A Closed-Loop CO_2 and Humidity Recovery System for Deep Space Missions

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Carbon dioxide (CO_2) removal is a critical component of life support systems used in human spacecraft and the International Space Station. Long-duration missions into deep space and to Mars will require a CO_2 removal system with higher performance, higher reliability, and the ability to recover the CO_2 for recycling back into oxygen, rather than discarding it to space. Up until now, solid sorbents have been preferred due to their familiarity and the ease of management of solids in microgravity. However, liquid absorbents have significant advantages over solid adsorbents. The ability to pump the absorbent from scrubber to stripper stages allows for continuous flow processing, which is generally more stable and reliable than alternate bed processing used in solid adsorbent systems, and eliminates complicated valve networks. Contacting methods, including membrane contactors and spray contactors, allow higher surface area and thus a system of lower estimated volume. Liquid may also be easily exchanged into the system without disassembly. Amine-based systems like those used in submarines are prone to outgassing of dangerous and odorous products, air oxidation, thermal degradation, and can be corrosive. Safe, stable ionic liquids allow the highly reliable and effective liquid absorbent system to be used in a human space environment. With numerous ionic liquids available, the ionic liquid can be tailored for stability and a high CO_2 capacity. Ionic liquids are also readily miscible with water, but, at the relative humidity concentrations of a spacecraft, water absorption will not have a strong negative effect on CO_2 capacity. This, along with the stability of ionic liquid with water, enables the system to act as a humidity removal system as well.

Progress in developing a compact combined CO_2 and humidity recovery system using ionic liquids and membrane ionic liquid contact will be described. Approaches to maximizing absorption and desorption kinetics lead to attractive estimated device volumes.

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Nomenclature

A	=	*membrane area (m^2)*
a_o	=	*area per volume ($m^2\ m^{-3}$)*
BMIM Ac	=	*1-butyl-3-methylimidazolium acetate*
C	=	*cooling (W)*
C_{eq}	=	*cooling equivalency factor ($kg\ W^{-1}$)*
c	=	*concentration ($mol\ m^{-3}$)*
CDRA	=	*Carbon Dioxide Removal Assembly*
CDRILS	=	*Carbon Dioxide Removal by Ionic Liquid System*
CO_2	=	*carbon dioxide*
CT	=	*crew time (h)*
CT_{eq}	=	*crew time equivalency factor ($kg\ h^{-1}$)*
D	=	*Diffusion coefficient ($m^2\ s^{-1}$)*
d	=	*hollow fiber or droplet diameter (m)*
EMIM Ac	=	*1-ethyl-3-methylimidazolium acetate*
ESM	=	*Equivalent System Mass*
ISS	=	*International Space Station*
K_G	=	*overall mass transfer coefficient ($kmol\ m^{-2}\ h^{-1}\ kPa^{-1}$)*
k	=	*mass transfer coefficient ($m\ s^{-1}$)*
M	=	*mass (kg)*
MFC	=	*mass flow controller*
n	=	*mole flux ($mole\ m^{-2}s^{-1}$)*
P	=	*power (W)*
P_{eq}	=	*power equivalency factor ($kg\ W^{-1}$)*
p	=	*pressure (torr)*
R	=	*Gas constant*
Sh	=	*Sherwood number*
T	=	*Temperature (K)*
∇	=	*molar volume ($mol\ m^{-3}$)*
v	=	*linear velocity ($m\ s^{-1}$)*
V	=	*volume (m^3)*
V_{eq}	=	*volume equivalency factor ($kg\ m^{-3}$)*
VLE	=	*Vapor Liquid Equilibrium*
Z	=	*hollow fiber length (m)*
η	=	*viscosity (poise)*
ρ	=	*density ($g\ m^{-3}$)*
φ	=	*packing factor*

I. Introduction

NASA's next human space missions involve taking humans beyond low earth orbit and into deep space. For life support systems, this means that resources like oxygen and water must be recoverable from metabolic waste products and that the systems used to recover these resources must be as efficient, regenerable, long lasting, and as reliable as possible. In addition, the nature of these missions preclude emergency resupply of resources from Earth and a quick return to Earth. Therefore, subsystems need to be very reliable, minimize resources, and use less mass, volume, and power to reduce the costs of such missions.

Past carbon dioxide removal systems for spacecraft employed solid adsorbent systems containing solid amines and zeolite adsorbents. These solid adsorbent systems involved sorbent beds which alternated between sorbing and desorbing CO_2 to enable continuous removal. Although solid systems like the International Space Station (ISS) Carbon Dioxide Removal Assembly (CDRA) met and exceeded the performance requirement to maintain CO_2 partial pressures below the required 3.9 torr,[1] astronauts on ISS have experienced headaches and eye degeneration that may be attributed to the high levels of CO_2.[2] This has led to a lower CO_2 partial pressure requirement of 2 torr for deep space vehicles. For the more difficult 2 torr requirement, a solid adsorbent system would dramatically increase in size, since limited adsorption kinetics dominate the system sizing. Solid adsorbent systems may also be compromised by contact with liquid water. Excessive humidity and possible water leaks into the ISS CDRA from upstream systems

can compromise the ability of the sorbent to remove carbon dioxide and cause dust formation from the zeolite. Likewise, water in a solid amine sorbent system may accelerate the degradation of amines.[3]

Liquid absorbent systems have significant advantages over solid adsorbent systems. Liquid absorbent systems are more capable of maintaining lower cabin CO_2 partial pressures with a smaller system volume. Liquid absorbent systems employ scrubber (absorption) and stripper (desorption) stages in which the liquid absorbent is pumped between the stages. In the scrubber, the sorbent contacts and removes the CO_2 in the air and is pumped into the stripper, where the sorbent is regenerated by removing the CO_2 via heat and/or vacuum pump. This method of continuous processing is generally smaller and more reliable than alternate bed processing used in solid adsorbent systems. A similar system employing liquid amines and thermal regeneration has been used in submarines for CO_2 removal for many decades due to the efficiency, reliability, and low cost of the system. The approach additionally eliminates complicated and high-mass valve networks, and allows the replacement of degraded or outdated liquid into the system without disassembly. In addition, liquid systems may employ a gas–liquid contactor in the scrubber and stripper to allow the maximization of surface area and kinetics, allowing for a lower size and weight compared to solid adsorbents when more stringent CO_2 removal is required. Using methods like direct liquid contact, in which the CO_2 is contacted with small liquid absorbent droplets, or membrane contact, in which CO_2 is contacted with fibers of flowing absorbent, allows higher surface area and thus a system of significantly lower estimated volume.

II. Advantages of Ionic Liquids

Amine-based CO_2 removal systems like those used in submarines are known for their efficiency, reliability, and low size, weight and power compared to solid sorbent systems. However, amines are prone to outgassing of dangerous and odorous products, air oxidation, thermal degradation, and corrosion. Although they are suitable in a submarine environment, the use of amines poses higher risks and costs to human spacecraft. Ionic liquids have been identified as a safe, stable, highly reliable and highly effective CO_2 absorbent for the human space environment.[4]

Ionic liquids are salts, generally comprised of an anion and organic cation, that are liquid at their temperature of use. They have effectively zero vapor pressure, eliminating odors and reducing the likelihood of contaminating the purified air. They are generally nontoxic, and have sufficient stability to resist deterioration. Ionic liquids typically contain relatively large organic cations (quaternary ammonium, imidazolium or phosphonium compounds) and any of a variety of anions, both of which can be tailored to obtain desired characteristics. As a result of this versatility, there are many to choose from and they are often called "designer solvents." In addition, they are relatively easy to make, and major chemical manufacturers have begun to make major classes of ionic liquids available in large quantities. Ionic liquids can both physically dissolve carbon dioxide and have specific chemical interactions with it. As a class, almost every ionic liquid is water soluble and hygroscopic, meaning that they will absorb moisture from the air, removal of which is necessary in spacecraft in addition to CO_2 removal. At the relative humidity of a spacecraft, water absorption will not significantly affect the capacity for CO_2. Due to the negligible volatility, the water can be removed by evaporation either by elevating the temperature or reducing the water partial pressure. Because a very large number of ionic liquids exist, and both the cation and anion can be tailored to obtain the desired characteristics, this class of compounds has a lot of promise and flexibility as the liquid absorbent for a carbon dioxide removal system for human spacecraft.

Ionic liquids have been studied by several groups as potential carbon dioxide absorbents, but almost exclusively at higher carbon dioxide partial pressures than those relevant to environmental control. Zhang *et al.*[5] screened numerous ionic liquids to evaluate approaches to recapture of CO_2 at large point sources, and Brennecke[6] has described several ionic liquids specifically designed for CO_2 uptake. Stevanovic *et al.*[7,8] focused on ionic liquids containing carboxylate anions since they and others have noted that they have particularly high capacity for CO_2. We have chosen to focus our initial work on 1-butyl-3-methylimidazolium acetate (BMIM Ac) because it has a high CO_2 capacity and well understood physical properties, and Honeywell has demonstrated proof of concept with this material. In parallel, we continue to compare the performance of various other ionic liquids with that of BMIM Ac. Ultimately, either an available ionic liquid will be selected, or we will design an ionic liquid specific to the need based on Honeywell's 15 years of experience in ionic liquid research and development.

BMIM Ac is an example of a set of ionic liquids that satisfies the basic requirements for an absorbent in a manned vehicle. According to a safety data sheet, the clear liquid is "not a hazardous substance or mixture" and has no hazards otherwise classified[9]. The pH of an aqueous solution is 6.1, and the autoignition temperature is 435°C. Other useful physical properties[10,11,12] for BMIM Ac are provided in Table 1. The surface tension is similar to that of a polar organic solvent, and the density is similar to that of water. The onset for thermal degradation sets the upper temperature limit for processing, and is comfortably above the temperature needed for desorption of either water or CO_2. The viscosity

for this ionic liquid is significantly higher than that of water. Viscosity strongly affects how well the ionic liquid can be distributed into high surface area droplets or media, and also plays a role in determining mass transfer rates for CO_2 absorption and desorption. Control of viscosity is therefore important to reduce the weight and volume of the scrubber. Fortunately, viscosity is reduced by raising the temperature or water content, such as in normal use where the ionic liquid absorbs both CO_2 and water.

Table 1: Selected physical properties of 1-butyl-3-methylimidazolium acetate (BMIM Ac)

Property	Value	Temperature/Water Concentration	Reference
Molecular weight (g mol^{-1})	198.26	-	
Density (g mL^{-1})	1.055	25˚C/anhydrous	Almeida _et al._[10]
Surface Tension (mN m^{-1})	36.4	25˚C/anhydrous	Almeida _et al._[10]
Heat Capacity (J mol^{-1} K^{-1})	210	25˚C/anhydrous	Strechan _et al._[11]
Onset of thermal degradation (˚C)	216	-	Cao _et al._[12]
Viscosity (mPa-s)	406	30˚C/anhydrous	*
	263	30˚C/2% water	*
	152	30˚C/5.5% water	*
	111	50˚C/anhydrous	*
	79	50˚C/2% water	*
	52	50˚C/5.5% water	*

*Estimated using Eq. 4 of Stevanovic[7]

III. System Overview

The Carbon Dioxide Removal by Ionic Liquid System (CDRILS) is a continuous liquid system that uses ionic liquid as a sorbent for carbon dioxide. Figure 1 shows the CDRILS process in which the cabin air, consisting of nitrogen, oxygen, carbon dioxide and water vapor, passes through a dust and particulate filter to enter the CDRILS. The input to the process is air from the cabin at an assumed 2 torr carbon dioxide partial pressure. In the scrubber, the air is contacted with clean ionic liquid which selectively absorbs the carbon dioxide and water, returning CO_2 free air to the cabin. Meanwhile, the rich ionic liquid containing CO_2 and water will pass into a stripper where heat and/or vacuum will be used to desorb the CO_2 and water in the form of vapor, allowing the ionic liquid to be reused. The stripper will both separate the liquid phase from the gaseous CO_2 and water, as well as separate the CO_2 and water for further processing and storage. Methods for water removal may include condensers and/or membrane
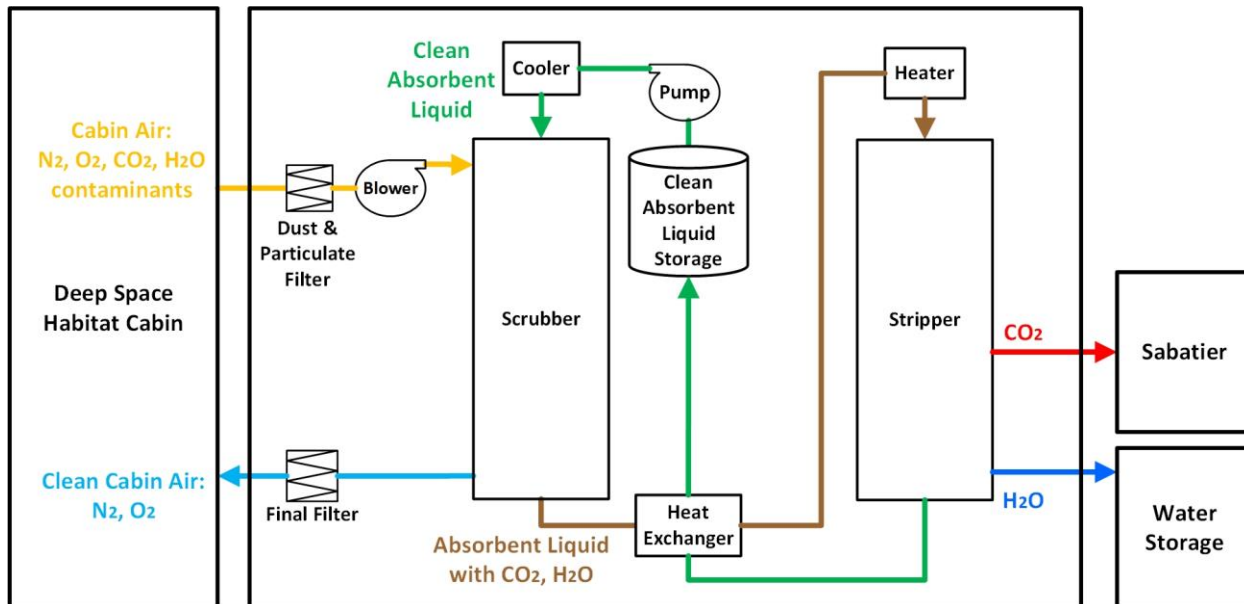

Figure 1: CDRILS general schematic.

dehumidification, as noted later in this paper. The system will be compatible with downstream processing of carbon dioxide for oxygen recovery by, for instance, a Sabatier reactor.

IV. Scrubber and Stripper Design

A. Importance of good mass transfer kinetics

The heart of the CDRILS design is that of the scrubber and the stripper. Both are, in essence, contactors in which a gas stream is contacted with the ionic liquid stream, and carbon dioxide and water are transferred from one stream to the other. In the scrubber, air from the cabin is contacted with the liquid, which absorbs carbon dioxide and water. In the stripper, higher temperature and lower pressure are used to remove these components and restore the ionic liquid for re-use. A number of processes are involved in mass transfer, including gas-phase transport, interfacial transfer, complexation reactions, and liquid-phase transport. Gas-phase transport is likely to be very fast, relative to the other processes, so our attention focuses on the interface and the liquid phase. The size of each system is strongly correlated with the rate of these mass transfer processes. The design of the scrubber and stripper units need not be the same, but for this discussion, we will focus on the common features.

Gas–liquid contactors must manage the flow of the two fluids, placing them in close contact, and then separating them. High interfacial area is important to getting good mass transfer, and must be done within a compact volume. One can achieve high surface area in some systems by dispersing the gas phase as small bubbles in the liquid phase; however, this approach is better suited for applications with a lower gas–liquid ratio than is required for the current application. Falling films and similar devices operate by spreading the liquid phase across a large surface and then re-collecting it. Providing high enough surface area while containing the liquid is a challenge because in zero gravity, the dominant force keeping the liquid in place against the surface is surface tension. This presents challenges in a zero gravity environment that are not well understood. Spray contactors divide the liquid phase into small droplets dispersed in the gas phase, but the droplets must then be coalesced into a continuous liquid phase. Alternatively, membrane contactors spread the liquid and gas phases over a large porous surface while separating the two phases with the membrane. This facilitates re-consolidation of the liquid phase but introduces the membrane as an additional barrier between the two phases.

Krupiczka *et al.*[13] and others have concluded that mass transfer for a system involving ionic liquid absorption is dominated by liquid-phase mass transfer. This is convenient for comparison since it is likely common across all the various contactors, and makes comparison easier. The Sherwood number, Sh, which describes the ratio of mass transfer to the diffusion rate (Eq. 1), is frequently a key parameter and can be estimated using correlations specific to each device. Thus, if we can estimate the Sherwood number and the diffusion coefficient, D, the mass transfer coefficient, k, is accessible. For imidazolium-based ionic liquids, Morgan *et al.*[14] has developed a correlation between the diffusion coefficient of carbon dioxide, D_{CO_2}, as a function of the liquid viscosity, η, and the molar volume of CO_2, $\bar{V}_{CO_2}$ (Eq. 2). The viscosity, in turn, can be estimated for BMIM Ac, since Stevanovic *et al.*[8] have determined the coefficients (C_1, C_2, T_0) for the Vogel-Fulcher-Tammann equation (Eq. 3) as a function of water content. Thus, with a knowledge of the temperature, T, and the water content of our ionic liquid, we can estimate the viscosity, and hence the CO_2 diffusion coefficient for our process. If we, in addition, can estimate the Sherwood number, then the mass transfer coefficient can also be estimated. Note that, by these criteria, the most rapid mass transfer is associated with higher temperatures and higher water content. However, we have seen from the isotherm data discussed earlier that higher temperatures and water content also reduce the CO_2 capacity in the ionic liquid.

$$Sh = \frac{k\,d}{D} \tag{1}$$

$$D_{CO_2} = 2.66 \times 10^{-3} \frac{1}{\eta_{IL}^{0.66} \bar{V}_{CO_2}^{1.04}} \tag{2}$$

$$\eta = C_1 \sqrt{T}\ e^{\left(\frac{C_2}{T-T_0}\right)} \tag{3}$$

The scale of the contactor is determined in part by the system requirements for a Deep Space mission. For illustration, if a crew size of four is assumed with a CO_2 generation rate of 1.04 kg day^{-1} person^{-1}, with a cabin pressure of 70.3 kPa, the minimum air flow rate through the scrubber will be 604 L min^{-1} (Eq. 4). More air will need to be processed if mass transfer is incomplete. If we use our measured CO_2 capacity for BMIM Ac at 2 torr, we can estimate that the minimum flow rate of ionic liquid should be 114 mL min^{-1} (Eq. 5). Again, more liquid will be required if mass transfer is incomplete. The gas–liquid volumetric flow rate ratio is thus roughly 5300. Note that these calculations

assume infinitely fast mass transfer. In reality, mass transfer will be incomplete, and the scale of the contactor will be determined by the mass transfer coefficient and the number of transfer units required to achieve the desired CO_2 removal efficiency.

$$4 \left(1.04 \frac{kg}{day}\right)\left(\frac{70.3 kPa}{2\ torr}\right)\left(\frac{R \cdot 296°K}{44\ g\ mol^{-1}\ 70.3 kPa}\right) = 604\ L\ min^{-1}\ air \tag{4}$$

$$4 \frac{(1.04\ kg\ day^{-1})}{\left(0.0253 \frac{g\ CO_2}{g\ IL}\right)(1.03\ g\ cm^{-3})} = 114\ mL\ min^{-1}\ BMIM\ Ac \tag{5}$$

A. Spray systems

Thanks to the great interest in carbon dioxide recovery to reduce the environmental impact of combustion processes, there has been great interest in CO_2 removal processes. Spray systems involving a liquid absorbent are very common. Recent reviews by Mirzaei *et al.*[15] and Wang *et al.*[16] provide useful summaries. Almost all of these studies, however, are for CO_2 concentrations orders of magnitude higher than concentrations encountered in occupied cabin air. The U.S. Navy has used a system involving a spray contactor and monoethanolamine on submarines for CO_2 management for many years, demonstrating that the technology is practical at the concentrations of CO_2 in occupied environments. We have evaluated two designs for a spray contactor adapted for use in zero gravity (Figure 2). In the simpler design, the absorbent liquid is forced through a spray nozzle, and mixed with the air to be treated. A liquid mist is generated, which is carried by the air flow through the contactor until it reaches a layer of packing material. Since the mist droplets are very small, surface area is large and mass transfer is rapid. The packing material serves two purposes. It intercepts the liquid mist, allowing the mist droplets to coalesce into larger droplets which are carried through the packing to the outlet of the contactor. It also serves as a secondary mass transfer surface, since the liquid absorbent will cover all surfaces, and be exposed to the passing air. At the exit, a centrifugal separator isolates air from liquid, to produce the two product streams.
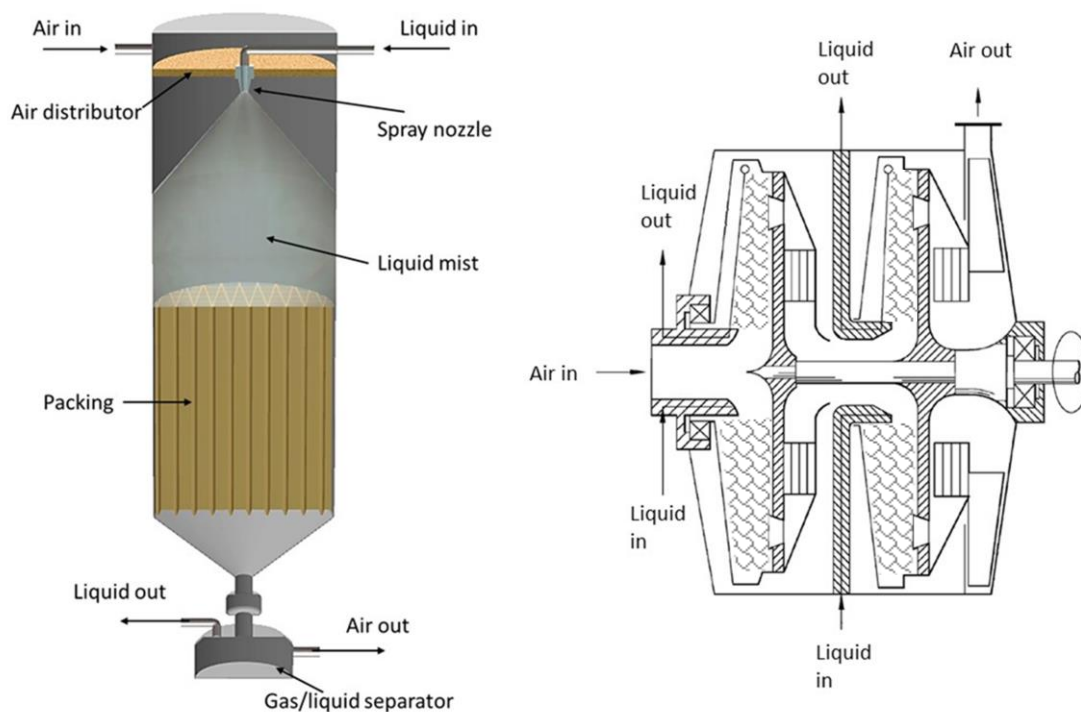

Figure 2: Possible CO_2 scrubber designs. Aerosol mist and packed bed contactor (left); rotating disk contactor (right).

In the rotating disk contactor, also shown in Figure 2, the same functions are arranged a bit differently. Here the mist of absorbent liquid is sprayed at a rotating disk and dense packing material, creating thin film on the surfaces.

The air, simultaneously entering the rotating device, contacts the liquid on these surfaces and in the spray and selectively absorbs the CO_2 and water vapor. Centrifugal force pulls the CO_2- and water-rich liquid to the circumference, where it is collected by pitot pumps. The air passes through a secondary back-up filter and then to the outlet.

For both of these designs, the importance of mass transfer is clear. To obtain a reasonably small contactor volume with the fixed inlet air flow rate, either the mass transfer coefficient or the interfacial area between gas and liquid should be high. Kuntz and Aroonwilas[17] studied a co-current spray scrubber to remove carbon dioxide from air which provides a useful comparison. Their study used aqueous monoethanolamine instead of ionic liquid, and 5-15% carbon dioxide concentrations. They measured a volumetric overall mass transfer coefficient $K_G a_0$ of 3.4 kmol m^{-3}hr^{-1}kPa^{-1}. The volumetric overall mass transfer coefficient is the product of the overall mass transfer coefficient K_G and the ratio of surface area to volume a_0. If we use this value with our CO_2 load and partial pressure, we would expect a reactor volume of 4.3 L. However, this estimate neglects that the liquid-specific mass transfer constant K_G for BMIM Ac is expected to be a factor of 6.7 lower than that for 15% monoethanolamine.[13] We must therefore increase the surface area a_0 to maintain a low contactor volume. The Kuntz study used a BETE P-40 nozzle to generate their spray, which, according to manufacturer data, has an average droplet size of 159 μm. Using this droplet size and the dimensions and flow rates from the paper,[18] we estimate that the surface area a_0 corresponding to the Kuntz overall mass transfer coefficient was 6.0 x 10^3 m^2 m^{-3}. Given that the gas–liquid flow rate ratio will be higher in our system than the Kuntz ratio of 50, it is necessary to greatly reduce the droplet size to maintain the mass transfer rate.
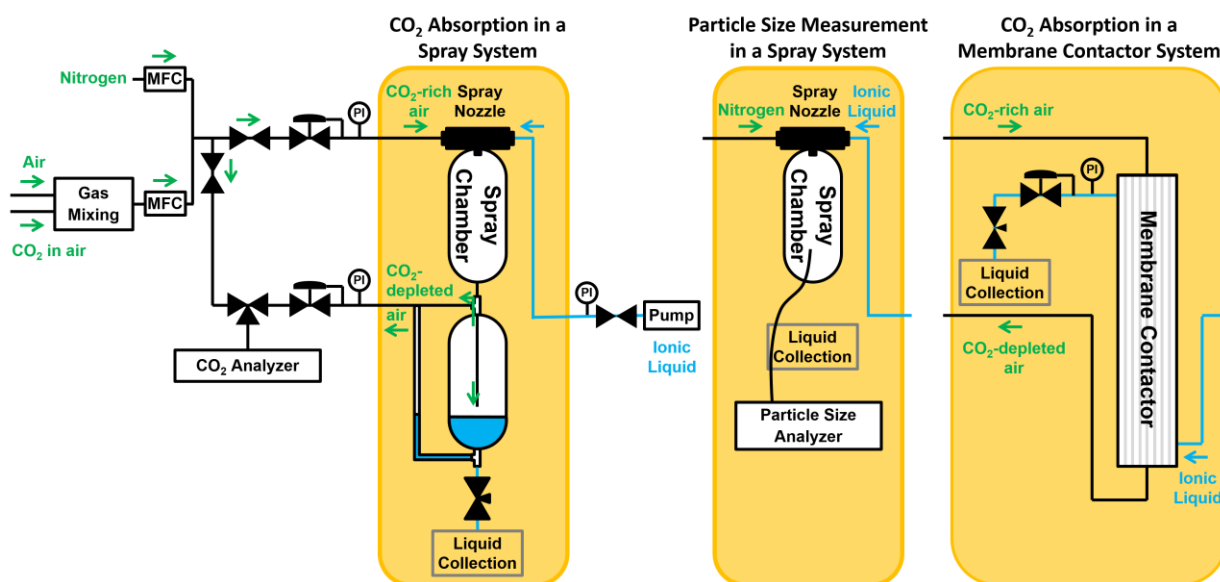

Figure 3: Schematic of test stand for CO_2 absorption by ionic liquid spray or membrane contactor.

The ability of the ionic liquid droplets produced by a BETE model XR-SA-050 spray nozzle to absorb CO_2 was tested on a laboratory test stand (Figure 3). The two-phase nozzle allows for a gas–liquid ratio consistent with the capacity of the ionic liquid that we have measured previously for CO_2 at the concentrations of interest (1–4 torr). A dry air stream of controlled CO_2 concentration and flow rate was provided to the spray nozzle by an Environics Series 4000 gas mixing system, and the ionic liquid stream was provided by a Teledyne Isco 1000D syringe pump. The gas provides the driving force for atomization of the liquid.

The objective of our droplet size measurement experiments was to measure the concentrations of smaller particles, since our analysis shows that these are essential to meet our mass transfer rate goal. The liquid droplet size distribution was measured using an Aerodynamic Particle Sizer 3321 (TSI Inc.), which detects particles from 0.5 to 20 µm, and an Electrostatic Classifier 3087 paired with a Condensation Particle Counter 3775 (TSI Inc.), which detects particles down to 4 nm. The particle distribution produced from a 5% water/95% ionic liquid mixture flowed at 1 mL min^{-1} with 5 L min^{-1} gas flow is shown in Figure 4. Additional results for experiments with varied water content and liquid flow rate are summarized in Table 2. The mean particle size and distribution of particle sizes detected was relatively independent of water concentration and liquid flow rate with no observable trend.
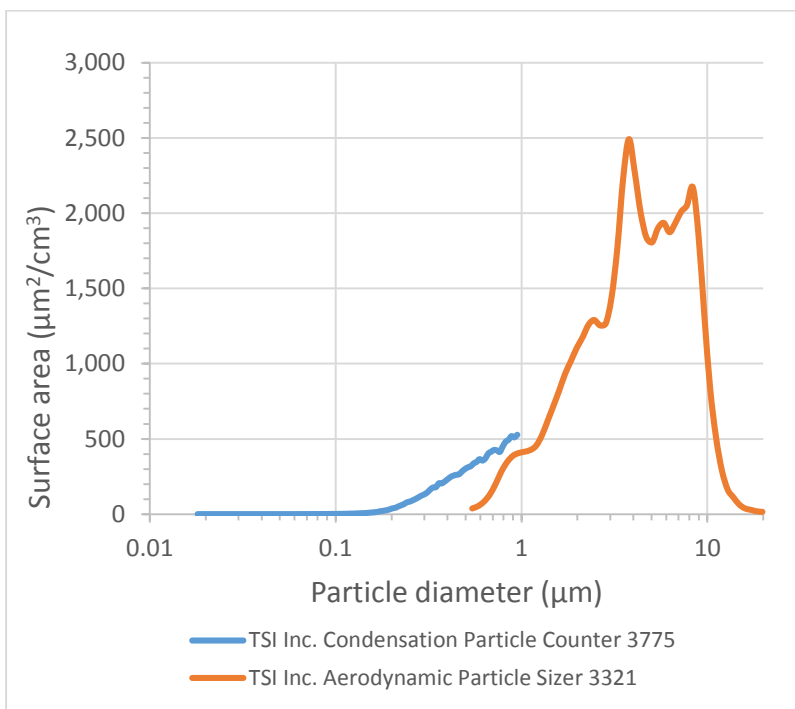

Figure 4: Particle size distribution obtained using a BETE model XR-SA-050 nozzle with 1 mL min^{-1} 95:5 BMIM Ac:water and 5 L min^{-1} air.

Table 2: Particle size data from BETE XR-SA-050 nozzle experiment

% weight ionic liquid (%)[1]	Liquid flow rate (mL min^{-1})	Mean particle size (µm)[2]	% of liquid mass detected (%)
95	1	4.78	0.020%
95	2	3.79	0.012%
90	1	4.19	0.036%
90	2	4.50	0.024%
[1] The balance is water.			
[2] The mean particle size is the mean particle diameter based on particle surface area. It is calculated only from the measurements collected by the instrument in the 0.5 to 20 µm range.			

The particle detection instruments also quantify the total mass of liquid detected per volume of air. We assume a liquid density of 1.05 g mL^{-1}, which is the density of the ionic liquid before dilution with water. At the liquid and gas flow rates provided to the spray nozzle, 200 µL liquid per liter of air is expected, but only 0.040 µL liquid per liter of air or 0.020% of the expected liquid quantity was detected in these experiments. The remainder of the liquid likely was sprayed as larger particles than the range of detection, coalesced with other small particles to form larger particles before detection, and/or was lost to the walls of the spray chamber and the walls of the tubing before reaching the detector. Usually, the majority of the liquid appears to be sprayed in a fine mist, so we conclude that our low level of detection results at least partially from loss of particles to coalescence and to the walls. However, we do observe that the amount of liquid detected increases with decreasing weight percent ionic liquid and with decreasing liquid flow rate. Both are explained by the high viscosity of the liquid. As the liquid is diluted with water, it becomes less viscous and is more easily atomized. As liquid flow rate is increased, too much liquid is provided to the spray nozzle for the air to effectively atomize it.

We concluded from these results that the use of this style of spray nozzle will not meet our mass transfer rate requirements. In further discussions with the manufacturer of the nozzle, it became clear that there is not much experience atomizing a viscous liquid with as low an gas–liquid ratio as we require, and that a system with this nozzle does not meet our mass transfer goal. We are currently evaluating other nozzles, including ultrasonic nozzles which do not depend on the gas–liquid ratio for proper operation.

B. Membrane contactors

Membrane contactors are an alternative approach for both the scrubber and the stripper steps and offer several advantages over spray technology for zero gravity operation. In a membrane contactor, the gas and liquid streams are separated from each other by a microporous membrane, and mass transfer occurs via the pores in the membrane (Figure 5). The membrane is frequently, but not always, a hollow fiber membrane, and in this format the module consists of a cylinder tightly packed with hollow fibers with two end-caps acting as distributors to separate the gas and liquid feeds. Advantages of this approach compared to the two-phase spray nozzle include that it allows for countercurrent operation, and the interfacial surface area, which corresponds to the membrane area, is independent of gas–liquid flow ratios. Membrane contactors are also gravity-independent, meaning rotating separator hardware is not required. They are thus more easily adapted to a modular design, allowing for redundancy without significantly impacting the size, weight, and power of the hardware. The pioneering work of Kreulen *et al.*[19] has demonstrated that membrane contactors are particularly well-adapted to use with relatively viscous liquids. More recently, other
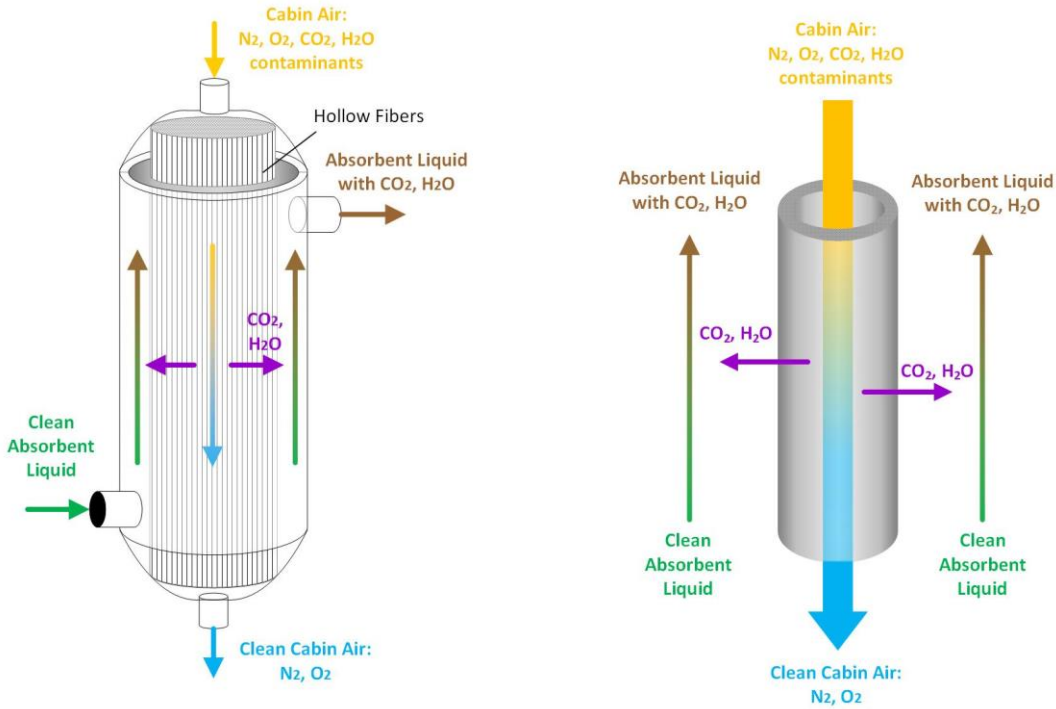

Figure 5: Hollow fiber membrane contactor (left). Single hollow fiber (right).

groups[20,21,22] have demonstrated the viability of the technology for CO_2 removal using ionic liquids.

For mass transfer in membrane systems, we must consider transport in the gas phase, transport through the membrane, and liquid-phase mass transport. Gas-phase transport will be fast relative to the other processes, and it is possible to minimize the resistance to mass transfer through the membrane by proper material and morphology choices, leaving liquid phase mass transfer as the rate-determining process. To prevent the membrane from significantly slowing mass transfer, a non-wetting membrane material should be chosen, since, liquid-filled pores create stagnant zones that inhibit liquid flow. For liquid-phase mass transfer, the mass transfer coefficient is expected to be strongly dependent on the diffusion coefficient, as shown in Eq. 1, and this, in turn, depends primarily on the ionic liquid viscosity. The ratio between the mass transfer coefficient and the diffusion coefficient is determined by the Sherwood number. The Lévèque-Graetz (Eq. 6) and Kartohardjono (Eq. 7) approaches to estimating this number include dependencies on the velocity of flow through the fiber, liquid viscosity and the diffusion coefficient for CO_2 in the liquid.

$$Sh = \sqrt[3]{3.67^3 + 1.62^3 \frac{v\,d^2}{DZ}} \tag{6}$$

$$Sh = 0.1789\varphi^{0.86}\left(\frac{\rho v d}{\eta}\right)^{0.34}\left(\frac{\eta}{\rho D}\right)^{\frac{1}{3}} \tag{7}$$

Avoiding wetting the membrane pores not only improves mass transfer but also prevents leakage of ionic liquid into gas lines. Such leakage would necessitate subsequent separation. The ability of the liquid to penetrate pores depends on the surface tension, the viscosity, the dimension of the pores and the contact angle. Because ionic liquids are polar and BMIM Ac has a surface tension of 36.4 mN m^{-1},[7] these considerations guide us to investigate relatively hydrophobic membrane materials with low critical surface tensions, such as polytetrafluoroethylene (PTFE). We measured the contact angle for BMIM Ac on a porous PTFE surface to be 81.3°, showing that it will not

Figure 6: Measurement of the contact angle of BMIM Ac on a porous Teflon surface .

wet this material unless significant force is applied (Figure 6). Kreulen and Dai each describe the addition of a composite layer to prevent pore-filling with very little effect on mass transfer.
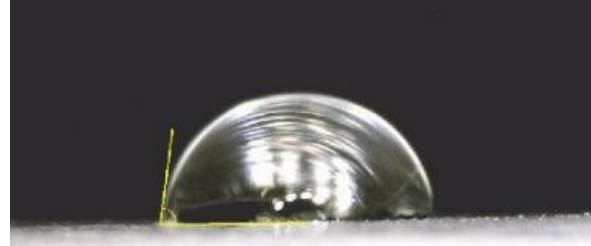
Initial experimental results using a membrane contactor were obtained using the laboratory test stand shown in Figure 3. A hollow fiber microfiltration module was used for the contactor, with 90:10 BMIM Ac:water as the liquid phase, and air containing 1 to 4 torr partial pressure of CO_2 at atmospheric pressure as the vapor phase. The pressures of both the liquid and the gas phases were controlled at up to 6 psi in operation. The ionic liquid may either be directed through the lumina of the hollow fibers or through the shell surrounding them, and we evaluated both options. When the ionic liquid passes through the lumina, the pressure drop is higher because of the viscosity of the ionic liquid, and there is less opportunity for bypass due to the small diameter of these fibers. In fact, we observed little difference between results from these two configurations. A commercially available

Figure 7: Molar flux of CO_2 transferred from air to a 90:10 BMIM Ac:water solution versus the CO_2 partial pressure in the air.

microfiltration module[23] was compared with a module containing proprietary membrane fibers developed for this application by Honeywell's membrane experts. Figure 7 shows a plot of the results of experiments in which the molar flux of CO_2 was observed as a function of its partial pressure. The CO_2 mass fractions in the ionic liquid reached 0.08-0.4%, depending on the concentration of CO_2 in the air, and were almost identical for the two modules. The slope of the linear fit to this equation provides a value for the mass transfer coefficient as shown in Eq. 8, which can be expressed either as a function of the partial pressure difference or the CO_2 concentration difference. Table 3 shows these calculated mass transfer coefficients. Eq. 8 defines the mass transfer coefficient as the ratio of the molar flux to driving force (either concentration difference or partial pressure difference), and has been used to estimate the membrane area required for a CO_2 load of 4.15 kg day^{-1}, representing a likely load from four crew members in a deep space vehicle.
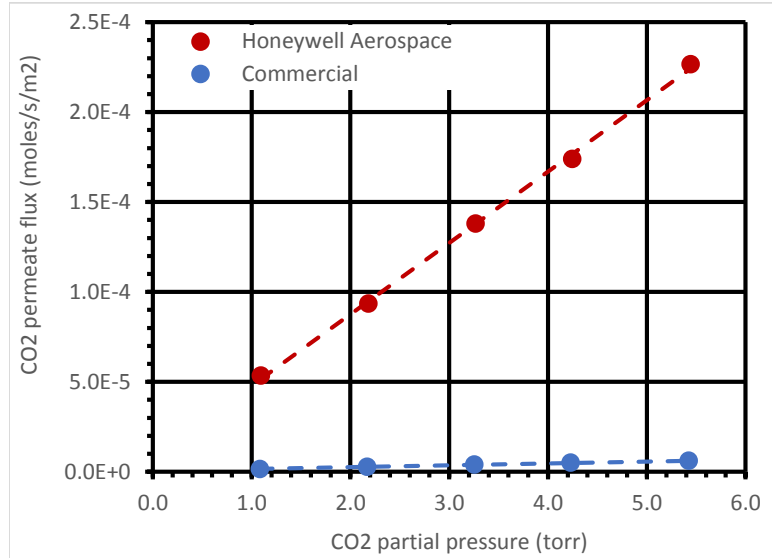
$$k = \frac{n_{CO2}}{A\Delta c_{CO2}} = \frac{n_{CO2}RT}{A\,\Delta\,p_{CO2}}$$

(8)

Table 3: Mass transfer coefficients calculated from initial membrane contactor experiments

	Mass transfer coefficient (mol s^{-1} m^{-2} torr^{-1})	Mass transfer coefficient (m s^{-1})	Membrane area required for 4.15 kg day^{-1} CO_2 flux (m^2)
Commercial membrane	1.16 x 10^{-6}	2.17 x 10^{-5}	470
Proprietary membrane	4.17 x 10^{-5}	7.80 x 10^{-4}	13.1

V. Design for Compatibility with Closed-Loop Processes

Design of the CDRILS process must focus on the inlet conditions presented by the occupied cabin, and the output streams required for downstream processes. In particular, the presence of water vapor in the inlet stream strongly influences all subsequent operations. While for solid zeolite adsorbents, water directly competes for active sites with carbon dioxide, ionic liquids can dissolve a significant amount of water without loss in CO_2 capacity. In our prior paper we showed that dilution of the ionic liquid results in reduced viscosity, but if the water content in the ionic liquid exceeds 20 weight %, it will reduce the CO_2 capacity. Since the solubility of water in ionic liquids is very high, the overall process must be designed to control water content as well as deliver CO_2. The output CO_2 must be relatively free of water if it is to be used by a downstream Sabatier process.
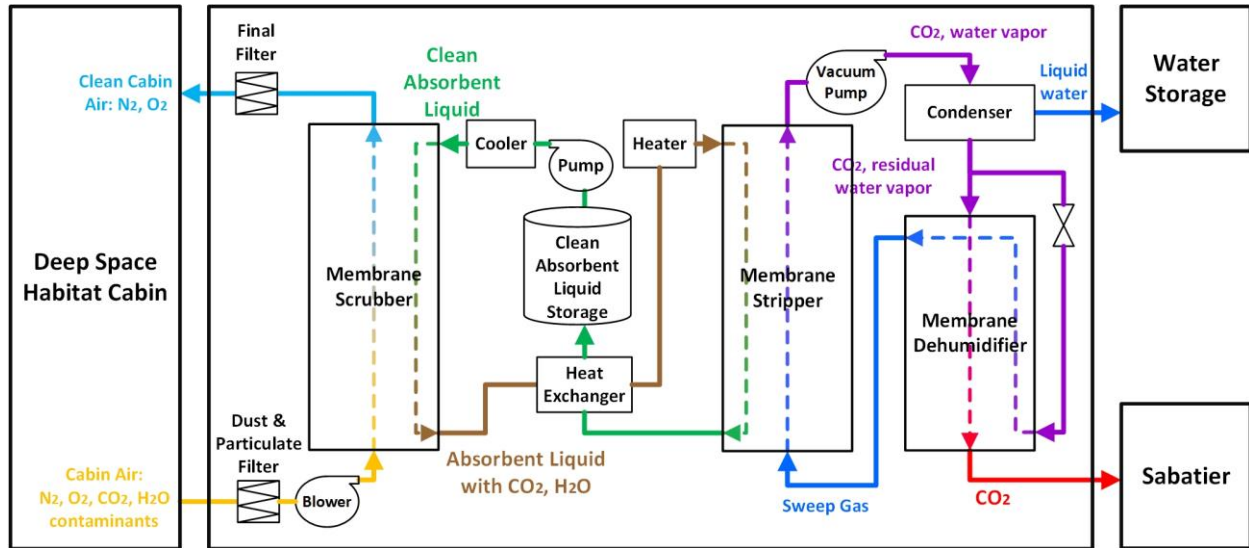

Figure 8: A schematic of the Carbon Dioxide Removal by Ionic Liquid System (CDRILS).

Figure 8 shows a potential schematic for the CDRILS system using the example of membrane contactors for the scrubber and stripper. Air containing CO_2 and humidity enters the system and both water and CO_2 are transferred to the ionic liquid. The liquid is then heated and enters the stripper. In the stripper, the CO_2 and water must be removed, restoring the ionic liquid so that it can be returned to the scrubber. As we noted above, it is not necessary or desirable that all of the water be removed, but it is essential that the rate of water removal in the stripper match the rate of water uptake in the scrubber. Otherwise the water content in the ionic liquid will increase continuously.

To understand the conditions required in the stripper to remove both CO_2 and water, we need vapor-liquid equilibrium (VLE) data for water in the ionic liquid. Fortunately, Passos *et al.*[24] have measured VLE data for BMIM Ac, and Römich *et al.*[25] have published even more complete data for 1-ethyl-3-methylimidazolium acetate (EMIM Ac). From this data, we can see that water sorption by ionic liquids does not follow ideal Henry's law behavior and that the activity coefficient varies with the mole fraction of water. Neither paper provides water partial pressure data at mole fractions below 0.5, but extrapolation to our concentration range is not controversial. Figure 9 shows the Römich EMIM Ac data in terms of weight fraction, with extrapolation to zero concentration. It is apparent that the vacuum required to remove all traces of water from one of these ionic liquids is much higher than would be practical in a low weight space application. Instead, we will select a temperature and pressure for the stripper step corresponding to a residual water concentration that is less than that required to impair CO_2 uptake in the scrubber step, and run the process with a constant residual water concentration corresponding to this selection. This has the additional benefit of reducing the viscosity of the ionic liquid.
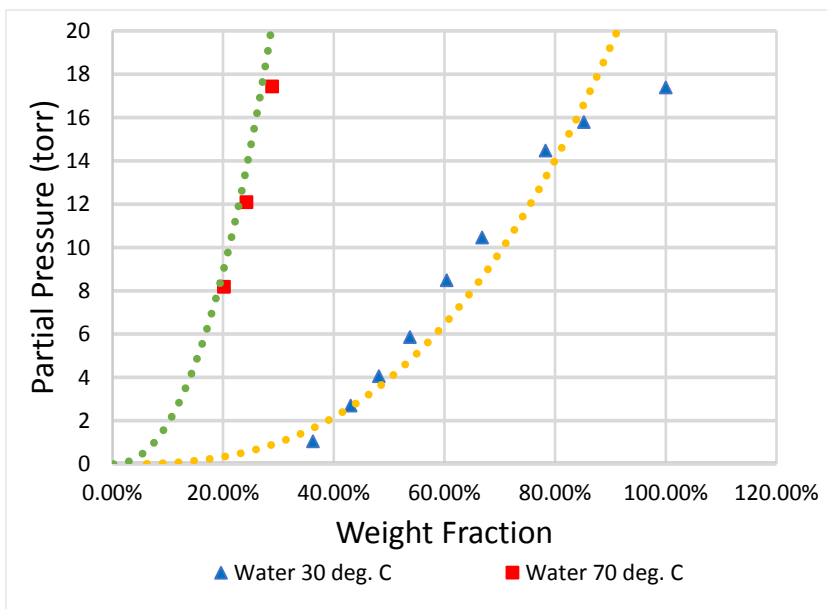
Figure 9: Vapor-liquid equilibrium data for EMIM Ac from Romich _et al._ recalculated to weight fraction vs. vapor pressure.

To better understand how a stripper might operate using realistic concentrations of water and CO_2, we ran a thermogravimetric analysis–mass spectrometry (TGA-MS) experiment. A sample of BMIM-Ac was diluted with water to contain 20% water and bubbled with air containing 5000 ppm CO_2 for several hours. The sample was heated in the TGA instrument from room temperature to 70˚C and held at that temperature under inert gas flow. The weight was observed, and a mass spectrometer was used to quantify the amounts of water and CO_2 in the effluent gas. The combined TGA-MS data were used to calculate the weight of each gas remaining in the ionic liquid over the course of the experiment, assuming that the total weight loss equaled the sum of the loss of water and of CO_2.

Figure 10 shows the results of this experiment versus time. The total weight is plotted as a percent of initial weight, while the H_2O and CO_2 weights are plotted as percentages of the total weight at the time. The temperature program is also shown versus time. Stripping of CO_2 from the ionic liquid is faster than that of water and is accelerated by higher temperature. The equilibrium condition corresponds to a decrease in the CO_2 concentration from 2.6% to essentially zero. If in the CDRILS unit a small "heel" of unrecovered CO_2 remained, it would, according to Figure 8, be returned to the scrubber where it would reduce the quantity of CO_2 scrubbed in the next cycle. According to Figure 10, water was stripped from the ionic liquid to a final concentration of 3.2%, which appears to be the equilibrium concentration under the conditions of the experiment. From our analysis in previous work[4], this water concentration is not high enough to impair the CO_2 capacity, and, since it will improve mass transfer by reducing the viscosity, is suitable for our process.

The quantity of water scrubbed from the cabin air by the scrubber, and therefore provided by the stripper to downstream processes, will not be limited by solubility in the ionic liquid. At a cabin pressure of 70.4 kPa, a temperature of 23˚C, and a relative humidity of 60%, the vapor pressure of water in the inlet air will be 1.69 kPa (12.7 torr), corresponding to a water concentration of 1.9%. The equilibrium concentration of water in the ionic liquid at that vapor pressure will be very high. Instead, the rate of water capture will be limited by the air flow rate through the scrubber and the mass transfer rate. The maximum rate, assuming infinitely fast mass transfer and the air flow rate from Eq. 4, is calculated in Eq. 9. This is therefore the maximum load on downstream processes.

$$\frac{(604\ L\ min^{-1})(70.4\ kPa)(1.9\%)(18g\ mol^{-1})}{R(296K)} = 8.4\ kg\ day^{-1}\ water \qquad (9)$$

The gas exiting the stripper (Figure 8) can then be compressed to the pressure required for further processing such as in a Sabatier. Compressing the gas and cooling it to 23˚C will result in CO_2 and water partial pressure of 610 torr and 302 torr, respectively. Since the saturation water vapor pressure at this temperature is only 24 torr, we are able to condense 92% of the water from the system, leaving a CO_2 stream that is 86% pure.

The CO₂ purity can be further increased by inclusion of a membrane dehumidifier following the condenser in Figure 8. These membranes are well-understood and widely used and consist of a hollow fiber module using a membrane material that is high in flux and selectivity for water over CO_2. For example, a silicone membrane has a permeability for water of 36,000 barrer and a permeability for CO_2 of only 3250 barrer (selectivity = 11.1). A small slip stream of feed to the dehumidifier is removed and allowed to expand through a needle valve to a lower pressure. This pressure drop and the sweep gas drive the flow of water through the walls from the other side of the membrane. The resulting sweep gas stream

Figure 10: TGA-MS Experiment with BMIM Ac containing 20% water and saturated at room temperature with carbon dioxide.

consists largely of water vapor and is then used as a sweep gas for the membrane stripper, to accelerate stripping from the ionic liquid, returning this water again to the condenser for removal. The data sheet for a commercially available membrane[26] promises 60% water removal. This would boost our CO_2 product purity to 92%.

While the schematic in Figure 8 describes the simplest possible approach to a CDRILS unit, it is not the only possible one. It may be preferable to reduce the water load on the scrubber so as to avoid swings in the ionic liquid water concentration. An alternative design would be to switch the membrane dryer from the end of the process to the beginning. If the bulk of the water is removed and condensed before the scrubber, the load on the scrubber and the stripper can be reduced.

Ionic liquids are, in general, good solvents, and will dissolve many contaminants present in parts per billion concentrations in cabin air, including siloxanes.[27] We expect that many volatile organic contaminants may be removed from the air stream by the scrubber, and dissolved in the ionic liquid. If the ionic liquid is then stripped to recover CO_2 and water by raising the temperature and lowering the pressure, these contaminant compounds may be desorbed. Depending on their vapor pressure and partition coefficient with water, these compounds may end up as contaminants in the CO_2 stream or water stream, or may remain in the ionic liquid. In either case, although the concentrations will be small, the destination of these contaminants should be identified and downstream processes should be evaluated to ensure that the systems are robust to these contaminants.
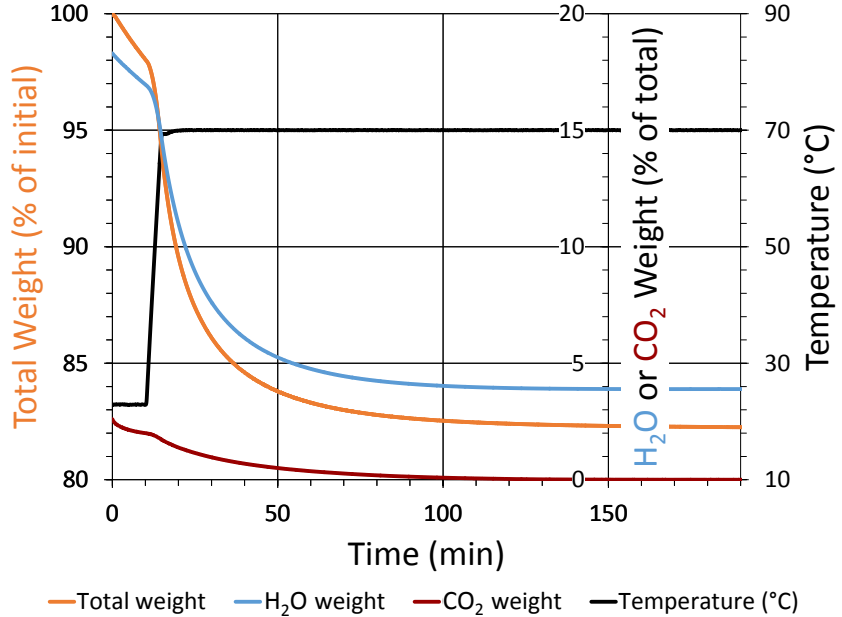
VI. Equivalent System Mass

The benefits of the CDRILS system include a low volume and weight, due to the maximization of kinetics in the scrubber and stripper, and low power and cooling, due to the low regeneration energy associated with ionic liquids. At a spacecraft system level, reducing weight, volume and power requirements reduces the equivalent system mass (ESM). ESM is a tool used to estimate the cost of operating a technology in a spacecraft. Since a large portion of a mission cost is associated with launch, and the launch costs are proportional to the mass of the spacecraft, the mass of a system in terms of ESM can help users estimate the cost of a technology.

The ESM incorporates (Eq. 10) the mass of a hardware, M, as well as the mass necessary to operate that subsystem, including the mass of the spacecraft pressurized volume, V, mass of the power supply, P, the mass of the cooling system, C, and the crew time required for the hardware, CT. V_{eq}, P_{eq}, C_{eq} and CT_{eq} are equivalency factors unique to each mission which allow conversion of volume, power, cooling and crew time to mass values.[28,29]

$$ESM = M + \left(V \cdot V_{eq}\right) + \left(P \cdot P_{eq}\right) + \left(C \cdot C_{eq}\right) + \left(CT \cdot D \cdot CT_{eq}\right)$$

(10)

Table 4: Equivalent System Mass of CDRA, CDRILS (spray contact), and CDRILS (membrane contact).

		Value	ESM	Source
ISS CDRA	Weight	185.10 kg	326.1 kg	Calculated from Handford *et al.*[30]
	Volume	0.44 m^3		
	Power	556 W		
	Cooling	556 W		
CDRILS (spray contact)	Weight	106.4 kg	159.5 kg	Yates[4]
	Volume	0.109 m^3		
	Power	261 W		
	Cooling	392 W		
CDRILS (membrane contact)	Weight	86.4 kg	130.2 kg	Calculated from the membranes discussed in this work.
	Volume	0.093 m^3		
	Power	261 W		
	Cooling	392 W		

The ESM was calculated for the ISS CDRA, a CDRILS using spray scrubbing, and a CDRILS using membrane scrubbing from the values in Table 4 and displayed in Figure 11. Both are based on a crew of 4 for a Deep Space Habitat/Mars Transfer Vehicle. For the simplicity of this estimation, we have left out the cost of crew time. Although crew time is not included in this analysis, the reliability of the continuous liquid system is expected to be very high based on similar systems. Additionally, many of the parts of the CDRILS were derived from datasheets on ISS-proven parts which now have hundreds of thousands of flight hours.

The comparison shows a great advantage to using either of the two CDRILS systems. The CDRILS spray contact system reduces the ESM by more than 50% versus the CDRA, while the CDRILS membrane contact technology reduces the ESM by more than 60% versus the CDRA. The reduction in mass of the CDRILS spray system is due to the maximization of kinetics in the scrubber and stripper, as well as the absence of large, heavy desiccant beds. The reduction in mass, volume, power and cooling between the CDRILS spray system and the CDRILS liquid system reflects the absence of the rotary separator, as separation is performed by the membranes. The decrease in power for both CDRILS systems is due to the low regeneration energy required by ionic liquids.
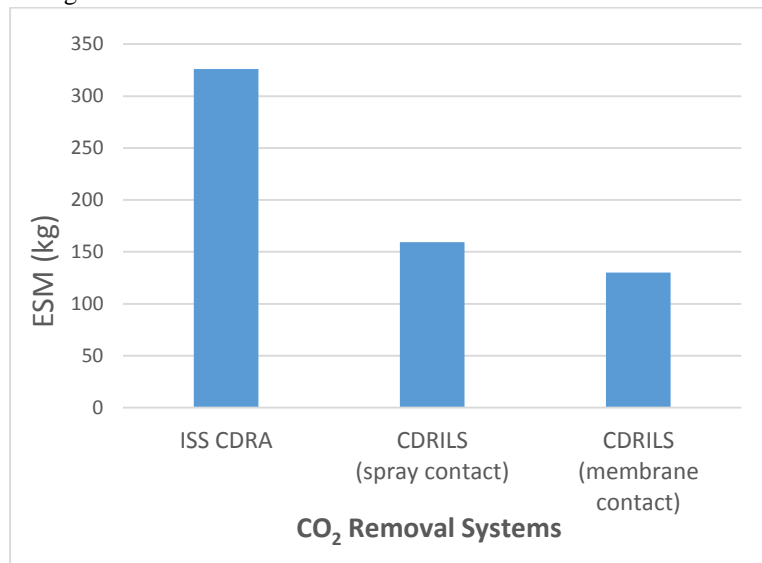

Figure 11: Equivalent System Mass (ESM) comparison.

Since the CDRILS systems will also perform trace contamination control and humidity removal, the CDRILS also reduces the load needed by the Trace Contaminant Control Subassembly (TCCS) and the Temperature and Humidity Control (THC) System. The resulting reduced mass on other systems is not shown in our estimates.

VII. Conclusion

CO_2 removal systems for spacecraft have used solid adsorbent systems up until now. The liquid absorbent approach utilizing ionic liquids and either spray or membrane contactors offer many advantages. Ionic liquids are safe, stable, highly efficient and reliable absorbents of CO_2. Proof-of-concept experiments have shown that the Honeywell's membrane technology has a mass transfer rate almost forty times greater than commercial membranes, and Honeywell is working to improve the mass transfer further. The use of a liquid system allows for the maximization of kinetics and estimates of the system have shown greater mass and volume savings in comparison with the current state-of-the-

art CDRA system. The use of ionic liquid, which has a significantly lower regeneration temperature, allows for greater power and cooling savings.

Acknowledgments

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