SPACE 2011 Abstract

Mars Atmospheric Capture and Gas Separation

Anthony Muscatello, Edgardo Santiago-Maldonado, Tracy Gibson, Robert Devor, and James Captain

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 un-reacted 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 and presentation will summarize the results of an extensive literature review and laboratory evaluations of candidate technologies for the capture and separation of CO_2 and other relevant gases.

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Mars Atmospheric Capture and Gas Separation

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Outline

- Introduction
- CO_2 Freezing and Liquefaction
- Membranes
- Ionic Liquids
- Acid-Base Chemistry
- Preparative Chromatography and Molecular Sieves
- CO_2 Freezer Design for Mars ISRU Test
- Conclusions

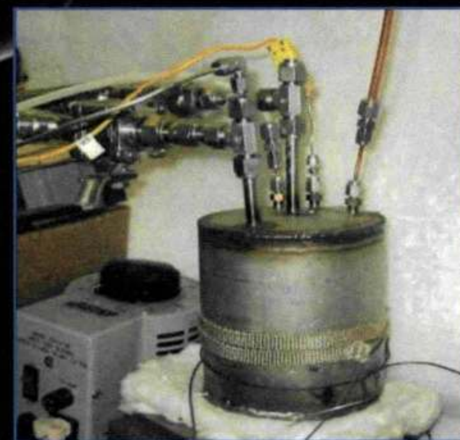
Introduction

- Review status of Mars atmospheric capture and gas separations for ISRU technologies
- Carbon dioxide capture, purification, and pressurization
- Buffer gas capture and separation
- Summarized results in a report to ISRU Program Manager Bill Larson
- Details in the conference paper

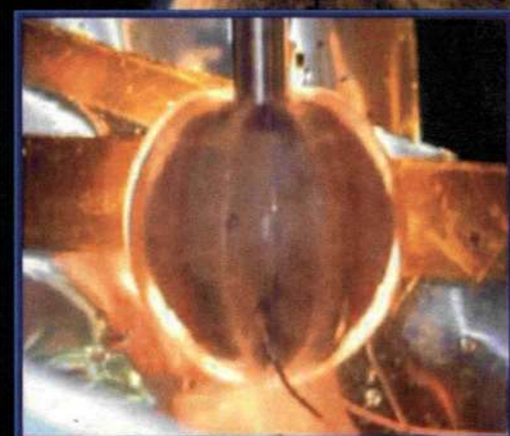
CO_2 Capture - Freezing

- <u>CO_2 Freezers Look Promising</u>
- CO_2 freezers have been tested by Pioneer Astronautics and Lockheed-Martin
- Results show accumulation rates of ~20, 13, and 80 g/hr using lab-scale systems (equiv. 5-30 g/hr CH_4)
- N_2/Ar was not measured or purified
- Rapp estimated a CO_2 freezer for 0.5 kg/hr needs ~1/3 the power and 11% the mass of a compression pump/membrane CO_2 purifier
- JPL investigated liquefaction of the Martian atmosphere, but power requirements are high
- Adsorption beds also rejected because of high mass, volume, and power

TRL 3-4

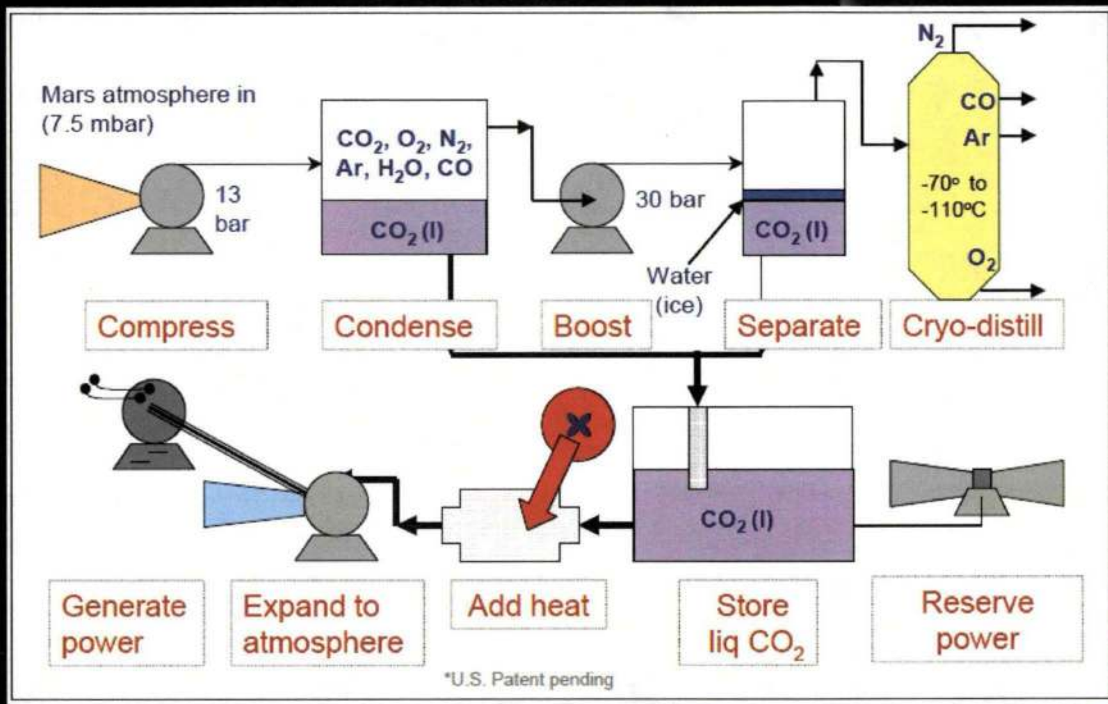


Pioneer MACDOF



Lockheed Cryocooler Freezer

CO_2 Capture - Liquefaction



Mars Atmosphere Resource Recovery System

TRL 1-2

- CO_2 Liquefaction and Collection of Other Gases
- Compress very large volumes of the atmosphere to the high pressures required to liquefy CO_2
- Geared toward larger scale operations: settlements
- Requires very high power source - nuclear reactor
- Not appropriate for Mars Sample Return or early human exploration

Alternative Approach - Direct Mars Atmospheric Gas Processing

- ISRU processes (SOE, RWGS, Sabatier) may not require high purity CO_2.
- Pioneer Astronautics ran a combined RWGS-Sabatier process with $CO_2/N_2/Ar$ for 5-continuous days without degradation of catalyst.
- N_2 and Ar were not separated from feed, but were removed during condensation or cryodistillation of products
- Gas separation downstream from CO_2 reduction process may be easier and still provide useful buffer gases
- Mechanical compression is required, and may require more power but was claimed to be less complex.
- A mass comparison needs to be done, as well.

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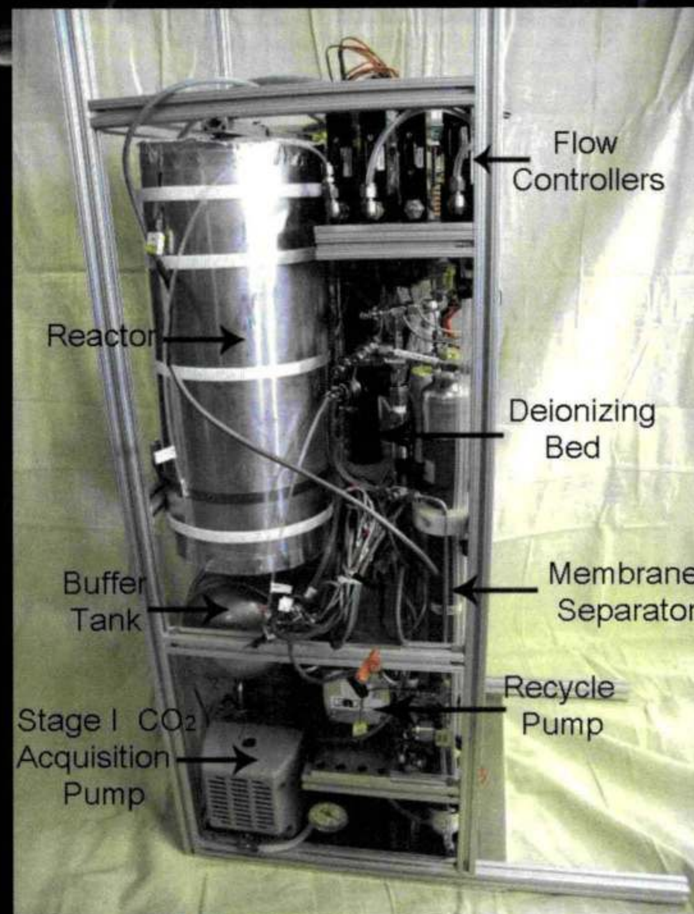
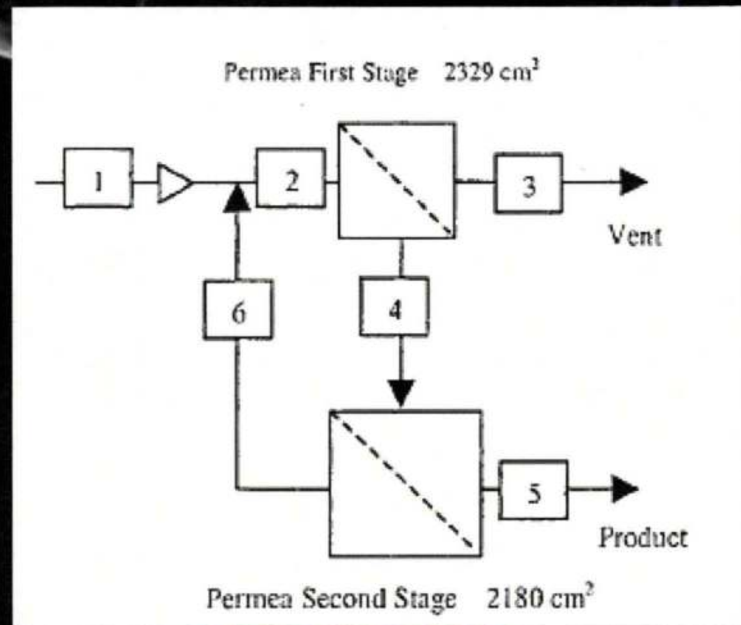


Pioneer IMISPPS

Buffer Gas Separation

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

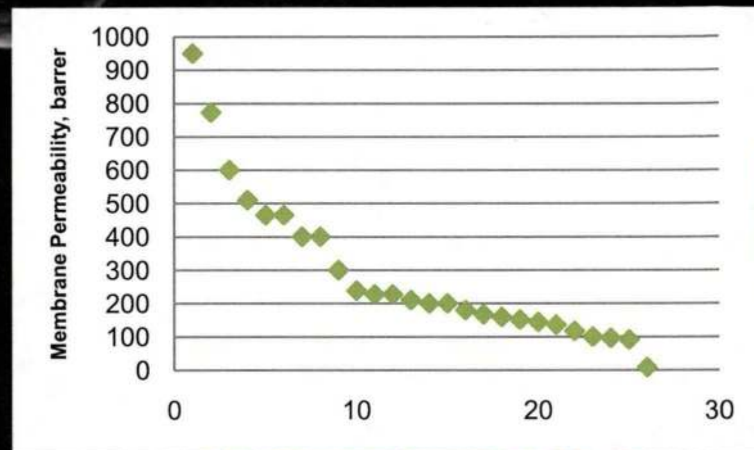
TRL 3-4



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

Other Membranes – CO_2 Capture

- Evaluated 28 other membrane materials
  - Top 10 identified
- Mainly polymeric-based: poly-acetate, polyimides, polyamides, poly-sulfone, polycarbonates, and polyethylene, plus zeolite membranes
- Selectivity and permeability are inversely related
- Pressurization is required (1-10 atm)
- Polyacetylene and polydimethylsiloxane have the highest permeability
- Trades are needed for selectivity vs permeability and power to compress the CO_2 for separation
- Synthesis required in some cases



Distribution of membrane permeability. Note: For clarity, the top two ranked materials are not included in this graph (1 barrer = 7.5×10^{-14} (cm^3(STP)-cm)/(cm^2-s-Pa)).

TRL 2-3

Chemical Processes - Membrane Separations

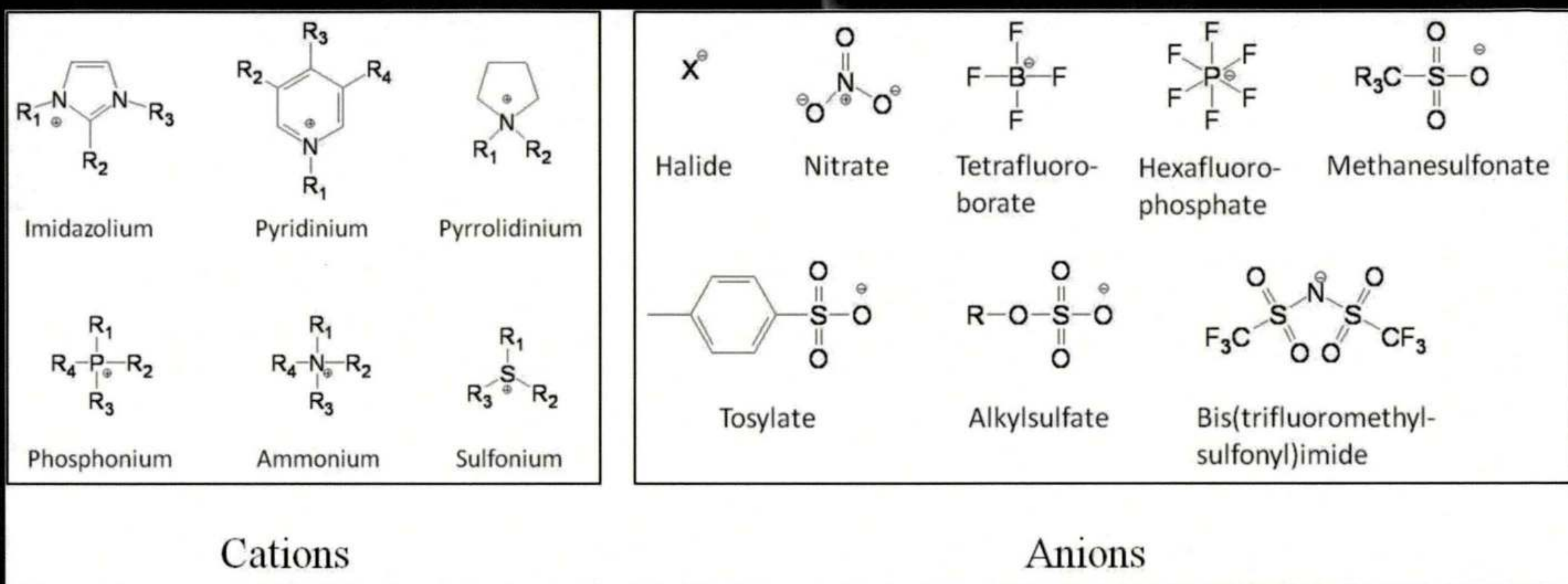
- Permea modules have been tested by LMA, Pioneer Astronautics and KSC
  - KSC results are good with minor H_2 losses (0.26% average)
- 28 other candidate membrane materials evaluated
  - Top 10 identified
- Selectivity and permeability are inversely related
- Pressurization is required (1-10 atm)
-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

	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

KSC RWGS Membrane Results

TRL 3-4

Ionic Liquids for CO_2



Typical cations and anions for ILs

Ionic Liquids are ionic compounds that are liquid at or near room temperatures

Ionic Liquids for CO_2 Capture

IL	Formula	H (10 °C)	H (25 °C)	H (50 °C)
1-n-butyl-3-methylimidazolium hexafluorophosphate	[bmim]PF_6	38.7 bar	53.4 bar	81.3 bar
1-n-butyl-2,3-dimethylimidazolium hexafluorophosphate	[bmmim]PF_6	47.3 bar	61.8 bar	88.5 bar
1-n-butyl-3-methylimidazolium tetrafluoroborate	[bmim]BF_4	40.8 bar	56.5 bar	88.9 bar
1-n-butyl-2,3-dimethylimidazolium tetrafluoroborate	[bmmim]BF_4	45.7 bar	61.0 bar	92.2 bar
1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	[emim]TF_2N	25.3 bar	35.6 bar	51.5 bar
1-ethyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide	[emmim]TF_2N	28.6 bar	39.6 bar	60.5 bar

Carbon Dioxide Solubility in Several ILs

Ionic Liquids for CO_2 Separations

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_2N	298	37	36	15
[EMIM]Tf_2N	313	50	24	12
[BMIM]BF_4	298	56		
[BMIM]BF_4	313	76		
[BMIM]PF_6	313	61		
[BMIM]Tf_2N	298	33		
[HMIM]Tf_2N	298	34	29	10
[HMIM]Tf_2N	313	42	20	8

Solubility and Selectivity Data for CO_2, N_2, CH_4 in ILs

Supported Ionic Liquid 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 (Barrer) and Selectivity Results for [hmim]Tf_2N-Biodyne Membranes

Biodyne® 1 and Biodyne® 2 are two crosslinkable nylon supports

Ionic Liquids for CO_2 - Summary

TRL 2

- 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

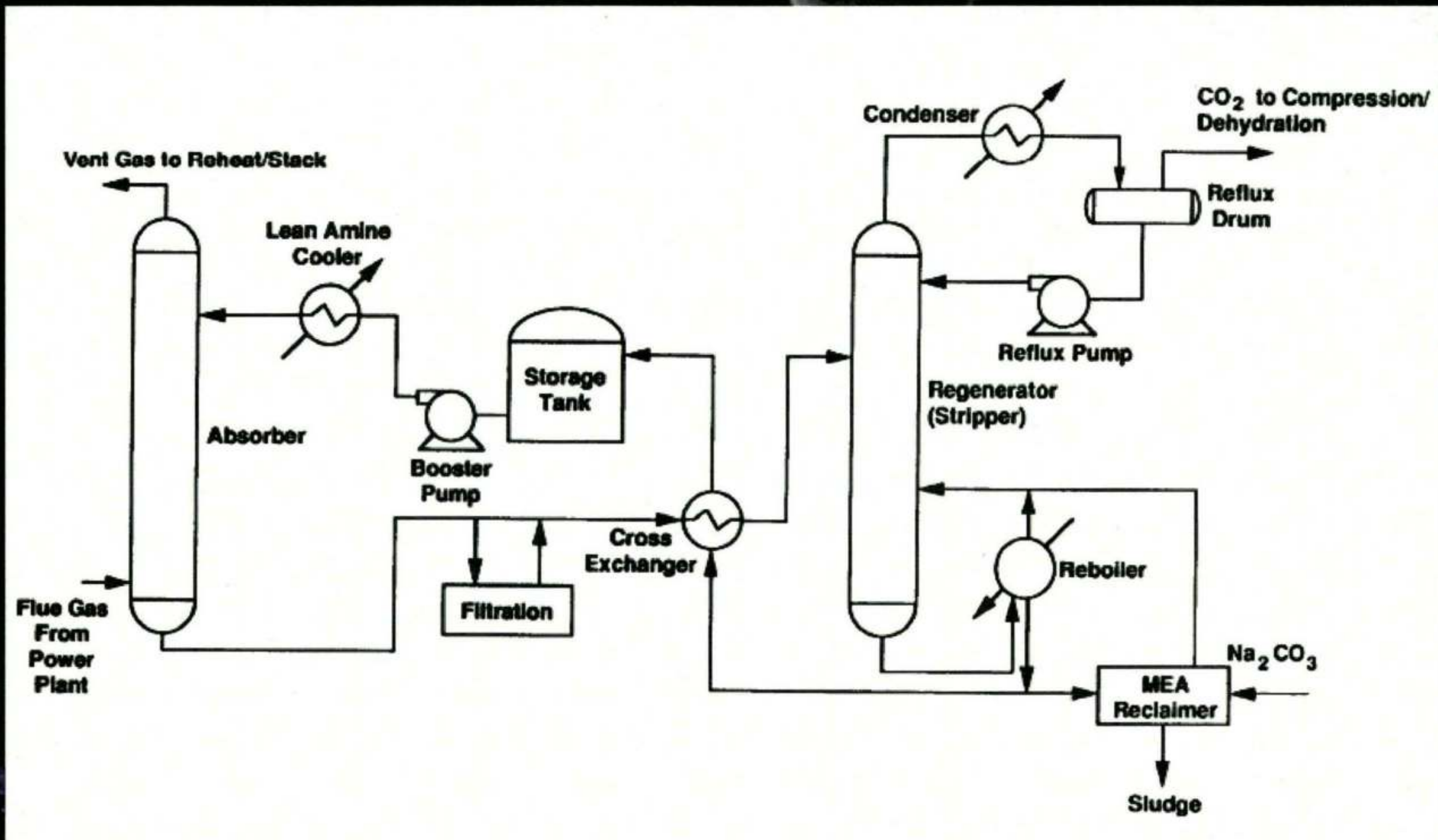
- Some major challenges for ILs that still need to be addressed:
  - Limited commercial availability
  - Limited understanding of the reaction mechanisms and kinetics

- 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

Acid-Base Chemistry

- Most commonly used technology today for low concentration CO_2 capture,
  - Natural gas industry (post-combustion)
- Amine-based solvents such as monoethanolamine (MEA) diethanolamine (DEA), methyldiethanolamine (MDEA), or diisopropanolamine (DIPA).
- $2(R\text{-}NH_2) + H_2O + CO_2 \leftrightarrow (R\text{-}NH_3)_2CO_3$
  - R = amine

Acid-Base Chemistry



Process flow diagram for the amine separation process (Herzog, et al., 2009)

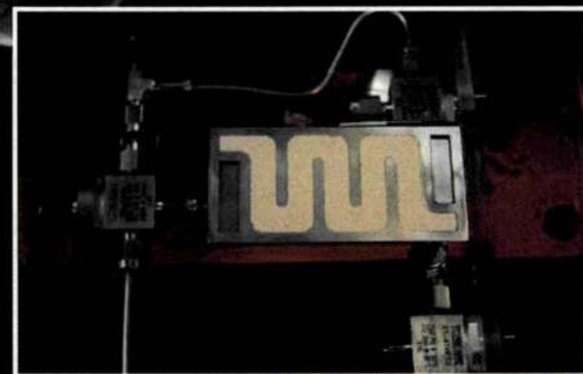
Acid-Base Chemistry - Summary

- Most promising (primarily due to the fact that it is the most mature) is chemical absorption,
  - MEA or through an alkali-metal salt such as potassium carbonate
- Regenerable
- Power concerns
- Requires cold traps to recapture lost water

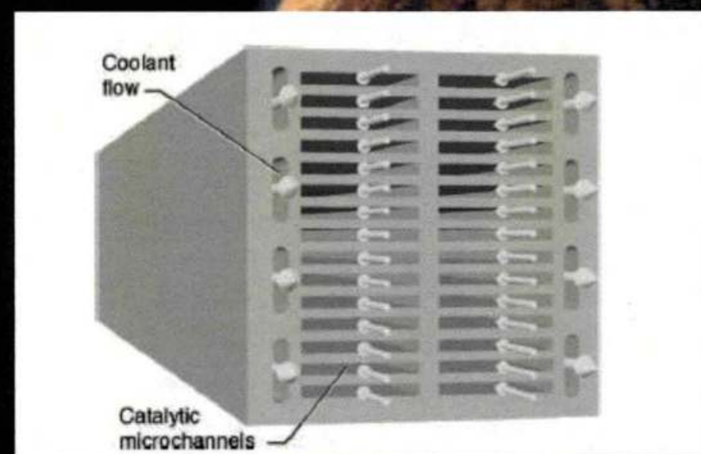
TRL 2

Microchannel Technologies

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



PNNL Microchannel Zeolite CO2 Absorber



TRL 3 PNNL illustration of a section of microchannel reactor.

Preparative Chromatography

- Ability to separate gases of almost any kind simply by changing the stationary phase
- Used in simple binary systems as well as for complex multi-gas mixtures
- Capillary columns are commonly used over packed columns,
  - Increased separation efficiency and lower operating temperatures
  - Ability to handle much larger quantities of analyte because of the larger amount of stationary phase present vs. single layer films coated inside capillary columns

Preparative Chromatography (cont.)

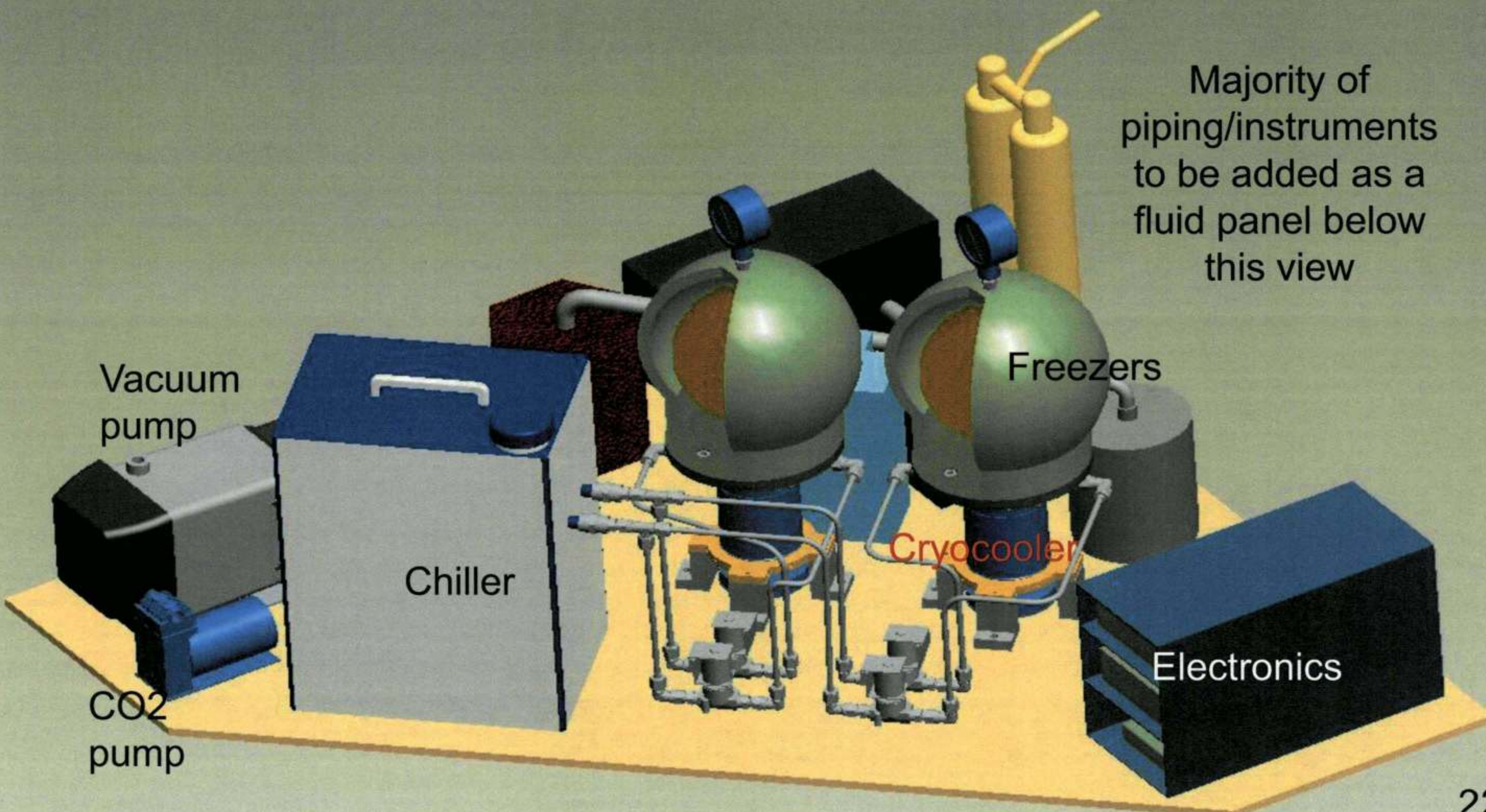
- Molecular sieve 3A commonly used in packed beds
  - Could separate water from methane gas in the products of a Sabatier reactor or carbon monoxide gas in the products of a RWGS reactor
  - May separate buffer gases (nitrogen and argon) downstream from a carbon dioxide freezer
- Molecular sieve 4A used in the purification of argon
- Carbon molecular sieves used in the separation of nitrogen and methane.
- Layered packed bed systems for various combinations of hydrogen, carbon monoxide, methane, nitrogen, and carbon dioxide

Preparative Chromatography - Disadvantages

TRL 2

- Highly temperature and pressure dependent
  - Requires high pressure (up to 250 psia) to drive the adsorption process
  - difficult to provide with low atmospheric pressure on Mars (<0.1 psia)
- Large quantities of gas to process
  - Size of molecular sieve systems can be quite large
- TSA (temperature swing adsorption) systems with large bed diameters requires a carrier gas
- Heating a molecular sieve will desorb captured gas, but it cannot be removed from the bed for storage
  - Vacuum desorption is slow due to diffusion
  - Carrier gas requires another gas separation to separate the carrier gas from the capture gas
- Implementing a molecular sieve gas separation system on Mars is an engineering challenge
- Molecular sieves might work well as a secondary separation when used in conjunction with other methods of gas separation, such as freezing
- <u>As a primary gas separation tool it does not seem practical</u>

CO_2 Freezer Design for Mars ISRU Test at JSC



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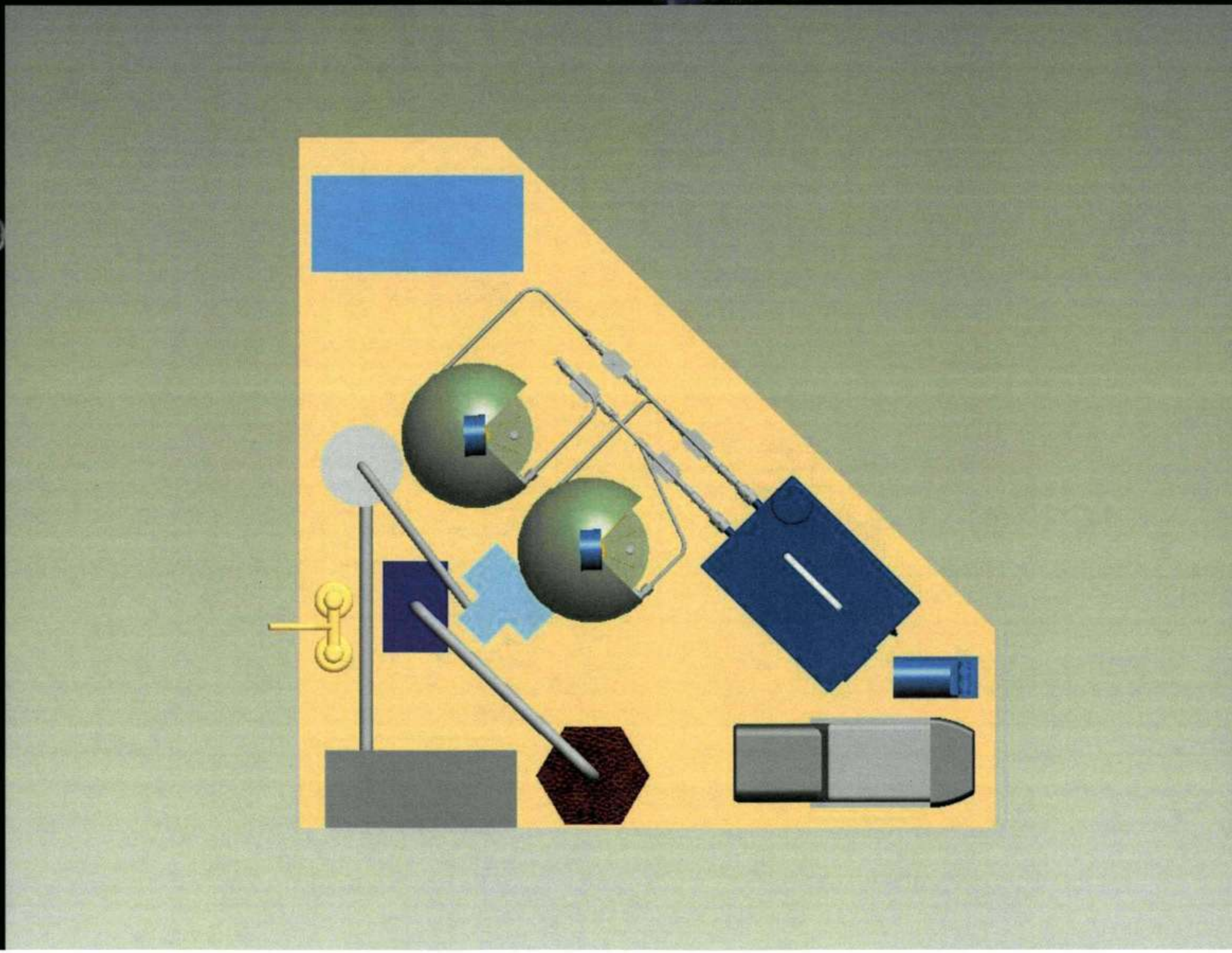

Conclusions

- 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
- Wide range in 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
  - Initial discussion at PTMSS/SRR
  - Full paper at AIAA ASM 2012