

## **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<sub>2</sub> 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<sub>2</sub>-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<sub>2</sub> and other relevant gases.

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# Mars Atmospheric Capture and Gas Separation

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# Outline

- Introduction
- CO<sub>2</sub> Freezing and Liquefaction
- Membranes
- Ionic Liquids
- Acid-Base Chemistry
- Preparative Chromatography and Molecular Sieves
- CO<sub>2</sub> 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



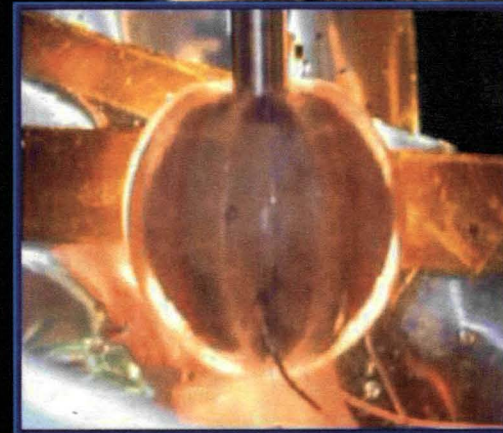
# CO<sub>2</sub> Capture - Freezing

- CO<sub>2</sub> Freezers Look Promising
- CO<sub>2</sub> 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<sub>4</sub>)
- N<sub>2</sub>/Ar was not measured or purified
- Rapp estimated a CO<sub>2</sub> freezer for 0.5 kg/hr needs ~1/3 the power and 11% the mass of a compression pump/membrane CO<sub>2</sub> 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



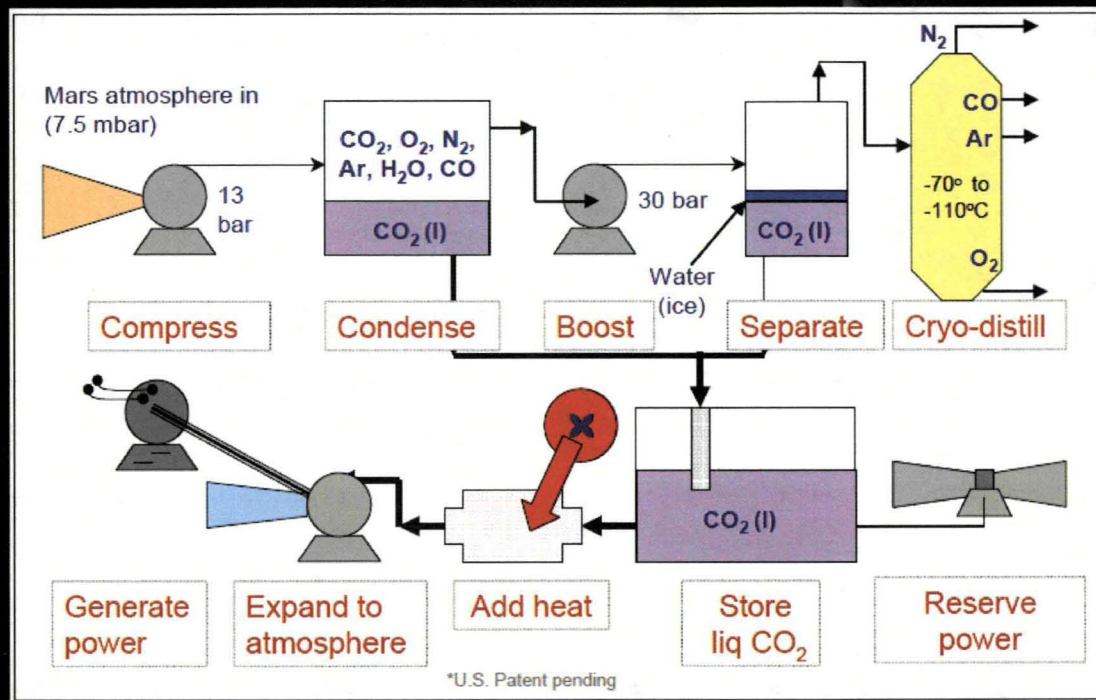
Pioneer MACDOF



Lockheed Cryocooler Freezer 4



# CO<sub>2</sub> Capture - Liquefaction



## Mars Atmosphere Resource Recovery System

TRL 1-2

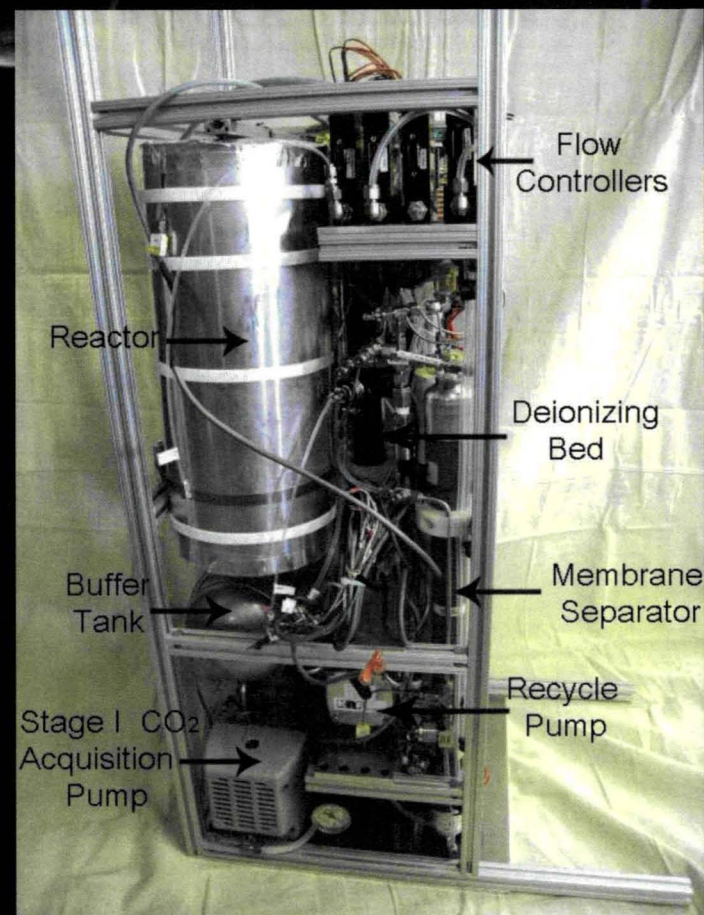
- CO<sub>2</sub> Liquefaction and Collection of Other Gases
- Compress very large volumes of the atmosphere to the high pressures required to liquefy CO<sub>2</sub>
- Geared toward larger scale operations: settlements
- Requires very high power source - nuclear reactor
- Not appropriate for Mars Sample Return or early human exploration



# Alternative Approach - Direct Mars Atmospheric Gas Processing

- ISRU processes (SOE, RWGS, Sabatier) may not require high purity CO<sub>2</sub>.
- Pioneer Astronautics ran a combined RWGS-Sabatier process with CO<sub>2</sub>/N<sub>2</sub>/Ar for 5-continuous days without degradation of catalyst.
- N<sub>2</sub> and Ar were not separated from feed, but were removed during condensation or cryodistillation of products
- Gas separation downstream from CO<sub>2</sub> 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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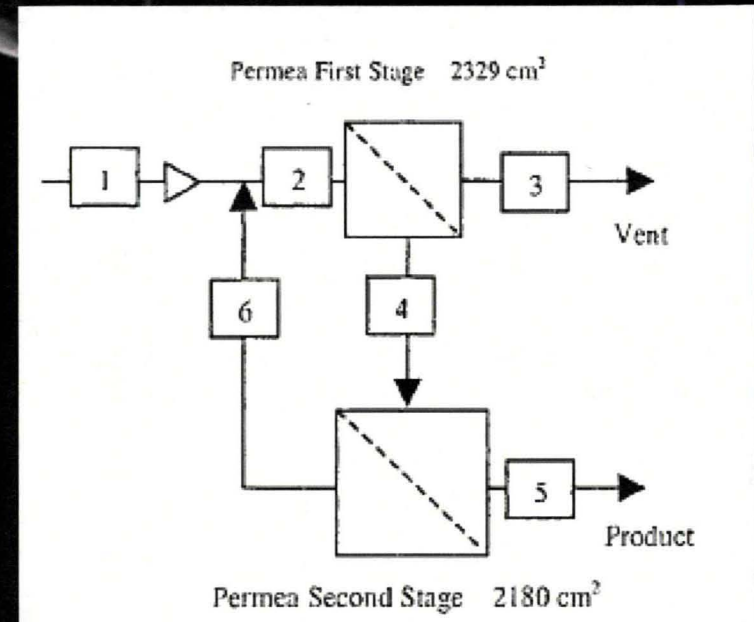
Pioneer IMISPPS



# 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<sub>2</sub>, 26% Ar, and 40% N<sub>2</sub>.
- Predicted product = 6 lpm, 600 ppm CO<sub>2</sub>, 38% Ar and 62% N<sub>2</sub>.
- 47% recovery of the feed.
- Work is needed on Ar/N<sub>2</sub> separation.
  - Ar leads to potential bends issue.

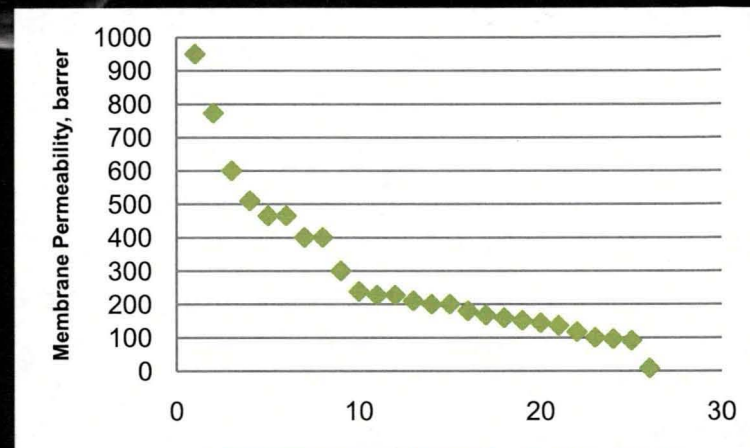
TRL 3-4



Membrane purification  
of feed from the  
capture of CO<sub>2</sub>  
(Parrish, 2002)

# Other Membranes – CO<sub>2</sub> Capture

- Evaluated 28 other membrane materials
  - Top 10 identified
- Mainly polymeric-based: polyacetate, polyimides, polyamides, polysulfone, 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<sub>2</sub> 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 =  $7.5 \times 10^{-14}$  (cm<sup>3</sup>(STP)-cm)/(cm<sup>2</sup>-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<sub>2</sub> 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

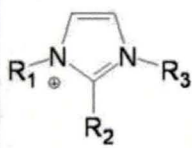
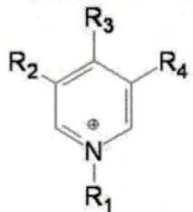
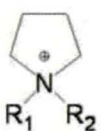
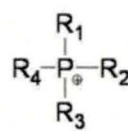
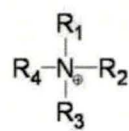
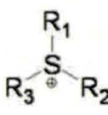
		Calculated	Measured	Calculated	Measured	Calculated	Measured
	Stream	H <sub>2</sub> (slpm)	H <sub>2</sub> (slpm)	CO <sub>2</sub> (slpm)	CO <sub>2</sub> (slpm)	CO (slpm)	CO (slpm)
Base Case	Feed	16.825	16.861	7.56	7.522	2.114	2.116
	Permeate	16.812	16.812	7.547	7.547	1.126	1.126
	Reject	0.013	0.013	0.013	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





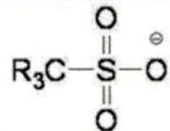
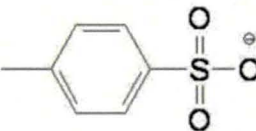
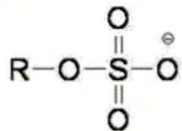
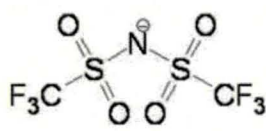
TRL 3-4



# Ionic Liquids for CO<sub>2</sub>

		
Imidazolium	Pyridinium	Pyrrolidinium
		
Phosphonium	Ammonium	Sulfonium

Cations

				
Halide	Nitrate	Tetrafluoro- borate	Hexafluoro- phosphate	Methanesulfonate
				
Tosylate	Alkylsulfate	Bis(trifluoromethyl- sulfonyl)imide		

Anions

Typical cations and anions for ILs

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



# Ionic Liquids for CO<sub>2</sub> Capture

IL	Formula	H (10 °C)	H (25 °C)	H (50 °C)
1-n-butyl-3-methylimidazolium hexafluorophosphate	[bmim]PF <sub>6</sub>	38.7 bar	53.4 bar	81.3 bar
1-n-butyl-2,3-dimethylimidazolium hexafluorophosphate	[bmmim]PF <sub>6</sub>	47.3 bar	61.8 bar	88.5 bar
1-n-butyl-3-methylimidazolium tetrafluoroborate	[bmim]BF <sub>4</sub>	40.8 bar	56.5 bar	88.9 bar
1-n-butyl-2,3-dimethylimidazolium tetrafluoroborate	[bmmim]BF <sub>4</sub>	45.7 bar	61.0 bar	92.2 bar
1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	[emim]TF <sub>2</sub> N	25.3 bar	35.6 bar	51.5 bar
1-ethyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide	[emmim]TF <sub>2</sub> N	28.6 bar	39.6 bar	60.5 bar

## Carbon Dioxide Solubility in Several ILs



# Ionic Liquids for CO<sub>2</sub> Separations

IL	Temperature (K)	H (atm)	CO <sub>2</sub> /N <sub>2</sub>	CO <sub>2</sub> /CH <sub>4</sub>
[EMIM]BF <sub>4</sub>	298	80	89	36
[EMIM]BF <sub>4</sub>	313	100	38	20
[EMIM]dca	313	96	51	21
[EMIM]OTf	313	71	37	17
[EMIM]Tf <sub>2</sub> N	298	37	36	15
[EMIM]Tf <sub>2</sub> N	313	50	24	12
[BMIM]BF <sub>4</sub>	298	56		
[BMIM]BF <sub>4</sub>	313	76		
[BMIM]PF <sub>6</sub>	313	61		
[BMIM]Tf <sub>2</sub> N	298	33		
[HMIM]Tf <sub>2</sub> N	298	34	29	10
[HMIM]Tf <sub>2</sub> N	313	42	20	8

**Solubility and Selectivity Data for  
CO<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub> in ILs**





# Supported Ionic Liquid Membranes

T (°C)	37			50			100		
Support	CO <sub>2</sub>	H <sub>2</sub>	CO <sub>2</sub> /H <sub>2</sub> Selectivity	CO <sub>2</sub>	H <sub>2</sub>	CO <sub>2</sub> /H <sub>2</sub> Selectivity	CO <sub>2</sub>	H <sub>2</sub>	CO <sub>2</sub> /H <sub>2</sub> 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 <sub>2</sub>	H <sub>2</sub>	CO <sub>2</sub> /H <sub>2</sub> Selectivity	CO <sub>2</sub>	H <sub>2</sub>	CO <sub>2</sub> /H <sub>2</sub> Selectivity	CO <sub>2</sub>	H <sub>2</sub>	CO <sub>2</sub> /H <sub>2</sub> 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 <sub>2</sub>	H <sub>2</sub>	CO <sub>2</sub> /H <sub>2</sub> Selectivity
Biodyne® 1	825	567	1.44
Biodyne® 2	1165	918	1.27

**Permeability (Barrer) and Selectivity Results for [hmim]Tf<sub>2</sub>N-Biodyne Membranes**

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

# Ionic Liquids for CO<sub>2</sub> - Summary

- In general, the benefits of ILs that were listed were:  
TRL 2
  - 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

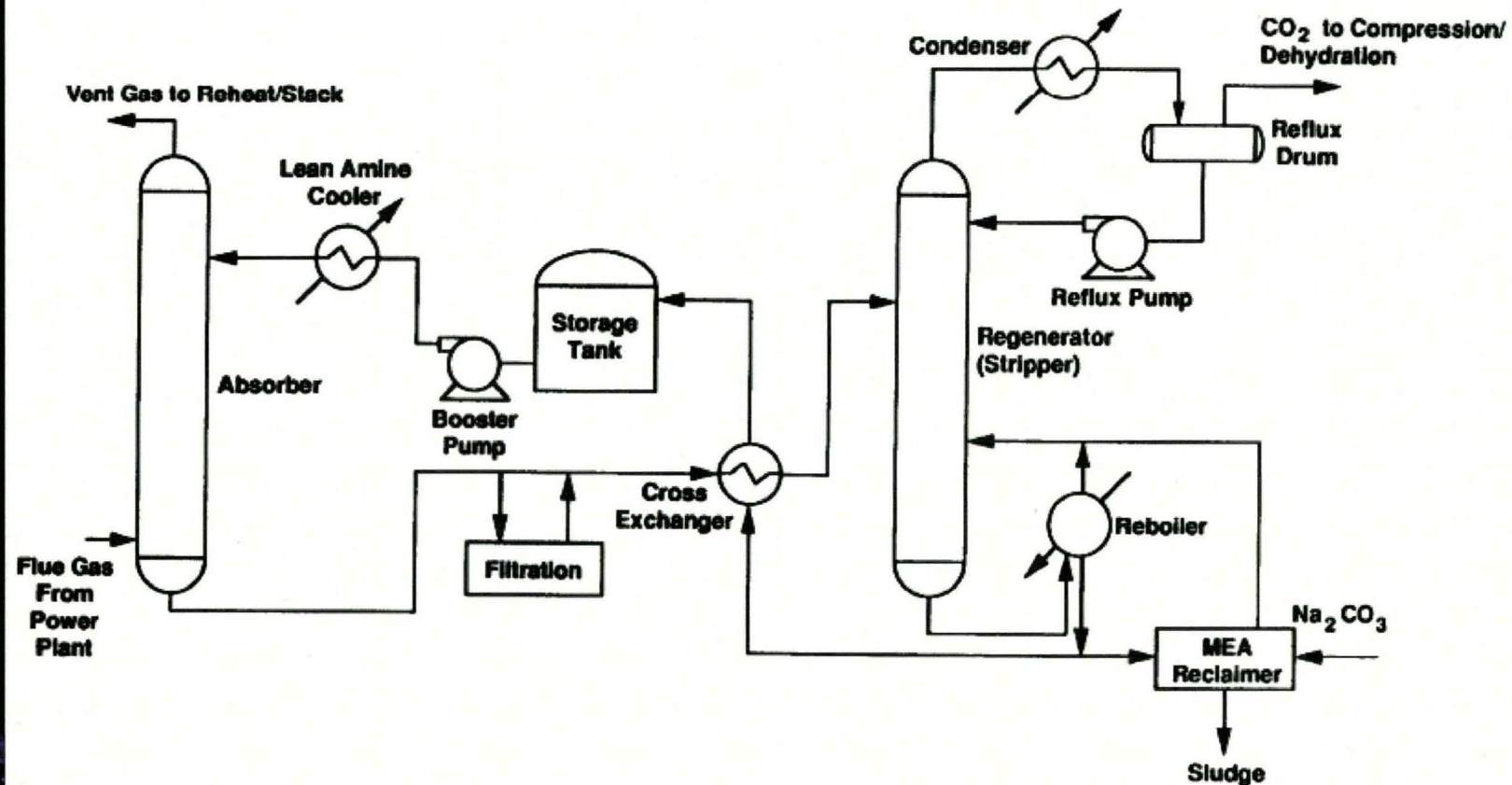


# Acid-Base Chemistry

- Most commonly used technology today for low concentration CO<sub>2</sub> capture,
  - Natural gas industry (post-combustion)
- Amine-based solvents such as monoethanolamine (MEA) diethanolamine (DEA), methyldiethanolamine (MDEA), or diisopropanolamine (DIPA).
- $2(\text{R-NH}_2) + \text{H}_2\text{O} + \text{CO}_2 \leftrightarrow (\text{R-NH}_3)_2\text{CO}_3$ 
  - R = amine



# Acid-Base Chemistry



Process flow diagram for the amine separation process (Herzog, et al., 2009) 16

# 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

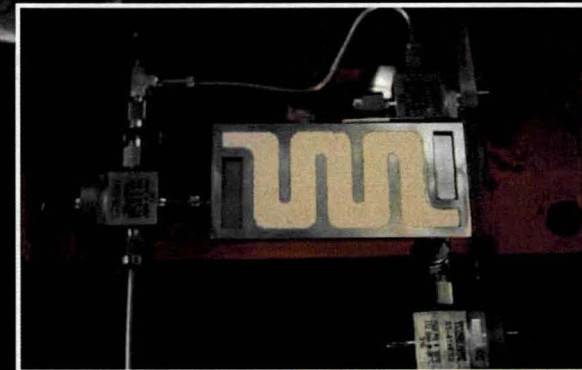


# Microchannel Technologies

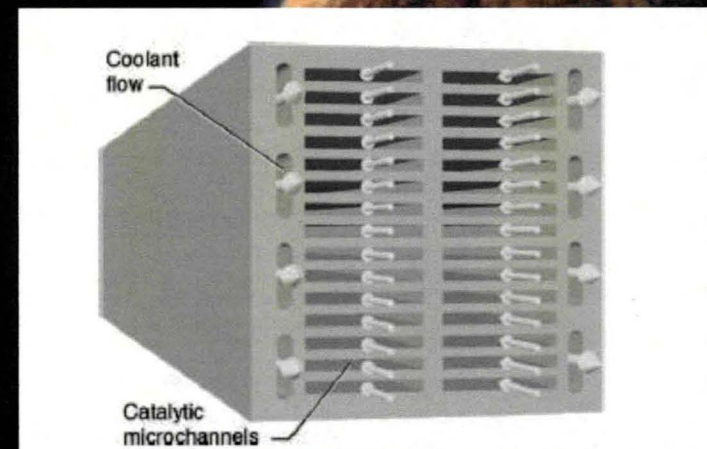
- Microchannel reactors offer:
  - Better temperature control of the catalyst bed
  - Reduce temperature gradients and localized “hot spots”
  - Prevent sintering of a packed bed catalyst
  - Large mass savings over the traditional packed bed reactor design,
  - Penalty of increased pressure drop and increased probability of complete catalyst deactivation.

- Potentially improved CO<sub>2</sub> absorption for concentration
  - Lower mass, volume, and power

- Further development is justified



PNNL Microchannel Zeolite CO<sub>2</sub> 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

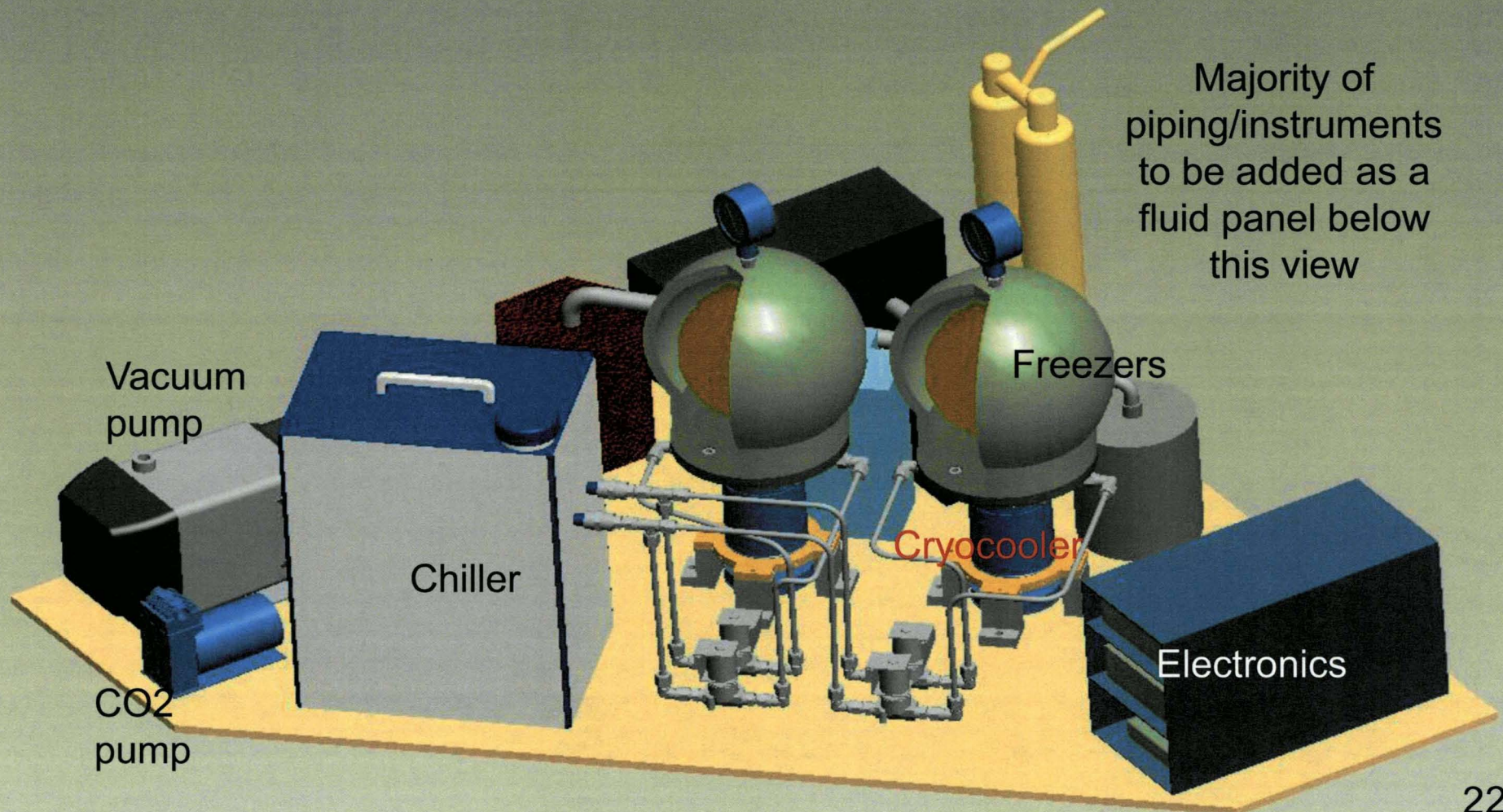
TRL 2

- 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
- As a primary gas separation tool it does not seem practical



# CO<sub>2</sub> Freezer Design for Mars ISRU

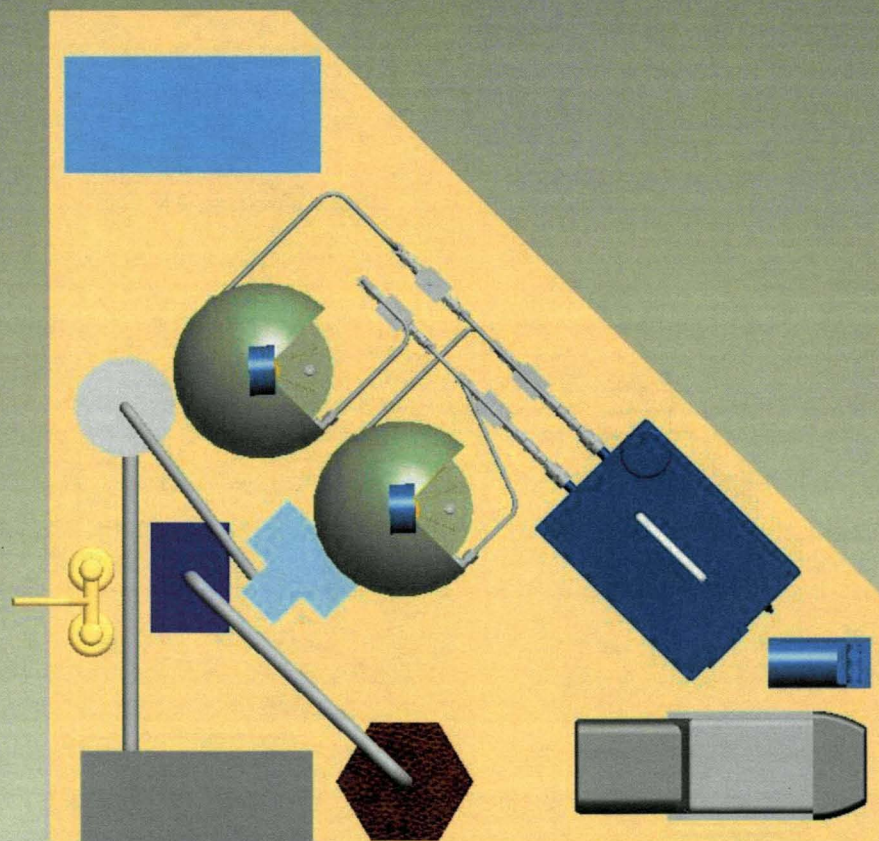
## Test at JSC





# CO<sub>2</sub> Freezer Design for Mars ISRU

## Test at JSC





# 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