

Dynamic Maintenance of CO₂ Levels in Closed Environments

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ABSTRACT

Carbon dioxide (CO₂) management is critical for all life forms and certainly for all human space-flight missions. CO₂ must be extracted and removed or recycled safely, reliably, and rapidly while maintaining CO₂ levels within allowable limits independent of crew activity. In view of ESM considerations the system should minimize mass, volume, energy and crew maintenance. Such considerations favor regenerable systems.

Our efforts in this direction are focused on a contained liquid membrane design enzyme catalyzed by carbonic anhydrase that exhibits high permeance, ca. 5×10^{-7} moles CO₂ / m² s Pa, very high selectivity vs. nitrogen and oxygen, and is non-responsive to a wide variety of VOCs. Over the last year we have addressed five issues: scale-up, integrated water management, enzyme immobilization, system modeling, and process engineering design. We have developed a membrane element (10 cm X 10 cm X 0.67 cm) capable of removing 0.09 kg/d CO₂ from a 0.5% feed stream. The overall reactor includes a Nafion membrane dehumidifier allowing regulation of return gas humidity level. We have expanded our 1-Dimensional Reactive Transport efforts to introduce enzyme kinetic equations. Finally, we have generated a full-up process engineering design that allows calculation of pressure drops, enthalpy changes, and energy requirements for this isothermal, catalyzed reactor design.

INTRODUCTION

The objective of this project is to create an integrated system for air revitalization and temperature/humidity control that is applicable to spaceships, space suits, planetary bases, and surface rovers. The key to this objective is the air revitalization component. Air

revitalization deals with both management of carbon dioxide (CO₂) and control of volatile organic compounds (VOCs). Our work focuses on the former. As is always the case with space hardware it has to have low mass, small volume, low power, high reliability, low maintenance and require little in the way of consumables. Of the many candidate methods for CO₂ separation historically only two have achieved flight status – molecular sieves and metal hydroxides. Many other methods have been studied for use alone or with another, generally physicochemical, CO₂ removal system.

At present, the principal CO₂ capture technologies applied or pursued under Advanced Life Support (ALS) to manage respiratory CO₂ fall under three categories: biological approaches, physical adsorption materials, and materials used for chemical absorption. Biological approaches involve the use of algae and higher order plants to capture the CO₂. These systems are difficult to maintain and are not flexible in responding to changing loads. Physical adsorption materials include devices such as molecular sieves and activated carbons. Chemical absorbers fall into two categories: Non-regenerable materials such as metal hydroxides (e.g., lithium hydroxide – LiOH) and regenerable materials that include metal oxides (e.g., silver oxide – Ag₂O) (1) and solid and liquid amines (2).

LiOH scrubbers have been used extensively on nuclear submarines and past space missions including the Apollo program. LiOH spontaneously and exothermically reacts with CO₂ to produce solid lithium carbonate (Li₂CO₃). However, the reaction chemistry is such that regenerating LiOH is difficult; this makes LiOH scrubbers non-regenerable. The technique is less than ideal for a prolonged mission where scrubbers for hundreds of EVAs would have to be brought from Earth.

Metal oxides have also been used in past missions and are being used in the current spacesuit (EMU – extravehicular mobility unit). This system relies on the formation of MCO_3 as a final product. However, the energy required to calcine the CO_2 is low enough that an onboard oven can be used as a regeneration device. While reusable, the heavy metal substrates result in appreciable increases in system mass. This problem is less significant when the system is deployed in micro-gravity. However, the size increase required makes the system impractical for long duration EVAs (extravehicular activity) (1). For this, as well as most other systems, the adsorption or absorption step is readily accomplished. The desorption step is generally energy dependent and tends to limit both the rate of production and the quality of the product.

APPROACH

In contrast to the previously described methods, we have developed a novel, enzyme-based, contained liquid membrane (EBCLM) reactor to capture CO_2 from the respiratory gas stream and to enrich it for disposal, distribution to a plant growth chamber or for delivery to a CO_2 reduction apparatus.

The enzyme carbonic anhydrase (CA – E.C. 4.2.1.1), used as the CO_2 facilitating agent, is the fastest CO_2 catalyst known. It accelerates the conversion of CO_2 to bicarbonate and the converse by about 2000-fold vs. the uncatalyzed condition. The membrane design is such that there are three steps to the extraction-transfer process. In the first, CO_2 is converted to bicarbonate at the feed side gas-liquid interface. Second, the bicarbonate either diffuses or is convected across the membrane. Third, at the sweep side gas-liquid interface the enzyme converts bicarbonate to CO_2 which then evolves into the sweep stream exiting the reactor as the permeate. While non-reactive gases will dissolve cross the membrane their rate and magnitude is severely limited by dissolution kinetics and solubility limits (3-6). The thermal stability of the enzyme is quite robust (it denatures at $\sim 65^\circ\text{C}$), and it has been shown that immobilized CA can enhance its stability (7).

The use of CA provides us with a regenerable method for removing CO_2 that is kinetically driven in contrast to traditional thermodynamically driven methods seen in other physical and chemical adsorption devices. Our approach also allows us to integrate air revitalization and temperature/humidity control systems towards a simpler, smaller, lighter and more robust device. A single platform applicable to all components of space activities will allow us to reduce consumables and simplify servicing.

At both reactor level and at system level, this is a very complicated process with large numbers of interdependent variables. The last makes it impossible, within a reasonable time, to optimize a set of system variables using experimental methods alone. A key

guiding approach is systems analysis and sophisticated modeling. Modern computer cost/capability matches along with ever more sophisticated software makes the simulation approach more readily available, more approachable and more desirable. Simulations are however, inherently limited by our current understanding of system components and the underlying assumptions of their operation. The utility of modeling can only be validated by experimentation.

To achieve our goals we have developed sophisticated simulation models, which include chemistry components within the CLM and mass transport across the liquid membrane. Chemistry and transport are inherently an integrated system.

There are several chemical reactions associated with CO_2 -CLM (water + salt), and over 8 major chemical species involved in these reactions as well as transport process. It becomes even more complicated with the presence of CA (isozyme α -II). We have explored mechanisms of these chemical reactions, with or without CA enzyme, and implemented them in the simulations.

The overall mass transport across the liquid membrane and hollow fiber membranes composed of the following resistances illustrated in Figure 1:

1. feed-side gas boundary layer resistance
2. feed-side hollow fiber membrane resistance
3. liquid film resistance at feed fiber membrane-CLM interface
4. resistance across the liquid membrane
5. liquid film resistance at CLM-sweep fiber membrane interface
6. sweep-side hollow fiber membrane resistance
7. sweep-side gas boundary layer resistance

We have estimated mass transfer coefficients in the gas phase and membrane for both the feed-side and the sweep-side using available mass transfer correlations (8). Mass transfer resistance is small in the gas phase as compared to membrane and liquid phase. Due to very fine pores in the membrane wall, Knudsen diffusion is operative and contributes to the effective membrane diffusivity. Based upon experimental conditions, mass transfer coefficients in the membranes are estimated to be about 0.02 m/s.

The mass transport process in the CLM is more complicated. Most of the chemical species in the CLM are ionized. Differences in their diffusivities results in the formation of a diffusion potential across the liquid film necessitating the use of the Nernst-Planck equation. System constraints include electroneutrality and zero current flow. First, all of the chemical reactions are assumed to be at equilibrium resulting in the maximum mass transport possible. Then, we used the chemical reaction rate expressions to simulate real transport process in the CLM which are not proceeding at chemical equilibrium.

The governing mass transport equation is given as (9):

$$\frac{d^2 c_{CO_2}}{dx^2} = \alpha_1 + \alpha_2 \quad (1)$$

Where

$$\alpha_1 = \frac{k_1 L^2}{D_{CO_2}} \left(c - \frac{2K_3}{K_2 K_W [M^+] - c_{HCO_3^-}} \right) \left(1 + \frac{k_2 K_W [M^+] - c_{HCO_3^-}}{2k_1 K_3 c_{HCO_3^-}} \right) \quad (2)$$

And

$$\alpha_2 = \frac{k_p [E]_0 L^2}{D_{CO_2} K_{MS}} * \frac{c_{CO_2} - \frac{2K_3}{K_2 K_W [M^+] - c_{HCO_3^-}}}{\left(1 + \frac{c_{CO_2}}{K_{MS}} \right) \left(1 + \frac{c_{HCO_3^-}}{K_{MI}} \right) \left(1 + \frac{2K_3}{K_H [M^+] - c_{HCO_3^-}} \right)} \quad (3)$$

α_1 represents the uncatalyzed reaction rate, and α_2 represents CA-catalyzed reaction rate. Different expression of α_2 was also available in the literature (10).

The Finite Difference Method was used to solve the above equations. All programs were written and solved using Matlab.

RESULTS

We can model the integration of the CO₂ reactor and the temperature/humidity control systems with Process Engineering. The Process Engineering modeling helped to define the heat exchanger network, water transport requirements, pressure drop limitations, enthalpy changes, mass transport thermal events, vacuum levels for optimum recovery and energy utilization. Comparing the model to tested results from the test modules is necessary to perfect the process model further. Preliminary results show that it is reasonable to achieve CO₂ concentrations in the supply air below 0.1%. Using this reactor as temperature control device in addition to the CO₂ removal activities further improves the simplicity of the system for EVA and varying the vacuum level of the sweep can be effectively used to respond to varying heat loads in response to the astronaut activity. Integration of these components together also provided the basis for keeping the dew point of return gas to the astronaut down to 8°C. A sample system design can be seen in Figure 2.

Sample calculated results with no external mass transfer resistance (gas-phase CO₂ concentration at gas-liquid interface is equal to that in the bulk gas) are shown in Table 1. In our simulations, no inhibition to CA-catalyzed reaction was considered except HCO₃⁻. Some ions are strong inhibitors to the reaction, and CA-catalyzed reaction rates will decrease to some extent. Thus the actual CO₂ flux, permeance and facilitation factors should be lower than predicted at the same simulation conditions. We will consider the effect of inhibitors in our future work. For the case with external mass transfer

resistance, Figure 3 shows normalized concentration profile across the CLM under conditions as given in the plot. For the feed containing 1% CO₂, the CO₂ permeance is 2.42*10⁻⁷ mol/m² s Pa, and facilitation factor is 151.0.

CONCLUSION

By modeling air streams of different CO₂ composition and calculating the permeance that is expected with different CLM compositions, we can optimize selection of CLM and performance of the EBCLM reactor. The best of the modeled situations can be implemented and tested in bench-top devices. This will not only validate our modeling efforts but can also provide real world data for further development towards a final device.

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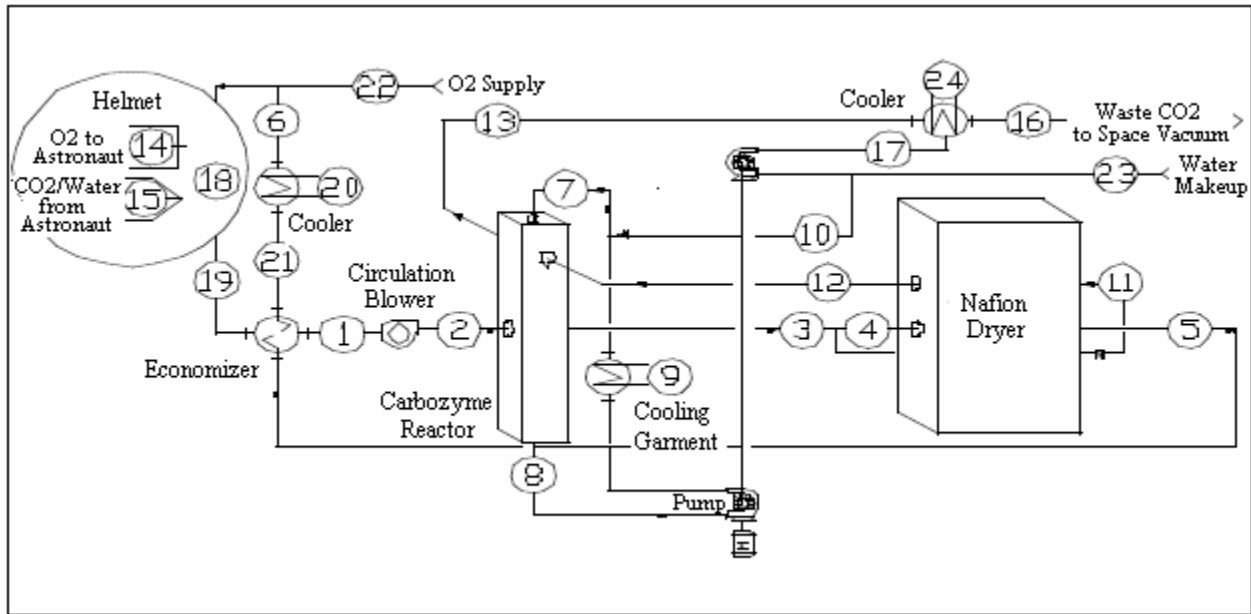


Figure 2: EVA Air Revitalization and Temperature/Humidity Control System Design

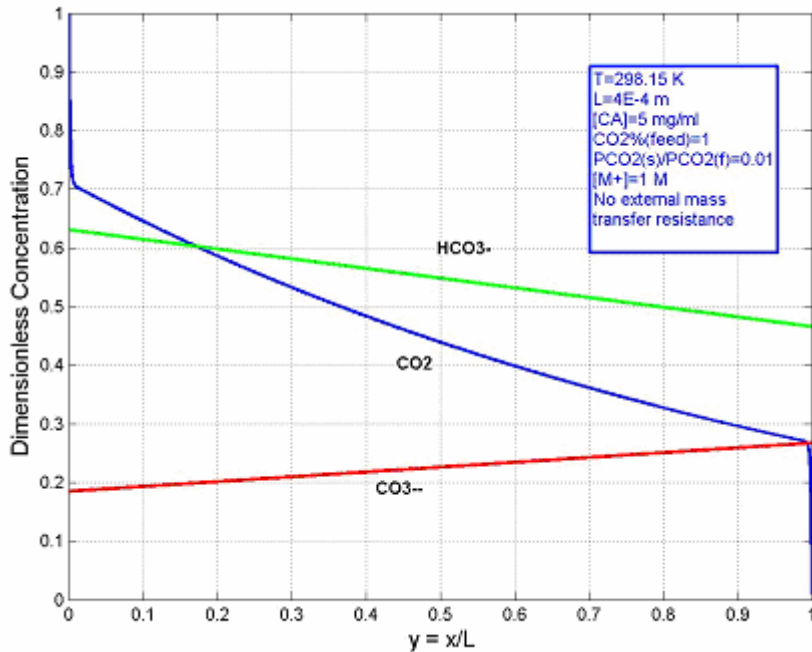


Figure 3: Normalized concentration profile of solubilized carbon dioxide and its ions across the CLM

Table 1. Calculated results for CO_2 transport through a CLM containing CA. The two different runs calculate Flux, Permeance, and the facilitation factor for different amounts of CO_2 in the feed stream.

	Parameters	Simulation Run #1	Simulation Run #2
Input	Temperature (K)	298.15	298.15
	CLM Thickness (m)	$4 \cdot 10^{-4}$	$4 \cdot 10^{-4}$
	[E] ₀ , mg/ml	5	5
	CO ₂ % (f)	1	5
	P _s /P _f	0.01	0.01
Output	CO ₂ Flux (mol/m ² s)	$2.425 \cdot 10^{-4}$	$3.24 \cdot 10^{-4}$
	CO ₂ Permeance (mol/m ² s Pa)	$2.42 \cdot 10^{-7}$	$7.1 \cdot 10^{-8}$
	Facilitation Factor	151.0	44.4