SEPARATION OF CARBON MONOXIDE AND CARBON DIOXIDE FOR MARS ISRU – CONCEPTS

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ABSTRACT
Solid oxide electrolysers, such as electrolysis cells utilizing yttria-stabilized zirconia, can produce oxygen from Mars atmospheric carbon dioxide and reject carbon monoxide and unreacted carbon dioxide in a separate stream. The oxygen-production process has been shown to be far more efficient if the high-pressure, unreacted carbon dioxide can be separated and recycled back into the feed stream. Additionally, the mass of the adsorption compressor can be reduced. Also, the carbon monoxide by-product is a valuable fuel for space exploration and habitation, with applications from fuel cells to production of hydrocarbons and plastics.

In our research, we will design, construct, and test an innovative, robust, low mass, low power separation device that can recover carbon dioxide and carbon monoxide for Mars ISRU. Such fundamental process technology, involving gas-solid phase separation in a reduced gravitational environment, will help to enable Human Exploration and Development of Space.

Figure 1. Diagram of system for conversion of the Mars atmosphere to a N₂-Ar mixture, high-pressure CO₂, O₂, and CO.

The separation device will be scaled to operate with a CO₂ sorption compressor and a zirconia electrolysis device built at the NASA Ames Research Center and the University of Arizona,
respectively. Figure 1 is a diagram of the overall system, incorporating the three critical elements of compression, electrolysis, and separation.

For the CO/CO₂ separator, we envision a thermally-driven adsorption-based separation system that combines elements of TSA, PSA, and adsorption compression. One such possible system is shown in Figure 2.

![Four-step adsorption cycle for separation of CO and CO₂. CO is produced at the feed pressure (e.g., 1 bar); CO₂ product is expanded to a pressure determined by the requirements of the zirconia cell. Two beds are needed. The steps are as follows: (1) Feed step: the bed is fed with the CO/CO₂ mixture. The bed contains a CO₂ selective adsorbent, and CO is produced as product. Little CO is adsorbed. (2) Heating step: as the bed is heated, the pressure increases. (3) Blowdown step: CO₂ at high pressure is allowed to pass into a storage tank at a pressure sufficient to feed the zirconia cell. (4) Cooling step: the bed is cooled prior to returning it to the feed step.

Research needs for the design shown in Figure 2 are as follows:
- The best adsorbent for the process must be determined.
- Adsorption isotherms must be measured, both for pure components and mixtures.
- Mathematical modeling must be performed to provide a solid framework for design.
- The separation system must be constructed and tested.
- System integration must be studied.
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Introduction

Solid oxide electrolyzers, such as electrolysis cells utilizing yttria-stabilized zirconia, can produce oxygen from Mars atmospheric carbon dioxide and reject carbon monoxide and unreacted carbon dioxide in a separate stream. The oxygen-production process has been shown to be far more efficient if the high-pressure, unreacted carbon dioxide can be separated and recycled back into the feed stream. Additionally, the mass of the adsorption compressor can be reduced. Also, the carbon monoxide by-product is a valuable fuel for space exploration and habitation, with applications from fuel cells to production of hydrocarbons and plastics.

In our research, we will design, construct, and test an innovative, robust, low mass, low power separation device that can recover carbon dioxide and carbon monoxide for Mars ISRU. Such fundamental process technology, involving gas-solid phase separation in a reduced gravitational environment, will help to enable Human Exploration and Development of Space.
Mars atmosphere: 95% CO₂, 3% N₂, 2% Ar, 0.007 bar

- Adsorption compression (NASA Ames)
  - CO₂ (1 bar)
- CO₂ electrolysis (Arizona)
  - O₂
- CO + CO₂
- CO₂ separation (Vanderbilt)
  - CO
  - CO₂

N₂-Ar
Adsorption Compressors

NASA Ames Research Center
Solid Oxide Electrolysis Cell: Yttria-Stabilized Zirconia (YSZ)

D.C. voltage source

- Cathode
- Anode
- YSZ electrolyte
We envision a thermally-driven adsorption-based separation system that combines elements of TSA, PSA, and adsorption compression. A four step cycle is shown. CO is produced at the feed pressure (e.g., 1 bar); CO\textsubscript{2} product is expanded to a pressure determined by the requirements of the zirconia cell. Two beds are needed.
Cycle Steps & Path

(1) Feed: bed is fed with CO/CO$_2$ mixture. It contains an adsorbent selective to CO$_2$. CO is produced as product. Little CO is adsorbed.

(2) Heating: as the bed is heated, the pressure increases.

(3) Blowdown: CO$_2$ at high pressure is allowed to pass into a storage tank at a pressure sufficient to feed the zirconia cell.

(4) Cooling: the bed is cooled prior to returning it to the feed step.

CO$_2$ isotherms on NaX zeolite (Finn). Path is for cycle between 273 K and 373 K.
Sample Calculations

Basis: 1 kg/day O₂; 50% conversion/pass in YSZ cell; NaX adsorbent; adsorption at 273 K and heating at 373 K (integrated with Martian day and zirconia cell thermal envelope).

From material balance, 2.75 kg/day of CO₂ must be compressed.

Path points (equilibrium loadings and pressures):
- End of feed: loading of CO₂ (at 273 K, 0.5 bar) will be 18 wt %.
- End of blowdown: loading of CO₂ (at 373 K, 1 bar) will be 9 wt %.
- End of cooling: pressure of CO₂ (at 9 wt %, 273 K) will be 10 torr.
  (The product of the feed step will be more than 98% CO.)

Desorbing at higher temperatures will increase the CO product purity. For example, if desorption were at 448 K, the residual loading would be only 3 wt %, giving a residual partial pressure of CO₂ in the feed product stream of only 0.4 torr, corresponding to 99.95% CO in the product.
Calculations show the following:

- Losses of CO\textsubscript{2} will be small. With the 373 K desorption temperature, the CO\textsubscript{2} partial pressure in the CO stream is only 10 torr.

- With 50% conversion in zirconia cell, only about half the CO\textsubscript{2} needs to be compressed by the compressor, compared to a process without the separator. The adsorption compressor and zirconia cell can be smaller.

- The purity of the CO stream can be adjusted by changing the desorption temperature (or the adsorption temperature).

- Although residual CO\textsubscript{2} pressures are small after regeneration, the CO\textsubscript{2} loading is not small, e.g., 9 wt %. (A vacuum step would waste CO\textsubscript{2}).

- Beds of NaX for a process to make 1 kg O\textsubscript{2} and 1.75 kg CO over a 6 hr period would contain 3.8 kg NaX or over a 25 hr period would contain 0.92 kg NaX. Basis: a bed on stream for CO\textsubscript{2} recovery for 30 minutes; 6 wt % CO\textsubscript{2} loading swing on adsorbent (e.g., 9 wt % to 15 wt %).
Design Goals

Design goals for the separator are as follows:

• to permit essentially complete conversion of CO₂ to products O₂ and CO

• to permit essentially complete recovery of CO

• to separate unreacted CO₂ such that it can be recycled back to the zirconia cell
  - this requires a CO₂ product pressure of 1 bar
  - high purity CO₂ in the recycle is not required since the reaction continues to produce CO

• to be able to generate CO product at various purities
Research Needs

Research needs for the design shown are as follows:

- The best adsorbent for the process must be determined.
- Adsorption isotherms must be measured, both for pure components and mixtures.
- Mathematical modeling must be performed to provide a solid framework for design.
- The separation system must be constructed and tested.
- System integration must be studied.