The atmosphere of Mars has many resources that can be processed to produce things such as oxygen, fuel, buffer gas, and water for support of human exploration missions. Successful manipulation of these resources is crucial for safe, cost-effective, and self-sufficient long-term human exploration of Mars. In our research, we are developing enabling technologies that require fundamental knowledge of adsorptive gas storage and separation processes. In particular, we are designing and constructing an innovative, low mass, low power separation device to recover carbon dioxide and carbon monoxide for Mars ISRU (in-situ resource utilization). The technology has broad implications for gas storage and separations for gas-solid systems that are ideally suited for reduced gravitational environments. This paper describes our separation process design and experimental procedures and reports results for the separation of \( \text{CO}_2 \) and \( \text{CO} \) by a four-step adsorption cycle.

![Diagram of a system for conversion of the Martian atmosphere to \( \text{O}_2 \) and \( \text{CO} \) at moderate pressures.](image-url)

**Figure 1:** Flow diagram of a system for conversion of the Martian atmosphere to \( \text{O}_2 \) and \( \text{CO} \) at moderate pressures.
As illustrated in Figure 1, this work comprises one-third of an overall process for producing O$_2$ and CO at moderate pressures from the Martian atmosphere. An adsorption compressor, developed by Dr. John E. Finn at NASA Ames Research Center, adsorbs CO$_2$ from the atmosphere and compresses it to a pressure of 1 bar. The CO$_2$ is then passed to a solid oxide electrolysis cell developed by K. R. Sridhar at the University of Arizona. This electrolysis cell makes use of yttria-stabilized zirconia to produce oxygen from the compressed planetary CO$_2$ and will then reject CO and unreacted CO$_2$ in a separate stream. The efficiency of the oxygen-production process is greatly improved if the unreacted CO$_2$ is separated and recycled back into the feed stream. The separation will also have a positive impact on the mass of the adsorption compressor because less CO$_2$ will needed from the atmosphere. Additionally, the CO by-product is a valuable fuel for space exploration and habitation, with applications from fuel cells to production of hydrocarbons and plastics.

Our separation device contains a CO$_2$-selective sorbent such that when the mixture is fed from the electrolyzer, CO$_2$ adsorbs and CO passes through the bed with minimal adsorption. The cycle is illustrated by Figure 2. The mixture is fed at a temperature of 273K. When the bed reaches capacity, it is isolated and heated with no flow at 398K to desorb the CO$_2$. CO$_2$ at high pressure is then allowed to pass to a storage tank at sufficient pressure to feed the electrolyzer. The bed is then cooled back to 273K prior to returning to the feed step. We envision a two-bed system in which one bed is onstream for the feed step while the other is undergoing regeneration and blowdown of CO$_2$.

![Figure 2: Depiction of four-step adsorption cycle between CO$_2$ adsorption isotherms on NaY zeolite.](image)

We have a working prototype and have performed the proposed cycle. We have developed process models and are continuing to optimize the separation. All of these results will be discussed.
Separation of Carbon Monoxide and Carbon Dioxide for Mars ISRU

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ABSTRACT
The atmosphere of Mars has many resources that can be processed to produce useful materials like oxygen, fuel, buffer gas, and water for support of human exploration missions. In this research, we are designing and constructing a low mass, low power separation device to recover carbon dioxide and carbon monoxide for Mars ISRU (in-situ resource utilization). The separation is accomplished by a four-step adsorption process. The technology has broad implications for gas storage and separations for gas-solid systems that are ideally suited for reduced gravitational environments.

Overall Process Description

Adsorption Compressor
The adsorption compressor adsorbs CO₂ from the atmosphere and vents N₂ and Ar. It reaches capacity and is heated to desorb the CO₂, raising the internal pressure. CO₂ then diffuses through the bed with minimal adsorption. CO₂ is then allowed to pass to a storage tank at sufficient pressure to feed the electrolyzer. The bed is then cooled back to 273 K prior to returning to the feed step. We envision a two-bed system in which one bed is on-stream for the feed step while the other is undergoing regeneration and blowdown of CO₂.

Yttria-Stabilized Zirconia Electrolyzer
Dr. K. R. Sridhar
University of Arizona

YSZ Electrolyzer
CO₂ diffuses through the electrode and liberates an oxygen atom through thermal dissociation and electrocatalysis. The oxygen atom acquires two electrons from the cathode to form an oxygen ion. The electric field drives the ion through the electrolyte. The ion transfers its charge to the anode as it reaches the anode-electrolyte interface and combines with another oxygen atom to form O₂, then diffuses out of the anode. CO and unreacted CO₂ will pass to the separation device.

Adsorptive Separation
CO₂ selective sorbent

The adsorption compressor adsorbs CO₂ from the atmosphere and vents N₂ and Ar. It reaches capacity and is heated to desorb the CO₂, raising the internal pressure. CO₂ then diffuses through the bed with minimal adsorption. When the bed reaches capacity, it is isolated and heated with no flow at 398 K to desorb the CO₂. CO₂ is then allowed to pass to a storage tank at sufficient pressure to feed the electrolyzer. The bed is then cooled back to 273 K prior to returning to the feed step. We envision a two-bed system in which one bed is on-stream for the feed step while the other is undergoing regeneration and blowdown of CO₂.

4-step Adsorption Cycle

Experimental Apparatus

The device is heated or cooled by an environmental chamber. Mass flow controllers allow constant feed of the mixture at prescribed rates. A mass flow meter measures the product flow and a pressure controller maintains downstream pressure at setpoint. An additional mass flow controller is used to control the flow to the CO₂ compressor. A gas chromatograph allows analysis of the composition of the product stream. The process is automated by National Instruments LabVIEW software.

CO₂ Breakthrough Curve

CO₂ begins to breakthrough the bed around 1 hour and 10 minutes after the feed step has begun for the first cycle. For the subsequent 2 cycles, CO₂ begins to breakthrough earlier after a feed duration of approximately 1 hour. Before CO₂ breakthrough, we are producing mostly pure helium with small traces of CO₂. We expect similar behavior for a mixture of CO and CO₂ based on binary adsorption measurements.

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Comparison of binary adsorption data with values calculated from multsite Langmuir fits.