RWGS Process

The RWGS/Electrolysis process has been developed for Mars in situ propellant production (ISPP) purposes for several years. The process is based on the conversion of Martian carbon dioxide into oxygen and carbon monoxide
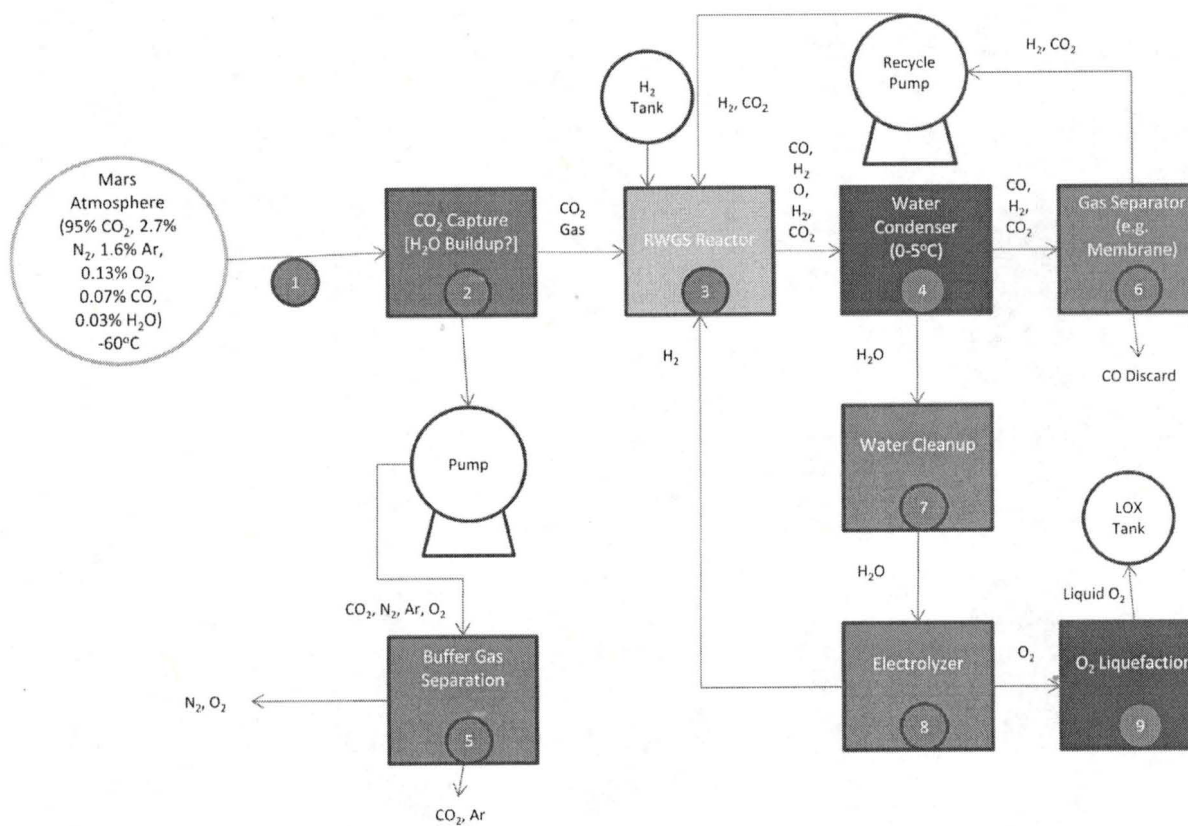
Figure 2. Schematic representation of the RWGS/Electrolysis process for oxygen production.

via hydrogen reduction of carbon dioxide into water and CO, with electrolysis of water to produce oxygen and hydrogen for recycling. Theoretically, the process yields infinite leverage (i.e. the mass of oxygen product divided by the mass of hydrogen brought from Earth), but some loss of hydrogen is inevitable. Nevertheless, the process can give very high leverage in the production of oxygen for both propellant and for life support functions on Mars. Figure 2 shows a simplified schematic of the RWGS process to enable discussion of available and potential technologies for process optimization.

The RWGS process starts (Steps 1, 2) with the collection and concentration of carbon dioxide from the ambient atmosphere of Mars. If desired, potentially useful buffer gases such as nitrogen and argon may be collected as well and possibly separated (Step 5). Depending on the collection process, a pump may be needed to bring the atmosphere into the collection device. Carbon dioxide is sent to the RWGS reactor (Step 3) where it is combined with hydrogen (either from Earth or from indigenous water electrolysis). Normally, the RWGS reaction is incomplete:

$$CO_2 + H_2 \Leftrightarrow CO + H_2O \qquad (4)$$
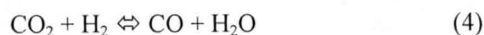
Reaction (4) is slightly endothermic with a ΔH of +9 kcal/mol. To improve the yield, the gases are separated and recycled, incorporating more carbon dioxide feed and make up hydrogen, if needed. After the RWGS reactor, the reaction gases are fed to a water condenser (Step 4) where liquid water is collected, deionized (Step 7), and electrolyzed (Step 8) into hydrogen, which is recycled into the RWGS reactor, and oxygen, which is liquefied and stored (Step 9). Alternatively, hot gases could be scrubbed of contaminants before water condensation (not shown). After removal of water vapor, the remaining gas, which consists of carbon monoxide and unreacted hydrogen and carbon dioxide, is passed through a separator, usually a membrane module that removes the carbon monoxide, which is normally discarded, but could be used to produce other hydrocarbons when combined with more hydrogen over the proper catalyst. The carbon dioxide and hydrogen are pumped back into the RWGS reactor to improve the conversion, as noted above.

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Previous Mars ISRU efforts (before Phoenix Lander) have included RWGS and SOE as secondary CO_2 processing process in order to produce oxygen in a ratio, with respect to methane, that is appropriate for the propulsion used. The oxygen-to-methane mass ratio produced after electrolysis of the water produced in reaction 2 is 2:1, which is short of the typical 3.4:1 oxidizer:fuel mass ratio used in methane-oxygen engines. Hence, SOE and RWGS provide an oxygen production process option without the consumption of hydrogen brought from Earth. In the new era of Mars exploration and resource utilization, oxygen would be generated from water mined from the soil or subsurface water ice.

D. Electrolysis of Carbon Dioxide in Ionic Liquids

Another method for the production of oxygen from the Martian atmosphere is the electrolysis of carbon dioxide in ionic liquids at much lower temperatures than SOE, i.e. <100°C. The solubility of CO_2 in ionic liquids makes this a potentially promising technology in terms of combining CO_2 capture and oxygen production as well as energy efficiency. However, the Mars Design Reference Architecture 5.0[11] notes that this process is at too low a TRL for consideration:

> It should be noted that while other technologies and methods for CO_2 processing are possible and have been evaluated, these processes were considered to be too low of a TRL to be evaluated at a system level for mission applicability. These alternative, low-TRL technologies include: molten carbonate electrolysis, non-aqueous electrolysis of CO_2, ionic liquid electrolysis, liquid CO_2 electrolysis, and lower-temperature mobile oxide ceramics. Finding H_2O in sufficient amounts, and of sufficient accessibility, provides an alternative to these low-TRL technologies, via use of electrolysis.

A thorough literature search found very few publications focused on oxygen production using this process beyond a few scouting experiments at KSC and some work by Rosen at the University of Illinois at Urbana-Champaign,[12] The KSC tests had little success in making oxygen because the two ionic liquids tested started decomposing during electrolysis. It was felt that other ionic liquids would be more successful. Rosen concluded that "1-ethyl-3-methylimidazolium tetrafluoroborate (EMIM BF$_4$) has many favorable characteristics that can enable the reduction of CO_2 at less negative potentials compared to previous work, as well as at low temperatures." Unlike the KSC work, Rosen used the ionic liquid with 1 M water added, which participated in the electrolysis. He observed the production of hydrogen, oxygen, and carbon monoxide in the same gas stream, attributing some of the oxygen to reduction of CO_2. Use of Martian water would make this approach feasible, but the purpose is unclear if the point is to make oxygen, which could be obtained from water electrolysis alone, unless the power required could be reduced. Rosen's lab scale apparatus also suffered a short working life as the ionic liquid diffused through carbon paper and coated the cathode catalyst. During a Phase II NASA SBIR project, Kimble et al.[13] investigated the process with two ionic liquids ([emim-BF$_4$] and [emim-tFMS]), each absorbed into Nafion membranes. Oxygen was produced, but some problems were encountered with the long-term operation of the electrochemical cells and poisoning of the Pt electrodes by carbon monoxide.

Lueck[14] has summarized the issues encountered for the electrolytic reduction of CO_2 to oxygen:

"Hurdles for Ionic Liquids
- Find one that carbonate is soluble in, or carbonate is the anion.
- (Working with Prof. R. Rogers @Univ. of Alabama)
- Confirm CO_2 reduction, preferably to CO.
- Confirm O_2 production at anode (2:1, CO_2/O_2).
- Confirm long term stability and balanced cell reactions.
- Minimize cell voltage.
- Electrode materials
- Minimize I*R drop → thin electrolyte film, highly conductive.
- Construct porous support for electrolyte (similar to carbonate).
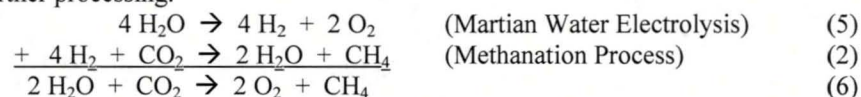- Construct cell manifolds and multi-cell assemblies."

The lack of significant progress in this area over the past decade is likely due to the difficulty in fulfilling the requirements listed above and the fact that there is little need for this process on Earth. More work should be encouraged by the ISRU program, especially in acedemia.

E. Electrochemical Reduction of CO_2 to Hydrocarbons

During the literature review for the above topic, it was realized that there is an alternative approach that becomes feasible with the known presence of large amounts of water on Mars. This technology is the combined electrolysis of CO_2 and water to produce hydrocarbons. This process has been the subject of intense research for several years and viable methods are emerging. The most relevant study by Sammels[15] was done for NASA JSC to improve the Sabatier process for use on the ISS. The authors state "A typical cell used to implement the process includes a polymer solid-electrolyte membrane, onto which are deposited cathode and anode films. The cathode film is catalytic for electrolytic reduction of CO_2 at low overpotential. The anode film is typically made of platinum. When CO_2 is circulated past the cathode, water is circulated past the anode, and a suitable potential is applied, the anode half-cell reaction is $4H_2O \rightarrow 2O_2 + 8H^+ + 8e^-$. The H^+ ions travel through the membrane to the cathode, where they participate in the half-cell reaction $CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O$." The net reaction is $CO_2 + 2H_2O \rightarrow CH_4 + 2O_2$. The reaction occurs at room temperature and appears to be efficient, based on the limited technical information available. The Tech Brief refers to a future Ph.2 study, but confirmation that it is underway was not found. This work and similar work also based on copper catalysts for this intriguing reaction should be pursued as a potentially high-payoff technique for fuel and oxygen production on Mars in a single chemical step, avoiding high temperatures, catalysts prone to deactivation, heat exchangers, water condensers, demisters, gas separation membranes, and a separate water electrolysis step. The CO_2/H_2O electrolysis process would provide enough oxygen to burn all the methane plus extra for life support systems (see discussion below).

III. Mining Martian Water

Recent robotic missions to Mars have reported the presence of water ice in subsurface deposits. The water ice deposit can be mined to extract hydrogen and oxygen that can be used for the production of propellants, as well as drinking water and oxygen for life support systems. From a mission architecture perspective, a combination of water electrolysis and methanation process provides a mass ratio of oxidizer:fuel just above the 3.4 oxidizer:fuel typically used for liquid oxygen-methane engines. As shown below, the Mars water-methanation combination provides an oxygen:methane mole ratio of 2 or a mass ratio of 4, which has the potential to provide sufficient oxygen for life support without any further processing.

$$4\,H_2O \rightarrow 4\,H_2 + 2\,O_2 \qquad \text{(Martian Water Electrolysis)} \qquad (5)$$
$$+\ \ 4\,H_2 + CO_2 \rightarrow 2\,H_2O + CH_4 \qquad \text{(Methanation Process)} \qquad (2)$$
$$2\,H_2O + CO_2 \rightarrow 2\,O_2 + CH_4 \qquad\qquad\qquad\qquad\qquad (6)$$

Clearly, Martian water mining will require excavation systems to obtain the water ice. The ISRU program has begun collaborating with Human Robotic Systems (HRS) to develop excavation implements for roving platforms for lunar applications, which are likely to be applicable to Mars surface systems. However, a different excavation implement will be required for water ice, as the excavation forces will be completely different and the sublimation of water on Mars may be significant. Further development of excavation techniques for Mars application should be pursued given the latest data from Mars.

Extracting water from Martian soil will require the development of soil processing reactors. Although the Mars water extraction process may not be at as high a temperature as those for lunar ISRU, typical terrestrial components have temperature limitations around, and not much higher than, the boiling point of water. Mars soil processing process would require processing temperatures higher than $100°C$; hence, technology development on high temperature seals, fluid components (valves, sensors, etc), soil feed systems, and energy efficient thermal design (to minimize the dependency on electrical power) will be required to enable the capability to extract water from Martian soil.

IV. Mars ISRU Supporting Unit Operations

A. Mars Atmospheric Gas Capture

There are several ways to capture and pressurize carbon dioxide from the Martian atmosphere, which is required to purify it from the minor components and to pressurize it sufficiently to obtain a significant feed rate. The literature review we recently performed[16] evaluated several technologies available for this step, which included freezing at cryogenic temperatures, mechanical compression, and adsorption pumping. That study concluded that freezing was the most advantageous process because it required less power than compression pumping, gave high collection rates, purified the carbon dioxide, yielded high pressure feed upon warming, and required less mass than

other options, especially adsorption pumping. Care must be taken that any material used to increase the condensation surface area does not adsorb other Martian atmospheric components, as occurred in one study that used activated carbon .[17]

Polymeric membranes have been considered for Mars atmospheric capture and gas separations, but their utility appears to be better for a feed that is already compressed to operating conditions. Thus, membranes will be evaluated below for buffer gas preparation because argon creates problems when used at high concentrations as a component in breathing gas. Membranes are also important devices for process gas separation.

We have also surveyed ionic liquids were also surveyed for carbon dioxide capture.[16] This is an intense area of study for terrestrial carbon dioxide capture and many candidate materials provide good separations from nitrogen, methane, and hydrogen. However, ionic liquids are expensive or require synthesis to prepare and processes using them for Mars applications are at low TRL. Given that there are no clear advantages for them relative to freezing, their pursuit for only this purpose is not recommended at this time, but they could be candidates for proposals to the NASA Office of the Chief Technologist (OCT). Developments should be monitored, however, and OCT has recently funded project formulation activities at KSC for combining carbon dioxide capture and electrolysis of the CO_2 to oxygen and CO or oxygen and methane. The latter process has the potential to greatly simplify the conversion of Martian CO_2 into propellant by combining capture and conversion in a single process vessel at room temperatures as compared to the high temperatures and many unit processes and vessels required for the Sabatier/Electrolysis process.

Similarly there are several other carbon dioxide capture technologies being studied for use on Earth, but some work is aimed at Mars. Amines, amino acid salts, cold dimethyl ether (Selexol), and cold methanol (Rectisol) are commercial CO_2 capture reagents that can be used selectively on flue gases. Although they work on Earth, they do not provide the capability to work at very low Martian pressures and do not provide high pressure CO_2 as a product as freezing does. Brooks and coworkers at the Pacific Northwest National Laboratory (PNNL) have investigated microchannel 13X zeolite absorbers[18] to overcome some of the disadvantages of sorption beds, i.e. being heavy and slow. PNNL calculated a productivity of >2 g CO_2 per kg of hardware for multiple parallel units for a compression ratio of 100, but they did not compare their results to other options. A rough estimate using several assumptions show the PNNL system may have a mass comparable to a CO_2 freezer of the same capacity, but this is a low confidence estimate. On the other hand, Precision Combustion, Inc. has a novel reactor concept that combines CO_2 separation from the Martian atmosphere and conversion to methane using the same lightweight, compact catalyst bed.[19,20] Such combinations of two or more steps in propellant production technologies should be pursued if they can be shown to save mass, power, volume, etc.

However, if trace gases are not required to be separated from CO_2, mechanical compression of atmospheric gases would have to be considered as an option. This option would require dust filtration technology and reliable and low power design, providing long life-cycles (possibly longer than 5 yrs of operation).

1. Development of a Carbon Dioxide Freezer

Following our own advice that the best current technology for CO_2 capture is cryofreezing,[16] we have been designing a CO_2 freezer to provide feed to a Sabatier reactor as part of the MARCO POLO (Mars Atmosphere and Regolith COllector/PrOcessor for Lander Operations) project being led by JSC. The purpose of the MARCO POLO project is to demonstrate the conversion of Martian CO_2 and water from regolith into methane/oxygen bipropellant on the scale needed for a Mars Sample Return mission. The requirements are to provide 88 g of >99% pure CO_2/hr at 50 psia for a 14-hr day with an initial power limit of 500 W (later increased to 900 W). We selected a Sunpower Cryotel GT cryocooler with 34 W of lift at 150 K, the amount of cooling estimated to freeze the CO_2 and offset heat leaks to the environment. Figure 3 shows a notional drawing of the current design of the module with the Sabatier reactor module in the background. Unlabled parts of the module include the fluid system, valves, regulators, pressure transducers, a CO_2 pump, and the freezer vessels. The design is still underway and fluid connections for the CO_2 storage tanks remain to be added. Two cryocoolers are required for one to collect dry ice while the other supplies it to the Sabatier reactor. The CO_2 storage tanks are needed because the flange on the cryocooler cannot withstand elevated pressures and the CO_2 pump is used to transfer gaseous CO_2 to the tanks.

We have initiated testing of the freezing process and the cold head size and shape required to collect sufficient dry ice. An initial finned copper cold head based on prior work turned out to be too heavy (1.3 kg), resulting a cool down time too long (43 min) to meet the requirements and minimal dry ice collection. A second test with only the cryocooler tip (1" o.d. x 1.33" long) with a small solid copper cylinder (0.75" o.d. x 1.5" long) attached was much more successful, with a cool down time of only 4.5 min. After 1hr, 15 min (including cool down time) at 150 K or less and a CO_2 pressure of 11 mbar, a layer of dry ice ~0.2-0.3" thick accumulated on the copper parts (Figure 4). Much of the dry ice was chipped off and it weighed 40 g. Some was lost by sublimation and uncaptured chips. Based on measured thickness, ~78 g of CO_2 was collected in 1.25 hr or 62.4 g/hr, which is 71% of the goal.
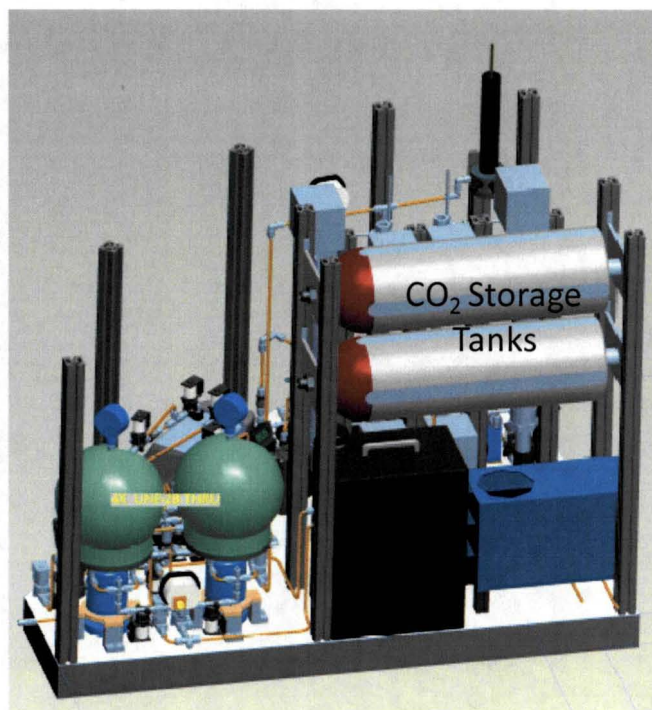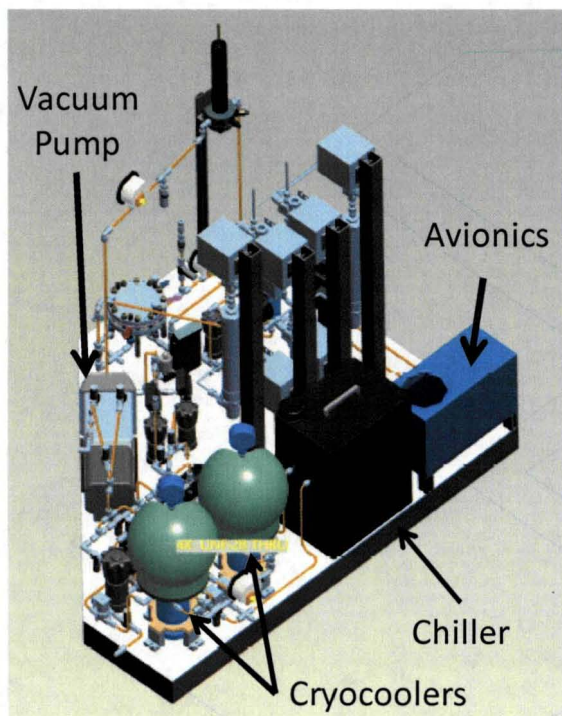
Figure 3. Drawing of the CO₂ Freezer module. The CO₂ Storage Tanks are omitted on the left for clarity.
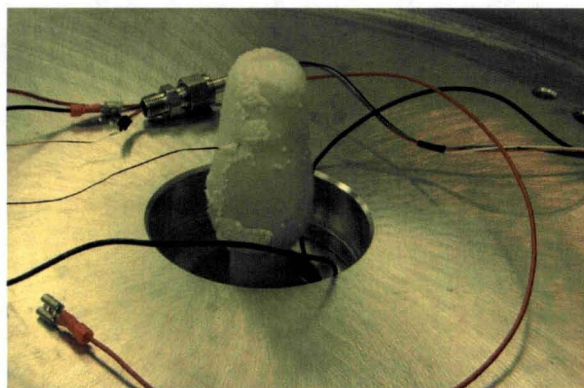

Figure 4. Photo of dry ice collected at 10 mbar CO₂ pressure and 150 K on the cryocooler cold tip plus a 1"x ¾"cold head.

Based on these results, we designed a new cold head that minimizes copper mass to minimize cool down time and maximizes surface area for dry ice collection. Figure 5 shows the new design that also takes into account the ability of our machine shop to make the item from solid copper. However, testing of the new design also failed to meet requirements. Testing and redesign of the cold head will continue until the desired freezing rate and mass is obtained.

B. Water Condenser

Water condensation is a straightforward cooling process to convert the water vapor into liquid water that has a very low vapor pressure just above 0°C. Previous testing in this process has not identified any issues. Effort must be taken to prevent misting loss of the water downstream for the sake of efficiency. No new development activities need to be undertaken in this area except implementation of a new light-weight material with high thermal conductivity (such as carbon foam).

Figure 5. Drawings of the new copper cold head. All units are in inches.

C. Gas Separation

The gas separation process is very dependent on the ISRU process under consideration. For example: (1) carbon monoxide, hydrogen, and carbon dioxide separation after water condensation

in the RWGS process, (2) unreacted hydrogen and methane after water condensation in the Sabatier process, and (3) volatile contaminants from the soil processing reactor. For the RWGS process, work by Whitlow and Parrish[21] showed the commercial Permea Prism membrane module was highly efficient. If the mass and volume of the membrane module could be reduced, it should be pursued, but not at a high priority because the existing Permea technology is adequate. For the Sabatier process, membranes separation and cryogenic condensation also offer a good solution to recover hydrogen from methane because the methane would have to be liquefied for ISRU purposes.

Trace gases, nitrogen and argon, are also a useful resource and would require purification and storage. Depending on the Mars atmospheric gas capture technique, buffer gas purification can take place before CO_2 reduction or as a final step in the process. As previously discussed, these trace gases are inert and should not affect the reduction of CO_2 in reactions 1-3. However, if the Sabatier reaction is carried slightly fuel rich (which may extend the life of the catalyst) and trace gases remain in the gas stream, a hydrogen-trace gas separation step would be required.

D. Water Cleanup

NASA's Phoenix lander mission to the northern hemisphere of Mars ($68°$ N) found significant amounts of water-soluble constituents in the Martian soil.[1,3] These constituents represent potential contaminants to water produced from soil processing. These constituents are potassium, calcium, sodium, magnesium, perchlorate, chloride, and carbonate. The ion exchangers used in the past for this process require large amounts of consumables for regeneration and are therefore not acceptable for Mars ISRU. Regenerable (non-consumable) contaminant removal systems to provide electrolysis-grade water will be required as part of the water extraction and electrolysis system. Various water purification techniques could be applicable to this application: membranes, distillation, reverse-osmosis, electrochemical filtration, among others. Technologies being developed for water cleanup from hydrogen or carbothermal reduction of regolith could be useful for this process as well. Development of all these technologies is needed.

E. Electrolyzer

Water electrolysis will be a critical step required to support Mars ISRU. Water electrolysis is a common need for multiple surface systems, and the ISRU project should continue collaboration in technology development with Power and Exploration Life Support System projects. Currently available water electrolyzers are already highly efficient, although electrolyzers that are not as sensitive to impurities would be a welcome improvement.

F. Cryogenic Liquefaction and Storage

Cryogenics liquefaction and storage has been outside the scope of ISRU for the last several years. This technology development is led by the Cryogenic Fluid Management project, and ISRU should continue to follow the effort as it is required for a complete ISRU architecture.

V. Technology Development Recommendations

The following recommendations are set forward by the authors with the best knowledge of the data presented in this point in time.

1. **Mars Atmospheric Gas Processing**: Select Sabatier (Methanation) Process for Fuel Production
   Research and Technology:
   - Lifetime of commercial catalyst
   - Efficient thermal control
   - Effect of pure CO_2 versus raw atmospheric gas on catalyst
   - Alternatives (for dissimilar redundancy): microchannel reactors (poison resistant/regenerable), ionic liquid electrolysis of CO_2, combined electrolysis of CO_2 and H_2O, improved SOE subsystems (ruggedized)

   Rationale:
   - Given the recent robotic mission findings, significant water is available on the surface of Mars
   - Water mining-Sabatier Process provides oxygen:methane in a ratio appropriate for propulsion

- This approach will reduce Earth departure mass (i.e. no hydrogen logistics)

2. **Mining Water**: Continue soil excavation system and soil processing reactor development

   Research and Technology:
   - High temperature seals, valves, sensors/instrumentation, gas pumps, auxiliary equipment
   - Efficient thermal design
   - Excavation systems: reliable, long life
   - Dust tolerant mechanisms

   Rationale:
   - Martian water provides a better architecture for ISRU (i.e. eliminates Earth-supplied hydrogen logistics)

3. **Mars Atmospheric Gas Capture**: Parallel developmental effort for CO_2 freezer and mechanical compression:
   Research and Technology:
   - High efficiency (freezer/compressor)
   - Efficient thermal design (freezer)
   - Long life (cryocooler compressor)
   - Improvements in microchannel absorbers and new approaches

   Rationale:
   - The gas capture technique downstream of CO_2 reduction unit depends on the gas capture technique employed to capture atmospheric CO_2

4. **Water Condenser**: Engineering design to take place during integrated system development effort
   Research and Technology:
   - None

   Rationale:
   - This is an engineering effort, not a technology development task

5. **Gas Separation**: Parallel effort of cryogenic condensation and membrane separation
   Research and Technology:
   - Polymer Electrolyte Membranes
   - Efficient cryogenic system (combine with cryocooler development above)
   - Solubility of gases in cryogenic liquids

   Rationale:
   - Methane purity and atmospheric gas capture selection will drive the final selection of the gas separation (separation of CH_4-H_2 or N_2-Ar-H_2-CH_4)

6. **Water Cleanup:** Continue regenerable water cleanup
   Research and Technology:
   - Regenerable water cleanup to meet electrolysis grade

   Rationale:
   - Clean water is required for electrolysis

7. **Electrolyzer:** Continue Small Business Innovation Research (SBIR) and collaboration with the NASA Evnvironmental Live Support project and the Power project; encourage industry development
   Research and Technology:
   - Contaminant resistant electrolysis

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Rationale:
- Electrolysis is a common sub-system for various surface system elements.
- Continue team collaboration and SBIR hardware.

8. **Cryogenic Liquefaction and Storage:** Continue collaboration with the Cryogenic Fluid Management project.
    Research and Technology:
    - Zero boil-off storage
    - High efficiency and reliable cryocooler

Rationale:
- Cryogenic storage is needed to provide methane and oxygen propellant
- Cryogenic storage provides high density storage of consumables.

VI. Conclusion

This paper has examined the technologies required to enable Mars In-Situ Resource Utilization (ISRU). Our understanding of Mars resources has changed significantly in the last five years as a result of recent robotic missions to the red planet. The indication of the presence of water in significant amounts at high latitudes, and possibly at lower latitudes, has the potential to change ISRU technology selection. A brief technology assessment is described for the most promising Mars atmospheric gas processing techniques: Reverse Water Gas Shift (RWGS) and Methanation (aka Sabatier), as well as an overview of soil processing technology to extract water from Martian soil. The authors conclude that the technologies needed to (1) concentrate carbon dioxide, nitrogen, and argon on Mars, (2) separate them, (3) process them into oxygen, methane, and buffer gases, and (4) store them for use are already available at a sufficiently high level of development at the component level that further efforts should be focused on engineering development and field demonstrations of integrated systems of these processes. A few technologies that promise improvements in the performance of these subsystems, such as ionic liquids for carbon dioxide collection and electrolysis to oxygen, low temperature electrolysis of carbon dioxide and water to methane and oxygen, and microchannel collectors and reactors, deserve closer scrutiny and possibly more development through the proper funding channels. Furthermore, current lunar soil processing technologies (i.e. excavation, soil reactor, and fluid processing) have applicability to Mars soil processing to extract water and these efforts should continue further development. It is expected that these integrated system engineering units will reveal remaining vulnerabilities caused by interactions of the various subsystems that are currently unknown, leading to new technological needs. Once satisfactory performance is demonstrated in the laboratory, oxygen, propellant, and buffer gas engineering units should be demonstrated at analog Mars sites along with other surface systems to demonstrate a full operational cycle (resource acquisition, processing, purification, storage, and utilization) to raise the TRLs to the 5-6 range. The time is right to push the development of these technologies to convince mission planners that Mars ISRU is a powerful tool for reducing costs and expanding exploration capabilities for Mars missions.

Furthermore, this paper recommends that the ISRU position on whether hydrogen for oxygen and propellant production on Mars should be imported from Earth or obtained from Martian water sources should be the use of Mars water resources. Years of debate on whether it is feasible to transport hydrogen in liquid or slush form to Mars is not likely to be resolved in the near future. The best strategy, which also enables future Mars ISRU, is to use the water resources that are already known by direct measurement to exist on Mars. The problem then is simplified to something we can address: the development and demonstration of efficient Mars water mining and refining technologies, which would also provide pure water, another extremely useful supply item for human missions for both drinking water and radiation shielding. One other extremely important advantage of this strategy is that the amount of oxygen and propellant that could be produced would no longer be limited to the amount of hydrogen brought from the Earth; a virtually unlimited supply would become available, restricted by only the lifetime of the hardware needed and the energy supply. Looking to the more distant future, this strategy is precisely what needed for a Mars outpost and a future Martian civilization. The availability of local Martian water resources will limit landing sites somewhat to known locations, but this is a minor disadvantage because Mars is a large planet with the same surface area as the continents of Earth. In addition, sites with water would enhance the possibilities of finding signs of past or current Martian lifeforms, a significant scientific goal for Mars exploration.

VII. Acknowledgments

VIII. References

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Mars In Situ Resource Utilization Technology Evaluation

Anthony Muscatello and
Edgardo Santiago-Maldonado

NASA – Kennedy Space Center

Outline

- Background
- Purpose
- Methodology
- CO_2 Capture and Buffer Gases
- Chemical Processes
- Recommendations
- Conclusions

Background – Our Changing View of Mars

- Mariners – dry, dusty, cold, Moon-like
  - Evidence for ancient water flow
- Vikings – dry, dusty, cold, but intermediate between Moon and Earth
  - RH ~100% (?)
  - Oxidizers in soil, no life (?)
- Pathfinder/Mars Global Surveyor – dry, dusty, cold, but interesting
  - Possible current liquid water flows
- Mars Odyssey – evidence for extensive water ice
- Mars Rovers – in situ proof of ancient, long duration surface water
- Mars Phoenix – in situ proof of near-surface water ice
  - Near neutral pH, perchlorate oxidizer

Water, water everywhere!
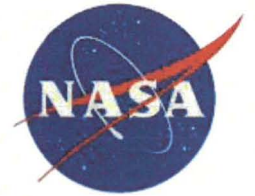
Lower-Limit of Water Mass Fraction on Mars

4
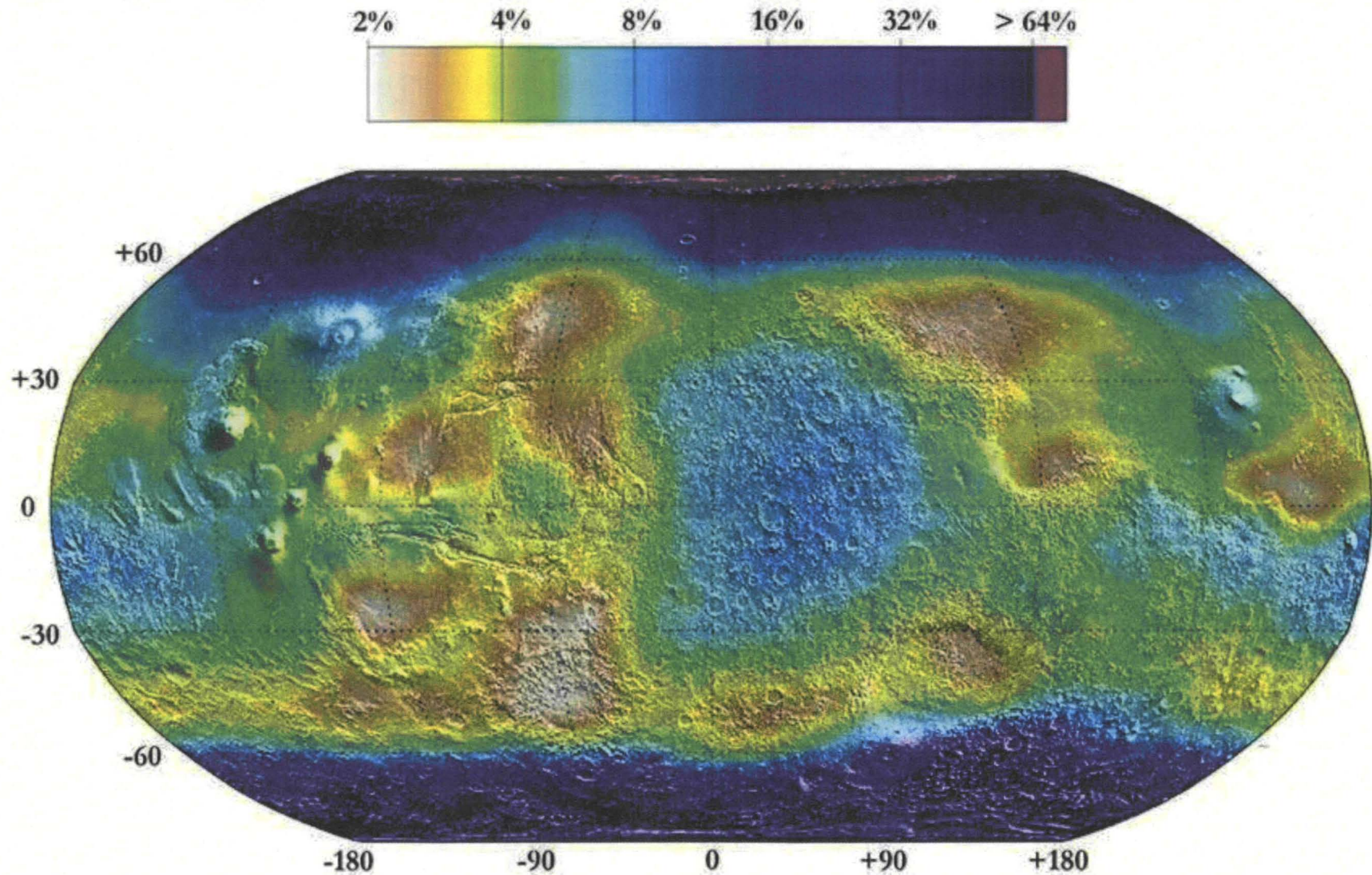
Purpose

- Update status of Mars ISRU technologies
- Provide guidance for future investments
- Provide basis for Mars ISRU planning
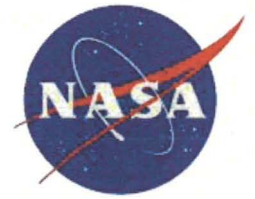
Methodology

- Evaluated CO_2 capture and gas separation technologies
  - Included new options: ionic liquids, amine-based solvents, preparative GC
- Selected RWGS and Sabatier systems
  - Examined unit processes for TRL status
- Summarized results in a report to ISRU Program Manager Bill Larson
- Full paper in 50th AIAA ASM Proceedings

CO$_2$ Capture Technologies

- **CO$_2$ Freezers Look Promising**
- **CO$_2$ freezers have been tested by Pioneer Astronautics and Lockheed-Martin**
- **Results show accumulation rates of ~20, 13, and 80 g/hr using lab-scale systems (equiv. 5-30 g/hr CH$_4$)**
- **N$_2$/Ar was not measured or purified**
- **Rapp estimated a CO$_2$ freezer for 0.5 kg/hr needs ~1/3 the power and 11% the mass of a compression pump/membrane CO$_2$ purifier**
- **JPL investigated liquefaction of the Martian atmosphere, but power requirements are high**
- **Adsorption beds also rejected because of high mass, volume, and power**

TRL 3-4
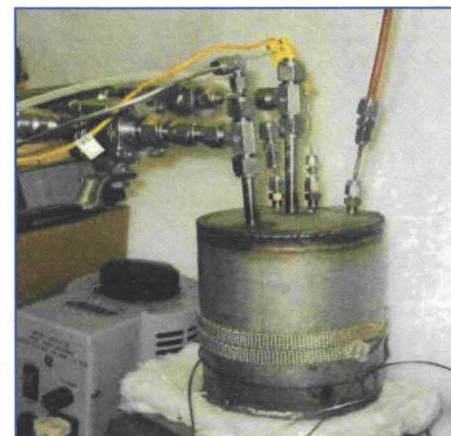
Pioneer MACDOF
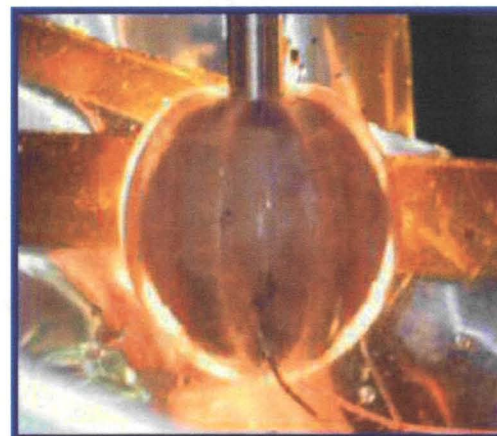
Lockheed Cryocooler Freezer 7

CO$_2$ Freezer Development

Followed own advice

- Designing/building/testing cryofreezer to test process and separate buffer gases
- Joined forces with MARCO POLO project
- Currently procuring equipment and developing freezer cold head

3-D Model of Atmospheric Processing Module

Vacuum Pump

CO$_2$ Storage Tanks

Chiller

Avionics

Cryocoolers

CO_2 Freezer Development

Sabatier Module

CO_2 Freezer Module

Vacuum Pump
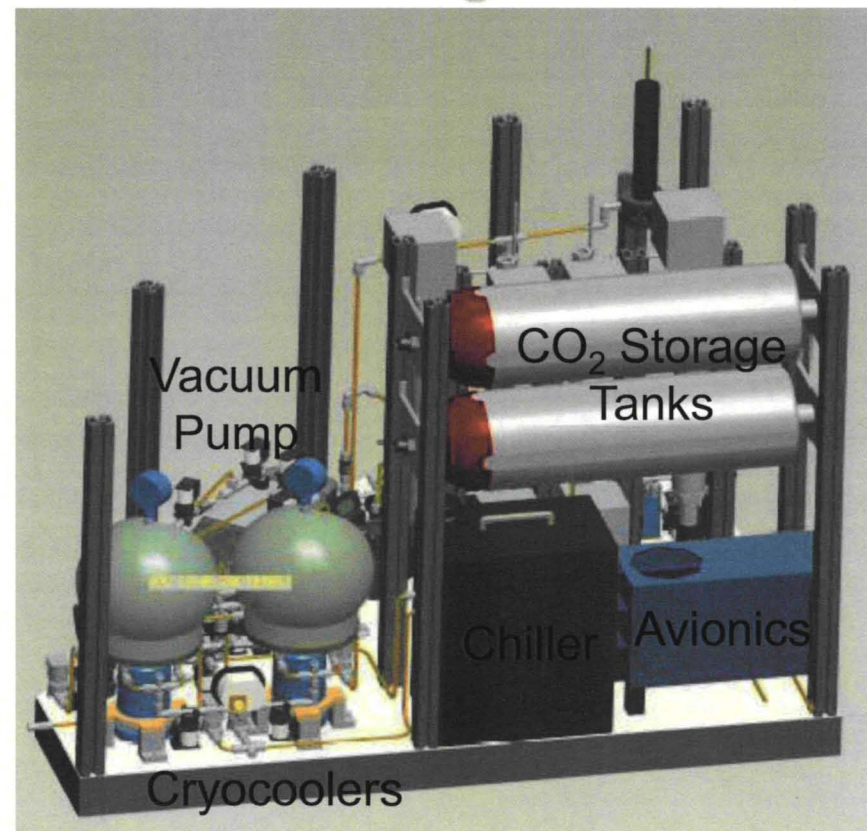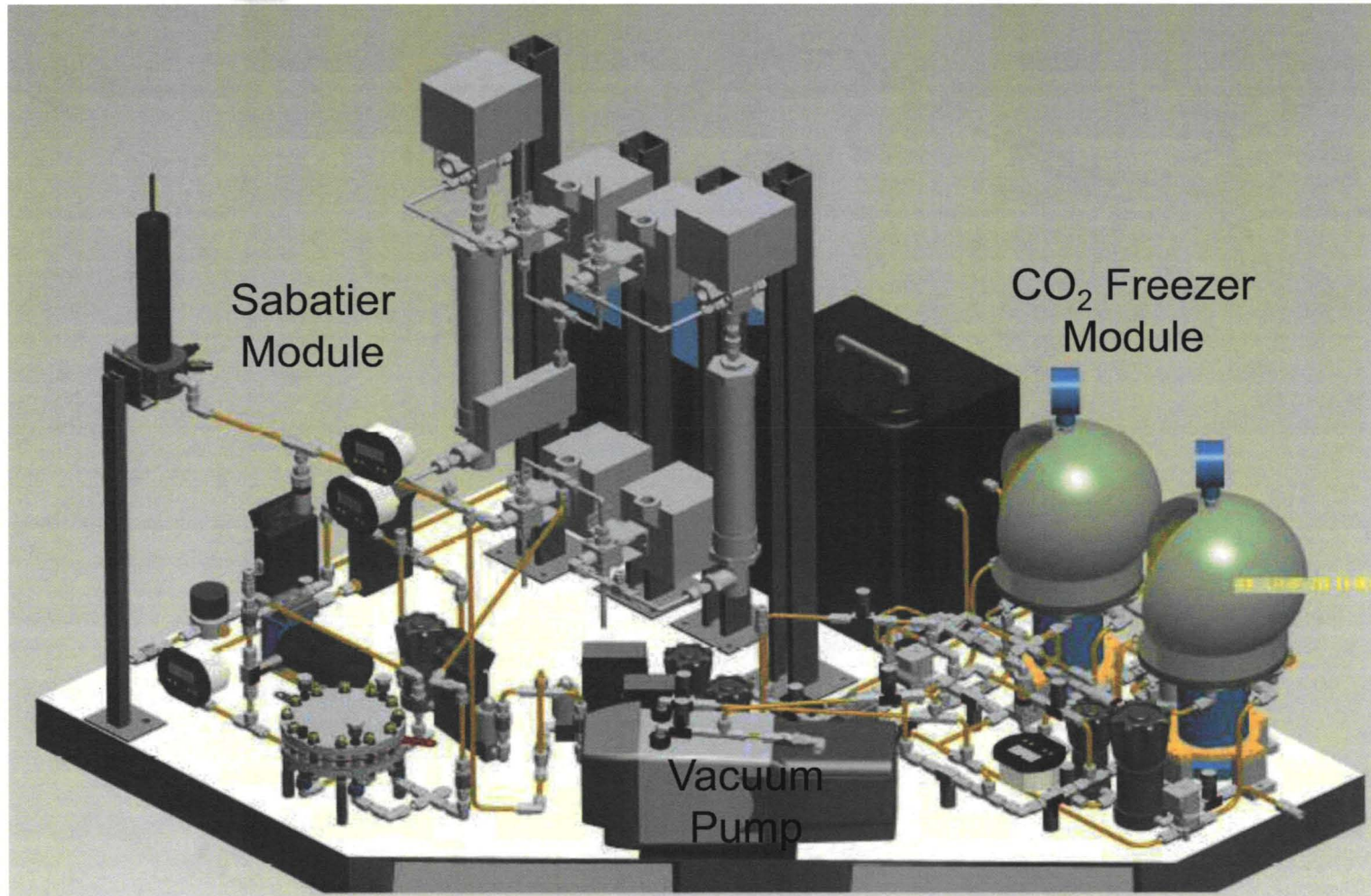
3-D Model of Atmospheric Processing Module (CO_2 Tanks Omitted)

9

CO$_2$ Freezer Development
Requirement: 88 g CO$_2$/hr @ 50 psia
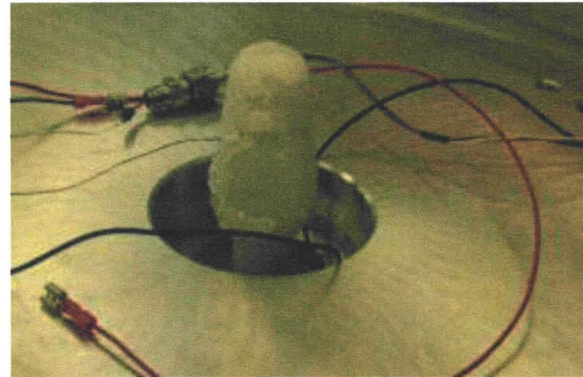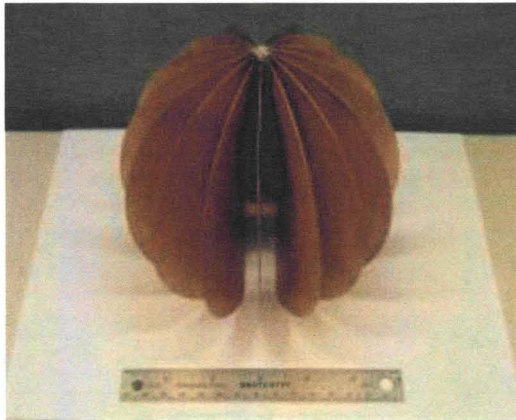
**Cold tip + 1x3/4" rod
~60 g/hr**

**Based on Lockheed
6" fins
~5 g/hr**
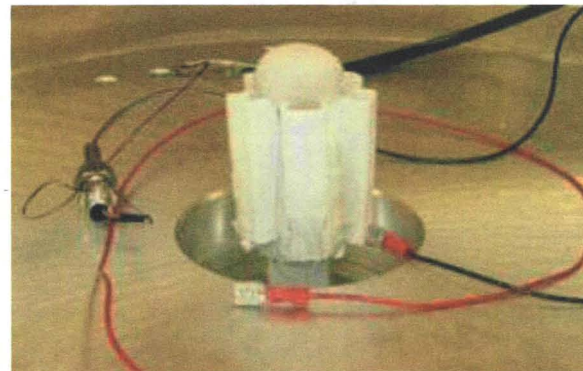
**Cold tip + 1x3/4" rod + Al fins
~20 g/hr**
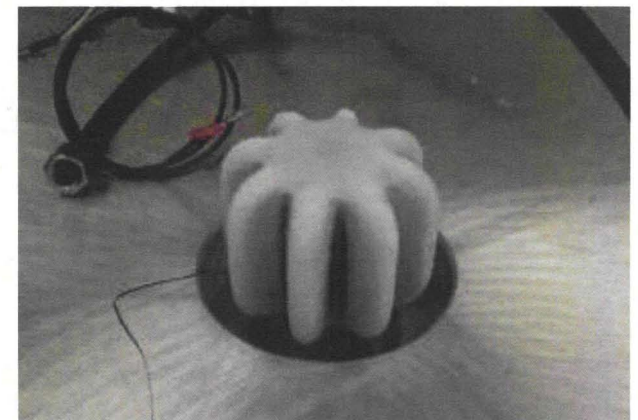
**2x2.5" machined fins
~35 g/hr**

10

Alternative Approach- Direct Mars Atmospheric Gas Processing

- ISRU processes (SOE, RWGS, Sabatier) may not require high purity CO_2.

- Pioneer Astronautics ran a combined RWGS-Sabatier process with $CO_2/N_2/Ar$ for 5-continuous days without degradation of catalyst.

- N_2 and Ar were not separated from feed, but were removed during condensation or cryodistillation of products

- Gas separation downstream from CO_2 reduction process may be easier and still provide useful buffer gases

- Mechanical compression is required, and may require more power but was claimed to be less complex.
  - 240 W for 0.6 lpm (71 g/hr) @ 5 bar

- A mass comparison needs to be done, as well.

TRL 3-4
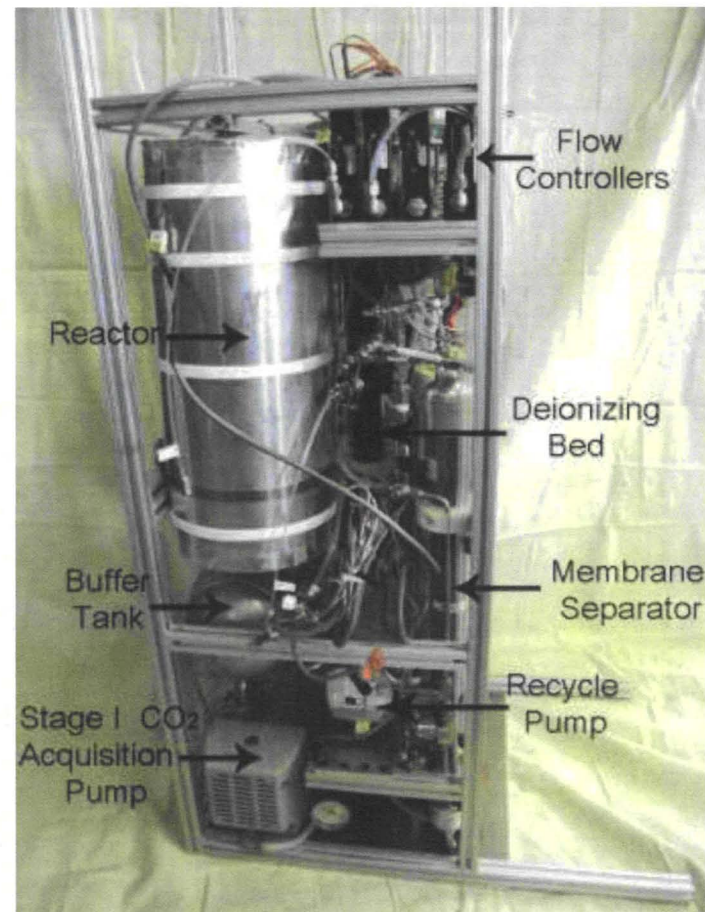
Pioneer IMISPPS

Buffer Gas Separation

- **COTS Membrane Modules Are Adequate**
- **Parrish (KSC, 2002) performed a study of several commercial membranes:**
  - Permea Prism® Alpha Separators PPA-20.
  - Neomecs GT #020101 .
  - Enerfex SS.
  - Enerfex SSP-M100C Membrane sheet.
- **Temperatures = -45°C to +30°C.**
- **Variety of pressures.**
- **Designed a system that would operate at -44°C and 780 mm Hg (1.03 atm)**
- **Feed = 30% CO_2, 26% Ar, and 40% N_2.**
- **Predicted product = 6 lpm, 600 ppm CO_2, 38% Ar and 62% N_2.**
- **47% recovery of the feed.**
- **Work is needed on Ar/N_2 separation.**
  - Ar leads to potential bends issue.

<div align="center">TRL 3-4</div>

Permea First Stage   2329 cm³

Vent

Permea Second Stage   2180 cm²
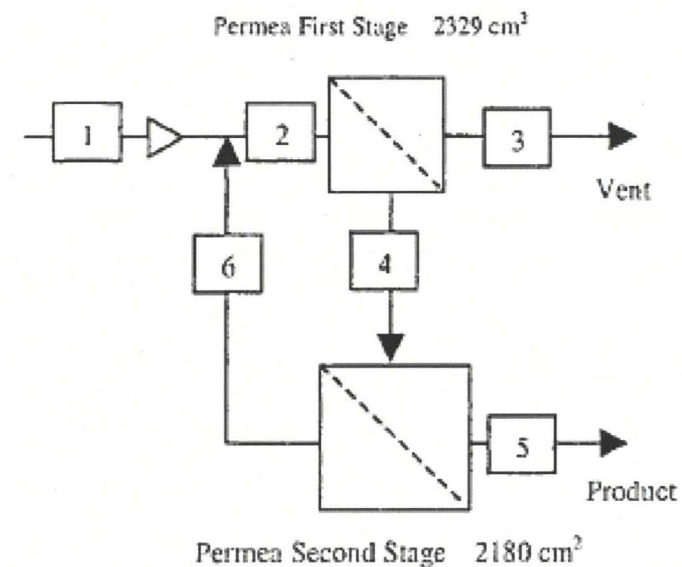
Product

Membrane purification of feed from the capture of CO_2 (Parrish, 2002)
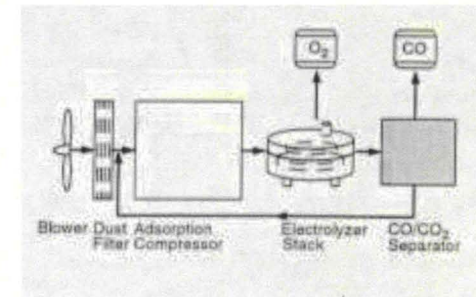
Chemical Processes

- **Solid Oxide Electrolysis:**
  $$2\ CO_2 \rightarrow 2\ CO + O_2 \tag{1}$$
- **Sabatier:**
  $$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \tag{2}$$
- **RWGS:**
  $$CO_2 + H_2 \rightarrow CO + H_2O. \tag{3}$$
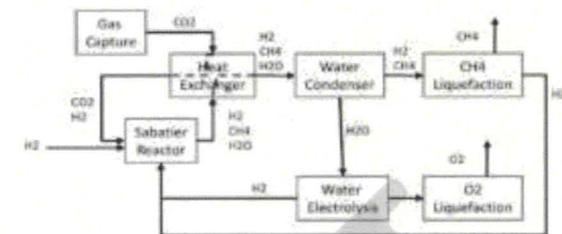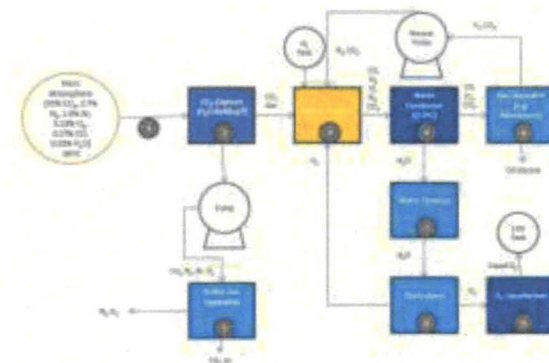- **SOE: fragile ceramic membrane, but new developments at Bloom Energy**
- **RWGS: produces only oxygen, but recycles hydrogen many times**
- **Sabatier: well known, but need to take H_2 to Mars and makes only half the oxygen needed**
- **So?**

TRL 3-4

SOE Process


Sabatier Process

RWGS Process

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# Major Recommendation – Use Mars Surface Water Resources

- Considered by DRA 5.0
- We know where the water (ice) is and how much (Phoenix and Mars Odyssey)
- Combined with Sabatier, we can make H_2 on Mars and get the right ratio of CH_4/O_2 with surplus O_2 for life support
- Avoids difficulty of LH_2 storage
- Requires surface mining
  - Base on lunar mining technologies
- Provides a path forward for human exploration and settlement
  - i.e. water for life support and shielding

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Chemical Processes – Ionic Liquids for CO_2
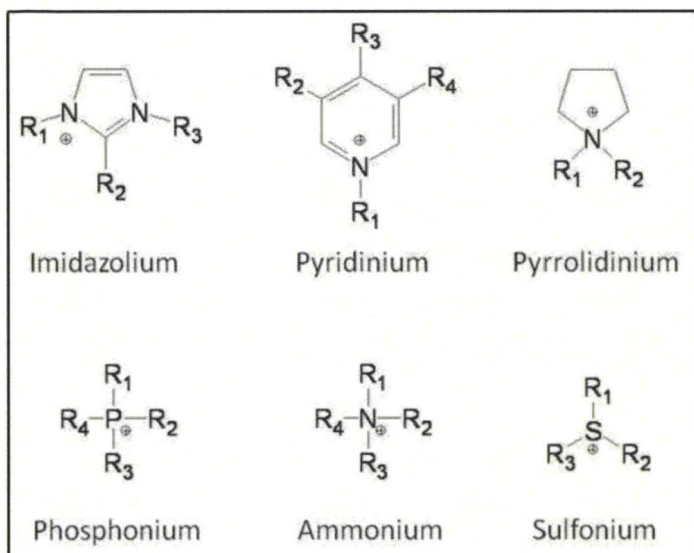
Cations
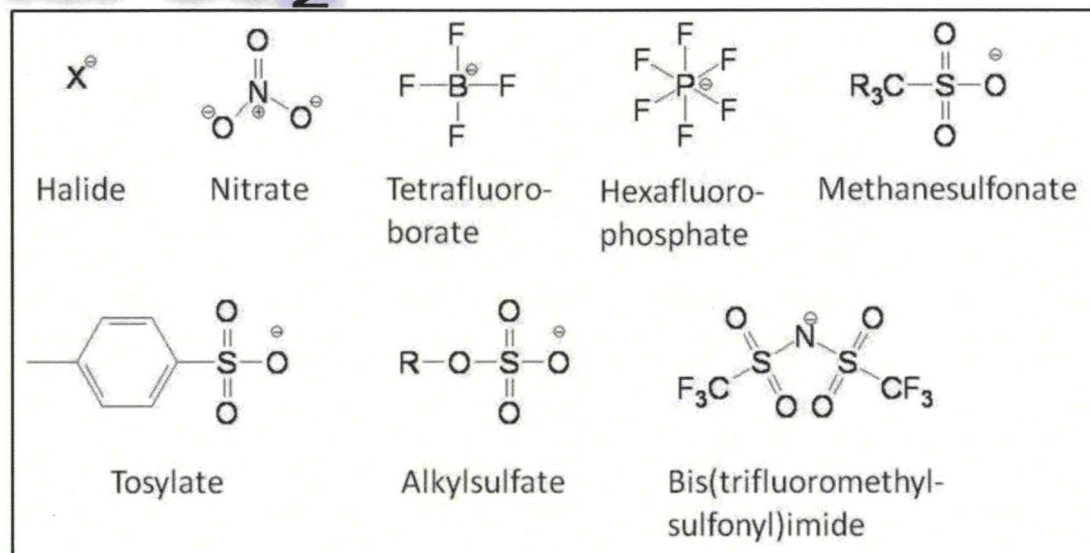
Anions

Typical cations and anions for ILs

- **Ionic Liquids are ionic compounds that are liquid at or near room temperatures**
- **Absorb up to 7% CO_2**

Chemical Processes - Ionic Liquids for CO_2

- Electrolysis of CO_2 in ionic liquids
  - Low TRL, but simplifies processing
  - Requires compression of Martian atmosphere
  - OCT project formulation at KSC
- Electrocatalylic reduction of CO_2 and H_2O to CH_4 and O_2
  - Room temperature, low voltage
  - Also low TRL, but very promising
  - Eltron Research for JSC for ISS application

TRL 1-2

Chemical Processes - Membrane Separations

- **Permea modules have been tested by LMA, Pioneer Astronautics and KSC**
  - **KSC results are good with minor H_2 losses (0.26% average)**
- **28 other candidate membrane materials evaluated**
  - **Top 10 identified**
- **Selectivity and permeability are inversely related**
- **Pressurization is required (1-10 atm)**
- **Synthesis required in some cases**

TRL 3-4

	Stream	Calculated H2 (slpm)	Measured H2 (slpm)	Calculated CO2 (slpm)	Measured CO2 (slpm)	Calculated CO (slpm)	Measured CO (slpm)
	Feed	16.825	16.861	7.56	7.522	2.114	2.116
Base Case	Permeate	16.812	16.812	7.547	7.547	1.126	1.126
	Reject	0.013	0.013	0.013	0.013	0.988	0.988
	Feed	26.265	25.333	7.265	8.126	1.793	1.864
Sim-1	Permeate	26.058	26.205	7.162	7.189	0.64	0.65
	Reject	0.207	0.059	0.103	0.076	1.153	1.144
	Feed	30.748	30.555	7.984	8.07	1.537	1.644
Sim-2	Permeate	30.011	30.48	7.681	7.801	0.3831	0.541
	Reject	0.737	0.267	0.303	0.184	1.154	0.996
	Feed	29.552	29.428	8.605	8.696	2.028	2.047
Sim-3	Permeate	29.324	29.463	8.486	8.523	0.723	0.834
	Reject	0.228	0.09	0.119	0.082	1.305	1.194
	Feed	25.603	25.099	7.035	7.332	1.779	1.986
Sim-4	Permeate	25.515	25.563	6.987	6.96	0.753	0.747
	Reject	0.088	0.04	0.048	0.076	1.026	1.032
	Feed	16.507	17.248	8.921	8.323	2.47	2.327
Sim-5	Permeate	16.43	16.5	8.843	8.909	1.032	1.384
	Reject	0.077	0.007	0.078	0.012	1.438	1.086
	Feed	20.591	20.864	7.036	6.786	1.983	1.96
Sim-6	Permeate	20.552	20.564	7.008	7.007	0.952	1.024
	Reject	0.039	0.026	0.028	0.029	1.031	0.959

**KSC RWGS Membrane Results (Whitlow and Parrish, 2003)**

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Microchannel Technologies

- Microchannel reactors offer:
  - Better temperature control of the catalyst bed
  - Reduce temperature gradients and localized "hot spots"
  - Prevent sintering of a packed bed catalyst
  - Large mass savings over the traditional packed bed reactor design,
  - Penalty of increased pressure drop and increased probability of complete catalyst deactivation.
- Potentially improved CO_2 absorption for concentration
  - Lower mass, volume, and power
- Further development is justified
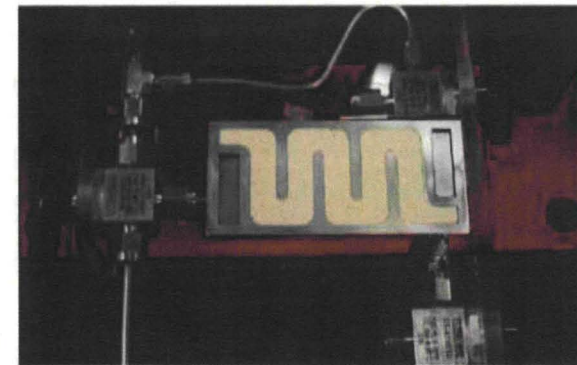
PNNL Microchannel Zeolite CO_2 Absorber
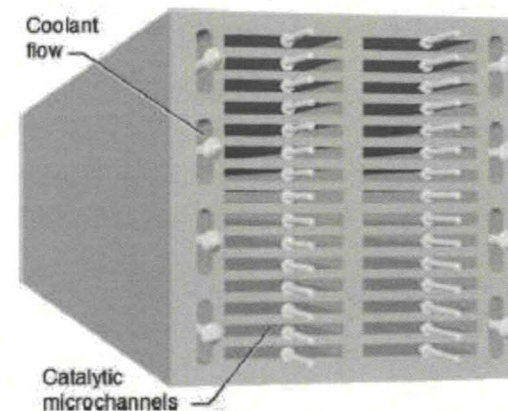
TRL 3   PNNL illustration of a section of microchannel reactor.

18

Recommendations

1. **Mars Atmospheric Gas Processing: Select Sabatier (Methanation) Process for Fuel Production**

   Research and Technology:
   - Lifetime of COTS catalyst
   - Efficient thermal control
   - Effect of pure CO_2 versus raw atmospheric gas on catalyst
   - Alternatives (for dissimilar redundancy): microchannel reactors (poison resistant/regenerable), ionic liquid electrolysis of CO_2, combined electrolysis of CO_2 and H_2O, improved SOE subsystems (ruggedized)

   Rationale:
   - Given the recent robotic mission findings, significant water is available on the surface of Mars
   - Water mining-Sabatier Process provides oxygen:methane in a ratio appropriate for propulsion
   - This approach will reduce Earth departure mass (no hydrogen logistics)

2. **Mining Water: Continue soil excavation system and soil processing reactor development**

   Research and Technology:
   - High temperature seals, valves, sensors/instrumentation, gas pumps, auxiliary equipment
   - Efficient thermal design
   - Excavation systems: reliable, long life
   - Dust tolerant mechanisms

   Rationale:
   - Martian water provides a better architecture for ISRU (i.e. eliminates Earth-supplied hydrogen logistics)

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Recommendations

3. **Mars Atmospheric Gas Capture: Parallel developmental effort for CO_2 freezer and mechanical compression:**

   Research and Technology:
   - **High efficiency (freezer/compressor)**
   - **Efficient thermal design (freezer)**
   - **Long life (cryocooler compressor)**
   - **Improvements in microchannel absorbers and new approaches**

   Rationale:
   - **The gas capture technique downstream of CO_2 reduction unit depends on the gas capture technique employed to capture atmospheric CO_2**

4. **Water Condenser: Engineering design to take place during integrated system development effort**

   Research and Technology:
   - **None**

   Rationale:
   - **This is an engineering effort, not a technology development task**

Recommendations

5. **Gas Separation: Parallel effort of cryogenic condensation and membrane separation**

    Research and Technology:

    - **PEM-based membranes**
    - **Efficient cryogenic system (combine with cryocooler development above)**
    - **Solubility of gases in cryogenic liquids**

    Rationale:

    - **Methane purity and atmospheric gas capture selection will drive the final selection of the gas separation (separation of CH_4-H_2 or N_2-Ar-H_2-CH_4)**

6. **Water Cleanup: Continue regenerable water cleanup**

    Research and Technology:

    - **Regenerable water cleanup to meet electrolysis grade**

    Rationale:

    - **Clean water is required for electrolysis**

Recommendations

7. **Electrolyzer: Continue SBIR and collaboration with ELS and Power; encourage industry development**

   Research and Technology:
   - **Contaminant resistant electrolysis**

   Rationale:
   - **Electrolysis is a common sub-system for various surface system elements.**
   - **Continue team collaboration and SBIR hardware.**

8. **Cryogenic Liquefaction and Storage: Continue collaboration with CFM.**

   Research and Technology:
   - **Zero boil-off storage**
   - **High efficiency and reliable cryocooler**

   Rationale:
   - **Cryogenic storage is needed to provide methane and oxygen from propellant**
   - **Cryogenic storage provides high density storage of consumables.**

Conclusions

- Most of the technology needed for integrated Mars ISRU demonstrations is at a high enough TRL
- Further development is required on more efficient and high-reliability options for a large-scale, fully operational system for human missions
  - Microchannel devices
  - Catalysts
  - CO_2 Freezers