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Gabriela Cesar

Debraliz Isaac-Aragones

David M. Warsinger

Justin Weibel

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Gabriela Cesar[a], Debraliz Isaac-Aragones, David E. M. Warsinger, Justin Weibel[b]

[a]*Davidson School of Chemical Engineering, Purdue University, West Lafayette, IN 47906.*
[b]*School of Mechanical Engineering, Purdue University, West Lafayette, IN 47906.*

## Abstract

Recently, NASA's ultimate goal has been to launch a crewed Mars mission. However, the current system used for carbon dioxide ($CO_2$) removal in air revitalization in the International Space Station (ISS) is not equipped to handle beyond low-earth-orbit missions. The Carbon Dioxide Removal Assembly (CDRA) is a complex system that relies heavily on sorbent materials and faces challenges in reliability, energy efficiency, and material degradation. Although the CDRA has operated well in the ISS for the past two decades, health effects from high $CO_2$ levels are amongst the most common complaints from and challenges for astronauts. Recent developments in membrane technology prove to be a promising alternative to sorbent-based systems for $CO_2$ removal. Maintaining high selectivity for $CO_2$ with a reasonable permeability, at such low partial pressures and in the presence of water, is among the main challenges of using membranes in this application. In this work, we have created a membrane-based model with appropriate conditions to identify the membrane technology for this application. We expect to determine a working range of critical parameters such as permeability, selectivity, and membrane area for successful $CO_2$ separation. We will also be comparing the thermodynamic efficiency of a membrane-based process to that of the CDRA to pin-point areas of improvement.

*Keywords:*
Membranes, carbon dioxide removal, modeling, gas separation

## 1. Background and Introduction

Currently at the International Space Station astronauts live in somewhat similar conditions to people down on Earth, especially when it comes to the air they breathe. To create a livable environment for humans in space, research efforts have been focused on carbon dioxide ($CO_2$) removal systems. Humans exhale about 5 percent by volume of carbon dioxide, but do not consume any of this gas while inhaling. Meanwhile, more than 1 percent of $CO_2$ in the air can start to cause health problems, such as dizziness, dullness and increased pulse rates (1). The current system used by NASA is the Carbon Dioxide Removal Assembly (CDRA), and although it fulfills its purpose, it is not the most reliable nor efficient system. Recent studies have found that membranes might be a great alternative for this task, since they can easily separate gases while being energy efficient (2). The objective of this work is to test if membranes possess the characteristics needed for an air revitalization system that can support a crewed deep space exploration mission, such as going to Mars.

### *1.1. NASA's Carbon Dioxide Removal Assembly:*

The current $CO_2$ removal system used by NASA is the CDRA, which comprises two sets of a desiccant and adsorbent beds, a blower, a pre-cooler and a pump as can be seen in Figure 1 (3). The machine operates in half cycles to allow the beds to thermally regenerate and desorb, while the other half of the system is actually doing the removal. After the gas mixture enters the machine, it goes through a dessicant bed (orange in Figure 1) where the water vapor is adsorbed. Then it passes through the pre-cooler and blower to condition the dry air before entering the zeolite sorbent bed (green in Figure 1) where the $CO_2$ removal occurs through molecular sieve (3).

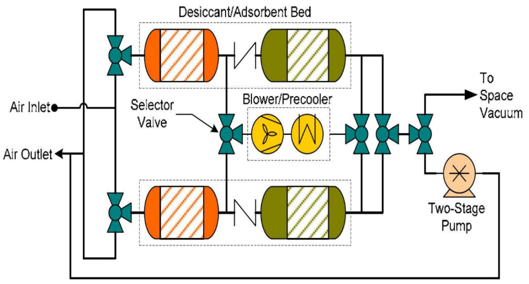

Figure 1: Four Bed Molecular Sieve CDRA schematic. Adapted from (3).

#### *1.1.1. CDRA limitations*

There are three main challenges that CDRA faces. First it is extremely unreliable. There are currently two CDRA devices aboard the ISS. Only one is operated, while the other is kept on standby as a preventive measure in case a system failure occurs (4). Second, the system is energetically inefficient. Having to cool the dried air before removing the $CO_2$ and having to heat it up again to obtain a better separation requires a great amount of energy (5). The sorbent beds must be thermally regenerated, which also requires an energy supply. Lastly, after adsorbing the $CO_2$, the gas is vented out to space rather than being reused

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in the ISS. A good use of the separated $CO_2$ would be the production of water through a Sabatier Process (4; 6). In addition to these main points, the $CO_2$ removal done by the CDRA is not enough to keep the partial pressure of this gas at desirable levels for the astronauts. As stated by astronaut Scott Kelly, the $CO_2$ partial pressures at the ISS can vary between 2 and 4 mmHg, but when closer to the higher boundary, the effects of such a high concentration of this gas in the air can include a sensation of burning eyes, congestion and heavy headaches (4).

### *1.2. Evaluation Criteria for $CO_2$ Removal System*

In spite of the CDRA's many limitations and complications, it has set the basis for any new technology that were to replace it. Some of the evaluation criteria set by NASA, using the CDRA as reference, refers to the system's mass, volume, power requirement, $CO_2$ removal performance, reliability, among many others. Some of the quantitative parameters that new developing technologies must aim for are: removal of 4.16kg/day of $CO_2$, while maintaining its partial pressure at 2mmHg; weigh 450 lbs or less; consume an average power of approximately 1000 Watts; and have a total volume of no more than 19 $ft^3$ (0.54 $m^3$)(7). In addition to that, the system must be able to separate the $CO_2$ from the cabin air, return the removed water back to the airstream, and deliver a steady state stream of the purified carbon dioxide. Lastly, NASA is looking for a system that can be used in a future Mars mission, and therefore it must be extremely reliable and need as little maintenance as possible (7). A summary of the main $CO_2$ removal technology criteria defined by NASA can be seen in table 1.

Table 1: Summary of Criteria for $CO_2$ Removal Technology

| Criteria | Value |
|---|---|
| Maximum Mass | 450 lbs |
| Average Power | 1000 Watts |
| Maximum Volume | 19 $ft^3$ |
| $CO_2$ Removal Rate | 4.16 kg/day |

### *1.3. Review of current $CO_2$ removal technologies being developed:*

Since 2018, one of NASA's primary goals has been developing more reliable and long-lasting $CO_2$ removal devices that could eventually help in a future Mars mission (8). Some of NASA's funded spacecraft $CO_2$ removal systems include the Mini-$CO_2$ Scrubber, a microfluidic separation unit and the Thermal Amine Scrubber, which uses desiccant and sorbent beds hardware to remove $CO_2$ from the air. These technologies are still in the development phase and have not yet been implemented for actual use. Another promising technology being developed is the Carbon Dioxide Removal by Ionic Liquid Sorbent (CDRILS). It is an innovative system that uses ionic liquid sorbents, instead of a solid desiccant bed or a membrane for the gas separation. It shows numerous benefits compared to other systems with the same functionality. Ionic liquids have negligible vapor pressure, they eliminate odors and reduce the likelihood of contaminating the purified air and downstream systems since they are non-toxic. The CDRILS was originally designed for submarines over a decade ago, and it is still being used today for its reliability as well as efficient use of power, weight and volume (8).

In addition to the technologies listed above, there are some membrane based technologies that have a similar function to the CDRA .For example, Electrochemical Membranes are made of a thin film material with an ionic liquid and a chemical carrier and can separate $CO_2$ from a feed gas without having to remove the water first (9). Supported Liquid Membranes (SLM),which consist of porous membranes filled with ionic liquids that separate the gas through a diffusion process (10). Finally, Extracorporeal Membrane Oxygenation (ECMO), a membrane system that helps remove $CO_2$ as well as replace some $O_2$ from the blood stream by a diffusion process (11).

## 2. Overview of Membranes

An alternative method for removing carbon dioxide from the cabin would be using a membrane to do the $CO_2/H_2O/air$ separation instead of sorbents. Membranes are thin layers that have selective permeability, allowing it to separate a compound from another as can be seen of Figure 2 (12). There are many types of membranes with different sizes, shapes and functionalities. One broad category is inorganic membranes, which include membranes made of materials such as ceramic, carbon, silica, and zeolite. This type of membranes can be used for liquid and gas separations, is thermally stable, but has high production cost (13). On the other hand, we have organic, or polymeric membranes, which are a better option for gas separation, especially for this application. Organic membranes usually have lower cost and they work well when 100 percent purity is not essential (14). Additionally, organic membranes have high flexibility and high selectivity for gases. Within organic membranes we still find subcategories, such as porous versus non-porous and glassy versus rubbery. Current studies have shown that all these of membranes can be utilized for gas separation, although glassy polymer membranes show better selectivity while non-porous ones have higher efficiency (15). Finally, a membrane system can have continuous operation, as opposed to CDRA's batch process, and can be mechanically simpler, since there is no need for blowers and pre-coolers (9). Ideally the membrane would also be able to separate the $CO_2$ without having to take the humidity out of the feed gas first. This would make an even more efficient system as the separation would be done in only one step.

### *2.1. Membrane Performance Characteristics*

To optimally select a membrane fit for this task, we must first understand which variables and parameters affect the efficiency of a membrane. The most frequent criteria used when evaluating membrane effectiveness are permeability and selectivity. Permeability is a material dependent property that measures how much a compound permeates through the membrane in SI units of $mol * m * m^{-2} * s^{-1} * Pa^{-1}$, but often expressed in units of Barrer [ 1 Barrer = $3.35*10^{-16}$ $mol*m*m^{-2}*s^{-1}*Pa^{-1}$]

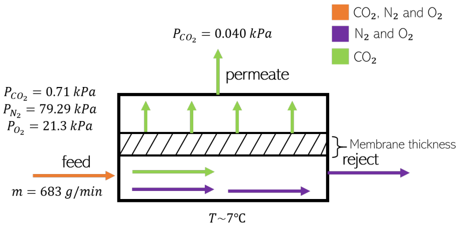

Figure 2: Membrane schematic for $CO_2$ separation under ISS operating conditions.

(15). Selectivity refers to how a membrane has a preference in letting some compounds permeate compared to others, and it is measured as the ratio between the permeabilities of two compounds (15).

The ideal membrane would have both high selectivity and permeability; however, these parameters are inversely proportional. For this reason, scientists have to settle for having either a high selectivity and only a moderate permeability, or vice-versa. However, recent studies have shown that the addition of nanofillers in the membrane fabrication can help increase the its permeability (16; 17). Some other properties that are essential in making a membrane a good $CO_2$ separator include being thermally and chemically stable, having a high $CO_2/N_2$ selectivity and being resistant to ageing and plasticization phenomena (18).

Additionally, membranes used for gas separation have found limited use in air revitalization due to the challenge of separating $CO_2$ at very low partial pressures, which is the case at the ISS (values around 700 Pa). The objective of this work is to provide a modeling framework that translates membrane characteristics, selectivity and permeability, into the membrane size needed for operation at the flow rate at the ISS.

## 3. Methods

### 3.1. Modeling Background

Using the solution-diffusion model, we estimated the flux and membrane area needed to successfully separate the carbon dioxide from the rest of the feed gas under CDRA operational conditions, as seen in Figure 2 (6). For simplicity, we also assumed the humidity in the air flow to be negligible.

In order to have a more accurate model, we first decided what type of membrane we would be working with, since gas diffusion vastly varies from a one type of membrane to another. We selected polymer membranes because scientists have seen the most success in gas separation applications using this type of membrane (15). More specifically we worked with dense/non-porous membranes (as seen in Figure 3) since they provide high selectivity at low transport rates (19). This model allowed us to calculate the $CO_2$ flux based on the permeability of the membrane material, the pressure difference across the membrane and the membrane thickness.

### 3.2. Data and Conditions

We collected permeability values ($R$) for multiple dense polymeric membranes from the literature (20), as can be seen in Table 2. A range of membrane thicknesses ($l$) from 0.1 to 0.5$\mu$m was also selected from literature (21).

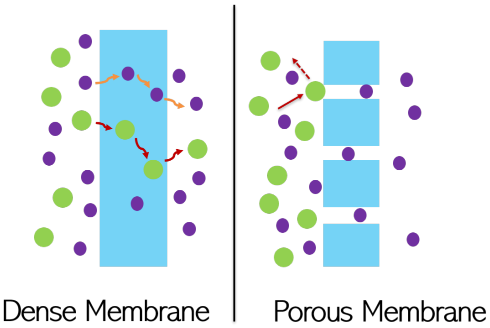

Figure 3: Difference between dense and porous polymeric membranes.

Table 2: Permeability values for different dense polymeric membranes (20)

| Polymer | $R_{CO_2}$ [Barrer] |
|---|---|
| Polyethylene | 17.2 |
| Polystryrene | 12.4 |
| Polycarbonate | 6.8 |
| Polysulfone | 5.6 |
| PMDA-ODA polymide | 2.7 |

To calculate the $CO_2$ flux ($J$) through the membrane we used equation 1, where $p_{in}$ is the gas pressure in the feed side and $p_{out}$ is the gas pressure in the permeate side. We assumed humidity in the air flow to be negligible for simplicity of the calculations.

$$J = \frac{R * (p_{in} - p_{out})}{l} \tag{1}$$

To calculate the minimum membrane area ($A$) necessary for a certain gas flux we used equation 2, where $J$ is gas flux and $n$ is molar flow rate.

$$A = \frac{n}{J} \tag{2}$$

## 4. Results and Discussion

Our results can be seen in figures 4 and 5 and they show the minimum membrane area necessary to provide a certain $CO_2$ flux for a specific membrane material and thickness.

To identify the membrane area needed, select a membrane material and thickness and determine the $CO_2$ flux. For example, for a Polyethylene membrane with a thickness of 0.25$\mu m$ the corresponding flux would be around 0.015 $mol/m^2$*s. Then, using the graph in Figure 5 find the minimum membrane area that corresponds to the flux needed. In this example, a membrane area of 17 $m^2$ would be needed.

On the other hand, if there is limited space and a maximum membrane area, you can determine the minimum thickness the membrane must have to achieve the necessary $CO_2$ flux. To do this just follow the reverse steps from above.

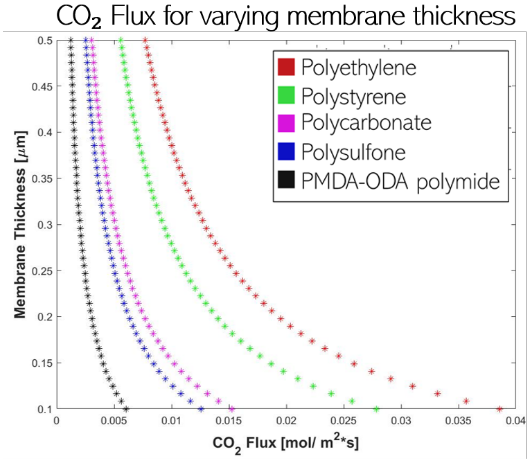

Figure 4: Different $CO_2$ fluxes for different polymer membranes with varying thickness

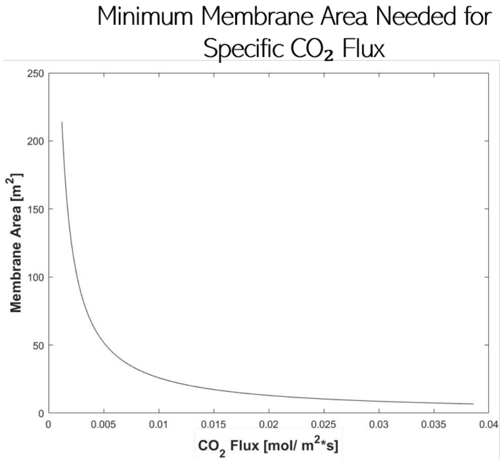

Figure 5: Minimum membrane area required for specific $CO_2$ flux

In Figure 4 we can observe two main trends. One is that the thicker the membrane is, the smaller the $CO_2$ flux. This is expected since the bigger the space the gas has to permeate, the longer it will take. The second trend is that the most permeable materials achieve higher fluxes, and that happens because the gas can more easily permeate some types of polymers, taking less time to reach the other side of the membrane.

In Figure 5, given that we have a constant molar flow rate of 0.26 mol/s of $CO_2$, the greater the gas flux, the smaller membrane area is needed.

### 4.1. Further Validation

To further validate the membrane area range calculated we performed a simple calculation to see how much volume a membrane in a spiral wound configuration would take (as seen in Figure 6). This type of configuration allows large membrane areas to occupy a reasonable amount of space depending on the packing density. For example, the usual range for spiral wound membrane packing density is 300 to 1000 $m^2/m^3$ (22). Assuming an average packing density of 650 $m^2/m^3$, for our largest predicted membrane area of $225m^2$ , the volume of the membrane system would be $0.35m^3$.

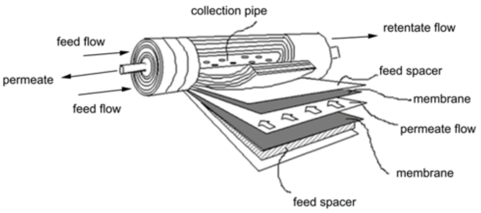

Figure 6: Spiral Wound Membrane Configuration (15)

## 5. Conclusions

From the modeling results, we were able to conclude that the membrane materials to further investigate should be Polyethylene and Polystyrene. These materials would require the lowest membrane areas and thicknesses because of their higher permeability values. However working with membranes that are too thin might cause complications since they can be very unstable (15).

In addition, as seen in section 4.1, the initial calculations for the volume that the membrane system would occupy are in the same order of magnitude of the volume of the CDRA, which demonstrates that it would be indeed feasible to implement this solution at the ISS. Most importantly, the preliminary results of this research seem to indicate that it is possible to engineer a reliable membrane system that would allow for deep space exploration missions. This system would ideally last more than 3 years and need minimum maintenance.

## 6. Future Work

### 6.1. Experimental validation of values

In the future we plan to experimentally validate the values obtained from the model with laboratory tests. Membranes with the materials recommended above should be ordered and ISS temperature and pressure should be simulated to accurately determine membrane areas.

### 6.2. Effects of humidity in the air flow

It is important to note that the effects of the water partial pressure were considered negligible in this work. This was done since the presence of humidity in the air flow can lower the overall performance of the membrane because of plasticization and competitive sorption (23). For future work it is important to determine whether it is necessary to filtrate the water prior to separating the $CO_2$.

### 6.3. Flux under transient conditions

Some other directions that can be taken forward are modeling the $CO_2$ flux under transient conditions, considering that the temperature is not constant over time under CDRA conditions (6).

### *6.4. Range of membrane selectivity*

Lastly, obtaining a range of membrane selectivity for the operating conditions would help determine the exact membrane material needed to successfully separate the $CO_2$ under the very low partial pressures.

## 7. Acknowledgments

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