Evaluation of Mars CO_2 Capture and Gas Separation Technologies

Anthony C. Muscatello [1] and Edgardo Santiago-Maldonado.[2]
National Aeronautics and Space Administration, Kennedy Space Center, FL 32899

and

Tracy Gibson,[3] Robert Devor,[4] and James Captain.[5]
QinetiQ NA, Kennedy Space Center, FL 32899

Recent national policy statements have established that the ultimate destination of NASA's human exploration program is Mars. 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, oxygen, and other consumables on Mars using the carbon dioxide atmosphere and other potential resources. The Mars Atmospheric Capture and Gas separation project is selecting, developing, and demonstrating techniques to capture and purify Martian atmospheric gases for their utilization for the production of hydrocarbons, oxygen, and water in ISRU systems. Trace gases will be required to be separated from Martian atmospheric gases to provide pure CO_2 to processing elements. In addition, other Martian gases, such as nitrogen and argon, occur in concentrations high enough to be useful as buffer gas and should be captured as well. To achieve these goals, highly efficient gas separation processes will be required. These gas separation techniques are also required across various areas within the ISRU project to support various consumable production processes. The development of innovative gas separation techniques will evaluate the current state-of-the-art for the gas separation required, with the objective to demonstrate and develop light-weight, low-power methods for gas separation. Gas separation requirements include, but are not limited to the selective separation of: (1) methane and water from unreacted carbon oxides (CO_2-CO) and hydrogen typical of a Sabatier-type process, (2) carbon oxides and water from unreacted hydrogen from a Reverse Water-Gas Shift process, (3) carbon oxides from oxygen from a trash/waste processing reaction, and (4) helium from hydrogen or oxygen from a propellant scavenging process. Potential technologies for the separations include freezers, selective membranes, selective solvents, polymeric sorbents, zeolites, and new technologies. This paper summarizes the results of an extensive literature review of candidate technologies for the capture and separation of CO_2 and other relevant gases. This information will be used to prioritize the technologies to be developed further during this and other ISRU projects.

Nomenclature

K = degrees Kelvin
v.p. = vapor pressure

I. Mars CO_2 Capture by Freezing

A. Introduction

Mars ISRU processes using carbon dioxide from the Martian atmosphere require increasing the density of the

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[1] Chemist, Surface Systems Office, NE-S-2, and AIAA Member.
[2] Chemical Engineer, Surface Systems Office, NE-S-2, and AIAA Member.
[3] Principal Scientist, Applied Science and Technology Group, ESC-24, and AIAA Member.
[4] Chemist, Applied Science and Technology Group, ESC-24, and AIAA Nonmember.
[5] Chemist, Applied Science and Technology Group, ESC-24, and AIAA Nonmember.

CO_2 ~1000 times for chemical processes and separation of other components, which could be used as buffer gases in life support systems. Several methods have been used to accomplish this task by various researchers. This report is a summary of the methods that are based on freezing the CO_2 into dry ice, which greatly increases its density and can separate other components that do not freeze at the temperature used. Where it is important for understanding the relative merits and problems of freezing CO_2 for ISRU, other methods of CO_2 capture will be discussed.

B. Basic Properties of the Atmosphere of Mars

The composition of the Martian atmosphere was measured by the Viking Landers to be as shown in Table 1 (The Internet Encyclopedia of Science [accessed Dec. 13, 2010] - http://www.daviddarling.info/encyclopedia/M/Marsatmos.html). The average surface density of the Martian atmosphere is 0.020 kg/m^3 which is 1.6% of that of Earth's at 1.23 kg/m^3 (http://www.imagineeringezine.com/e-zine/mars-data.html).

At 1 atm, carbon dioxide freezes at a temperature of -78.5°C (194.7 K) whereas nitrogen liquefies at -195.8°C (77.3 K) and argon liquefies at -185.4°C (87.8 K). The liquefaction and freezing temperatures of the components of the Martian atmosphere are shown in Table 2.

C. Capture by Freezing Carbon Dioxide

It is obvious from Table 2 that CO2 can be easily frozen out separately from almost all the other components by reducing the temperature to <195 K at 1 atm. However, the vapor pressure of CO2 is an important aspect of its capture. Figure 1 shows the vapor pressure of CO2 as a function of temperature. The capture of Martian CO2 by freezing requires that the gases be pumped through the system to avoid buildup of uncondensed gases, which would stop the freezing of additional CO2. To prevent excessive losses of the CO2 during pumping, the temperature could be reduced well below the freezing point, but above the condensation or freezing points of the other components, e.g. 170 K, where the vapor pressure is 0.1 bar or 0.01 MPa. However, this pressure is far above that of the Martian atmosphere and the gases must be pressurized to obtain the dry ice or the temperature reduced to 150 K where the vapor pressure of CO2 is ~10 mbar or approximately the same as its partial pressure in the Martian atmosphere. On Earth, liquid nitrogen is a convenient refrigerant at 77 K where the vapor pressure of CO2 is <<5 mbar. The effects of chilling to this temperature on the other components should be considered.

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	

Table 2. Boiling Points and Freezing Points of Mars Gases at One Atmosphere Pressure

Gas	Boiling Point, K	Freezing Point, K
Carbon dioxide	195 (sublimes)	195
Nitrogen	77	63
Argon	88	84
Oxygen	90	54
Carbon monoxide	82	68
Water vapor	373	273
Neon	27	25
Krypton	120	116
Xenon	165	161
Ozone	161	81
Methane	112	91

Figure 2 shows the vapor pressure of Ar and N2. At 77 K, the vapor pressure of Ar is ~0.25 bar and that of N2 is 1.0 bar, so in the absence of other factors, they should not condense with CO2 because their partial pressures in the Martian atmosphere are far below these values. Other gases with boiling points similar to that of N2, but in low concentrations should behave in the same way, such as oxygen and carbon monoxide. The vapor pressures of the other minor components at 77K are neon > 100 bar, krypton ~5 mbar, xenon ~10^{-2} mbar, ozone = ~5×10^{-2} mbar,[1] and methane = 20 mbar. The neon, krypton, and methane will not be an issue and the remaining minor components (xenon and ozone) are at such low concentrations that they can be ignored.

However, it should be noted that water vapor (at a partial pressure of 0.0021 mbar), even though it is a minor component of the Martian atmosphere, will freeze out with the CO2 and could build up in the freezer over time if it is used long enough and the temperature at which the CO2 is vaporized for use. The vapor pressure of water ice at very low temperatures is shown in Fig. 3[2]. At 110 K, the v.p. of ice is ~10^{-14} hPa or ~10^{-14} mbar. It is much lower at 77 K. Caution should be used in applying the data given above. If the Martian atmosphere is compressed before freezing the CO2, other components besides water could condense. Also, the use of adsorbents to increase the condensing surface area (as seen below) can alter the results drastically.
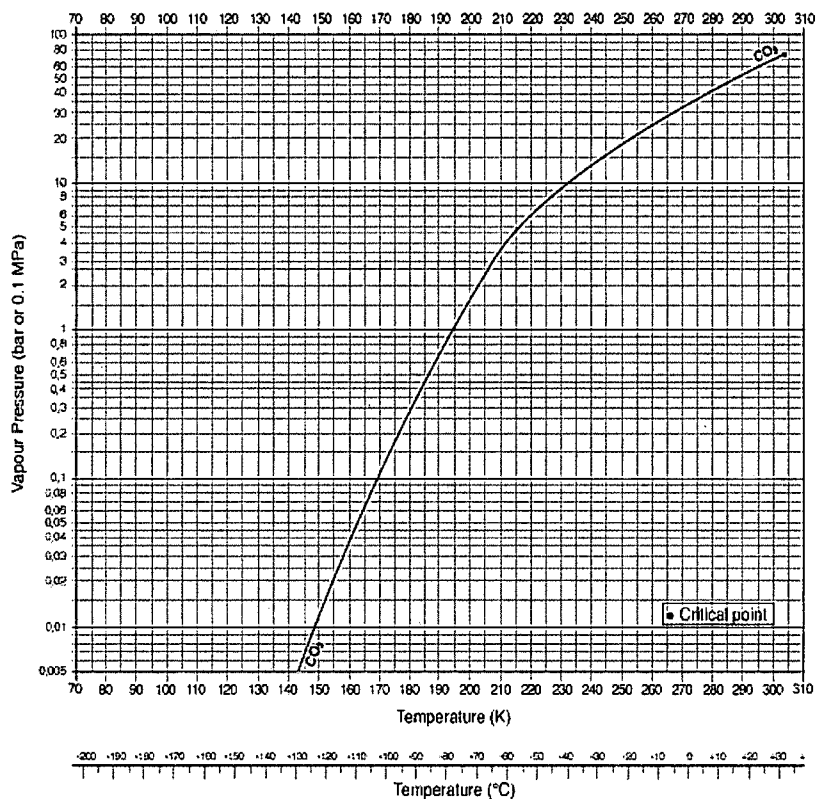

Figure 1. Vapor pressure of CO2 as a function of temperature (http://encyclopedia.airliquide.com/images_encyclopedie/VaporPressureGraph/Carbon_dioxide_Vapor_Pressure.GIF)

D. Research and Development for CO2 Collection on Mars

Several studies have been performed for the collection of CO2 on Mars, with some considering the generation of buffer gases from the atmosphere. This work is summarized below.

1. Robert Ash

Robert Ash, of the Old Dominion University, and others described a carbon dioxide freezer.[3] Ismail[4] has summarized their work as follows:

> An alternative concept is the CO2 freezer/collector, which was originally promoted as a component of a CH4 manufacturing system. This proposed system could be adapted for a CO2-collection-only scenario. Using a baseline average temperature as 210 K, Ash et al. calculated that ~80 W is required to cool down CO2 gas into the form of a solid, ~76 W of which is required for phase change. The power estimates were deducted from the assumption that the wind speed is 0.1 ms^{-1} & the known value for the latent heat of sublimation (598.6 kJ/kg). Other assumptions & operating conditions were as follows; the collector tube diameter is 1 cm; heat transfer coefficient for convection is between 1 & 8 Wm^{-2} K; flow rates vary from 1 ms^{-1} to 10 ms^{-1}; full range of pressures & temperatures; radiation of 60 Wm^{-2} & atmospheric gas is homogenous. The system uses a coolant, which passively freezes the CO2. The choice of coolant & its temperature as well as the collector's density & thermal conductivity are strong factors that affect the collector's
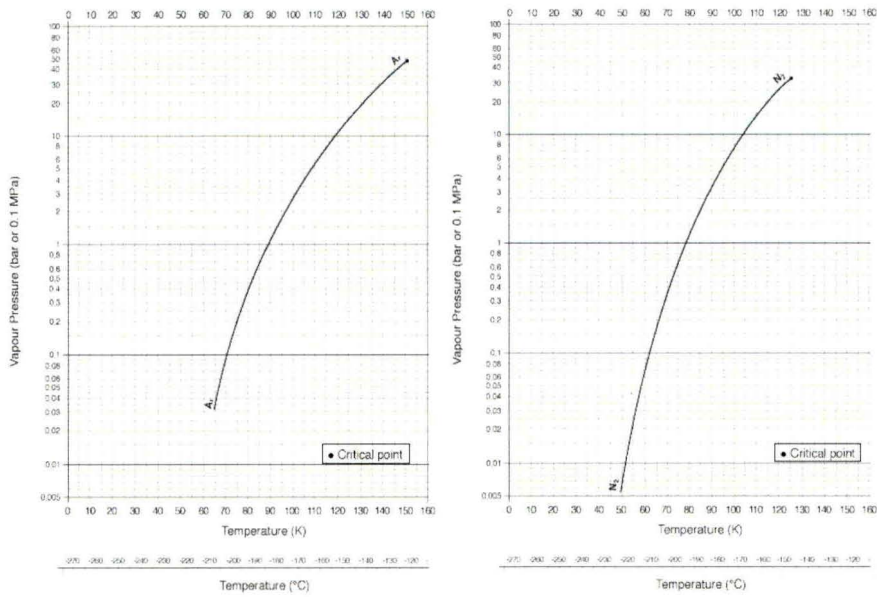
Figure 2. Vapor pressure of argon as a function of temperature.
(http://encyclopedia.airliquide.com/images_encyclopedie/VaporPressureGraph/Argon_
Vapor_Pressure.GIF and
http://encyclopedia.airliquide.com/images_encyclopedie/VaporPressureGraph/nitrogen_
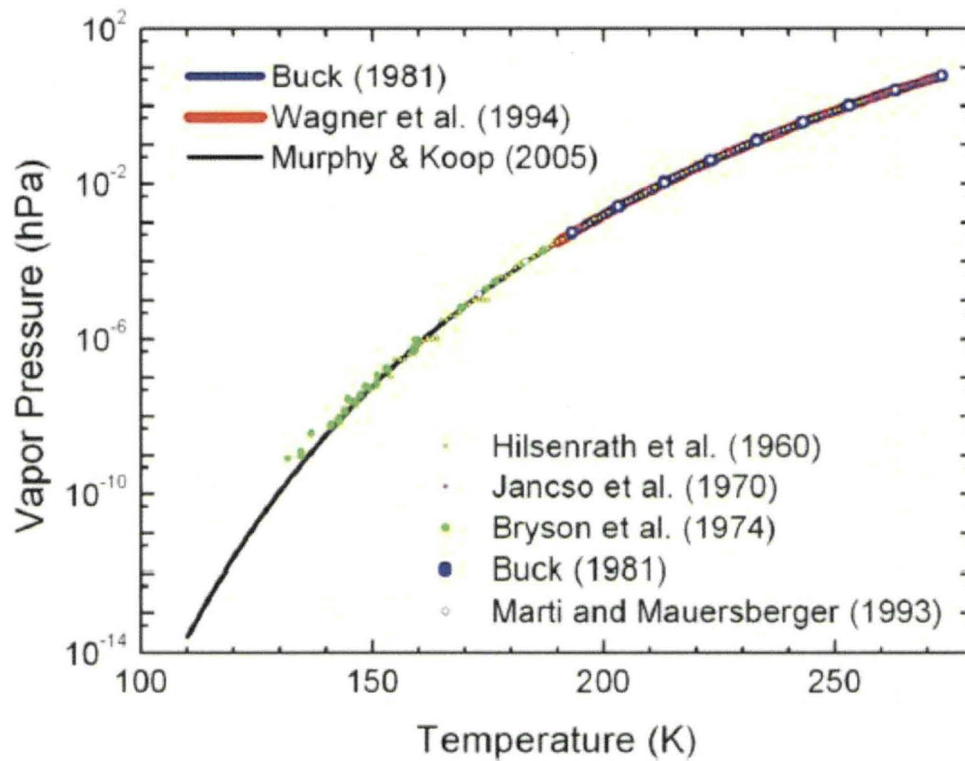**vapor_pressure.gif)**

Figure 3. Measurements or reference data for the saturation vapor pressure over a planar surface of pure water ice (Ref. 1).

performance. Since the concept was initially designed to produce methane, the researchers simply used a small quantity of the methane they produced to feed through the collector's coils. The CO_2 could then be scraped off the cooling coil, compressed to a pressure of ~70 bars fed into a storage tank, where the CO_2 is stored in the form of a solid. During the CO_2 frost extraction process, the introduction of heat could raise the temperature to ~218°K where the frost would liquefy & subsequently be redirected to a liquid CO_2 tank. Approximately 40 W of power would be required to heat the frost to liquefaction temperatures.

Two of Prof. Ash's students conducted a study of using a Peltier cooler to condense dry ice from a simulated Martian atmosphere ("Mars Airplane Carbon Dioxide Propellant Generator Using Thermoelectric Cooling") (http://www.paulrosensteel.com/ECE486_DesignII_FinalReport.doc), but failed to do so because the experimental setup required changes. In theory the concept should work according to the authors. [However, see comments below.]

2. Pioneer Astronautics

Robert Zubrin and coworkers at Pioneer Astronautics near Denver, CO have developed and demonstrated a Mars atmosphere CO_2 freezer designated the MACDOF (Mars Atmosphere Carbon Dioxide Freezer). Ismail[3] has summarized Pioneer's work as follows:

> Mechanical roughing pumps require power, moving parts and must operate without maintenance over long periods of time. Depending on the method of generating power, i.e. solar arrays, the pump may only be operable for 50% of the Martian day. Sorption pumps use a bed of active carbon or zeolite, on the other hand, are heavy, brittle and can operate once a day.

> Faced with these problems, Pioneer Astronautics, headed by Dr. Robert Zubrin, developed a system which they referred to as a Mars atmospheric carbon dioxide freezer or MACDOF. This system was designed as a component of a larger system to produce CO and LOX with the baseline NASA Johnson Space Center's human Mars mission as a reference. This mission calls for the production of 100 kg of CO_2 per day. Therefore, their logic in some cases does not apply to the production of just CO_2.

> In principal, the MACDOF actively freezes carbon dioxide from the atmosphere and produces on the order of 700 grams per day. It is less massive than a passive adsorption pump and yet, it has twice the capacity and 40% the storage capability. The experimental module was built out of steel whereas the adsorption pump was made from aluminium. It was determined that if the MACDOF was also made out of aluminium, then the mass would have been ¼ of the adsorption pump.

> An adsorption bed can store on the order of 10% of the adsorbent mass whereas the MACDOF is capable of storing 100% dry ice. Based on the logic of equal capacities, the freezer can store up to five times that of an adsorption bed. The freezer material is either diffuse copper or aluminium wool is much less dense than the adsorbent material. For example, copper wool is ~240 grams per litre which is over three times less dense than activated carbon as an adsorbent material. The MACDOF is capable of acquiring a consignment of CO_2 every five hours which, based on the use of solar arrays, affords an opportunity to collect CO_2 twice per day, at best. The hours after sunrise and prior to sunset may reduce the solar flux so ten hours, or twice a day, may be somewhat of an over exaggeration. This system would more likely be able to produce CO_2 1.5 times per day, which is still a 50% increase over passive or active adsorption pumps. Pioneer takes the position that a nuclear reactor will power the in-situ propellant production (ISPP) system and therefore such a system will be able to operate at least four times a day. So, with 1/5th the volume, 1/3rd the interior density and 1/4th the cycle, this works out to be 1/60th the mass of an adsorption pump and the shell is assumed to be 1/20th the mass of equivalent capacity. For of a low-cost sample return mission, the employment of a nuclear power plant is out of the question and solar arrays will be the most likely form of power generation. At worst case, the production rate of one times a day relates to 1/15th the mass of the adsorption pump of equal capacity; which is still a remarkable improvement.

> During Pioneer's experiments, 300 grams of CO_2 was produced in a 1-litre bed, which was subsequently rejuvenated over the five-hour period. Approximately 400 W of power was required
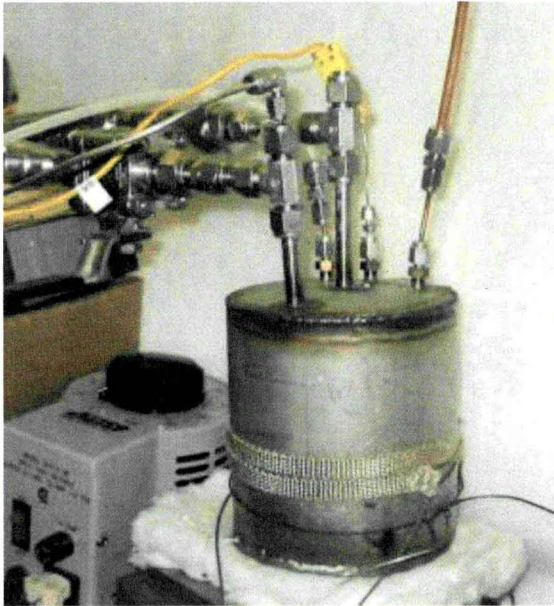
Figure 4. MACDOF System for Acquiring CO_2 from a Simulated Martian Atmosphere.

for this operation. The adsorption pump was found to require a 20 litre capacity bed to produce the same quantity. For a CO_2 production capacity of 300 gram per day or less, it was found that the adsorption pump was less massive than the MACDOF. But, for CO_2 quantities of up to 4 kg/day, the copper wool filled, solar powdered MACDOF proved to be the superior performer. During these comparisons, the supporting hardware for the MACDOF, such as refrigerators, heat sinks and heating units were not included. Also, the experiments were developed to test systems and were not optimised for mass and power consumption. As with terrestrial refrigerators, electric power is used to dispose of thermal energy from the freezer to ambient temperature. The refrigerator will also have to be thawed, to clear its contents following one production cycle. This could be performed via solar heating during the Martian day but active heating would increase the turn-around time. The power required for freezing depends on the heat rejection temperature:

$$\beta = \frac{T_C}{T_H - T_C}$$

where β Coefficient of Performance

                          T_H Heat Rejection Temperature

                          T_C Freezing Temperature

At a CO_2 vaporization temperature of 218 K, the vapor pressure of water ice would be ~10^{-6} bar according to Fig. 2, where volatilization would be extremely slow, leading to accumulation in the freezer (or the CO_2 tank in the process described by Ash, above). Assuming capture of 100 kg of CO_2/day, the water content would be ~32 g, which would accumulate in the freezer. A human Mars mission will require propellant production to occur over a six month time frame so that the process will be complete before the crew departs Earth for Mars. If the freezer had an active volume of 100 liters, the 300 cycles needed would accumulate 9.6 kg of water ice, which would occupy <10% of the freezer volume, which sounds tolerable. If needed, the freezer temperature could be allowed to rise to ambient Mars conditions and the atmosphere pumped through it to sublimate the water ice.

Pioneer Astronautics utilized a MACDOF (Fig. 4) in a Mars in situ propellant production project,[5] but encountered adsoption of small amounts of air that leaked into the system. The solution was "to warm the MACDOF to 200-240K and vent until the air decreased to <<1%, a tolerable level in the system. Being held less tightly by the activated carbon, the air vaporizes before the majority of the dry ice, leaving virtually pure CO_2 feed to the Sabatier system… [W]e ran the MACDOF for over 85 hr collecting CO_2 from a simulated Mars atmosphere at 8 mbar and collected about 1 kg of CO_2. Note that in the earlier runs this included adsorbed air in unknown amounts. The later runs had lower acquisition rates because the CO_2 lost by venting to remove the air was not included in the acquisition rates. The MACDOF could be improved by using a less active activated carbon or another substance such as copper mesh, etc. that would not adsorb air in significant amounts."

Muscatello *et al.* ran the MACDOF at a temperature below 153 K, but did not simulate the Martian atmospheric composition except for the pressure with 100% CO2. The behavior of other gases was not determined except that air contamination was eliminated by heating the container to 200-240 K before use of the CO2 to allow air removal with minimal loss of CO2. Comparing these operating conditions to Table 2 indicates that water vapor would also be captured. The preliminary warming would release any adsorbed xenon, ozone, nitrogen, argon, etc. except water. The authors recommend against use of the high surface area, activated carbon material to avoid adsorption of gases not desired for the subsequent chemical processes.

3. Other R&D CO2 Freezing Systems

A brief search of other R&D studies of CO2 freezing systems reveals one fairly recent publication. Yu et al.[6] present a flowchart for such a system as a collection system for a thermal CO2 rocket for a "gashopper" (Fig. 5), but they did not build any hardware. The freezing process was deemed to be preferable to mechanical pumping and sorption pumps because sorption pumps are large and heavy, whereas the CO2 freezer "can reach a compression ratio of over 10000, a value that would require several stages of mechanical compressors, and can meet the pressure level of the propulsion [system]." This study is essentially duplication of the Pioneer Astronautics MACDOF, but without actually testing hardware. However, it is reassuring to see that independent workers confirm the Pioneer approach.

In addition, Clark et al.[7] have built and tested a CO2 freezer somewhat different from the Pioneer MACDOF, making several pertinent observations:

> If N2 and Ar are highly desired products, a much greater separation between CO2 and N2/Ar can be obtained in the freezer by investing additional power in an inlet compressor instead of a blower. By operating the freezer at higher pressure, the vapor pressure of CO2 becomes a much smaller fraction of the overall pressure, and therefore the resulting gas stream contains much less CO2.

> Heat is allowed to enter the freezer from the surroundings to begin warming the frozen CO2 and increasing the pressure in the freezer. The conditions in the freezer will rapidly reach the CO2 triple-point, at which time liquid CO2 forms and drops to the bottom of the storage vessel, increasing the heat transfer rate. The outlet valve is then opened and an extremely pure stream of CO2 is delivered to the downstream process at a pressure at or above the triple point pressure of 75 psia.

> Using an average incoming gas temperature of 210 K, cooling the gas to the freezing point requires 29 Joules/gram and heat of sublimation is approximately 598 J/g for a total of 627 J/g. Pulse-tube cryocoolers have achieved significant efficiencies with recent improvements and can
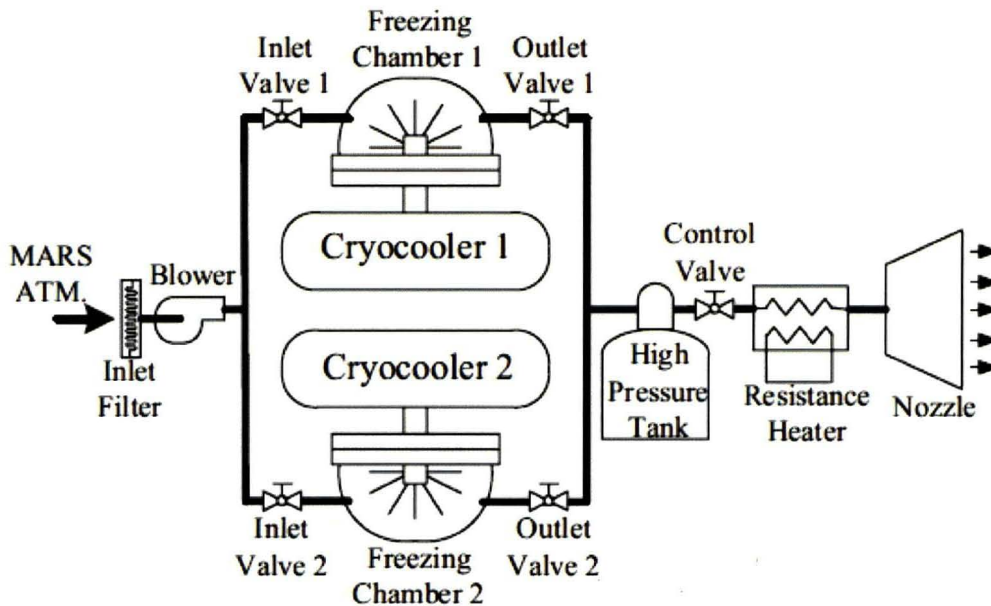

Figure 5. CO$_2$ thermal rocket system for Mars (Yu 2009)[6]

offer a Watt of cooling power for five Watts of electrical power, leading to an ideal power requirement of 0.871 Watt-hour/gram for acquiring the solid CO2.

Flow is forced through the chamber by a miniature centrifugal blower, either by drawing atmosphere out of the chamber or pushing it in. Forced flow is necessary to remove non-condensable gasses from the chamber and maintain acquisition rate.

[T]he best performance was at the higher pressures and cryocooler settings, where in under four hours 50 grams of CO2 was acquired.

Freezing of the CO2 occurs at approximately 150 K. Temperature of the copper heat exchanger drops slightly over the course of the test as solid CO2 thickness increases, causing a drop in thermal conductivity. Constant circulation through the freeze chamber is required to remove buffer gasses. A thermocouple located on the gas outlet showed that very little if any heat was taken out of the waste gasses, preserving the efficiency of the system.

CONCLUSIONS

Acquisition of atmospheric carbon dioxide on Mars can be accomplished very effectively with the frozen compression method. The purity of the delivered product is very high and is supplied at useful pressures in a single compression stage. The entire system is very compact with the majority of the volume going for the cryocooler and valves. The volume of the storage vessel is marginally greater than the volume required for the solid CO2 mass. The concept is readily scaled to greater quantities with a linear relationship of cooling power to acquisition rate. The process also lends itself to further distribution using the dense liquid as an easily transferred commodity similar to terrestrial CO2 storage.

The frozen CO2 method compares favorably to other processes under consideration for collecting CO2 on Mars. Two methods that appear the most promising are direct mechanical compression and adsorption pumping. Mechanical compression is clearly achievable, but the large mass and poor efficiency of a multi-stage device to achieve compression ratios of this magnitude are prohibitive. Additionally. The rotating machinery with sliding seals limit operating lifetimes. Modern pulse-tube cryocoolers use flexure springs and clearance seals to achieve greater than ten year, maintenance-free operational lifetimes. Mechanical pumping also provides no additional product purification. Sorption compressors have been demonstrated for these applications, but the large volumes of sorbent beds required to collect and store significant CO2 quantities require heavy pressure vessels and large blowers to keep the bed completely purged of non-condensable gases that quickly reduce the acquisition efficiency. Additionally, the entire mass of sorbent, gas and pressure vessel must be heated and cooled to the full temperature excursion of the sorption cycle. The mass of the sorbent and vessel is typically 10 to 20 times the mass of the acquired product, requiring large amounts of heat to reach and maintain operating pressure and similar cooling requirements to get the bed back down to a temperature at which the CO2 can again be collected.

It would be preferable that quantitative comparisons be used for the CO2 freezing, mechanical compression, and sorption compressors, but Clark's analysis agrees with that by Pioneer Astronautics, at least for the sorption pump vs. the freezer. Note that recent improvements in mechanical compressors may alter the conclusions one would reach as to which process is preferable for ISRU applications. Simon et al.[8] also summarize the Clark's results as follows:

<u>CO$_2$ Collection Method: Solidification Pump</u>
Lockheed Martin Astronautics is exploring thermal solidification as a means of acquiring and conditioning CO$_2$ from the Martian atmosphere as part of an activity funded through JSC. The initial program examined the major solidification pump subcomponents, such as the acquisition pressure vessel, circulation blower, and heat exchanger configurations, as well as a variety of operating scenarios. The test results from the initial characterization program were very encouraging. The prototype at approximately 4.4 inches in diameter was sized to contain 161

grams of solid CO_2 (Figure 1). The cooling was performed by a Magnavox Split Stirling Cycle cryocooler that operates on 50 Hz AC power and can provide 7 watts of cooling at 150 K with 115 watts of input power.

Figure 1. CO_2 Frozen Using Solidification Pump
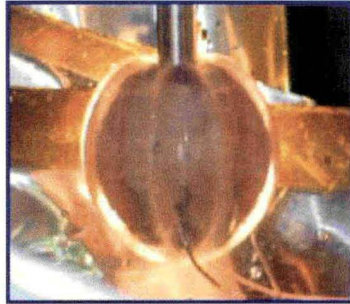
A second-generation solidification pump has been fabricated with the design goal of collecting 800 grams of solid CO_2. Initial testing has been performed with a peak collection rate of 80 grams/hour. Meltback and repressurization of the collected CO_2 was also successfully demonstrated. Based on the results from both units and continued modeling it is estimated that the power required for the entire process (power to the cooling device) of freezing the CO_2 can be calculated by the factor 0.871 watt-hour/gram.

Rapp et al.[9] have performed a preliminary analysis of a large scale Mars ISRU system, including CO2 capture. They also concluded that the CO2 freezer approach was superior to adsorption and mechanical pumping. A full analysis should also include the interactions of the various subsystems in addition to mass and power for each one.

4. Commercial CO2 Freezing Systems

A cursory review of commercial CO2 freezing systems was performed given that the conditions under which they would operate would be very different from those on Mars and therefore the design details would be unlikely to be
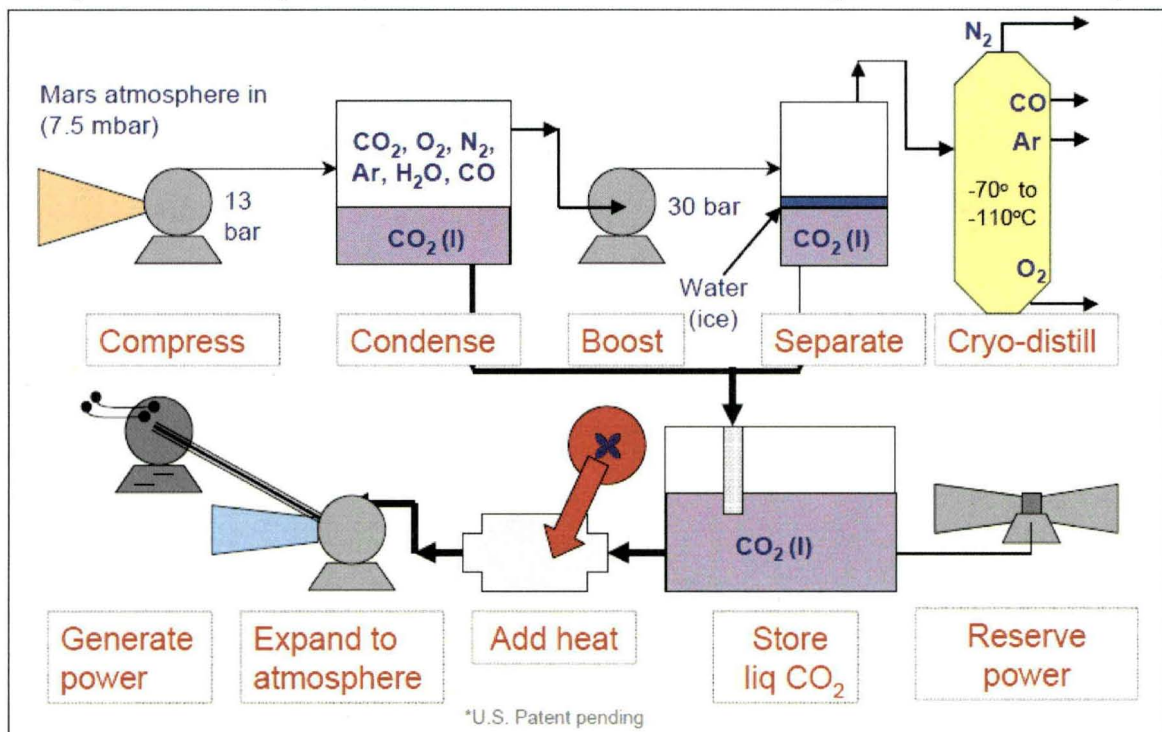

Figure 6. Elements of Atmospheric Resource Recovery on Mars (England, 2001)[13]

useful. One system examined in more detail is that undergoing commercialization tests by ExxonMobil called the Controlled Freeze Zone (CFZ) process. The CO2 is frozen, but is not collected in dry ice form. Instead, conditions are set so that the dry ice particles melt upon reaching the bottom of the CFZ section into liquid CO2, which is drawn off to separate it from the methane. Technical details are given by Northrop[10] and Thomas[11] as well as by a patent application (http://www.faqs.org/patents/app/20090266107) for a modification that allows higher hydrocarbons to go along with the methane instead of with the CO2. This process is feasible probably because the CO2 is from a high pressure natural gas well, which enables Joule-Thompson cooling instead of having to supply refrigeration. Consequently its utility for Mars is doubtful, but should be kept in mind.

5. Alternative to Freezing – Pressurization without Separation

Muscatello et al.[12] have extensive testing results that indicate CO2 acquisition on Mars can be accomplished by simple pressurization a scroll pump to raise the pressure to 1 atm with a second pump to raise the pressure to 5 atm. This system was possible because the nitrogen and argon were inert in the combined Sabatier/RWGS (Reverse Water Gas Shift) process that converted CO2 into CH4 and CO. The CH4 and CO were separated using cryogenic distillation to produce ISRU methane fuel and waste CO that carried off almost all the N2 and Ar. Such novel approaches should be considered in future processes.

6. Alternative to Freezing – Pressurization with CO_2 Liquefaction

Another alternative explored in a theoretical/design study uses pressurization of the Martian atmosphere to the conditions where the CO2 liquefies and separates from the buffer gases.[13] Figure 6 shows a schematic diagram of the process steps envisioned. The goal of the process is to accumulate oxygen and buffer gas by harvesting them from the Martian atmosphere without chemical reactions, only physical separation processes. A nuclear reactor was planned to be the power source for the extreme amount of energy required to compress the very large volumes of the atmosphere required to the high pressures required to liquefy CO2. Some of the energy could be regenerated by expansion of the CO2 back into the gas phase to run a turbine.

As noted by Sanders et al.,[14] the process has some disadvantages:

> Recently, an investigator at JPL received a Phase I NASA Institute for Advanced Concepts (NIAC) award to examine large scale acquisition of oxygen, water, N2, Ar, CO, and large amounts of CO2 from the Mars atmosphere through compression and liquefaction of the Mars atmosphere for life support, propulsion, hydrocarbon manufacturing and power generation. The process is power intensive, however, for extremely large production rates the process may be attractive since, nuclear power system mass growth may be less than conventional chemical processing system mass growth.

Although large amounts of power are required to produce oxygen and buffer gas by just physical processes, the scheme could be altered to produce liquid CO2 as feed for a chemical process, with the separation of the buffer gas through cryogenic distillation, as shown in Fig. 7. The advantages of this approach as compared to simple freezing of CO2 are not obvious, however, because of the high power required for compression.

E. Conclusions

Capture of Martian CO2 by freezing appears to be a very promising method for obtaining fairly pure CO2 at very high pressures (after melting and either liquefaction or sublimation) as well as providing an enriched feed for buffer gas preparation. Parrish et al.[15] estimate that "if the CO2 freezer operates at 140K, the composition of the inert gas would be approximately 21 percent CO2, 50 percent nitrogen, and 29 percent argon." Freezing should do well in comparison to other potential processes especially because of its relative simplicity, although power requirements should be compared as well as other process parameters such as mass, volume, TRL, durability, and versatility. Testing is required to verify the selectivity of the freezing process is adequate when inactive support materials are used. More work is required to understand the implications of the simultaneous capture of water vapor as to whether this is a serious issue or perhaps another advantage, given that additional water is a valuable resource on Mars.

II. Membranes

This section summarizes the literature evaluation of the applicability of membranes to capture and separate CO_2 from various gas mixtures. The literature reviewed was focused to reports from the last 10 years and primarily from technical journals such as: Advances in Polymer Technology, AIChE Journal, Journal of Applied Polymer Science, and Journal of Membrane Science. In total, more than 50 papers were reviewed.

The use of membranes for CO_2 separation has been investigated for some time now. Commercially available membranes are mainly polymeric-based: poly-acetate, polyimides, polyamides, polysulfone, polycarbonates, and polyethylene. Not surprisingly, these are the basic polymeric materials that continue to be studied for CO_2 gas

separation, with the addition to zeolite membranes. Except for the zeolite membranes, which separate gases mainly by size exclusion, CO_2 separation via non-porous polymeric material is characterized by the solubility of CO_2 in the membrane matrix, the diffusivity through the membrane matrix, and finally the dissociation of CO_2 from the membrane matrix on the permeate side of the membrane.

Figure 7. **Distribution of membrane permeability.** *Note: For clarity, the top two ranked materials are not included in this graph*

The absorption and desorption of the gas of interest on the membrane matrix is related to the gas solubility in the matrix. This gas solubility is governed by Henry's Law of solubility, which is directly proportional to the pressure of the gas on the feed side of the membrane. Hence, the use of a polymeric membrane to capture CO_2 from the Martian atmosphere will require the feed gas to be compressed to increase the solubility of the gas in the polymeric membrane material.

The diffusion, or permeability, of the gas through the membrane matrix is related to the polymeric structure. It is believed that gas molecules transport from "gap to gap" within the membrane matrix. Bulky polymeric structures, with high free volume, tend to provide higher gas permeability. Polymer structure also provides polymer chain flexibility, which affects the diffusion of the gas through the membrane.

The area of CO_2 capture and separation using polymeric membranes has been heavily studied mainly for applicability to CO_2 capture from energy production processes. Significant data is available on a wide variety of polymer and co-polymer materials. Table 3 summarizes the polymeric material performance of the "top performing" materials found during this literature search, which are those membranes considered with the highest CO_2 permeability and highest CO_2 selectivity (CO_2 to N_2 selectivity). The data in Table 3 is organized by decreasing CO_2 permeability rate (1 barrer = 7.5×10^{-14} (cm^3(STP)-cm)/(cm^2-s-Pa)). All the information available in the study was included in the table, including permeability of other gases of interest to ISRU Mars processes.

The performance of each membrane material is characterized by the ability to selectively transport CO_2 gas molecules. A balance exists with respect to the permeability and selectivity; typically, higher permeability results in lower selectivity. As can be seen from Table 3, the membranes with the highest permeability - polyacetylene, polydimethylsiloxane, and polyethylenimine, are the least selective membrane material. Polyethylene oxide membranes seem to be a leading candidate material for the CO_2 separation with CO_2 permeability in the range of 8-700 barrer and a selectivity of CO_2:N_2 of 40-140. However, the high CO_2 selectivity of 140 is achievable at the low permeability rate 8 barrer at 25°C and 7.8 atm feed pressure.

Figure 7 shows graphically the distribution of permeability of all the materials tabulated in Table 3. The majority of the membrane materials' permeability falls between 100 and 300 barrer. From this sub-group (100-300 barrer CO_2 permeability), the material that resulted in the highest CO_2:N_2 selectivity is poly(amide-6-b-ethylene oxide) (PEBAX ®). The poly(amide-6-b-ethylene oxide) demonstrated a CO_2 permeability of 122-227 barrer and a CO_2:N_2 selectivity of 71-79 at 25°C and 3 atm feed conditions. Another material with high CO_2 permeability rate and CO_2:N_2 selectivity is poly(vinyl alcohol), with 200-300 barrer and 40-60, respectively, at slightly higher feed pressure 2-8 atm.

As mentioned earlier, permeability is directly proportional to feed pressure, and at lower feed pressure (0.96 atm) the following cross-link polymeric membrane materials showed significant performance with CO_2 permeability above 100 barrer and CO_2:N_2 selectivity greater than 30: DM14/MM9 (30/70), DB30/MM9 (100/0), DB69/MM9 (90/10).

Selecting an optimum membrane material for capturing Martian atmospheric CO_2 is heavily dependent on the specific process in which the CO_2 will be utilized. Given the high concentration of CO_2 in the atmosphere of Mars (95%), membrane selection may prefer a lower permeability and a high selectivity because the abundance of CO_2 in the atmosphere. However, this option may trade poorly if the technique to acquire and condition (i.e. pressurize) the Mars atmospheric gases are costly (mass, power, volume). If the CO_2 conversion process is not sensitive to the trace gases in the atmosphere (Ar, N_2), then a higher permeability and lower selectivity membrane may be more attractive.
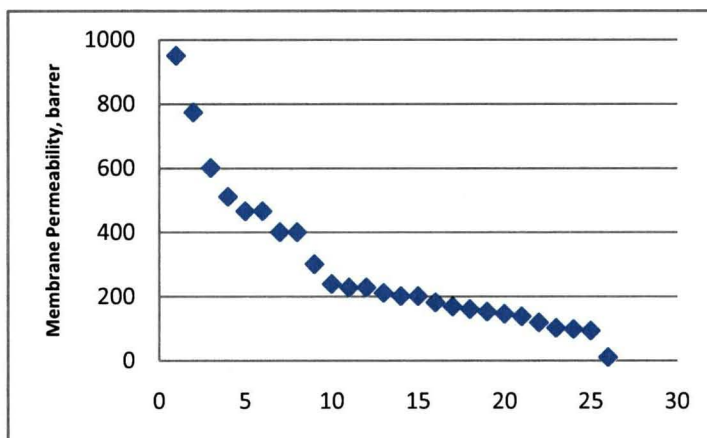
Two commercially available membranes are available for CO$_2$ separation: Prism by Air Products and Separex by UOP. Detailed data on these membranes were not available from the manufacturers in order to compare them to those materials described in Table 3. The membrane materials utilized in those studies summarized in Table 3 were synthesized in house by the research team and would require polymer synthesis material expertise in order to develop such membranes to improve on the technology.

Parrish[16] performed a study of several commercial membranes at various temperatures with the express purpose of separating nitrogen and argon buffer gases from CO$_2$ on Mars. He evaluated the Permea Prism® Alpha Separators model PPA-20 module, the Neomecs model GT #020101 module, an Enerfex SS Membrane module, and an Enerfex SSP-M100C Membrane sheet supported in a stainless steel filter housing at temperatures as low as -45°C to +30°C, depending on the membrane and at a variety of pressures. Parrish

Permea First Stage 2329 cm³

Vent

Permea Second Stage 2180 cm²

Product

Figure 8. Membrane purification of feed from the capture of CO$_2$.[16]

used the data with a proprietary membrane system design tool from Enerfex to design a system that would operate at -44°C and 780 mm Hg (1.03 atm). The membrane system consisted of two Permea membranes in series (Fig. 8) that accepted the gaseous effluent of a CO$_2$ freezer. The effluent was assumed to be 30% CO2, 26% Ar, and 40% N$_2$. The calculated performance predicted that the system would produce 6.0 L/hr of a product that met the buffer gas specification of 600 ppm CO$_2$ in 38% Ar and 62% N$_2$ with a 47% recovery of the feed.

In addition, Whitlow and Parrish[17] used the Permea Prism® Alpha Separators model PPA-20 module as part of an RWGS ISRU system to produce oxygen from Martian CO$_2$. These authors note the importance of not losing hydrogen from the process through the membrane modules. Table 4 from this work shows both calculated and actual performance of the RWGS system. The average hydrogen loss for the seven runs is only 0.26%, which is good, but must be observed over the life of the process to determine whether it is acceptable and does not get worse due to degradation of components.
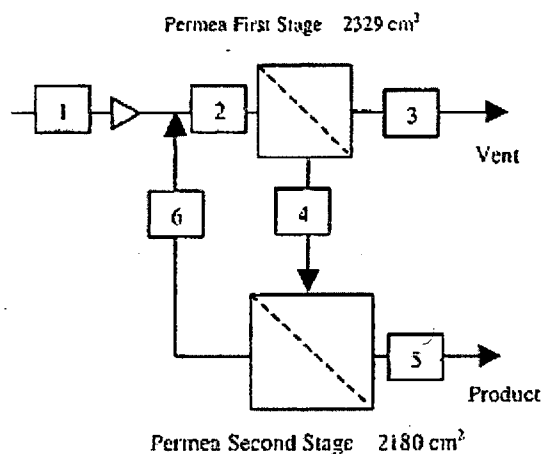
Table 3. Summary of the top performing polymeric membrane material. The data in this table is organized by decreasing CO_2 permeability.

Perm rank	select rank	Membrane Material	Temp [C]	Press [atm]	CO2 Perm [barrer]	N2 Perm [barrer]	O2 Perm [barrer]	H2 Perm [barrer]	CH4 Perm [barrer]	He Perm [barrer]	CO2 Selectivity
1	27	Polyacetylene[18]	25	tbd	15-19000	1.0-1800	n/a	n/a	n/a	n/a	5.0-23 (CO2/N2)
2	28	Polydimethylsiloxane[19]	35	1.0-15	4000	600	1000	1500	1500		6.7 (CO2/N2)
3	25	polyethylenimine-polyvynilbutyral-epoxy-water[20]	20-50		400-950	7.0-50	10.0-60				19-27 (CO2/N2)
4	2	polyethylene oxide[18]	25-45	4.4-14.6	8-773	.07-16.8	n/a	n/a	n/a	n/a	40-140 (CO2/N2)
5	20	Polyimides[18]	25-35	1.0-10.0	0.6-600	.01-35	n/a	n/a	n/a	n/a	16-37.7 (CO2/N2)
6	21	DB69/MM9 (90/10)[18]	50	0.96	510	14.2	n/a	n/a	n/a	n/a	36(CO2/N2)
7	24	6FDA-based polyimides[18]	25-55	1.0-10.0	1.9-465	.06-35	n/a	n/a	n/a	n/a	1.91-29 (CO2/N2)
8	26	6FDA-FDA/HFBAPP (1/1)[18]	30	1	465	19.9	n/a	n/a	n/a	n/a	23.4(CO2/N2)
9	23	DB69/MM9 (90/10) (heating)[18]	50	0.96	400	11.4	n/a	n/a	n/a	n/a	35(CO2/N2)
10	11	alginic acid[21]	25	2.0-8.0	300-400	9		11.5		11	35-55 (CO2/N2)
11	9	poly(vinyl alcohol)[21]	25	2.0-8.0	200-300	5		11		10.5	40-60 (CO2/N2)
12	5	poly(amide-6-b-ethylene oxide) (PEBAX®)[22]	25	3	122-277	1.71-3.52	5.84-11.3			18.6-32.2	71-79 (CO2/N2)
13	19	PMDA-pDDS/PEO4(80)[18]	35	2	238	4.9	n/a	n/a	n/a	n/a	49(CO2/N2)
14	1	perfluorosulfunic acid with ethylene diamine ions[23]	25	0.89	227 (pure CO2)						~~88-551~~ (CO2/CH4)
15	8	DM14/MM9 (30/70)[18]	25	0.96	210	3.3	n/a	n/a	n/a	n/a	63(CO2/N2)

|											
16	22	DB30/MM9 (100/0)[18]	50	0.96	200	5.7	n/a	n/a	n/a	n/a	35(CO2/N2)
17	18	Chitosan[21]	25	2.0-8.0	200	4		11		10.5	45-50 (CO2/N2)
18	13	polyethylene oxide copolymer with amide segments[18]	35	4	75-180	1.8-3.6	4.7-8.8	10.4-19.6	5.5-11.3	6.3-12.2	41-53 (CO2/N2)
19	15	PMDA-ODA/PEO4(80)[18]	35	2	167	3.2	n/a	n/a	n/a	n/a	52(CO2/N2)
20	17	PMDA-APPS/PEO3(80)[18]	35	2	159	3.1	n/a	n/a	n/a	n/a	51(CO2/N2)
21	14	PMDA-mPD/PEO4(80)[18]	35	2	151	2.9	n/a	n/a	n/a	n/a	52(CO2/N2)
22	7	DM14/MM9 (50/50)[18]	25	0.96	144	2.25	n/a	n/a	n/a	n/a	64(CO2/N2)
23	12	PMDA-APPS/PEO4(80)[18]	35	2	136	2.6	n/a	n/a	n/a	n/a	53(CO2/N2)
24	16	BPDA-ODA/PEO1(80)[18]	35	2	117	2.3	n/a	n/a	n/a	n/a	51(CO2/N2)
25	10	carboxyl methyl cellulose[21]	25	2.0-8.0	40-100	2		8		8	35-60 (CO2/N2)
26	6	DM14/MM9 (70/30)[18]	25	0.96	96	1.5	n/a	n/a	n/a	n/a	66(CO2/N2)
27	4	polyphenylene oxide and sulfonated polyphenylene oxide[24]	30-100	1	13.8-91	.16-6.06	.98-20.60			15-152	15-86 (CO2/N2)
28	3	polyvinylchloride on polyethyleneglycol[25]	25	20	0.1-8	.01-.05	.05-.1		.01-.05		15-110 (CO2/N2); 15-80 (CO2/CH4)

Table 4. Comparisons of Predicted and Measured Component Values[17]

	Stream	Calculated H2 (slpm)	Measured H2 (slpm)	Calculated CO2 (slpm)	Measured CO2 (slpm)	Calculated CO (slpm)	Measured CO (slpm)
Base Case	Feed	16.825	16.861	7.56	7.522	2.114	2.116
	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
Sim-1	Feed	26.265	25.333	7.265	8.126	1.793	1.864
	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
Sim-2	Feed	30.748	30.555	7.984	8.07	1.537	1.644
	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
Sim-3	Feed	29.552	29.428	8.605	8.696	2.028	2.047
	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
Sim-4	Feed	25.603	25.099	7.035	7.332	1.779	1.986
	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
Sim-5	Feed	16.507	17.248	8.921	8.323	2.47	2.327
	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
Sim-6	Feed	20.591	20.864	7.036	6.786	1.983	1.96
	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

III.   Ionic Liquids for CO$_2$ Removal from the Martian Atmosphere

A. Background

Ionic liquids (ILs) are a new class of ionic material that have unusually low melting points. They are purely ionic materials (cation and anion) with interesting solvent and conductive properties. Typical cations and anions for ionic liquids are shown in Figure 9.
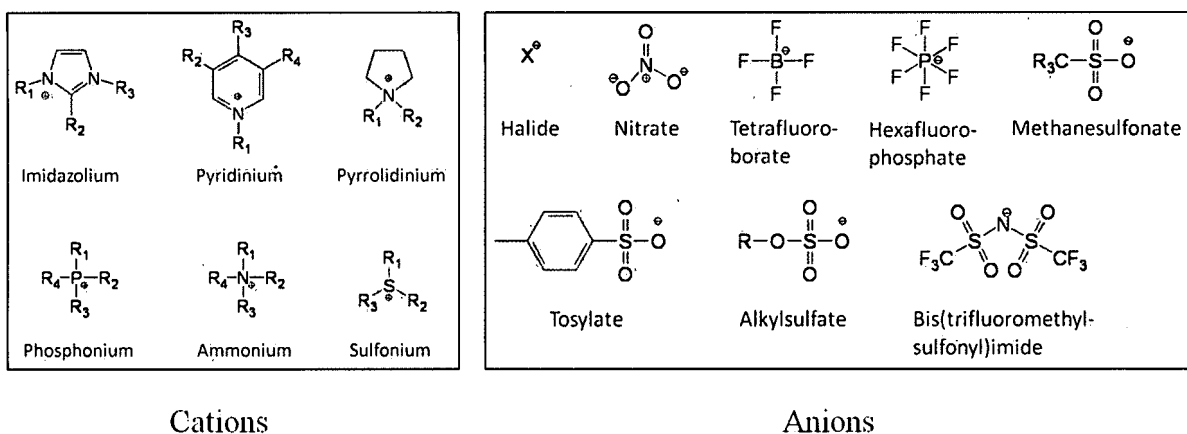
Cations   Anions

Figure 9. Typical cations and anions for ILs.

Many ionic liquids have melting points below 100 °C (the normal boiling point of water). More recently, many ionic liquids have been developed with melting points below room temperature. For example, for several ionic liquids with 1-ethyl-3-methylimidazolium cations ([emim][X]), the melting points range from 87 °C to -14 °C depending on the anion.[26]

Ionic liquids have become of increasing interest in the past decade as replacements for typical solvents used in many organic and catalytic reactions due to their high temperature stability and low volatility. Also, the use of ionic liquids in gas separation processes is becoming of increasing interest. Ionic liquids have shown to have a high affinity for several gases, including carbon dioxide, making them prime candidates for use in green technologies related to carbon dioxide removal.

In-situ resource utilization (ISRU) provides a means to "harvest" essential commodities to support long-term human and robotic exploration efforts. The Martian atmosphere contains many useful commodities that can be utilized for exploration efforts, including carbon dioxide that can be used to produce oxygen, methane, and water. An extensive literature search was performed regarding the use of ionic liquids for capture of carbon dioxide. More than one hundred references were reviewed and examples of the relevant data is reported in this document. We will start with discussing capture methods for materials typically not found in the Martian atmosphere and move to more relevant gas capture technologies related to the gases found in the Martian atmosphere.

B. Ionic Liquids for Gas Capture

1. Desulfurization of Gasoline

Studies were performed by Wang *et al.* to investigate the use of ionic liquids to desulfurize gasoline.[27] Several ionic liquids were used in the study, including N-butyl-pyridinium nitrate ([BPy]NO$_3$), N-butyl-pyridinium tetrafluoroborate ([BPy]BF$_4$), N-ethyl-pyridinium tetrafluoroborate ([EPy]BF$_4$), N-ethyl-pyridinium acetate ([EPy]Ac), and N-butyl-pyridinium acetate ([BPy]Ac). A model oil composed of thiophene dissolved in a solution of n-heptane and xylol and gasoline was used as the sulfur containing materials. All experiments were carried out at room temperature (25 °C) in a 100 ml glass flask with a 1:1 mass ratio of ILs to either the model oil or gasoline. The biphasic mixtures were agitated with stirring for 30-40 minutes to increase the rate of desulfurization. As much as 45% of the sulfur compound was removed from the model oil using IL [BPy]BF$_4$ and 38% of the sulfur compounds from gasoline using the same IL. When [BPy]BF$_4$ is used as the desulfurization agent, as much as 96% of the thiophene can be removed from the model oil when using multiple extraction cycles (6 cycles). The extraction efficiency for gasoline is less due to complexity of the sulfur-containing compounds. Also, it was shown that the ILs can be regenerated under vacuum at 100 °C or extraction with tetrachloromethane. In general, the longer the alkyl group on the cation, the higher the desulfurization ability.

2. Reversible Sorption of Sulfur Dioxide and Ammonia

A variety of 1,1,3,3-tetramethylguanidinium (TMG) -based ionic liquids were investigated for sulfur dioxide and ammonia capture by Huang *et al.*[28] Pure gases were passed through stirred samples of the ILs at a pressure of 1 bar at 20 °C. The TMG-based ILs were shown to be good absorbents for both SO$_2$ and ammonia. Mole fractions as high as 0.67 could be achieved for SO$_2$ absorption and 0.54 for ammonia absorption. Absorption capacity was improved by substitution of the [TMGH]$^+$ cation. Gas absorption was most influenced by the cation; the anion had little effect on gas absorption. Desorption of the gases was carried out between 20-140 °C in a step wise manner.

3. Separation of Biohydrogen using Supported Ionic Liquid Membranes

Neves *et al.* studied the enrichment of hydrogen from a gaseous mixture containing hydrogen, carbon dioxide, and nitrogen using supported ionic liquid membranes with ionic liquids based on the 1-n-alkyl-3-methylimidazolium cation.[29] The following ionic liquids were evaluated as part of this study: 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM]PF$_6$), 1-hexyl-3-methylimidazolium hexafluorophosphate ([HMIM]PF$_6$), 1-octyl-3-methylimidazolium hexafluorophosphate ([OMIM]PF$_6$), and 1-butyl-3-methylimidazolium tetrafluroborate ([BMIM]BF$_4$). The ionic liquids were incorporated in a polyvinylidine fluoride (PVDF) membrane for the study. Studies were performed in a constant pressure system at a constant temperature (30 °C). Permeability and selectivity were evaluated for each single gas. Two separate studies were performed to determine the cation and anion effects on permeability and selectivity. The alkyl chain length on the cation appears to affect the permeability but has little effect on the selectivity. The permeability and selectivity are both affected by the change in the anion. Improvements in both selectivity and permeability were shown when the BF$_4$ anion was used (the BF$_4$ anion produce less viscous ILs).

C. Comparison of Gas Solubilities in ILs

Jacquemin *et al.* investigated the solubility of several gases in the ionic liquid 1-buty-3-methylimidazolium tetrafluoroborate ([BMIM]BF$_4$) at temperatures between 283 K and 343 K and pressures close of atmospheric.[30] The gases that were evaluated as part of this study were carbon dioxide, ethane, methane, oxygen, nitrogen, hydrogen, argon, and carbon monoxide. Each gas was studied individually, with no gas mixtures evaluated. Carbon dioxide was the most soluble gas, with mole fraction solubilities of the order of 0.01. Ethane and methane were the next most soluble, with mole fraction solubilities of the order of 0.0001, which was an order of magnitude more soluble than the other five gases. Hydrogen had the lowest solubility. The solubility for most gases decrease with increasing temperature.

D. Solubility of CO$_2$ in Imidazolium-Based BF$_4$ ILs

The solubility of carbon dioxide in several imidazolium-based ionic liquids was investigated by Chen *et al.* between 305-325 K and pressures from 1-9 MPa.[31] Three different ionic liquids were evaluated during this study: 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM]BF$_4$), 1-hexyl-3-methylimidazolium tetrafluoroborate ([HMIM]BF$_4$), and 1-octyl-3-methylimidazolium tetrafluoroborate ([OMIM]BF$_4$). The purpose of the study was to determine how alkyl chain length affects carbon dioxide solubility. Results of the study indicate that carbon dioxide solubility increases with increasing pressure and increasing alkyl chain length, although the increase due to increased alkyl chain length was small. Solubility of carbon dioxide in the ionic liquids decreases with increasing temperature.

E. Low-Pressure Solubility of CO$_2$ in Room Temperature ILs

The solubility of carbon dioxide in nine room temperature ionic liquids at low pressure was measured by Baltus *et al.* using a quartz crystal microbalance.[32] The nine ionic liquids investigated were: 1-methyl-3-propylimidazolium bis[trifluoromethylsulfonyl]amide (C$_3$mimTf$_2$N), 1-butyl-3-methylimidazolium bis[trifluoromethylsulfonyl]amide (C$_4$mimTf$_2$N), C$_4$mimTf$_2$N with polyethylenimine, 1-n-hexyl-3-methylimidazolium bis[trifluoromethylsulfonyl]amide (C$_6$mimTf$_2$N), 1-methyl-3-n-octylimidazolium bis[trifluoromethylsuflonyl]amide (C$_3$mimTf$_2$N), 1-methyl-3-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecdafluorooctyl)-imidazolium bis[trifluoromethylsulfonyl]amide (C$_8$F$_{13}$mimTf$_2$N), 1,4-dibutyl-3-phenylimidazolium bis[trifluoromethylsulfonyl]amide, 1-butyl-3-phenylimidazolium bis[trifluoromethylsulfonyl]amide, and 1-methyl-3-propylimidazolium hexafluorophosphate (C$_3$mimPF$_6$). Henry's constants were obtained for carbon dioxide at 25°C with carbon dioxide pressures of 1 bar or less. Increased carbon dioxide solubility was observed for ionic liquids with fluorinated cations when compared to those without fluorinated cations. Lower carbon dioxide solubility was observed for the IL with the PF$_6^-$ anion when compared to the corresponding IL with the Tf$_2$N$^-$ anion. The length of the alkyl chain affected carbon dioxide solubility: the longer the alkyl chain the more soluble the carbon dioxide. The presence of phenyl rings on the imidazolium ring reduced carbon dioxide solubility when compared to ILs with alkyl chains on the imidazolium ring.

F. Oxygen and Carbon Dioxide Solubility in BMIM BF$_4$

Oxygen and carbon dioxide solubilities in 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM]BF$_4$) were measured at temperature between 303 – 343 K and at pressures near atmospheric.[33] Carbon dioxide was found to be one order of magnitude more soluble in the IL than oxygen and the carbon dioxide solubility decreased with increasing temperature. The solubility of oxygen slightly increased with increasing temperature.

G. Guide to CO$_2$ Separations in Imidazolium-Based ILs

Bara *et al.* reviewed the use of room temperature ionic liquids (RTILs) as a media for carbon dioxide separations.[34] A variety of gases have been studied, with most of the work focused on carbon dioxide, nitrogen, and methane. RTILs show potential for carbon dioxide separation by three different modes: physical solvents, supported ionic liquid membranes, and in combination with amines for carbon dioxide capture. Cation and anion impact on carbon dioxide solubility has been examined in great detail, as well as selectivities for the separation of CO$_2$/N$_2$ and CO$_2$/CH$_4$. Some typical results for carbon dioxide solubilities and selectivities are shown in Table 5.

Table 5. Solubility and Selectivity Data for CO_2, N_2, CH_4 in ILs.

IL	Temperature (K)	H (atm)	CO_2/N_2	CO_2/CH_4
[EMIM]BF$_4$	298	80	89	36
[EMIM]BF$_4$	313	100	38	20
[EMIM]dca	313	96	51	21
[EMIM]OTf	313	71	37	17
[EMIM]Tf$_2$N	298	37	36	15
[EMIM]Tf$_2$N	313	50	24	12
[BMIM]BF$_4$	298	56		
[BMIM]BF$_4$	313	76		
[BMIM]PF$_6$	313	61		
[BMIM]Tf$_2$N	298	33		
[HMIM]Tf$_2$N	298	34	29	10
[HMIM]Tf$_2$N	313	42	20	8

H. CO_2 Solubility in 1-(2-Hydroxyethyl)-3-methylimidazolium ILs

Jalili *et al.* discuss carbon dioxide solubility in a new series of ionic liquids based on the 1-(2-hydroxyethyl)-3-methylimidazolium ([hemim]$^+$) cation.[35] Three different anions were evaluated during this study: hexafluorophosphate (PF$_6^-$), trifluoromethanesulfonate (OTf$^-$), and bis(trifluoromethyl)sulfonamide (Tf$_2$N$^-$). Studies were carried out at temperatures ranging from 303 – 353 K. Carbon dioxide pressures up to 1.3 MPa were used in the study. The carbon dioxide solubility is highest in [hemim]Tf$_2$N and lowest in [hemim]PF$_6$. The solubility of carbon dioxide in [hemim] ILs is greater than that for the corresponding [emim] ILs, which are well known for their high carbon dioxide solubilities.

I. CO_2 Capture by Task-Specific Ionic Liquids

Bates *et al.* describe a new task-specific ionic liquid (TSIL) consisting of an imidazolium cation to which a primary amine moiety is tethered.[36] The anion for this TSIL is tetrafluoroborate. The synthesis of this new TSIL is also described. Results from studies indicate that mass gains as high as 7.4% can be achieved when the TSIL is exposed to bone dry carbon dioxide for 3 hours at 1 atmosphere at room temperature (295K). This mass gain of 7.4% is much greater than that for typical ionic liquids, such as 1-hexyl-3-methylimidazolium hexafluorophosphate ([hmim]PF$_6$), which shows a mass gain of 0.0881%. The carbon dioxide sequestration is reversible, with the carbon dioxide being extruded from the IL upon heating to 80-100 °C for several hours under vacuum. The recovered IL was repeatedly recycled for CO_2 uptake for five cycles without loss of efficiency.

J. Enhanced CO_2 Absorption of Poly(ionic liquid)s

Tang *et al.* evaluated the use of polymers from ionic liquids for carbon dioxide absorption.[37] Polymers of poly[1-(4-vinylbenzyl)-3-butylimidazolium tetrafluoroborate] (PVBIT), poly[1-(4-vinylbenzyl)-3-butylimidazolium hexafluorophosphate] (PVBIH), and poly[2-(1-butylimidazolium-3-yl)ethyl methacrylate tetrafluoroborate] (PBIMT) were prepared from the corresponding ionic liquids and carbon dioxide absorption was measured and compared to their corresponding monomers. Carbon dioxide absorption for 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM]BF$_4$) was 0.26 weight percent at 592.3 mm Hg CO_2 and 22 °C, which is consistent with literature values. The carbon dioxide absorption values for the polymer ionic liquids exposed to dry carbon dioxide for 1.5 hours under the same conditions are shown in Table 6. The sorption/desorption processes were shown to be very fast, with carbon dioxide sorption taking approximately 30 minutes and desorption taking 15 minutes (under vacuum). CO_2 absorption was also shown to be very selective; no weight increase was observed when the polymers were exposed to nitrogen or oxygen. Also, when a mixed gas of carbon dioxide/nitrogen was utilized, only the carbon dioxide was absorbed.

Table 6. Carbon Dioxide Absorption by Poly(ionic liquid)s.

IL	CO_2 Absorption (wt %)
PVBIH	0.322
PVBIT	0.305
PBIMT	0.241
[BMIM]BF$_4$	0.256

K. Improving CO₂ Solubility in ILs

Muldoon *et al.* conducted a study to determine the structural impacts on carbon dioxide solubility.[38] The overall goal was to develop a series of carbon dioxide-philic ionic liquids. It was shown that ILs containing fluorine have improved carbon dioxide solubility. The fluorines may be present in either the anion or cation moieties of the ILs. However, there are issues related to environmental impacts of fluorinated ionic liquids. For imidazolium-based ionic liquids, the longer the alkyl chain on the imidazolium cation, the higher the carbon dioxide solubility. This is most likely attributed to an increase in the free volume of the ILs.

L. Solubility of CO₂ in Imidazolium-based ILs

A study was conducted by Cadena *et al.* to determine the underlying mechanisms for the high solubility of carbon dioxide in imidazolium-based ILs.[39] Six different ionic liquids were evaluated as part of this study. Cation and anion impacts on carbon dioxide solubility was reported. The exact experimental conditions for the experiments conducted were not presented. The results are shown in Table 7. Data shows that the anion dominates the interactions with CO_2, with the cation playing a secondary role.

Table 7. Carbon Dioxide Solubility in Several ILs.

IL	Formula	H (10 °C)	H (25 °C)	H (50 °C)
1-n-butyl-3-methylimidazolium hexafluorophosphate	[bmim]PF₆	38.7 bar	53.4 bar	81.3 bar
1-n-butyl-2,3-dimethylimidazolium hexafluorophosphate	[bmmim]PF₆	47.3 bar	61.8 bar	88.5 bar
1-n-butyl-3-methylimidazolium tetrafluoroborate	[bmim]BF₄	40.8 bar	56.5 bar	88.9 bar
1-n-butyl-2,3-dimethylimidazolium tetrafluoroborate	[bmmim]BF₄	45.7 bar	61.0 bar	92.2 bar
1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	[emim]TF₂N	25.3 bar	35.6 bar	51.5 bar
1-ethyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide	[emmim]TF₂N	28.6 bar	39.6 bar	60.5 bar

M. Room-Temperature ILs and Composite Materials

Bara *et al.* explored the use of room-temperature ionic liquids (RTILs) in absorptive and membrane technologies for carbon dioxide capture.[40] It was shown that RTILs and composites based on RTILs can compete with, or improve upon, current technologies. A range of applications were presented, including postcombustion carbon dioxide capture and natural gas sweetening. The advantages and limitations of the systems were also presented.

N. Technology Needs for Carbon Capture Beyond 2020

A resource document from the Workshop on Basic Research Needs for Carbon Capture: Beyond 2020 presents a wide range of technologies used in carbon capture.[41] Materials for carbon capture are described, including amines, ionic liquids, and ionic liquid-supported membranes. The challenges and technology needs were discussed for each topic. With regard to ionic liquids (ILs), the value of being able to tune the IL for the desired properties was considered invaluable. There are virtually endless possibilities for cations, anions, substituents, and functional groups that can be incorporated into ILs.

The benefits of ILs were listed as follows:
- Low volatility
- Ability to regenerate over a wider temperature range
- Elimination of water as a solvent for the sorbent
- Less energy to regenerate
- Potentially lower corrosion
- Significantly lower parasitic energy loses
- Tunability

The major challenges for ILs were listed as follows:
- Many of the compounds are not commercially available

- Some of the best performing compounds will be susceptible to SO_2 poisoning
- Limited understanding of the reaction mechanisms and kinetics

The major challenges for IL membranes were listed as follows:
- Developing mechanically stable, commercially viable IL membrane platforms
- Improvements in fabrication/coating technologies to enable preparation of very thin, high permeance, defect-free selective layer films on a suitable support
- Commercial process for removal of smoke and oxides of sulfur

Gas transport properties for several supported ionic liquid membranes were presented in the document, as well as the associated references.

O. Ionic Liquids in Separation Techniques

A review discussing the use of ILs in separation processes was written by Berthod et al. in 2008.[42] The review covers the use of ILs in gas chromatography (GC), liquid chromatography (LC), and capillary electrophoresis. Physicochemical data is presented for more than 50 ILs, including molecular weight, melting point, density, and solubility in water. The use of ILs in gas chromatography was focused primarily in the area of ionic liquid-based stationary phases. Crosslinked dicationic ILs have been used in the separation of polyaromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs). The use of ILs in LC has involved the use of ILs as solvents for reversed-phase LC with water-IL solvents. Ionic liquids have also been evaluated as additives to the mobile phase for LC, as well as stationary phases for LC.

P. CO_2 Separation Membranes with ILs in a Nafion Matrix

Nafion® composite membranes using ionic liquids and Nafion® were designed and fabricated by Yoo et al. to efficiently separate carbon dioxide and methane.[43] Three ionic liquids were evaluated during this study: 1-n-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([hmim]Tf$_2$N), 1-hexyl-3-methylimidazolium tetrafluoroborate ([hmim]BF$_4$), and 1-hexyl-3-methylimidazolium hexafluorophosphate ([hmim]PF$_6$). Two different types of Nafion® membranes were prepared: dense Nafion® and electrospun Nafion®/polyethyleneoxide composite. Gas separation factors as high as 26 were obtained for the dense Nafion® layer for carbon dioxide/methane separation, implying a change in the microdomain of Nafion® in the presence of the IL.

Q. CO_2 Separation using Task-Specific ILs on Supported Liquid Membrane

Selective and facilitated carbon dioxide transport through novel membranes is described by Hanioka et al.[44] Three different ILs were utilized in the study: 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([C$_4$mim]Tf$_2$N), N-aminopropyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([C$_3$NH$_2$mim]Tf$_2$N), and N-aminopropyl-3-methylimidazolium trifluoromethanesulfone [C$_3$NH$_2$mim]CF$_3$SO$_3$). The membrane used for the support was a porous hydrophilic polytetrafluoroethylene (PTFE) membrane with a pore size of 0.1 µm, porosity of 71%, and thickness of 35 µm. The membranes were prepared by soaking the PTFE membrane with excess IL overnight, followed by removal of the excess IL using a wipe. The PFTE-containing membranes were sandwiched between hydrophobic PTFE membranes (pore size 0.1 µm, thickness 60 µm) to prevent leakage of ionic liquids from the membrane. The gas feed for the study consisted of carbon dioxide and methane, with the partial pressure of carbon dioxide approximately 2-50 kPa. The total pressure for the system was 1.01×10^5 Pa (1 atm). A total flow rate of feed gas was 200 cm^3/minute. Helium was used as the sweep gas at a flow rate of 10 cm^3/minute. Both gas streams were saturated with water before entering the permeation cell. The study indicated that the prepared membranes showed high selectivity and high stability for carbon dioxide separation from the gas mixture. Selectivities of greater than 100 can be achieved using these membranes.

R. CO_2/Helium Separation using Supported IL Membranes (SILMs)

Supported IL membranes were fabricated by impregnation of commercially available polymer films with the ionic liquid 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([hmim]Tf$_2$N).[45] Polysulfone and polyethersulfone polymeric porous substrates were used to fabricate the SILMs. The substrates were 75-85% porous with a nominal pore size of 0.2 µm. The substrates had thicknesses of 152 µm and 145 µm, respectively. The membranes were prepared by soaking the support film with excess IL for a minimum of 8 hours, followed by removal of the excess IL using an unmodified support by blotting. The experiments in this study were performed in a constant pressure system. Membranes prepared using polysulfone supports had good temperature stability up to

125 °C. In the temperature range from 37-125 °C to CO_2 permeability increases from 744 to 1200 barrer. Helium permeability increases from 86 to 270 barrer over the same temperature range. The CO_2/He selectivity decreases from 8.7 to 3.1 over the temperature range of 37-125 °C. It should be noted that carbon dioxide solubility in ionic liquids typically decreases with increasing temperature.

S. Polymerizable Room-Temperature ILs as Gas Separation Membranes

Studies were carried out to evaluate gas separation properties of membranes fabricated from room-temperature ionic liquids with polymerizable groups.[46] As described in the document, there is no "perfect" ionic liquid for carbon dioxide separation, i.e., one that possesses both high CO_2 solubility and CO_2/N_2 and CO_2/CH_4 selectivity. The best IL for the process depends on the requirements of the process. In this study, a series of IL monomers with varying alkly chain length were converted into polymer films. These films were evaluated for separation of CO_2, N_2, and CH_4. It has been reported in literature that polymer films prepared from pure room-temperature ionic liquids are too brittle to use in gas separation processes.[47] However, these membranes can be strengthened through the addition of a small amount of non-CO_2 interactive polymer cross-linker and the use of a porous support. This study utilized membranes produced from styrene-based and acrylate-based monomers. Permeability measurements were made at ambient temperature (20 °C) using single gases. The permeability study results are shown in Table 8 and the selectivity results are shown in Table 9.

Table 8. Permeability Results for Styrene-based and Acrylate-Based Poly(RTILs).

		Permeability (Barrer)		
Cross-Linker	Alkyl Chain	CO_2	N_2	CH_4
Styrene	Methyl	9.2	0.29	0.24
Styrene	Butyl	20	0.67	0.91
Styrene	Hexyl	32	1.4	2.3
Acrylate	Methyl	7.0	0.23	0.19
Acrylate	Butyl	22	0.71	0.97

Table 9. Selectivity Results for Styrene-based and Acrylate-Based Poly(RTILs).

		Permselectivity	
Cross-Linker	Alkyl Chain	CO_2/N_2	CO_2/CH4
Styrene	Methyl	32	39
Styrene	Butyl	30	22
Styrene	Hexyl	28	17
Acrylate	Methyl	31	37
Acrylate	Butyl	30	22

In general, these polymers were shown to have high carbon dioxide solubility and nearly constant permselectivity with increasing permeability as the n-alkyl substituent on the cation became longer.

T. Task-Specific ILs with Nitrile-Containing Anions

This study, performed by Mahurin et al., explored the performance of a series of 1-alkyl-3-methylimidazolium ionic liquids with nitrile-containing anions.[48] Three different ionic liquids were evaluated in this study and compared to the well-studied ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ([emim]Tf$_2$N). The ionic liquids studied were: 1-butyl-3-methylimidazolium dicynamide ([bmim]N(CN)$_2$), 1-butyl-3-methylimidazolium tricyanomethane ([bmim]C(CN)$_3$), and 1-ethyl-3-methylimidazolium tetracyanoborate ([emim]B(CN)$_4$). Supported ionic liquid membranes were formed by infusing the desired ionic liquid into a 47-mm Supor-100 porous fiber membrane filter from Pall Corporation. These membranes are hydrophilic polyethersulfone (PES) membranes with a pore diameter of 0.1 μm and a thickness of approximately 130 μm. For the IL [bmim]C(CN)$_3$, an anodic alumina membrane with a pore diameter of 0.1 μm and thickness of 60 μm was used since the IL was found to damage the PES membrane. The supported ionic liquid membranes were placed in a vacuum desiccators for a minimum of 12 hours to remove residual water and degas the sample. Excess IL was removed by wiping with Whatman filter paper. In general it was shown that permeation of the gas through the membrane proceeds via the following steps:
- Absorption of the gas into the ionic liquid from the high-pressure side of the membrane
- Diffusion of the gas across the membrane

- Desorption of the gas out of the low-pressure side of the membrane

This report shows that the separation properties of the supported ionic liquid membranes could be enhanced relative to previously reported data. For example, the [emim]B(CN)$_4$-based supported ionic liquid membrane showed a permeance of 2.55×10^{-9} mol/(m^2 Pa s) for carbon dioxide, which is 30% higher than the permeance of [emim]Tf$_2$N (which is considered one of the best separation systems). Also, the newly developed supported ionic liquid membrane showed a CO$_2$/N$_2$ selectivity of 53.

U. Stabilized Ionic Liquid Membranes

A novel pressure-assisted method is proposed by Vangeli *et al.* for the chemical stabilization of silane-functionalized imidazolium-based ionic liquids into the pores of ceramic nanofiltration membranes.[49] Several membranes were evaluated during this study, including two silica (1 nm pore size) and one gamma-alumina (5 nm pore size) membranes with 1-methyl-3-(1-trimethoxysilylmethyl)imidazolium hexafluorophosphate (C$_8$H$_{17}$N$_2$SiO$_3$PF$_6$) and one silica and one gamma-alumina with 1-methyl-(3-(3-trimethoxysilylpropyl)imidazolium hexafluorophosphate (C$_{10}$H$_{21}$N$_2$SiO$_3$PF$_6$). Carbon dioxide and carbon monoxide solubilities were measured using a gravimetric microbalance. Permeability and selectivity studies were performed in a flow apparatus in which the feed, permeate, and retentate gas compositions were analyzed using a GC. Considerable CO$_2$/CO separation capacity (25) and temperature stability (stable up to 250 °C) was observed for the developed membranes. Permeability values up to 2000 Barrer has also been observed.

V. Development of Supported Ionic Liquid Membranes: A Systematic Approach

Luebke *et al.* describes the study of a variety of ionic liquids in supported ionic liquid membranes for the capture of carbon dioxide from streams containing hydrogen.[50] This work was supported by researchers at the National Energy Technology Laboratory, who incorporated candidate ILs into supports and evaluated the membrane performance. The ILs utilized in this study were [hmim]Tf$_2$N, [NH$_2$C$_3$mim]Tf$_2$N, and [NH$_2$Cmpy]Tf$_2$N. Polyethersulfone, polysulfone, and crosslinkable nylon polymeric porous substrates from Pall Corporation were used as the supports for the study. Supported ionic liquid membranes were prepared by covering the substrates with excess IL and allowing them to absorb the liquid for a minimum of 8 hours. Excess IL was removed by blotting. A feed gas of 20% carbon dioxide, 20% hydrogen and the balance argon was used for most studies; one mixture containing 1% hydrogen sulfide was also used. The pressure used for the studies was approximately 108 kPa for the feed and the permeate pressure was less than 102 kPa. A sweep gas (argon) was added to the permeate side with a flow of 1.0-2.0 ml/minute. Results for the permeability study using two crosslinkable nylon supports (Biodyne® 1 and Biodyne® 2) and the ionic liquid [hmim]Tf$_2$N are shown in Table 10. Biodyne® 1 has larger pores than Biodyne® 2.

Table 10. Permeability (Barrer) and Selectivity Results for [hmim]Tf$_2$N-Biodyne Membranes.

T (°C)	37			50			100		
Support	CO$_2$	H$_2$	CO$_2$/H$_2$ Selectivity	CO$_2$	H$_2$	CO$_2$/H$_2$ Selectivity	CO$_2$	H$_2$	CO$_2$/H$_2$ Selectivity
Biodyne® 1	417	43	9.72	446	50	9.03	508	72	6.84
Biodyne® 2	502	54	9.30	571	67	8.47	772	123	6.24

T (°C)	150			200			250		
Support	CO$_2$	H$_2$	CO$_2$/H$_2$ Selectivity	CO$_2$	H$_2$	CO$_2$/H$_2$ Selectivity	CO$_2$	H$_2$	CO$_2$/H$_2$ Selectivity
Biodyne® 1	606	122	4.72	699	199	3.13	767	323	2.13
Biodyne® 2	861	205	4.18	1009	367	2.74	942	535	1.76

T (°C)	300		
Support	CO$_2$	H$_2$	CO$_2$/H$_2$ Selectivity
Biodyne® 1	825	567	1.44
Biodyne® 2	1165	918	1.27

Permeability and selectivity data were also collected for membranes fabricated from three ionic liquids and the Biodyne® 2 support. The data was collected at two temperatures: 37 °C and 300 °C. The results are shown in Table 11. In general, it was shown that carbon dioxide selective membranes can be fabricated from ionic liquids.

Table 11. Permeability and Selectivity Results for Membranes with Biodyne® 2 Supports.

T (°C)	37		
IL	CO_2 (Barrer)	H_2 (Barrer)	CO_2/H_2 Selectivity
[hmim]Tf$_2$N	502	54.0	9.30
[NH$_2$pmim]Tf$_2$N	80.5	10.8	9.58
[NH$_2$pmpy]Tf$_2$N	102	14.4	7.69

W. Gas Separations using Stabilized Room Tempeature Ionic Liquid Membranes

Scovazzo summarizes literature data, along with adding new data, on the permeabilities and selectivities of stabilized room temperature ionic liquid membranes (SILM) for the following pairs of gases: CO_2/N_2, CO_2/CH_4, O_2/N_2, ethylene/ethane, propylene/propane, 1-butene/butane, and 1,3-butadiene/butane.[51] It was shown that solubility selectivity dominates the permeability selectivity in stabilized ionic liquid membranes. For carbon dioxide separations, room-temperature ionic liquid molar volume and room-temperature ionic liquid viscosity are critical properties that affect SILM performance. Data indicates that for CO_2/N_2 and CO_2/CH_4 separations, the two best ILs for preparing SILMs are [emim]Tf$_2$N (based on permeability) and [emim]dca (based on selectivity). The author also presents a list of topics that could be addressed to improve SILM selectivity.

X. CO_2 Capture using Ionic Liquids

A master's thesis from the Department of Chemical and Biochemical Engineering from the Technical University of Denmark provides a great deal of information related to carbon dioxide capture using ionic liquids.[52] Information related to ionic liquids and their properties, theory of carbon dioxide capture and methods used, and research data for several ionic liquids are presented. The document contains far more data than can be summarized in this report and it is recommended that interested parties review the document for desired information.

Y. Reversible ILs for Energy Applications

Reversible, single component, ionic liquids were studied by Blasucci et al. for use in hydrocarbon extraction from crude oil and carbon capture from power plant flue gas streams.[53] The reversible ILs were derived from silylated amine molecular liquids which react reversibly with carbon dioxide to form ionic liquids. These new ILs are described as having dual-capture mechanisms: physical absorption and chemical absorption. The four silylated amines used in this study were (3-aminopropyl)-triethyoxysilane (TESA), (3-aminopropyl)-trimethoxysilane (TMSA), (3-aminopropyl)-triethylsilane (TEtSA), and (3-aminopropyl)-tripropylsilane (TPSA). The corresponding ionic liquids were TESAC, TMSAC, TEtSAC, TPSAC. Carbon dioxide solubility was measured using a Specas, Ltd. heated "Golden Gate" attenuated total reflectance (ATR) accessory with diamond crystal and ZnSe focusing lenses in combination with a custom high pressure reactor. The results for carbon dioxide capture at 35 °C and 62.5 bar carbon dioxide are shown in Table 12.

Table 12. Carbon Dioxide Capture Results at 35 °C and 62.5 bar.

IL	Density (g/cm^3)	Swelling (%)	CO_2 Absorption Capacity (mole CO_2/kg Amine)	CO_2 Reaction Capacity (mole CO_2/kg Amine)	Total CO_2 Capacity (mole CO_2/kg Amine)
TMSA	1.151	17	10.9	2.79	13.69
TESA	1.060	23	12.5	2.26	14.76
TEtSA	0.945	16	12.3	2.88	15.15
TPSA	0.907	31	17.9	2.32	20.2

Z. Summary

The two major methods of using ionic liquids for carbon dioxide capture that are addressed in this document are physical absorption and the use of ionic liquids in supported ionic liquid membranes (SILMs). Each case will be summarized in the following paragraphs.

4. Physical Absorption

A great deal of work has been performed investigating the solubility of carbon dioxide in ionic liquids, and more specifically, room temperature ionic liquids (RTILs). Most of the work has utilized ionic liquids with substituted imidazolium cations. The length of the alkyl chain on the cation plays a very important role in carbon dioxide solubility: the longer the alkyl chain, the greater the carbon dioxide solubility. Therefore, [BMIM]BF$_4$ will absorb less carbon dioxide than [HMIM]BF$_4$, which will absorb less carbon dioxide than [OMIM]BF$_4$. Also, for physical absorption, the solubility of carbon dioxide increases with increased carbon dioxide partial pressure. For example, at near atmospheric pressure approximately 0.001 mole fraction carbon dioxide is absorbed in [BMIM]PF$_6$, whereas the number increases to near 0.73 at 95 bar. It has also been shown that carbon dioxide solubility decreases with increasing temperature; for [BMIM]BF$_4$ the Henry's constant increases from 40.8 bar at 10 °C to 88.9 bar at 50 °C. The impact of fluorine on carbon dioxide solubility was also investigated, with results indicating that the presence of fluorine atoms on the alkyl sidechain of imidazolium cations improves carbon dioxide solubility when compared to imidazolium cations without fluorine atoms; fluoride atoms on the anion also improves carbon dioxide solubility, but the overall impact is not as well understood. Phenyl group substitution of the imidazolium cation reduces overall carbon dioxide solubility when compared to imidazolium cations with alkyl chain substitution.

Several research groups addressed the topic of task specific ionic liquids (TSILs). TSILs are ionic liquids with ions that contain functional groups that can interact with dissolved substrates. These ionic liquid systems absorb carbon dioxide by two modes: physical absorption and chemical absorption. They typically involve imidazolium ions to which reactive functional groups (such as amines) are tethered. TSILs have been shown to absorb as much as 7.4 % by weight carbon dioxide when exposed to 1 atmosphere of carbon dioxide for 3 hours at room temperature; [HMIM]PF$_6$ showed 0.09 % weight increase due to carbon dioxide absorption under similar conditions. One paper reports 20.2 moles carbon dioxide can be absorbed per kilogram of amine for TSILs.

5. Supported Ionic Liquid Membranes

A great deal of work has been conducted in the area of supported ionic liquid membranes (SILMs). For all of the membranes described in the literature the permeability of carbon dioxide increases with increased temperature and pressure. However, the selectivity for carbon dioxide decreases with increased temperature. Typical supports that were used to fabricate SILMs are PTFE, polysulfone, crosslinked nylon, polyvinylidenefluoride, and polyethersulfone. Membranes have been used for separating carbon dioxide, nitrogen, hydrogen, methane, and helium, as well as various other gases (oxygen, argon, carbon monoxide, etc.). Most of the studies conducted utilized single gases in the studies; very few mixed gas systems were evaluated. The selectivity of carbon dioxide versus nitrogen can exceed 75 and for carbon dioxide versus methane can exceed 25. The selectivity of carbon dioxide versus hydrogen can exceed 10. Some nitrile-containing ionic liquids have been shown to produce membranes with carbon dioxide solubility as high as 0.13 mol L^{-1} atm^{-1}. Some of the membranes identified have very high temperature stability (exceeding 300 °C); however, the selectivity of the membranes for carbon dioxide is very low at these temperatures. Some ILs can be polymerized, producing poly(ILs). Poly(ILs) membranes follow many of the same trends as typical ionic liquids: permeability increases with increase alkyl chain length and selectivity decreases with increased temperature.

In general, the benefits of ILs that were listed were:
- Low volatility
- Wide range of regeneration temperatures
- Less energy to regenerate
- Potentially lower corrosion
- High temperature stability
- Ability to tune performance

Some major challenges for ILs that still need to be addressed:
- Limited commercial availability
- Limited understanding of the reaction mechanisms and kinetics

Some major challenges for IL membranes that still need to be addressed:
- Improvements in membrane fabrication (in general)
- Improvements in large scale membrane fabrication
- Improvements in producing defect free coating for the membranes

IV. Acid-Base Chemistry

This section summarizes the literature evaluation of the applicability of both chemical and physical absorption and adsorption processes for the capture and separation of carbon dioxide from various gas mixtures as a possible Mars ISRU technology capability.

Initial research focused on the use of CO_2 capture from the gas processing industry, as this is a mature technology which has been developed for quite some time. This is a chemical absorption process based upon the acidic properties of gases such as carbon dioxide and hydrogen sulfide from natural gas streams that was developed over 60 years ago. It is the most commonly used technology today for low concentration CO_2 capture, primarily from the natural gas industry (post-combustion) using amine-based solvents such as monoethanolamine (MEA)[54] (see Fig. 10),[55] diethanolamine (DEA), methyldiethanolamine (MDEA), or diisopropanolamine (DIPA).[56,57,58]
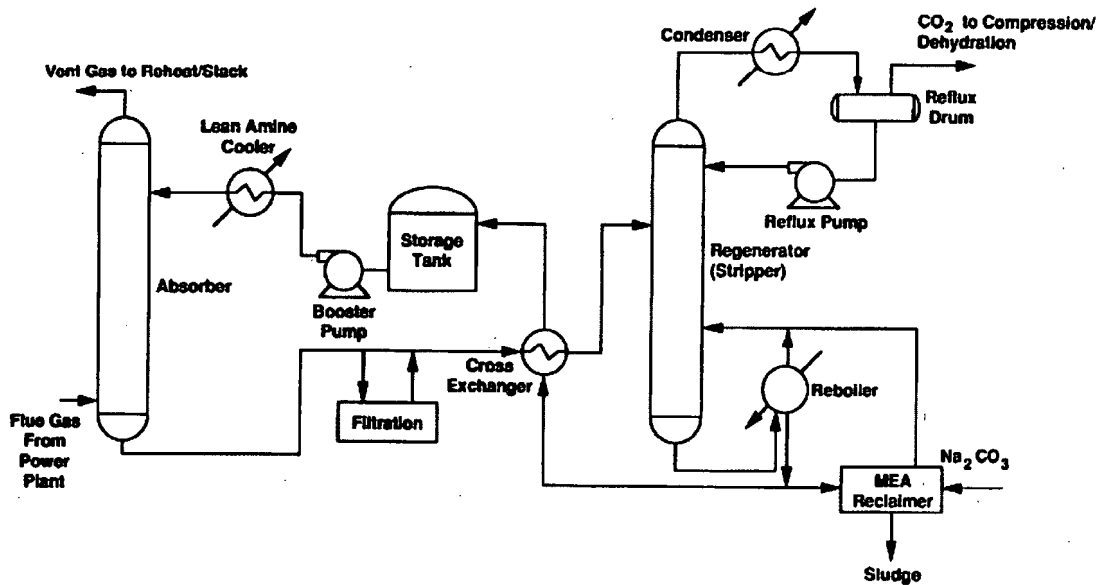
Figure 10. Process flow diagram for the amine separation process [55]

As stated above, amine solvents such as MEA are the preferred solvents for carbon dioxide capture. The general process is as follows:

1. CO_2 in the gas phase dissolves into a solution of water and amine compounds, the amines then react with the CO_2 in solution to form a protonated amine (AH^+), bicarbonate (HCO_3^-), and carbamate (ACO_2^-)

2. As these reactions occur, more CO_2 is driven from the gas phase into the solution due to the lower chemical potential of the liquid phase compounds at this temperature

3. When the solution has reached the intended CO_2 loading, it is removed from contact with the gas stream and heated to reverse the chemical reaction and release the high-purity CO_2

4. The CO_2-lean amine solvent is then recycled to contact additional gas[56].

An example of an actual patented CO_2 capture process using this technology is the Fluor Daniel ECONAMINE FG process. The equilibrium reaction is given below:

$$2(R\text{-}NH_2) + H_2O + CO_2 \leftrightarrow (R\text{-}NH_3)_2CO_3 \ [56]$$
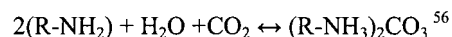
CO_2 is absorbed during the forward reaction, which is favored at temperatures between 20°C-70°C. The regeneration cycle, during which the release of CO_2 takes place, occurs at temperatures of 120°C-150°C.[54] The pressure is kept low during the regeneration process to aid in desorption of the CO_2 from the amine solvent, which should be relatively easy to achieve in a Mars atmosphere. The ionic strength is kept relatively low which results in a relatively high regeneration energy requirement, which may be prohibitive from a Mars ISRU standpoint, but it may be possible to choose a solvent system where this is less of a problem (or to change the ionic strength).

Problems of scale, efficiency, and stability become barriers when chemical solvents are used for high-volume gas flows with a relatively smaller fraction of valuable product.

A more common problem seen with the use of amine solvents has been the possible susceptibility of the capture system to elements of corrosion. The alkanolamines themselves are not corrosive to carbon steel; it is the dissolved CO_2 itself which acts as the primary agent of corrosion. The alkanolamines act as indirect corrosion agents, and the general trend is that the primary are most corrosive while the tertiary are least corrosive.[59] Oxygen content must also be controlled due to solvent degradation (to varying degrees) that occurs in oxidizing atmospheres. This should not be a large problem in a Mars atmosphere, however it may be an issue if oxygen were to be produced from a process such as ROXYGEN. Oxygen can also contribute to additional corrosion problems. Inhibitors have been shown to be effective in limiting both corrosion and solvent degradation, giving one possible control option. Other problems include gases incompatible with alkanolamines found within flue gas streams such as sulfur oxides, nitrogen oxides, and other particulate matter.[60]

Another type of chemical absorption method utilizes alkaline salt-based processes as the chemical reaction media for CO_2 capture. This method uses the alkali salts of various weak acids to physically absorb carbon dioxide gas. Many different salts have been put forth as possible chemical sorbents, including sodium and potassium salts of carbonate, phosphate, borate arsenite and phenolate. The most commonly used salts to date have been sodium carbonate and potassium carbonate, primarily due to low cost and minimal solvent degradation. These processes have not been used for low pressure, low concentration CO_2 flue gas applications in a commercial setting as of yet; they have been limited to bulk CO_2 removal from high pressure vapor streams or to produce high purity commodity streams of carbon dioxide. Typically, inhibitors and proprietary activators (i.e. an amine) are added to increase the mass transfer of carbon dioxide and to prevent/limit the amount of corrosion within the system.[61]

Another option for carbon dioxide capture and separation is physical absorption, where an analyte (in this case CO_2) is allowed to penetrate a solid or liquid under a specific set of conditions, then allowed to desorb under a different set of conditions. The rate of both absorption and desorption are temperature/pressure dependent. Physical absorption of carbon dioxide occurs when high partial pressures (based on Henry's Law) are applied to the gas at low temperature. This is a relatively low energy process (in terms of the actual chemical interaction that occurs, as the desorption step occurs more easily), but it does have the requirement of high pressures (which would require a compression stage for Mars ISRU).[62] The affinity of CO_2 for the absorbent is relatively weak compared to that of chemical solvents, which leads to a lower energy requirement necessary for the regeneration cycle step. The capacity of physical absorption can also be higher than that of chemical solvents, due to the fact that the system is no longer limited by stoichiometric requirements. The solvents are regenerated either by heating or pressure reduction. The most common solvents are Selexol (dimethyether of PEG) or Rectisol (cold methanol). Selexol has been used for decades for both bulk carbon dioxide and hydrogen sulfide removal from natural gas streams.[55,61]

A last technology for CO_2 capture and separation that will be examined is physical adsorption, which depends on upon the affinity for an analyte for the surface of a material without the formation of a chemical bond. Weak interactions such as van der Waals forces allow for the separation of specific analytes (such as carbon dioxide) from a vapor stream.[55,56,62] There is a difference in the chemical potential in the adsorbed and the free carbon dioxide (the adsorbed CO_2 has a lower chemical potential than that of the CO_2 in the gas mixture). Absorbents include materials such as activated carbon, zeolites, and hydrotalcites.[58] The process would consist of 2 major steps: adsorption followed by a controlled desorption. Adsorption requires a strong affinity between the adsorbent and the analyte (CO_2). Unfortunately, the stronger that initial affinity, the more difficult (i.e. energy intensive) it is to desorb the CO_2 from the adsorbent in the desorption phase. Compared to chemical absorption, physical adsorption can be simple and energy efficient in both operation and regeneration. This can be achieved using a pressure swing or temperature swing cycle (cycle in which either pressure or temperature is put through a absorption/desorption cycle in order to achieve separation).[56,61,62] Pressure swing adsorption has been used commercially for the separation of hydrogen from carbon dioxide, using zeolite as the primary adsorbent material. Further work would have to be done in creating CO_2 specific absorbent materials. One of the primary advantages of physical adsorption methods is the lowered energy requirements of regeneration as well as the quickness of the regeneration process associated with changing of the pressure.[61]

An example of recent innovative work using zeolite 13X as a CO_2 adsorber is summarized by researchers at PNNL in a report for JSC.[63] The authors state [original figure numbers and references have been preserved as they appeared in the report]:

> Several compact single-channel adsorbers, such as that shown in Figure 3.8, were fabricated and tested to demonstrate proof-of-concept CO_2 capture and subsequent delivery in rapid adsorption/desorption cycles (Rassat et al. 2001; Brooks et al. 2002; Wegeng et al. 2003, 2004). Integrating heat-exchange microchannels on both sides of a single adsorbent-filled mesochannel

results in devices that are well suited to thermal swing adsorption processes. (Here, "microchannels" are defined as those having a depth < 1 mm, whereas "mesochannels" may be up to 1-cm deep.) Heat-exchange fluid was delivered to and received from the heat-exchange microchannels using a common header/footer system, while an independent header/footer system was used to deliver and collect adsorbate gas species to and from the sorbent. A thin, solid heat transfer wall isolated the heat-exchange fluid from the adsorbent bed and through which heat was transferred to or from the adjacent layer of adsorbent. These single-adsorbent channel test units were flow through adsorbers, in which the adsorbate and carrier gas flowed through the interstices of the adsorbent bed.
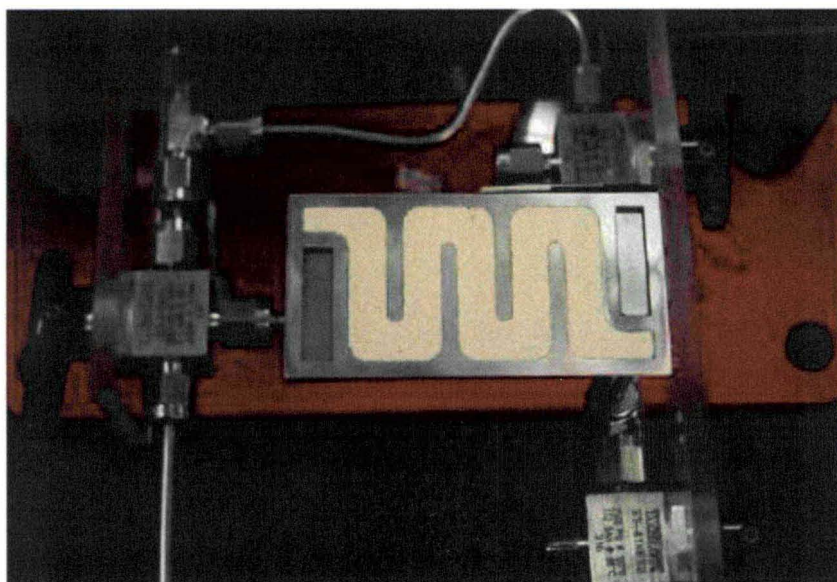
Figure 3.8. A stainless steel single-channel, microchannel adsorber filled with zeolite adsorbent. Another heat exchanger (not shown) covers the exposed adsorbent bed.

One of several proposed modes of operation to attain efficient thermal recuperation in a multi-cell adsorber is depicted in Figure 3.10 (Wegeng et al. 2003). Conceptually, the eight adsorption cells move clockwise through the cycle, while a heat transfer fluid circulates counter-clockwise through heat transfer channels in each cell. (In actuality, the cells may not be physically rotated; rather, virtual rotation can be accomplished with a valve system by transitioning the gas/vapor inlet and outlet points as well as the points where heat is provided to and removed from the system.) The highest temperature occurs in the cell at the top of the diagram where desorption is occurring. As the heat transfer fluid leaves this stage at its hottest temperature, it consecutively gives up heat to the cells on the left that are cycling toward the desorption step. At the bottom, the coldest cell is adsorbing gas or vapor. As the heat transfer fluid moves up through the cells on the right, it cools the cells moving down toward the adsorption step. In this manner, the majority of the heat associated with the thermal mass is effectively recuperated. Any "lost energy" is provided as heat at the hot end before entering the desorbing cell, and the heat transfer fluid is cooled prior to entering the adsorbing cell. A goal is to design, build, and operate a rapidly cycled, multi-cell adsorber that will achieve 80 to 90% thermal recuperation efficiency.
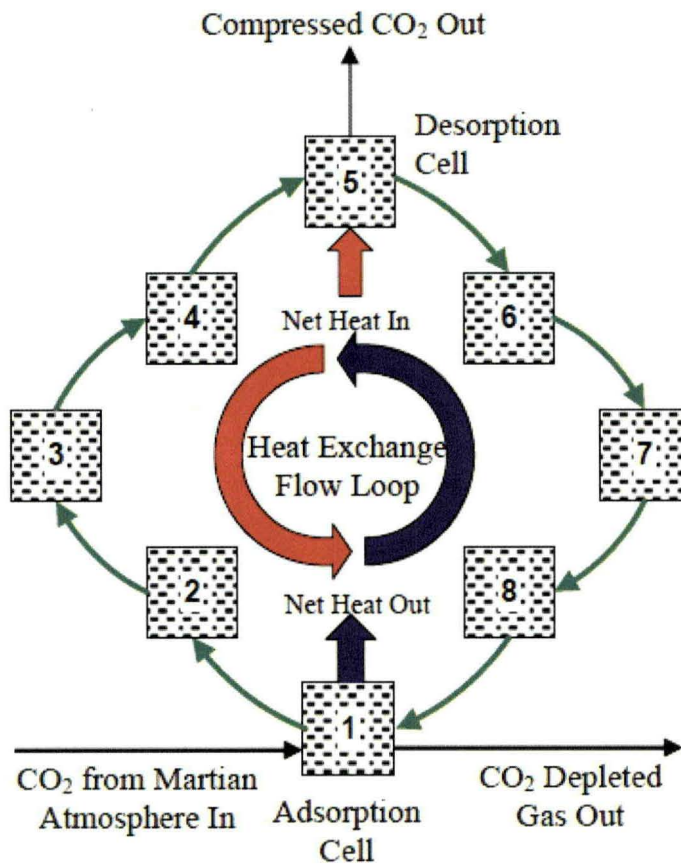
Figure 3.10. Schematic of an eight-cell CO2 sorption pump, with heat recuperation via a heat exchange flow loop.
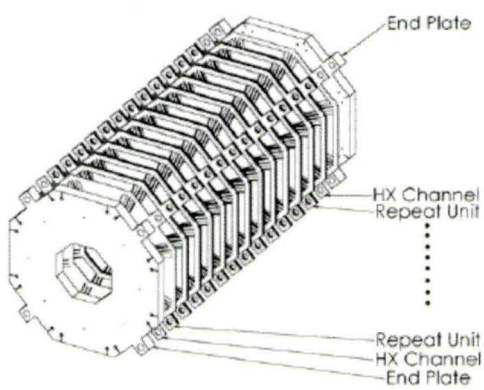
....

Figure 3.13. An exploded view of multiple repeat units, capping heat-exchange shims, and endplates arranged for bonding.
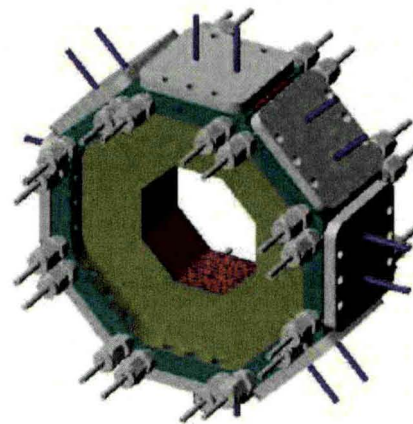

Figure 3.14. A completed adsorber with tube stubs for external adsorbate gas and heat-exchange fluid connections.

The eight-cell adsorber shown in Figure 3.14 is designed for a rapidly cycled TSA process with thermal recuperation using the mode of operation depicted in Figure 3.10 by proper linking and control of the heat-exchange fluid streams. The amount of heat that must be added to the desorber and removed from the adsorber from external sources is a function of the thermal recuperation efficiency and the heats of sorption. Since adsorption is typically exothermic and desorption is endothermic, energy must be removed or added from the adsorbent to affect the sorption cycle. These heats of sorption are the minimum thermodynamic energy cost to compress gas thermochemically in a heat-engine cycle.

Figure 3.14 is a model of the laboratory-scale CO2 thermochemical compressor designed for the NASA ISPP project. The plates on each of the eight cells are the header/footer ports for the fluid stream containing the adsorbate gas. In the case of collecting and compressing CO2 on Mars, Martian atmospheric gas is introduced into the cooled adsorption cell(s) through these ports. After isolating cells from the Martian atmosphere, the cells are heated, gas is desorbed from the adsorbent, and the CO2 partial pressure within the gas phase of the sealed cells increases. When the temperature nears or is at the maximum desorption operating temperature for the system, the ports on the desorption cell(s) are opened to provide compressed CO2 at a specified throughput and pressure to the microchannel reactors for propellant production.

Reference to the above work is not a recommendation that it be pursued as such, but it does show that the use of adsorption should be carefully considered for Mars atmospheric capture and processing. It should be noted that active pumping is required for adsorption systems to prevent stagnation of the process by buildup of a diffusion barrier by unadsorbed N2 and Ar.

In summary, this section explored various options for chemical and physical absorption/adsorption processes for possible use as carbon dioxide capture and separation techniques for use on Mars. Each of the proposed techniques has distinct advantages and disadvantages which are difficult to fully quantify and elucidate at this stage of the technology selection process. Of the technologies discussed, the one that seemed to demonstrate the most promise (primarily due to the fact that it is the most mature) was the chemical absorption, whether through the use of an amine solvent such as MEA or through an alkali-metal salt such as potassium carbonate. Both of these techniques are regenerable, although the energy requirements may vary depending on which solvent or salt is used. The MEA chemical absorption processes are also carried out at fairly low mole fractions of CO_2 and the pressures can be kept relatively low even for the desorption technique, which will be an advantage in a Mars-type environment. An advantage to the potassium carbonate technique is that it may be possible to couple this technology with an electrolysis fuel cell, using the products from one system as the source in another. This could prove to be extremely valuable, especially in the type of closed-system envisioned in this process. This would have to be explored more fully. One major disadvantage chemical absorption methods is that they are performed in an aqueous solution, so design controls (i.e. cold traps) to recapture lost water would have to be built into any system which utilized this method. Another regenerable method of carbon dioxide capture and separation is physical absorption (either solid or liquid) which is a relatively low energy process in terms of the regeneration step; however it does have the requirement of high pressures during the absorption phase which may be difficult to accomplish in a Mars atmosphere (pumps would be required). Further research would have to be done to determine whether or this was an efficient method to pursue, due to possibly prohibitive costs associated with the compression pumping necessary for the absorption phase of the process to occur. The last technology examined was physical adsorption, which uses a weak physical bond rather a chemical bond for the interaction that allows the separation to occur. This allows for it to be energy efficient specifically during the regeneration cycle (as compared to chemical absorption) but could require a much higher energy investment during the initial adsorption cycle, as higher pressures are required to increase the efficiency and speed of the CO_2 separation. Again, further research will have to be done to decide which avenue provides the most promise for Mars ISRU applications.

V. Preparative Chromatography and Molecular Sieves

Preparative chromatography is known for the ability to separate gases of almost any kind simply by changing the stationary phase. It can be used in simple binary systems as well as for more complex multi-gas mixtures. Capillary columns are commonly used over packed columns, particularly in sample analysis, due to a number of factors including increased separation efficiency and lower operating temperatures. A marked advantage to using packed

columns, the main reason for their consideration presented here, is the ability to handle much larger quantities of analyte because of the larger amount of stationary phase present as compared to the single layer films coated inside capillary columns.

A popular medium for the stationary phase in packed columns are molecular sieves. Molecular sieves are materials that contain a network of intermolecular pores of a definitive size and are commonly used in the adsorption of gases. There are a number of molecular sieves varying in pore size as well as chemical composition which have been utilized in a wide range of gas separation applications. Molecular sieves are typically used in adsorption/desorption systems where the compound of choice is adsorbed in a first step at some standard operating temperature and then desorbed in a second step at some elevated temperature.[64] This means that all operations would likely be performed in batches rather than a flow through system.

Molecular sieve 3A is a common material used as a dessicant. It can be used to separate water from methane gas in the products of a Sabatier reactor or carbon monoxide gas in the products of a RWGS reactor. When considering the presence of potential buffer gases in the Martian atmosphere (nitrogen and argon), a molecular sieve downstream from a carbon dioxide freezer could be a viable separation technique. Molecular sieve 4A has been used in the purification of argon and carbon molecular sieves are used in the separation of nitrogen and methane.[65,66] Work has also been performed showing the efficiency of separation of layered packed bed systems for various combinations of hydrogen, carbon monoxide, methane, nitrogen, and carbon dioxide – all important compounds in Martian ISRU systems[67].

The downside to molecular sieve systems is they are highly temperature and pressure dependent. Several of the applications mentioned above are employed in PSA (pressure swing adsorption) systems. These require high pressure (some as high as 250 psia) to drive the adsorption process which can be difficult to provide when the atmospheric pressure on Mars is so low (<0.1 psia).[68] Because of the quantities of gas requiring processing, the size of these molecular sieve systems can be quite large. This can pose a problem for TSA (temperature swing adsorption) systems, particularly for large bed diameters, when attempting to uniformly heat these systems for desorption.[69] Another problem is the need for a sweep or carrier gas. Without them, heating a molecular sieve will cause the desorption of the captured gas, but it cannot be removed from the bed for storage. A vacuum can be created above the bed, but desorption times becomes much longer due to the diffusion based removal of gas from the bed. The need for a carrier gas, however, introduces another issue in that another gas separation is required to separate the carrier gas from the capture gas, introducing another level of complexity to the process.

Implementing a molecular sieve gas separation system on Mars is an engineering challenge. A number of factors such as size and pressure requirements do not lend well to working in that environment. Molecular sieves might work well as a secondary separation when used in conjunction with other methods of gas separation, such as freezing, but as primary gas separation tool it does not seem practical.

VI. Conclusion

We have surveyed a variety techniques for the capture of carbon dioxide on Mars for processing into oxygen or propellant and the separation of other Martian gases for use as buffer gases and other uses. These technologies have a wide range in both their applicability and Technical Readiness Level for use on Mars. A deeper evaluation of the relative merits of these technologies and which of them should be further developed is the subject of future work that we will report in the near future.

Acknowledgments

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