

Scale-up of the Carbon Dioxide Removal by Ionic Liquid Sorbent (CDRILS) System

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The Carbon Dioxide Removal by Ionic Liquid Sorbent (CDRILS) system is designed for efficient, safe and reliable carbon dioxide (CO₂) removal from cabin air on long-duration missions to the Moon, deep space, and Mars. CDRILS integrates an ionic liquid sorbent with hollow fiber membrane contactors for rapid CO₂ removal and recovery. The liquid-based system provides continuous CO₂ delivery, which avoids complicated valve networks to switch between absorbing and desorbing beds and enables simpler integration to the Sabatier without the need for the CO₂ Management System (CMS). Ionic liquids are particularly desirable as liquid absorbents for space applications since they are non-volatile, non-odorous, and have high oxidative stability. The hollow fiber membrane contactors offer both high contact area and rigorous containment between the gas and liquid phases in a microgravity environment.

Scale-up of the CDRILS technology has presented a series of fascinating challenges, since the interaction between hollow fiber properties, ionic liquid properties and performance is complex. Properties measured with lab-scale hollow fiber contactors are used to estimate the performance of contactors that are similar in scale to flight-scale demonstrations. To accomplish this, component and system models have been built to relate the key scrubber and stripper design and operating variables with performance, and experiments directed to validate the models have been performed. System size, weight and power are determined by component selection, arrangement, and operating conditions.

Reliability will be extremely important for any long-range mission and depends on the stability of the ionic liquids and hollow fiber contactors. We report on our continuing long term stability experiments for the ionic liquid and contactor materials and our investigation of the physical properties of additional ionic liquids.

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Nomenclature

<i>AHA</i>	=	aprotic heterocyclic anions
<i>ATR-FTIR</i>	=	attenuated total reflectance Fourier-transform infrared spectroscopy
<i>CASIS</i>	=	Center for the Advancement of Science In Space
<i>CCAA</i>	=	Common Cabin Air Assembly
<i>CDRILS</i>	=	Carbon Dioxide Removal by Ionic Liquid Sorbent
<i>CHN</i>	=	carbon, hydrogen and nitrogen
<i>CMS</i>	=	CO ₂ Management System
<i>CO₂</i>	=	carbon dioxide
<i>DMSO</i>	=	<i>dimethyl sulfoxide</i>
<i>EMIM Ac</i>	=	1-ethyl-3-methylimidazolium acetate
<i>ESM</i>	=	Equivalent System Mass
<i>¹H NMR</i>	=	proton nuclear magnetic resonance
<i>H₂O</i>	=	water
<i>HTU</i>	=	height of a transfer unit
<i>MTC</i>	=	mass transfer coefficient
<i>N₂</i>	=	nitrogen
<i>NTU</i>	=	number of transfer units
<i>O₂</i>	=	oxygen
<i>P₆₆₆₍₁₄₎⁺</i>	=	trihexyltetradecylphosphonium

I. Introduction

THE Carbon Dioxide Removal by Ionic Liquid Sorbent (CDRILS) system is a next generation approach to removal of carbon dioxide from the air in an enclosed system, including vessels in Earth orbit or interplanetary missions. In contrast to other approaches, it avoids the use of solid carbon dioxide adsorbents in favor of ionic liquids that have a specific affinity for carbon dioxide over oxygen and nitrogen. This approach, similar in many ways to the technology used to revitalize air in submarines, is operationally simpler than approaches with solid adsorbents. While solid adsorbent-based approaches require a complicated valve system to switch the beds between adsorption and desorption modes, circulating liquid in CDRILS allows the scrubber and stripper each to have a fixed role. Since the liquid can be rapidly moved between absorption and desorption, less carbon dioxide absorbent is required, reducing weight and volume. The CDRILS process is inherently well-designed for zero gravity, since the ionic liquid is constrained within the system, and forced flow is always used. It has high reliability due to internal redundancies, and easy maintainability since ionic liquid can be readily withdrawn or replaced without disassembly.

The CDRILS system has been described in prior papers.^{1,2,3} The current paper discusses progress in scaling up and optimizing the technology, including design and construction of a scaled-up CDRILS brassboard unit and the associated model development. It also reports results of continuing testing to ensure the long-term stability of the ionic liquid and a new effort to evaluate other ionic liquids.

II. Background

The CDRILS process is enabled by the unique properties of the selected organic ionic liquids. These materials are liquid at room temperature, and, because they are salts, have a negligible vapor pressure. They are nonflammable, non-toxic, easily handled liquids with viscosities low enough for rapid mass transfer and fluid flow. While carbon dioxide is soluble in many ionic liquids, certain ionic liquids have a specific affinity for carbon dioxide and therefore are selective for carbon dioxide over nitrogen and oxygen. As described in earlier papers, 1-ethyl-3-methylimidazolium acetate (EMIM Ac) is the current choice ionic liquid used for CDRILS.

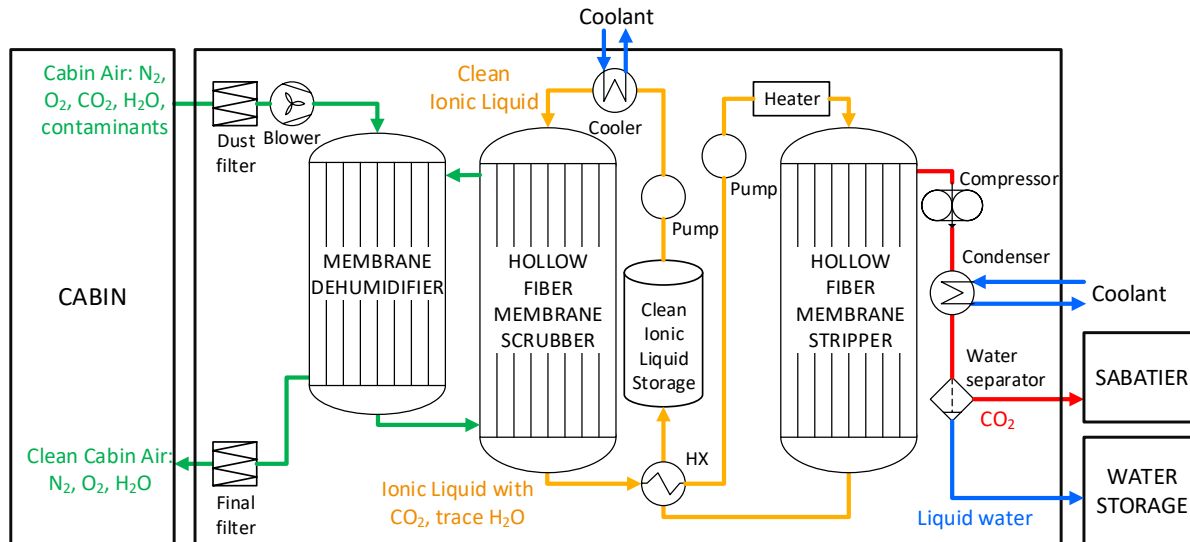


Figure 1: Generalized CDRILS System Schematic.

Figure 1 shows a schematic for the CDRILS process. Cabin air containing carbon dioxide, water, and possibly trace contaminants is drawn into the process by a blower. In some configurations, as in Figure 1, a membrane dehumidifier is used to remove water vapor for return of humidity to the cabin before the air enters the scrubber. The scrubber is a hollow fiber membrane contactor that allows intimate contact between the air and a stream of ionic liquid, while keeping these two streams physically separated. Carbon dioxide is selectively removed from the air, but, since water is quite soluble in the ionic liquid, water is also removed. The cleansed air is returned to the cabin. The CO₂-laden ionic liquid passes through a heat exchanger to heat to the stripping temperature (typically 50-60°C) before it enters the stripper. The stripper is also a hollow fiber membrane contactor, where carbon dioxide and water are drawn from the ionic liquid under vacuum, separated by condensation of water, and recovered as pure components for storage or for immediate use, such as by a Sabatier reactor as used on the International Space Station for the first step in recovery of oxygen from carbon dioxide.

Figure 2 shows the mass transfer processes in a hollow fiber membrane contactor used as a scrubber. Clean ionic liquid enters the bundle of hollow fibers at one end and leaves from the opposite end. Cabin air enters the shell surrounding the hollow fiber bundle at one side and leaves from the opposite side in a countercurrent configuration compared to the liquid flow. Air and its components contact the ionic liquid through the porous walls of the hollow fibers, and, driven by solubility, carbon dioxide and water transfer from the gas to the liquid phase. The ionic liquid and nitrogen and oxygen remain separated by the hollow fibers in the tube and shell sides, respectively. How effective this process is in removing carbon dioxide and water from the air depends on the capacity of the ionic liquid for each and on the mass transfer rate for each across the gas-liquid interface in the membrane.

The mass transfer processes in the hollow fiber membrane contactors at the stripper are similar. Ionic liquid containing carbon dioxide and water from the scrubber is fed in through the contactor. Carbon dioxide and water transfer through the porous hollow fiber walls from the liquid to the gas phase for

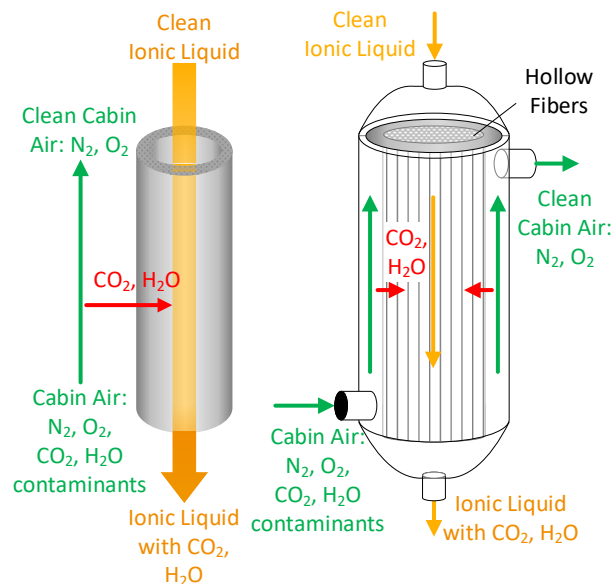


Figure 2: Membrane contactor in scrubber configuration.

recovery. Many of the contaminants present in the cabin air are absorbed into the liquid at the scrubber. Work is planned to further understand the fate of contaminants in the CDRILS system, such as in the work described in Section IV.

III. Long Term Stability of Ionic Liquids and Contacted Materials

A. Ionic Liquid Stability

This team has previously reported on the chemical analysis of samples of EMIM Ac aged under sparging dry air at room temperature for five months and at 60°C for 1 month.¹ The initially reported tests have been continued, and a third sample has been aged at 90°C, and aliquots have been taken periodically for analysis. The samples have been compared to control samples of pure EMIM Ac by ¹H NMR and ATR-FTIR spectroscopies and by elemental analysis for evidence of changes in chemical composition due to thermal oxidative degradation.

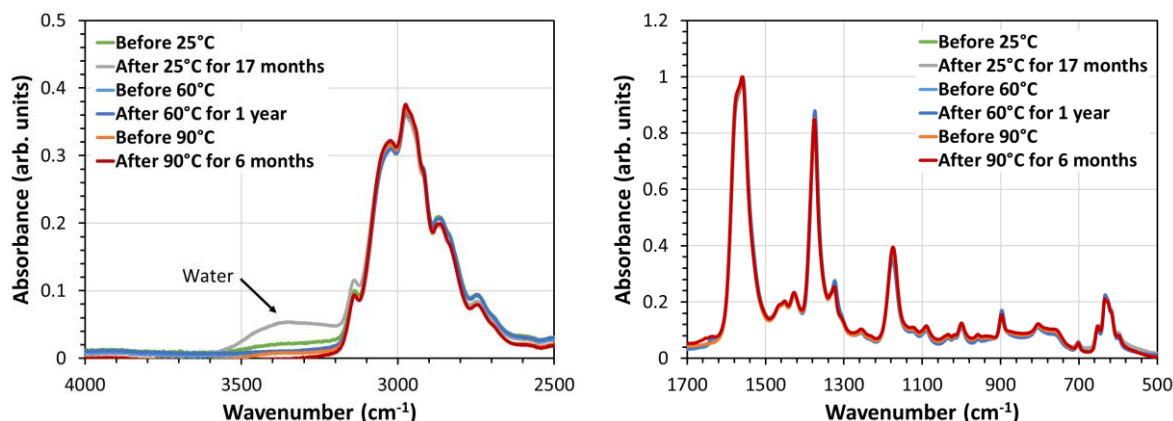


Figure 3: ATR-FTIR spectra for EMIM Ac before and after aging under air at 25°C, 60°C, and 90°C.

ATR-FTIR experiments and carbon, hydrogen, and nitrogen (CHN) elemental analyses of samples aged at room temperature for 17 months, at 60°C for 1 year, and at 90°C for 6 months show no change in chemical composition of the ionic liquid within the error of the methods. The ATR-FTIR spectra in Figure 3 show no changes in intensity or wavenumber bands, nor formation of any new bands, that would indicate the presence of any species in the sample other than EMIM Ac. Seven samples of fresh ionic liquid examined by CHN elemental analysis produced C/N wt%/wt% ratios of 3.40 ± 0.09 , which is in agreement with the stoichiometric ratio for EMIM Ac of 3.43. None of the liquids aged at any of the three temperatures have C/N ratios to date that are outside of the expected range (Table 1). The only experimentally significant change in liquid composition detected by either technique was variation in water content, which was consistent for each sample between both techniques and indicates only absorption and desorption of water from the air.

Table 1: Summary of combustion analysis for carbon, hydrogen and nitrogen for EMIM Ac after aging under air at 25°C, 60°C, and 90°C.

Temperature	C/N ratio (wt%/wt%, ± 0.09)			
	Fresh	Aged 6 months	Aged 12 months	Aged 17 months
25°C	3.52	3.34	3.26	3.45
60°C	3.45	3.36	3.48	-
90°C	3.46	3.39	-	-

Samples aged at each of the three temperatures were also compared by ¹H NMR spectroscopy in DMSO-d₆ (Figure 4). Figure 4A compares the overall spectra of a fresh sample versus the three aged samples, while Figures 4B-C magnify two regions of interest by 1500 and 375 times, respectively. Neither the samples aged for 17 months at room temperature nor the samples aged at 60°C for 1 year demonstrated an increase in or formation of impurities of greater than 0.5 mol% (experimental resolution). Note that the two impurity peaks detected at 3.2-3.1 ppm in the samples

aged at 60°C and 25°C were present in the starting samples and did not grow over time. The sample aged at 90°C for 6 months, however, did reveal several new peaks present at ~1-3 mol%. These most likely result from accumulation of trace products of thermal degradation. This observation indicates the importance of avoiding temperatures as high as 90°C in the CDRILS system.

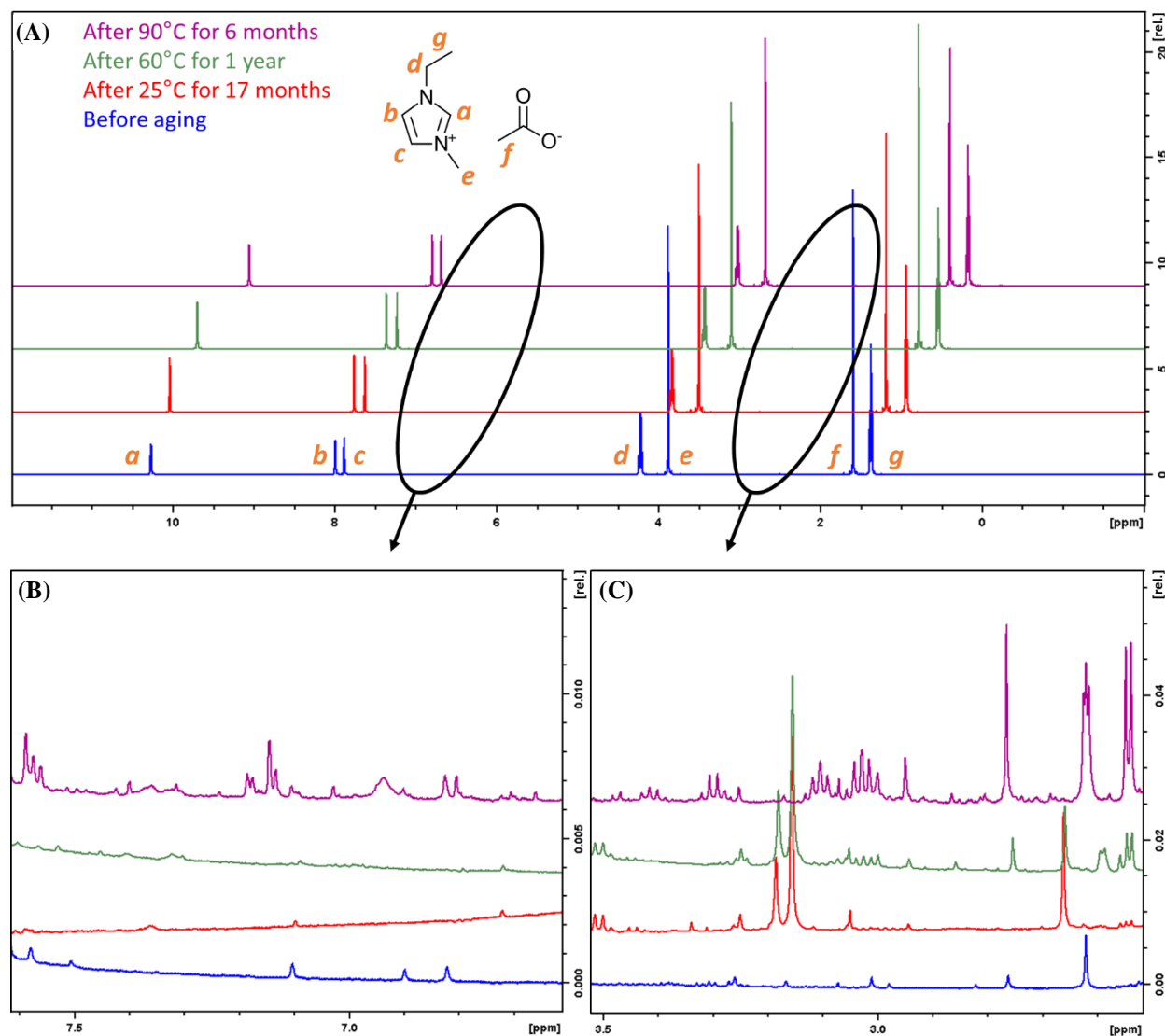


Figure 4: ^1H NMR spectra for EMIM Ac before and after aging under air at 25°C, 60°C, and 90°C.

The vapor pressure of EMIM Ac itself is too low to measure by conventional means, and to our knowledge there is no experimental vapor pressure for EMIM Ac available in the literature. To confirm the lack of volatility of EMIM Ac, a sample of pure, dry EMIM Ac was repeatedly heated to 70°C under vacuum for five hours and then weighed for evaporative loss. After more than 25 hours of heating and 33 hours under vacuum, the final weight of the ionic liquid was identical to the starting weight of the ionic liquid to five significant figures, with a standard deviation between the five measurements of 0.01%. This reproducibility supports the negligible vapor pressure of the ionic liquid. Thus, introduction of EMIM Ac vapors to the cabin air is not a concern for CDRILS, especially since the cabin air in CDRILS is exposed only to EMIM Ac at the scrubber, which is lower in temperature, at about 35°C, compared to the 70°C conditions explored in this test. Similarly, introduction of EMIM Ac vapor to processes downstream of the 60°C CDRILS stripper liquid is not a strong concern.

B. Membrane Contactor Stability

Three candidate hollow fiber types for use in our contactors were filled with ionic liquid and aged at room temperature or 60°C, and the contactors were tested for CO₂ scrubbing performance periodically. Testing conditions were identical between tests and between fiber types. Effective CO₂ mass transfer coefficients were computed and normalized compared to modules before aging to produce Figure 5. Each point represents the average of 2-3 aged modules. A small decrease in effective mass transfer coefficient is observed over time and can be expected in full-sized modules. Thus, the full-scale CDRILS system must be sized to account for this slow change. Lab-scale aging tests are ongoing with these and with larger modules.

The structural integrity of the contactor materials after prolonged exposure to ionic liquid and heating is also critical. The contactors are made of a metal housing, an epoxy-based tubesheet that anchors the fibers in place at the ends of the modules and separates the shell and tube sides of the contactor, and the fibers themselves. Housing materials are selected to be light-weight and resistant to corrosion by the ionic liquid. We have previously reported the structural integrity of tubesheet material exposed to ionic liquid¹. The force at break for fresh fibers and for fibers aged in ionic liquid at 25°C and 60°C is used to evaluate the strength of the fibers. With five samples per data point in Figure 6, the data for Fiber type #1 shows no experimentally significant change in either force at break or Young's modulus after 7 months compared to fresh fiber. Tests with the other two fiber types are ongoing.

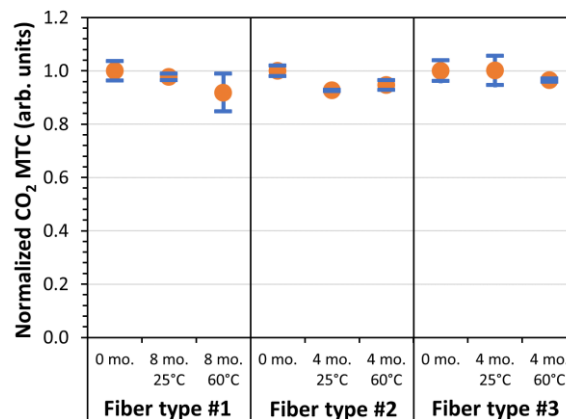


Figure 5: Normalized effective scrubber CO₂ mass transfer coefficients for lab-scale hollow fiber modules aged exposed to ionic liquid at 25°C and 60°C.

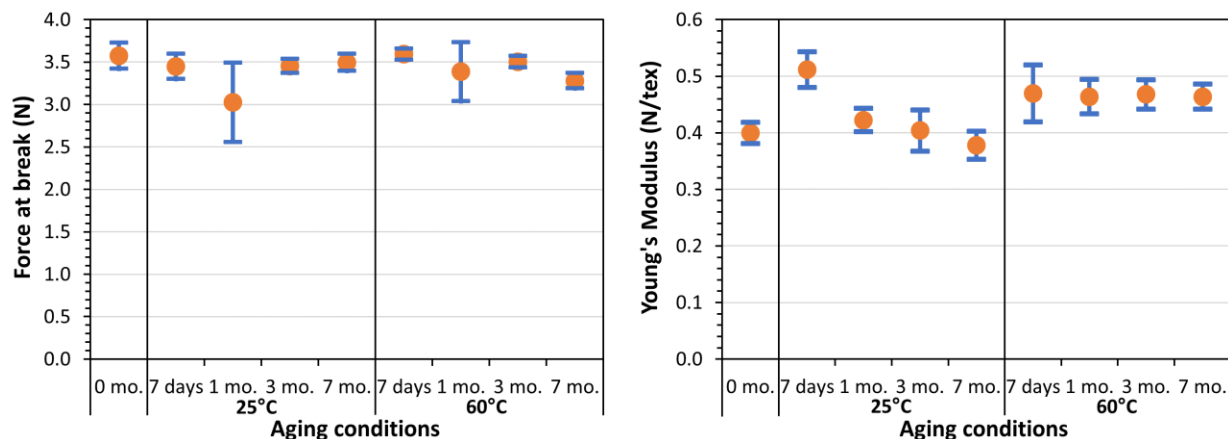


Figure 6: Force at break and Young's Modulus of hollow fibers aged at 25°C and 60°C exposed to EMIM Ac.

Strong adhesion of the fiber and tubesheet materials to each other after prolonged exposure to ionic liquid and heating is also important for structural integrity. Two studies designed to understand these properties were performed. In the first study, tubesheet samples were prepared with fibers extending several centimeters from one end of the tubesheet. The samples were aged dry at 60°C, and fibers were periodically pulled until either the fiber broke or slipped out of the tubesheet. Several types of custom tubesheet have been identified for which the force required to pull fibers from the tubesheet is higher than the force required to break them after 120 days of aging. This indicates strong adhesion between the fibers and the tubesheet. In the second study, vacuum of <5 torr was applied to the shell side of modulated fiber to evaluate the resistance of the tubesheet/fiber interface and of the hollow fiber itself to

leaking ionic liquid. Figure 7 demonstrates three approaches used in this study. Dye was added to the ionic liquid to facilitate visual detection of leaks. The first approach (Figure 7A) directly tests the leak resistance of the hollow fiber under vacuum, as the tube side of the fibers is connected to an ionic liquid reservoir and vacuum is pulled on the shell side. One such test of fiber leak resistance has demonstrated 6 months to date with no detectable ionic liquid on the shell side of the fiber. In the second approach (Figure 7B), the fibers are air-filled because they are uncut at both faces of the tubesheet, while ionic liquid fills a reservoir above the tubesheet and surrounding the fibers. One test on an optimized tubesheet design has so far survived over 4 months with no detectable ionic liquid on the shell side of the contactor or inside the hollow fibers. Finally, lab-scale contactors with looped fiber encased in tubesheet only at the top end allows the same type of tests to be conducted at elevated temperature (Figure 7C). Any contactors that do not resist leaks well begin to accumulate ionic liquid in the collection flask, which can be weighed periodically for comparison of various samples' ability to resist leaks. Whether a fiber is eventually wetted and begins to leak liquid depends on the fiber and liquid types, temperature, and pressure differential between liquid and gas. These and other tests of fiber and tubesheet long-term resilience to ionic liquid are ongoing.

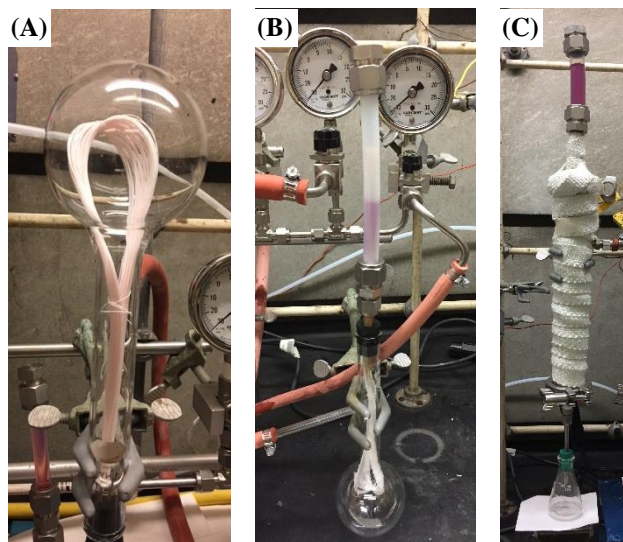


Figure 7: Vacuum tests on systems containing ionic liquid, hollow fiber, and tubesheet.

IV. Alternative Ionic Liquid Research

Recent computational and experimental studies have led to the identification and synthesis of a new class of ILs based on aprotic heterocyclic anions (AHA).⁴ Computer modeling suggested that the incorporation of aprotic anions would inhibit the formation of a hydrogen bond network between CO₂ adducts, thus preventing the increase in viscosity that is observed in most IL sorbents as CO₂ is absorbed. Experimental work with ILs based on the trihexyltetradecylphosphonium (P₆₆₆₍₁₄₎⁺) cation and several AHAs showed excellent CO₂ absorption for many of these ILs, particularly for lower partial pressures of CO₂, and no increase in viscosity with CO₂ uptake.⁵ However, the literature contains limited CO₂ capacity data for very low partial pressures of CO₂, little information about the kinetics or rates of CO₂ sorption and desorption, and no information on the long term stability of ILs when exposed to real world use conditions, all of which is required for the design of systems that use these ILs as sorbents.

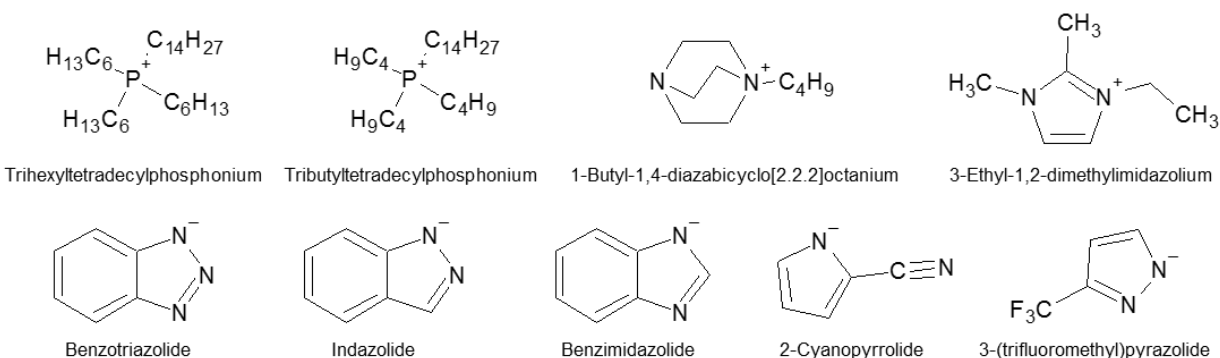


Figure 8. Cations and anions selected for study.

This study will fill these holes by examining a number of AHA-based ILs (Fig. 8) for use as drop-in replacements for the EMIM Ac sorbent currently used in the CDRILS system. AHA ILs based on the $P_{666(14)}^+$ were selected for study due to these ILs being well characterized in the literature, while the other three selected cations are likely to be water miscible as ILs and thus suited for use in a binary water-IL mixture such as the one currently used in CDRILS. The five anions were selected as ILs containing these anions have high affinity for CO_2 , even at low partial pressures.⁵

The performance of the candidate IL sorbents will be evaluated both for their effectiveness as CO_2 sorbents and for their compatibility with existing CDRILS hardware. In addition to measuring the CO_2 capacity for each IL, the rate of absorption and desorption will also be quantified, along with the viscosity of the ILs, and the selectivity of the ILs for CO_2 compared to N_2 or O_2 . The properties will be measured both for neat ILs and for ILs containing water. The compatibility of the new ILs with the materials used for wetted surfaces in CDRILS will also be determined through contact angle measurements and long duration corrosion testing. Additionally, the stability of the AHA ILs when exposed to common contaminants found in cabin air will be examined.

V. Scale-up

A. Brassboard CDRILS Design

Scaling the CDRILS test equipment from the previously reported lab-scale prototypes¹ to a brassboard unit has required a systematic approach. On the laboratory scale, the scrubber and stripper were built and tested separately then integrated to create the complete CDRILS unit. As separate units, the scrubber and stripper are effective tools to measure mass transfer coefficients and other parameters needed for scale-up and for model development, as discussed below. Following initial tests on the separate scrubber and stripper units, the two halves have now been integrated to establish proof-of-principle that the entire system can operate as expected. In the integrated system, continuous liquid recirculation between scrubbing and stripping allows the liquid composition and the scrubbing and stripping performance to reach an operating steady state. Since a stripper unit that removed effectively all of the carbon dioxide from the liquid would be unrealistically large or demanding in power, the ionic liquid returned from the stripper to the scrubber contains some residual carbon dioxide, while a scrubber tested separately typically receives rigorously clean ionic liquid. Similarly, water absorbs into the ionic liquid in the scrubber, while a fraction of the water in the liquid is removed in the stripper until both rates are equal and the process achieves steady state. The connection between CO_2 and water absorption and desorption provides valuable insight, even on the small scale, about expected steady state operation on a full-scale CDRILS unit. The construction of a second lab-scale prototype is also in progress. This integrated CDRILS breadboard prototype will be devoted to a long-term study to detect any changes in performance or failure modes over time.

In parallel with this effort, a CDRILS brassboard system has been designed, and its construction is nearing completion. The brassboard unit is designed to test and optimize full-scale hollow fiber contactors and other components at a range of operating conditions and to provide data for continued improvement of the system models. Scale-up presents a series of new challenges, including scale-up of the membrane contactors themselves, and must include proper design of the system around the contactor properties.

Design of a hollow fiber membrane module requires attention to a number of factors. Even a smaller module than the CDRILS design can hold $> 60,000$ fibers, and it requires skill and attention to smoothly lay these out into the shell. To minimize the number of modules, and thus the size of the system, higher packing densities are required, but too high a packing factor can lead to inefficient performance. The ends of the module are sealed with a tubesheet. This epoxy layer creates the boundary between the ionic liquid-filled manifold at the inlet and outlet and the gas-filled contacting zone and must therefore be durable and leak-free. Figure 9 shows the face of the tubesheet from a contactor module with a typical packing density.

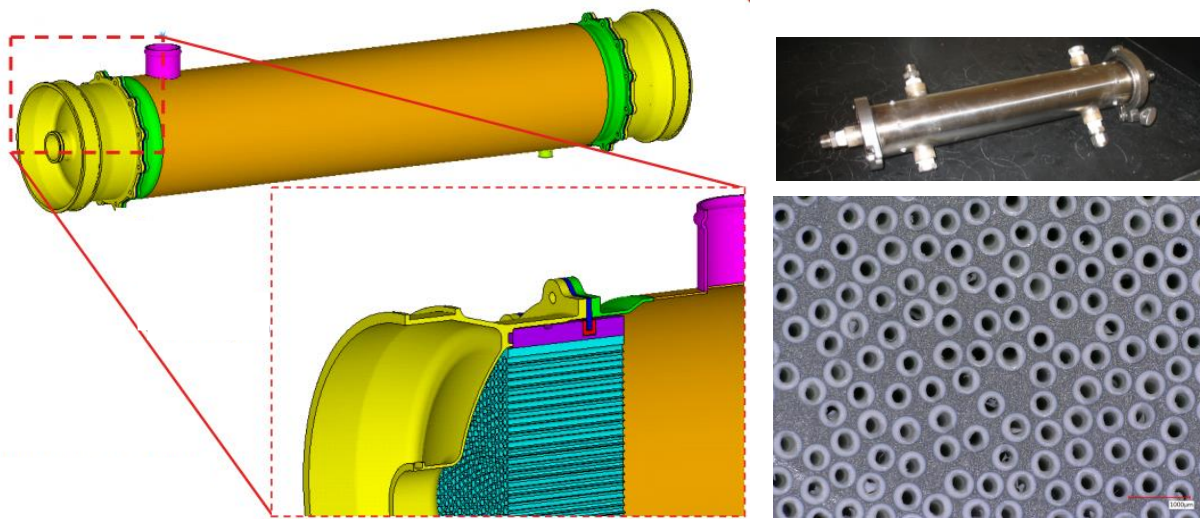


Figure 9: Tubesheet design for a hollow fiber membrane module and micrograph of fibers.

In contrast to modules for use in industrial applications, CDRILS modules must be short enough to fit into the locker sizes for possible missions. Since there is a practical limit to module diameter, the CDRILS approach is to have several scrubber or stripper modules mounted in parallel rather than to use a single contactor. This approach also allows for internal redundancy and easier maintenance. The brassboard unit as currently built accommodates four full-size contactors operated in parallel at the scrubber and four more in parallel at the stripper. Regardless of the number of contactors operated in parallel, any individual contactor should produce the same performance under the same individual operating conditions. Thus, scaling the module requirements for a larger or smaller CDRILS system simply involves increasing or decreasing the number of contactors in parallel.

Additionally, the brassboard is designed to incorporate other features not present in the lab-scale unit such as optional membrane dehumidification, a realistic vacuum pump and condenser, and more realistic thermal management. These features provide the opportunity to demonstrate some of the key features of CDRILS that were not readily demonstrated on the laboratory scale. The CDRILS brassboard can simulate cabin air that has been pre-dried by a membrane dehumidifier, as did the lab-scale unit, but it can also optionally incorporate (a) membrane dehumidifier module(s) between the simulated cabin air supply and the scrubber unit. This option allows for more thorough testing of the ability of CDRILS to act not only as a carbon dioxide scrubber but also as a humidity control system. As part of the humidity control system, water is stripped from the ionic liquid along with carbon dioxide at the stripper. The water must be separated from the carbon dioxide before being fed to the Sabatier. The preferred method for this separation is in a custom compressor/condenser that is currently under development. Finally, in order to minimize the power requirements of heaters and chillers as liquid is recirculated between the scrubber and stripper at different temperatures, the CDRILS brassboard unit makes use of a recuperative heat exchanger.

B. Brassboard CDRILS Unit

A schematic of the CDRILS brassboard unit is shown in Figure 10, and a photo of the test stand that is nearing completion of construction is shown in Figure 11. No attempt has been made to optimize size, weight or volume since the purpose of this unit is to demonstrate CO₂ removal performance on full-scale contactors and components and to collect operational data for further system and model optimization. Instead, additional sensors are included compared to a future flight unit, and the components are spread out for easy modification or maintenance. CO₂ concentrations and humidity of cabin simulant air before the scrubber and treated air after the scrubber are measured, as are the CO₂ and oxygen concentrations and humidity of the product CO₂ stream, and temperatures, pressures, and flow rates of gas and liquid streams at the module and system level. Treated air can also be sampled individually from each scrubber contactor to ensure consistent performance between contactors. Aliquots of ionic liquid can be removed for determination of water content by Karl Fischer titration. Liquid pumps and heaters provide steady flow and

temperature control on gas and liquid lines and on each contactor. A control system allows for semi-automated operation and continuous data logging.

The brassboard unit includes four parallel hollow fiber contactors at the scrubber and four at the stripper. In Figure 11, one module is shown in place for the scrubber and one for the stripper. The parallel plumbing is completed such that each module is in an identical environment to the other three. This ensures that any inconsistencies between contactors can be identified based on differences in sensor measurements to optimize the modulation process. Additionally, any performance observed on four modules can easily be scaled to expected performance on more or fewer modules. Equipment has been selected that allows air and liquid flow rates to be varied over a wide range so that the brassboard can be operated with as few as one module and up to more than four modules each at the scrubber and the stripper. This flexibility will aid in accurate scaling predictions from the data and facilitate optimization of the component and system models.

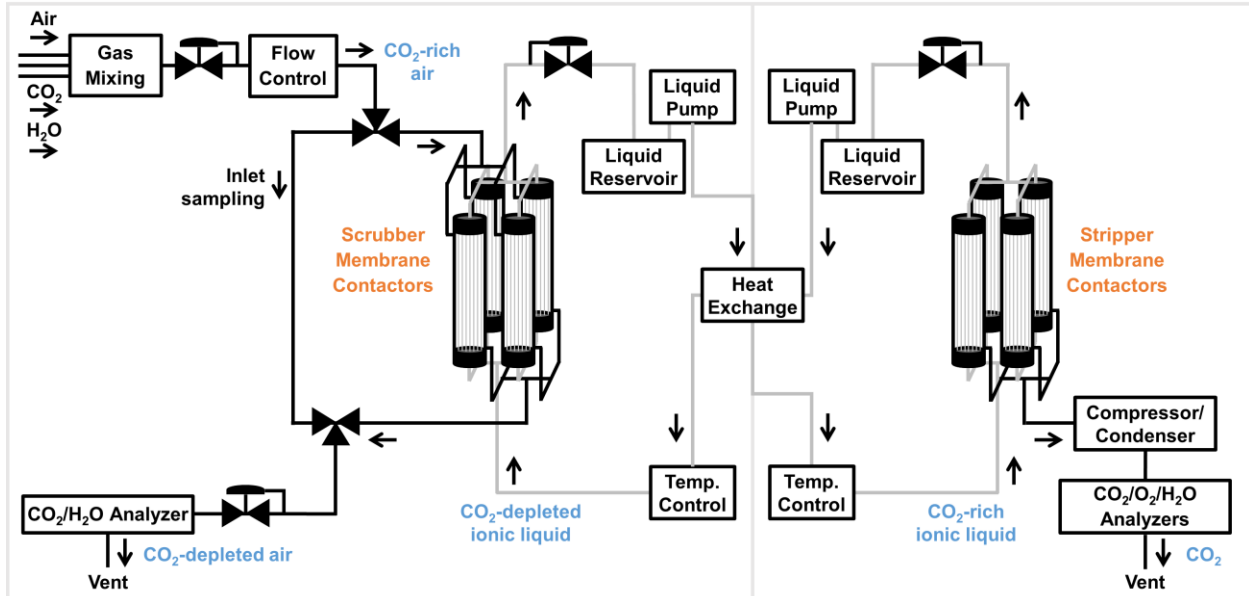


Figure 10: Schematic of the CDRILS brassboard unit.

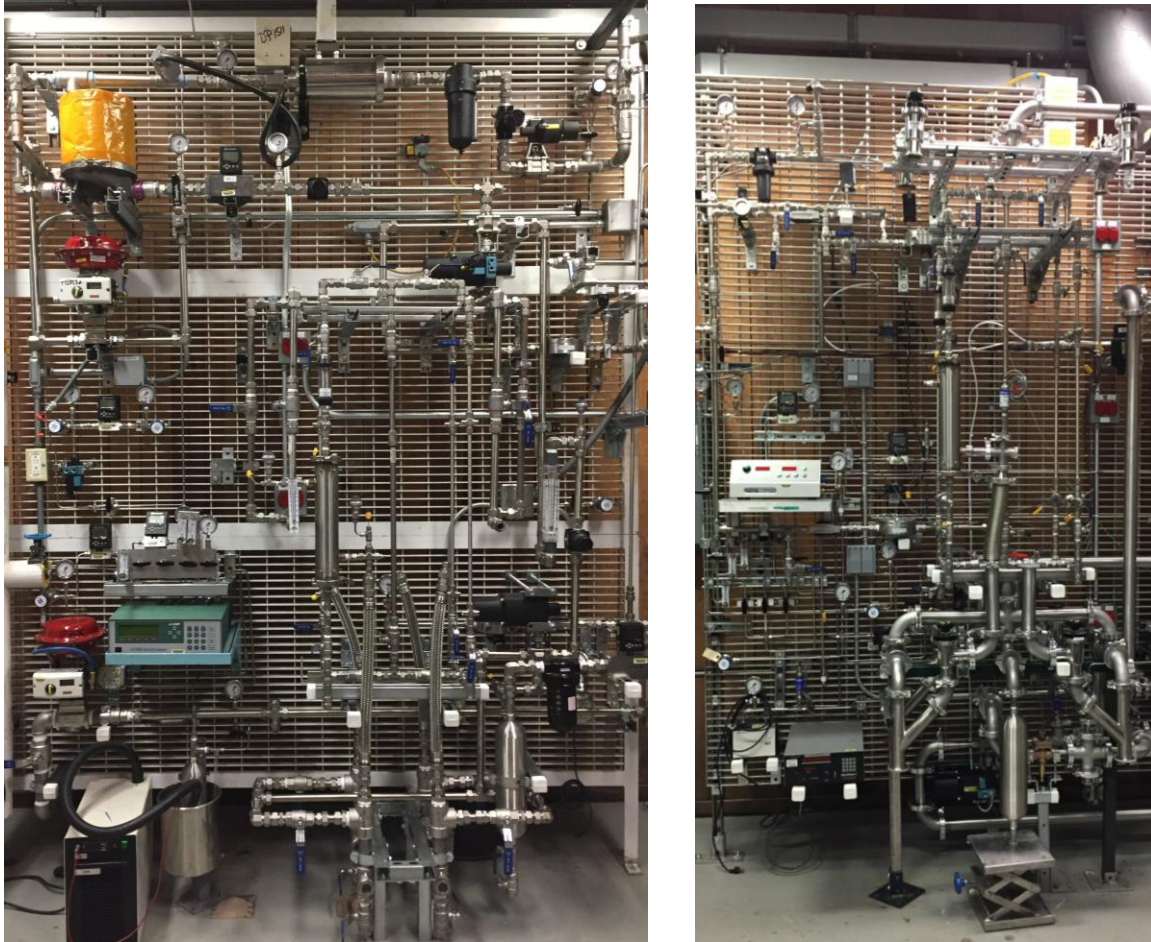


Figure 11: Pictures of the scrubber (left) and stripper (right) of the CDRILS brassboard unit.

VI. Component Model Development

While the experimental work reported in this and earlier papers has established the use of an ionic liquid to scrub carbon dioxide from air and recover it in a stripper, the connection between these lab-scale experiments and a full-scale CDRILS unit takes the form of multiple models. Component models are used to synthesize the experimental results into preliminary designs for larger scale units and will be validated and corrected using experimental data from the larger scale unit. These models then contribute to the system model of the entire CDRILS unit, which predicts size, weight, power and cooling. Separate but related component models are required for the scrubber and the stripper.

The scrubber modules can each be considered to be a continuous countercurrent contactor in which the gas phase (cabin air) and the liquid phase (ionic liquid) are continuously flowed through the device. Key variables include the length and active area of the contactor and the flow rates and compositions of the gas and liquid phases. To evaluate the efficiency of removal of carbon dioxide and water from the air, the equilibrium capacity of the ionic liquid for dissolved gases must be known. The modeling approach to the CDRILS scrubber must account for shifts in the composition of the two phases while passing through the contactor since they impact the equilibrium capacities and the rate of mass transfer between the phases.

Our basic approach to modeling carbon dioxide and water transfer in the scrubber is identical for the two components and can be illustrated graphically for carbon dioxide as in Figure 12, in which the two axes are the mole fractions of carbon dioxide in the gas phase and the liquid phase. The green isotherm line represents the capacity of the ionic liquid for carbon dioxide as a function of gas phase mole fraction and is shown as a straight line for simplicity. The red line, traditionally called an operating curve, represents a CO_2 species balance between phases over the modeled scrubber. The lower terminus of the red operating line is determined by the desired outlet CO_2 concentration

in the air (y_2) and the concentration of CO_2 remaining in the ionic liquid after the stripper (x_2), and the upper terminus is determined by the inlet CO_2 concentration in the air (y_1) and the design concentration of CO_2 loaded into the ionic liquid (x_1). Again, for purposes of illustration, the operating curve is shown as linear. Note that the theoretical liquid mole fractions of carbon dioxide at equilibrium corresponding to y_1 and y_2 are designated x_1^* and x_2^* , and the theoretical gas phase mole fractions corresponding to x_1 and x_2 are y_1^* and y_2^* . The desired transit down the operating line can be envisioned as a series of steps coming alternatively to equilibrium and then return to the operating line.

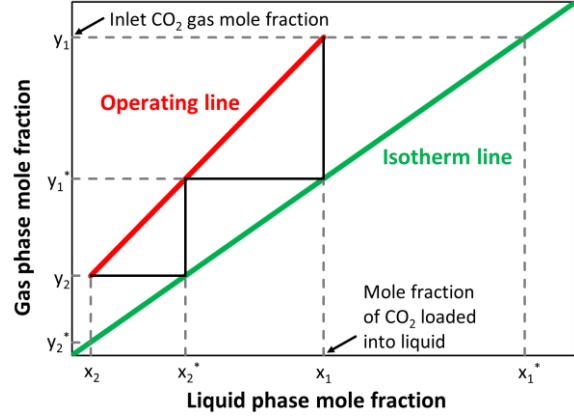


Figure 12: Scrubber operation conceptualized as a series of equilibrium stages

Each “step” in Figure 12 is a theoretical equilibrium stage, and this Figure allows for estimation of the number of theoretical equilibrium stages required to accomplish the specified separation. The column height equivalent of a theoretical stage is evaluated through experiment, and usually correlated to superficial flow rates, surface area, and other variables. Implicit in this approach is the assumption that enough opportunity is given to permit the mass transfer between phases to achieve equilibrium. The CDRILS scrubber model uses a transfer unit approach to model performance of the hollow fiber membrane module. The number of theoretical transfer units needed and the corresponding height of a transfer unit are computed from available information. The height of a transfer unit (HTU) is proportional to a number of key variables, principally the number of hollow fibers in the membrane bundle.⁶ To achieve the desired separation, the product of the NTU and HTU must equal the active length of the hollow fiber membrane module (Z). Assuming counter-current flow, dilute solutions, single component scrubbing, and constant slope isotherms, values for NTU and HTU can be calculated for each set of conditions using equations 2 and 3.

$$Z = NTU_G HTU_G \quad (1)$$

$$NTU_G = \int_{y_2}^{y_1} \frac{dy}{y - y^*} + \frac{1}{2} \ln \frac{1 - y_2}{1 - y_1} \quad (2)$$

$$HTU_G = \frac{G}{K_y a_0 (1 - y^*)_{LM}} \quad (3)$$

In these equations, NTU is the ratio of mass transfer conductance to the capacity rate for mass transfer. In equation 3, G is the gas phase flow rate, K_y is the overall mass transfer coefficient, a_0 is the ratio of the membrane area to the contactor volume, and the final term is the logarithmic mean of $(1 - y^*)$. The final term corresponds to an integrated driving force for mass transfer. As the mass transfer coefficient increases, the height of a transfer unit decreases, and the overall length of the module can decrease. Equation 3 also establishes a relationship between the height of a transfer unit and a_0 . Since a_0 accounts for the number and diameter of membrane modules, and hence the size and weight of the scrubber, equation 3 lays out the requirements for sizing the scrubber. For sizing a scrubber under specific operating conditions, an appropriate effective mass transfer coefficient should be applied, as its value varies based on operating conditions. For example, the mass transfer coefficient, assumed in these equations to be constant throughout a contactor, in fact changes with temperature and water concentration.¹ This needs to be borne in mind while modeling contactors using this approach. While this discussion has focused on carbon dioxide removal, an analogous treatment is used for water removal from air. Since the mass transfer coefficient for water is about 10 times that of carbon dioxide, a module designed for carbon dioxide removal will typically also be adequately sized for water removal.

This simplified scrubber model forms the basis for routine evaluation of laboratory results. Effective mass transfer coefficients are calculated from data measured with lab-scale modules. The model and these mass transfer coefficients have been used to size the modules and gas and liquid flow rates for the full-scale unit. Further evaluation and validation of the model will occur once the scaled-up CDRILS system is complete. Scale-dependent effects are expected for the hollow fiber contactors, including the effects of pressure and temperature distributions within the module and the increased likelihood of shell side mass transfer limitations. Shell side mass transfer is a frequent focus

in membrane module scale-up and results from stagnant zones developing where dense fiber arrays prevent free gas flow. In these regions the carbon dioxide concentration can be depleted without introduction of fresh gas, which reduces the driving force for mass transfer and thus the effectiveness of the module.

The CDRILS stripper model incorporates additional complexities that are present in the stripper, such as the fact that stripper operation is very sensitive to shell-side pressure. Since the shell-side pressure is very low and relative pressure gradients are high, almost all the simplifying assumptions used to develop the scrubber model are not applicable; a more general approach with more detailed assumptions is required. For example, the carbon dioxide permeating through the fibers becomes a significant component of the gas composition so that equations 2 and 3 no longer hold true.

VII. Trade Studies using System Model

As the models for key components like the scrubber and stripper have been refined, the insights from these models have been incorporated into a system-level model for the CDRILS system. This system level model includes the modules and the remaining components within CDRILS, including the blower, liquid pumps, heater, chillers, vacuum pump, condenser, and the membrane dehumidifier. The model accepts inputs for cabin conditions, such as the temperature, pressure, CO₂ partial pressure and relative humidity of the air, as well as system requirements, such as the number of crew and the CO₂ partial pressure requirement. The key system requirements for all examples discussed below are that the system remove CO₂ for 4 crew, or 4.2 kg/day,⁷ and maintain a CO₂ partial pressure requirement of 2 torr. Adjustable parameters for the model include scrubber and stripper performance inputs, such as air and liquid flowrates, temperatures and pressures. The model outputs the volume, weight, power, and cooling requirements of each component and of the entire system.

A. Optimizing scrubber efficiency

The system model was used to determine the optimal balance between the volumetric flowrate of cabin air into CDRILS and the scrubber volume and mass. A scrubber with 100% efficiency, or one that removes 100% of the CO₂ from the air that enters the scrubber, would be infinitely large. However, lower scrubber efficiencies increase the air flowrate required to remove the same CO₂ load. This increases not only the blower volume, weight and power, but also the quantity of water vapor that must be desorbed in the stripper. This additional water vapor in turn increases the volume, weight and power of the ionic liquid heater, vacuum pump, and condenser. Figures 13A and 13B show how scrubber efficiency can be varied in the system model to predict the optimal balance between a highly efficient scrubber and a high air flowrate. Note that selecting a high scrubber efficiency near 90% results in high volume and mass, while minimizing power and cooling. However, a similarly low power and cooling can be achieved at scrubber efficiencies between 40% and 80%, where the CDRILS volume is also at its lowest and the mass is also minimized. Therefore, assuming the conditions in the example, the optimum scrubber efficiency is expected to be in the broad range of 40-80%, and a desired design point or operating range can be selected based on the specific integration requirements of the broader life support system.

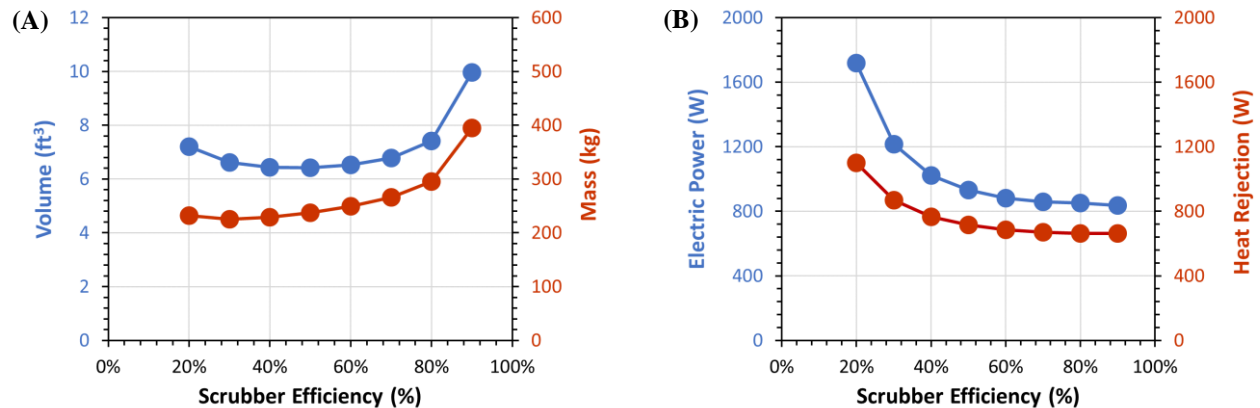


Figure 13: A) Volume and mass predictions, and B) electric power and cooling predictions for the CDRILS system model for 4 crew, as a function of scrubber efficiency.

This flexibility in scrubber efficiency stands in great contrast to solid carbon dioxide scrubbers. Solid adsorbent-based systems frequently include desiccant beds upstream of the CO₂ adsorbent because the solid adsorbent competitively adsorbs water over CO₂. Thermal desorption from both beds is required to recover the CO₂ from the adsorbent and the water from the desiccant. Because of their sizes and the heat capacities of their shells, heating and cooling the beds to proper desorption and absorption temperatures requires significant time in which beds perform little absorption or desorption. Solid sorbent systems are therefore designed to minimize the amount of time spent cycling between adsorption and regeneration modes. This translates into large adsorbent beds that are loaded to near capacity. To minimize the size, weight, and power required for the desiccant, a high CO₂ removal efficiency is required of the adsorbent to minimize the amount of water introduced into the system. The need for high CO₂ removal efficiency with long cycle times and loading to near capacity all contribute to larger adsorbent bed sizing. In contrast, in CDRILS, even without a membrane dehumidifier, the water absorbed into the liquid at the scrubber has a negligible effect on the capacity of the ionic liquid for CO₂ or the immediate CO₂ removal performance. The absorbed water is simply removed from the liquid at the stripper to avoid accumulation of water in the ionic liquid over time. Continuous liquid circulation allows for operation below the liquid capacity for CO₂, where CO₂ capture is more rapid. The temperatures of the scrubber and stripper do not change during operation, so extra adsorbent is not required as it is with solid beds to account for heating and cooling time. High CO₂ removal efficiencies are therefore not necessary, and scrubber size can be reduced. The tolerance of the CDRILS process to water also presents an opportunity for CDRILS to contribute to humidity management of the cabin air, as discussed below.

B. Optimizing water removal

In determining an optimal balance between system size and power, water management is important. Like other CO₂ absorbents, ionic liquid has affinity for both CO₂ and water. In CDRILS, any water that co-absorbs in the ionic liquid with CO₂ is desorbed in the stripper to maintain the humidity balance in the cabin and to prevent the CO₂ capacity of the liquid from decreasing slowly over time. However, desorption of water at the stripper increases the volume, weight and power of the heater, vacuum pump and condenser. To mitigate these negative impacts, the amount of water removed can be modulated by adjusting the size of the membrane dehumidifier, which returns the water vapor to the occupied space before it would otherwise be absorbed into the ionic liquid at the scrubber.

Figure 14 shows the predicted volume, mass, power and cooling for a CDRILS unit operating at 50% scrubber efficiency for 4 crew, while absorbing varying amounts of humidity, as controlled by the membrane dehumidifier. Without a membrane dehumidifier, absorption of humidity into the ionic liquid drives high power and cooling requirements (Figure 14B). When the amount of humidity allowed to absorb into the ionic liquid is minimized using a membrane dehumidifier, power and cooling are also minimized, but the volume of the membrane dehumidifier drives the total system volume higher (Figure 14A). From a volume and weight perspective, the optimal humidity absorbed is between 4 and 17 kg of water/day. The water vapor generation rate for crew members is within this range at an average of 7.4 kg/day,⁸ so CDRILS is capable of managing this humidity load in place of the condensing heat exchangers used today for humidity removal.

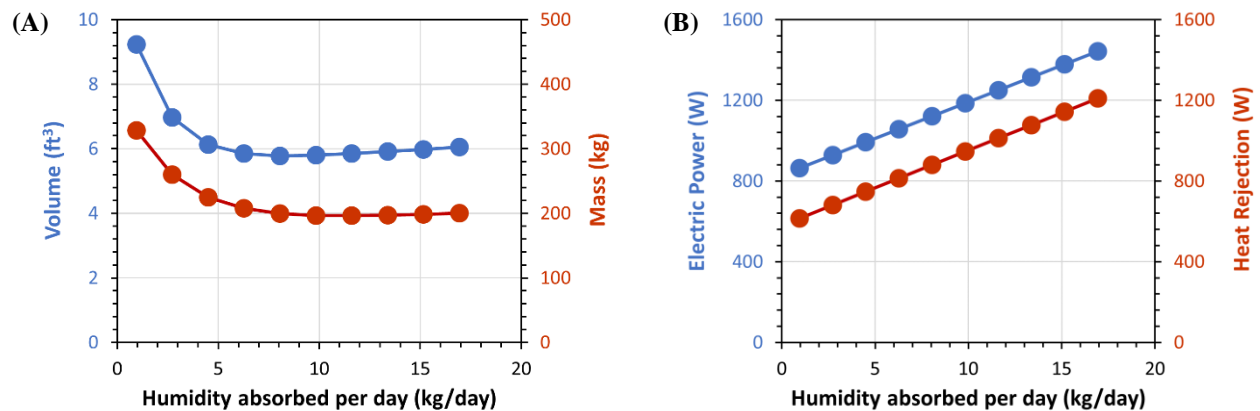


Figure 14: A) Volume and mass predictions, and B) electric power and cooling predictions for the CDRILS system model for 4 crew for various rates of humidity removal.

Humidity removal has been problematic on the International Space Station. The Common Cabin Air Assembly (CCAA) suffers from microbial growth, requiring two alternating condensing heat exchangers to allow for periodic dryouts. It is also implicated as a source of siloxane contaminants due to breakdown of a hydrophilic coating, which is used in part to prevent bacterial growth in stagnant water.⁹ CDRILS is likely to avoid these concerns for a few reasons. First, humidity removal occurs in the scrubber, where the relative humidity of the air never exceeds that of the habitat. Microbial growth in this unit is unlikely because no liquid water is present except that which is dissolved in the ionic liquid, which is antimicrobial. Water is carried in the ionic liquid to the stripper, where it is heated and removed under vacuum. Condensation of water occurs from a stream containing only carbon dioxide and water. Microbial growth is unlikely here since no oxygen is present in the stream. Because of the preconcentration of CO₂ and humidity in the condenser, the size of this condensing heat exchanger is much smaller than that required to condense the same quantity of water vapor from the air. The CDRILS system cannot replace all functions of the CCAA, since it does not cool the air or provide the air flowrates needed to ensure sufficient mixing of the cabin air, but use of CDRILS as the primary dehumidification approach, with a downsized system to maintain cabin temperature, should be considered for future vehicles.

VIII. Conclusions and Future work

The brassboard unit is soon to be completed and will be used to validate and refine our component models for predictions such as pressure drops and mass transfer coefficients at the full scale. Validation of our models will also allow us to validate our trade studies, and complete a number of other important studies to further refine the development of the CDRILS system. After completion of this brassboard unit, Honeywell will begin work on building a prototype for demonstration on the International Space Station, through the Center for the Advancement of Science In Space (CASIS). This prototype is currently envisioned to be similar to that shown in Figure 14. We anticipate refining this design over the next year to be ready for this important experiment.

In work with NASA AES, the studies of alternative ionic liquids are just beginning and may lead to the selection of alternative liquids with improved characteristics. An automated lab-scale CDRILS system is under construction with plans to operate continuously for at least six months to accumulate durability information and note any long-term trends. Extended operation of this unit will also improve our understanding of how a CDRILS system might operate at full scale. This test stand may later be used to test the performance of the alternative ionic liquids and determine optimal conditions for their use.

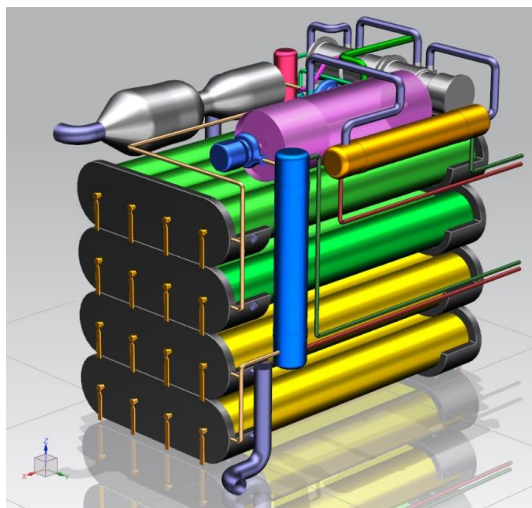


Figure 14: Conceptual Drawing of CDRILS unit for CASIS.

Acknowledgments

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