# Evaluation of Ionic Liquids for Closed Air Revitalization

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Final Report for 2018-2019 X-hab Project Course

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## Abstract

This document is the final report resulting from the work conducted by undergraduate students at the University of South Alabama during the 2018/2019 academic year and was prepared by the undergraduate students.
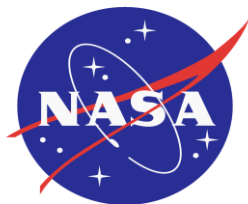
As NASA pushes the boundaries further into space, the current technologies within the various life support systems must be improved upon.  One such improvement is needed to the current air revitalization systems, specifically sorbents that can capture $CO_2$ more effectively from enclosed habitats.  Ionic liquids (ILs) have been considered as absorbents for flue gas, but little research has been done to test the ability of ILs at ambient pressures and relatively low concentration of $CO_2$. The experiment outlined below utilizes the task-specific ionic liquid, tetramethylammonium taurinate (TMN) , in a commercial off the shelf absorption system to capture $CO_2$. The $CO_2$ stream is combined with nitrogen to produce an inlet gas concentration relevant to close air revitalization applications.  At an inlet gas flow with a $CO_2$ partial pressure of 3.8 torr the system was capable of removing just under 97% of the inlet $CO_2$.  The concentration of $CO_2$ in the outlet stream, partial pressure 0.16 torr, was less than that of atmospheric air.  The duty required to separate the absorbed gas from the ionic liquid as well to cool the ionic liquid to be reintroduced to the column were acquired utilizing laboratory cooling/heating baths. These results show that TMN may be an efficient candidate for consideration in closed air revitalization.

**Introduction**

        Air revitalization is a vital aspect of life support in closed system environments and is one of NASA's mission priorities.  Systems such as permeable membranes, liquid amines, adsorbents, and absorbents are some of the methods being used today.  The current $CO_2$ removal system used in the International Space Station uses a dual desiccant bed. The dual desiccant bed has to remove approximately one kilogram of $CO_2$ per day per person to ensure survival.  At 100% performance, the CDRA (Carbon Dioxide Removal) system is able to remove enough $CO_2$ to support six people [1]. Utilizing ionic liquid absorption may provide an alternative to scrubbing $CO_2$ in a closed environment.  However, at present more research information about the performance of ionic liquid for low pressure $CO_2$ capture. Driven by the Lewis acid-base reaction, the anion of the compound captures the $CO_2$.  Unlike using liquid amines, TMN Taurinate have a low vapor pressure resulting in a negligible volatility.  Therefore, using TMN Taurinate for this experiment presents a more efficient, and safer, way of absorbing $CO_2$ when compared to using liquid amines which are known to be toxic and volatile.  Pure TMN is a non-volatile, hygroscopic, crystalline solid that can easily be dissolved in water to form an aqueous solution.   This allows TMN to be easily stored and used as needed.  Ionic liquids also have high thermal stability, which makes it an ideal candidate for closed environment systems such as the International Space Station.  To test the effectiveness of ionic liquids in absorbing $CO_2$, a commercial off the shelf absorber column was used to test the absorption capabilities of TMN at a range of partial pressure and temperatures.

**Schedule and Work Breakdown**

        Initial Research began Fall Semester of 2018 (August 2018-December 2018). Dr. Glover's Systems Engineering Class (CHE-490) aided in determining milestones for the project. Tasks included background research, system design, budgeting, creating a template for a testing and evaluation master plan, and procurement of equipment.  Periodic meetings with Dr. Eric Fox and associates from the Marshall Space and Flight Center concerning project milestones were held during the fall, and more were scheduled throughout the project.  During the Fall Semester of 2018, significant design options were explored and detailed trade-off analyses were completed to arrive at the design that is discussed in this report.  For clarity the various options that were not pursued are not discussed in this report but were documented with presentations provided to NASA throughout the Fall semester.

        Spring Semester of 2019 (January 2019-May 2019) consisted of continuing procurement, assembly, component & system test and evaluation, and data collection.  A summary of the schedule is shown as a Gantt Chart in Figure 1.  The Work Breakdown Structure is an important part of project planning that reduces complicated activities down to a collection of doable tasks. The Project was broken down into various tasks and sub-tasks as shown below:

1. Task-Specific Ionic Liquids (TSIL)
      1.1  Background Research

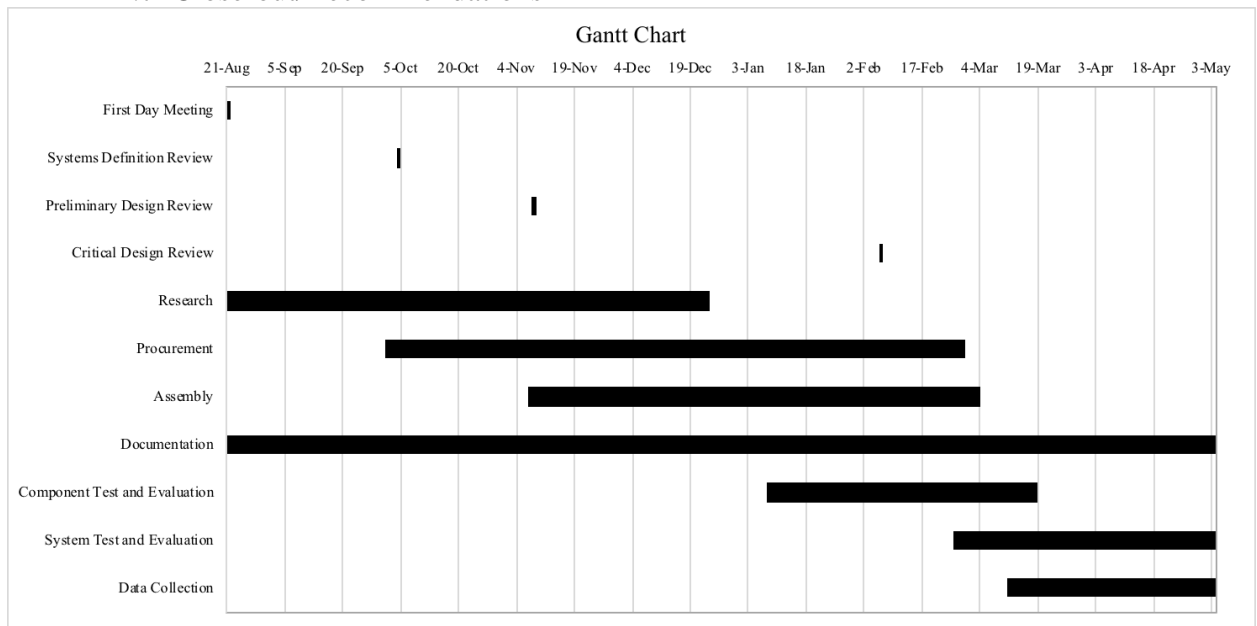**Figure 1.** NASA X-Hab $CO_2$ Scrubber Gantt Chart

**Equipment Selection and Assembly**

      The main objective of this experiment is to quantify the effectiveness of the ionic liquid, TMN Taurinate, to absorb $CO_2$ using a commercial off the shelf absorber column. The commercial system is shown in Figure 2. During the Fall Semesters it was determined that a second heat exchanger and pump would be required to regenerate the fluid. A block flow diagram of the preferred system design is shown in Figure 3. The modified absorber column is shown in Figure 4 and has the heat exchangers labeled. The heat exchanger that contains the green heat transfer fluid is the cold heat exchanger used to reduce the ionic liquid temperature after removing the CO2.

      Utilizing a combination of the block flow diagram in Figure 3 and Figure 4, the process path of the ionic liquid and CO2 can be discussed (a process flow diagram and piping and instrumentation diagram are provided in the appendix). Specifically, the ionic liquid was pumped from the bottom of the absorber, to a heater, then a regeneration flask. From the regeneration flask, the ionic liquid is drained to a chiller after which it is transferred to the top of the absorber. Simultaneously, $CO_2$ and nitrogen were released from the bottom of the absorber, where it came in contact with the ionic liquid flowing from the top of the absorber column through the ½" Raschig rings. The ionic liquid with the absorbed $CO_2$ (effluent $CO_2$) was pumped through the heater where it was heated to 85ºC and passed into a regeneration vessel. This is where the scrubbed $CO_2$ was released to the atmosphere. The ionic liquid was then drained from the regeneration vessel to the cooler to be cooled down to 23ºC and pumped back
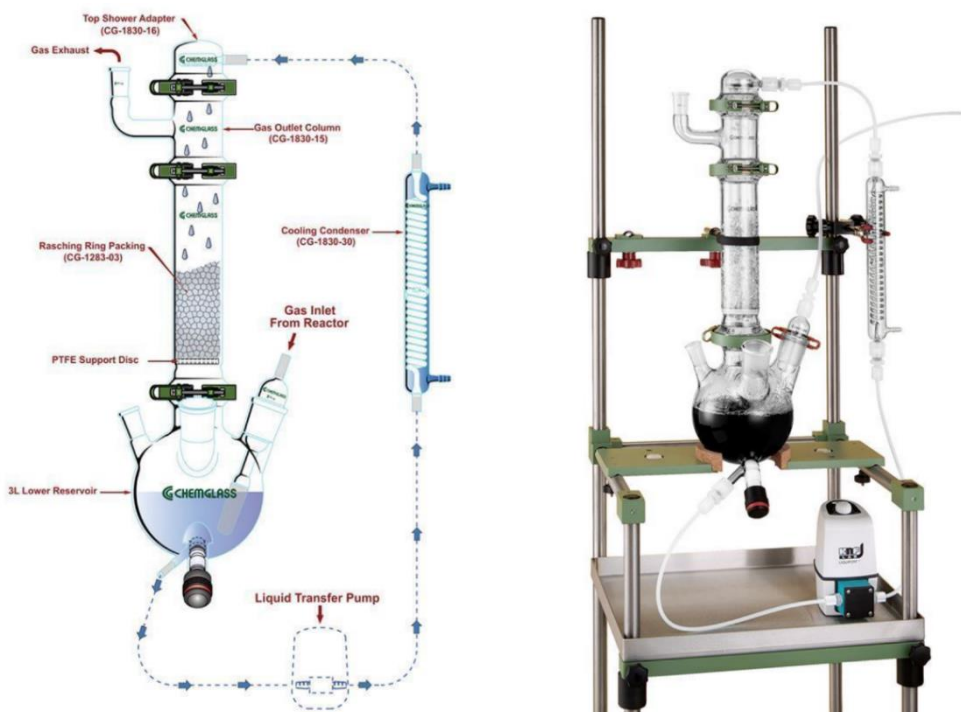


**Figure 2.** Chemglass 3L complete scrubber system as received. [2]

to the top of the column absorber.  Flow rates and temperatures were adjusted accordingly to achieve steady state within the process.
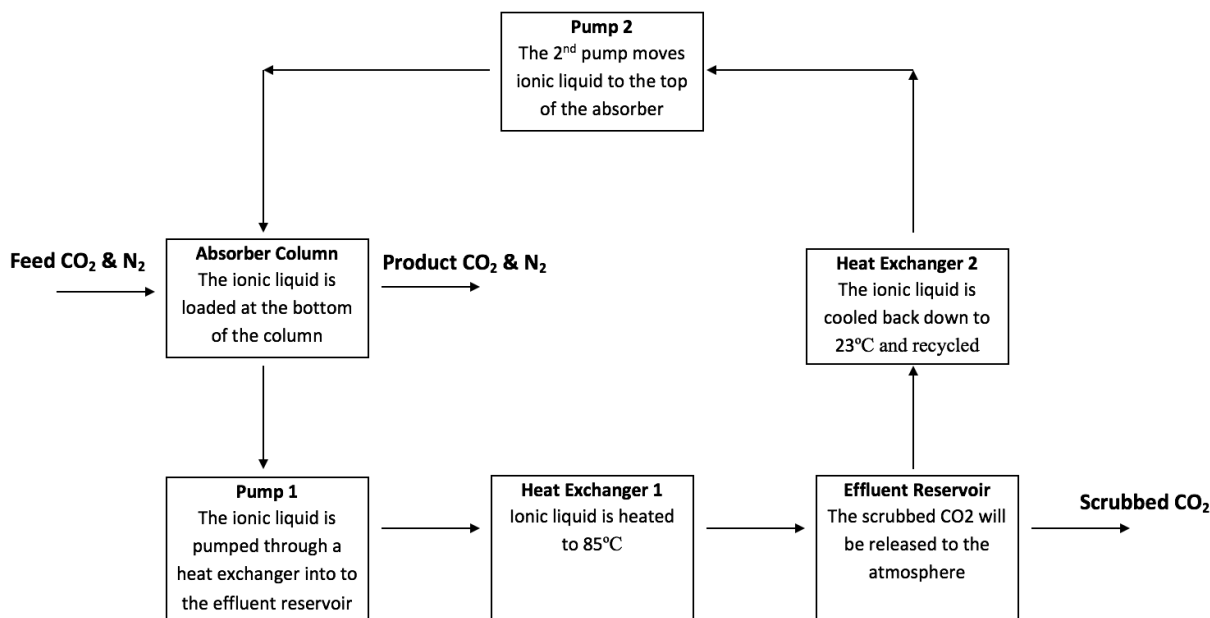


**Figure 3.** Block flow diagram - CO2 scrubbing apparatus

The commercial absorber used was purchased from ChemGlass and can contain three liters of ionic liquid.  The absorber consists of a 17" absorption column with a three liter reservoir, ½" glass Raschig ring column packing, PTFE diaphragm liquid transfer pump, a heat exchanger, and ¼" PTFE tubing. The tubing is used throughout the system and is connected by Swagelok fittings.

TMN Taurinate was pumped from the absorber using a diaphragm pump and was controlled by a variac voltage transformer.  The hot water bath will heat the ionic liquid up to 85℃ using a Thermo Scientific RTE-740 heater which was donated by Glover Research Group.  A three liter round bottom flask purchased from ChemGlass was used as the regeneration flask.  This volume will allow for the ionic liquid to be contained properly in case of overflow during the process.  From the effluent reservoir, the ionic liquid was drained to the PTFE Diaphragm Pump to a cooler regulated by an Across International Chiller C20-7.

## Sensors and Flow Controllers

From the beginning of the project, the choice of using a National Instrument Data Acquisition board (NIDAQ), was made due to the prevalence of National Instrument within a lab setting. The group concluded to go with the USB-6003 model for the required number of analog channels for the thermocouples, and the carbon dioxide analyzer. The NIDAQ board came with eight analog and digital channels or four differential channels that could acquire data simultaneously.  To collect the necessary data for the experiment, the use of a NIDAQ board was
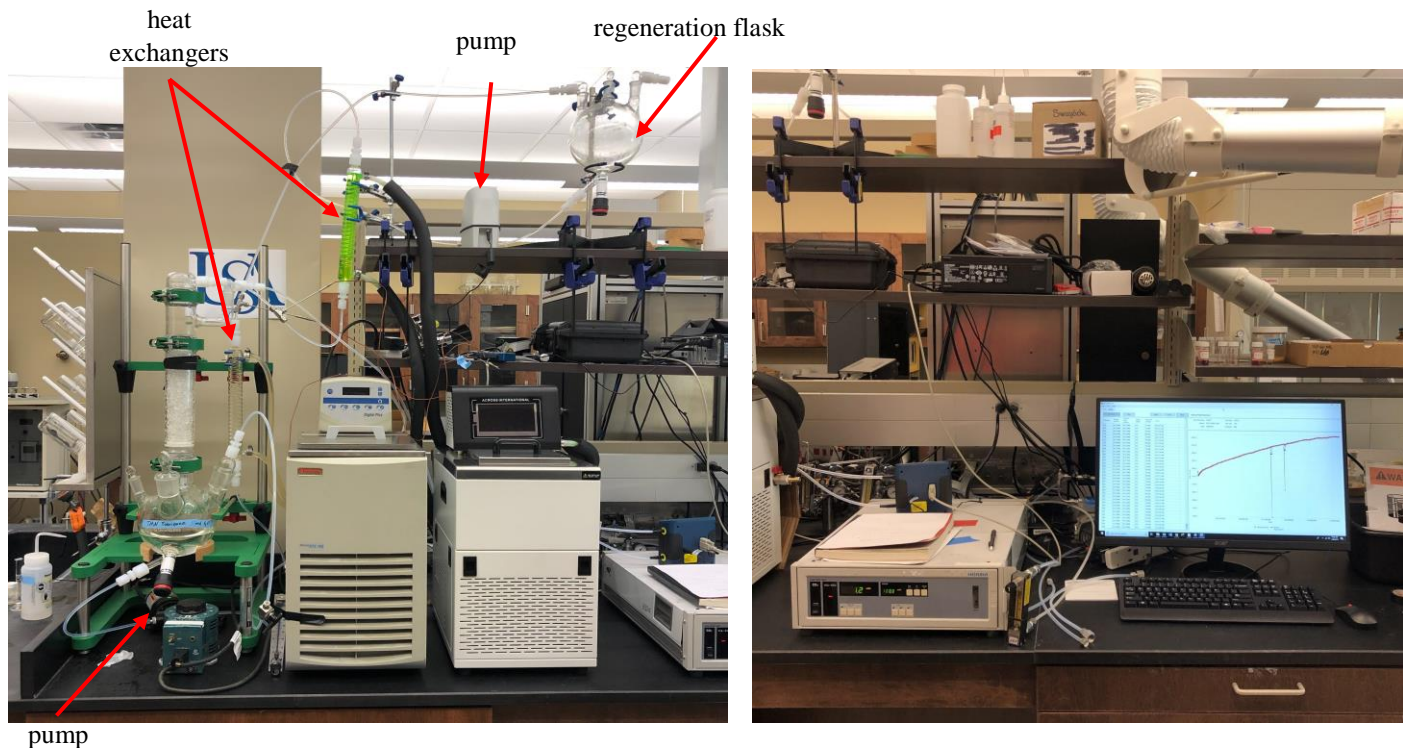
**Figure 4.** NASA X-Hab 2018/2019 ionic liquid absorption apparatus.

used in tandem with LabVIEW software. This program allowed the simultaneous collection of data points from the three K-type thermocouples as well as a voltage differential reading from the carbon dioxide detector. The working program started with a NIDAQ assistant piece that allowed the delegation of analog channels to the appropriate sensor. Both the thermocouples and the carbon dioxide analyzer had to be wired to two analog channels apiece in order to for a differential reading to be acquired. The software was set to a range of 0 to 100 degrees Fahrenheit and to continuous data collection from the thermocouples. The carbon dioxide analyzer was set to read between 0 to 10 volts and will collect data continuously. The DAQ assistant is designed to only collect data at the amount that is desired, therefore, a while loop was drawn for the program to continue collecting data at a rate of 2 samples every one to five seconds with timestamps on each set of data points.

The data that was collected comes in as raw data and had some interference and so a filter was needed to clean up the signal. At first, a Butterworth was chosen as the filter, but the data were flowing through sporadically and inconsistent, thus a smooth filter was used instead. This allowed for a much more consistent flow of data. After the filter, two waveform charts were inserted into the GUI to monitor the real time variations within the data. As depicted in Figure 5, two charts were used to report the thermocouple and CO2 concentration data. The actual LabVIEW coding is shown in Figure 6. The four dynamic-data attributes cells were used to arrange and organize the data collected into columns and were sent to the text file to be exported to Excel. A time delay with a controller was placed within the loop in order to slow down the collection of data and make it more suitable for plotting in Excel.

Omega rotameters for nitrogen gas and carbon dioxide were selected because they were individually calibrated for each gas, the flow rate range for each rotameter was suitable for the manipulation of inlet carbon dioxide concentration by independently manipulating each gas flow and were the most economically feasible option when compared to mass flow controllers. Type K thermocouples were used and contained metal sheaths to allow for the interface of the thermocouple with Swagelok pipe fittings. This type of thermocouple is selected because the chromel-alumel conductors have a broad range of operating temperatures and a Curie point, temperature at which output deviation occurs due to magnetism, well beyond the operating temperatures of the process.

**Experimental Plan and Conditions**

The main goal of this experiment was to measure the absorption of $CO_2$ at input partial pressures of 5, 2, and 1 torr in a dry gas stream. The sensitivity of the process to temperature change was tested by varying the system temperature between 35, 45, 55, and 65 °C. The initial functionality test of the scrubber system was completed using nitrogen and water. The purpose of the initial testing was to identify fluid leaks in the tube fittings before running the system with the
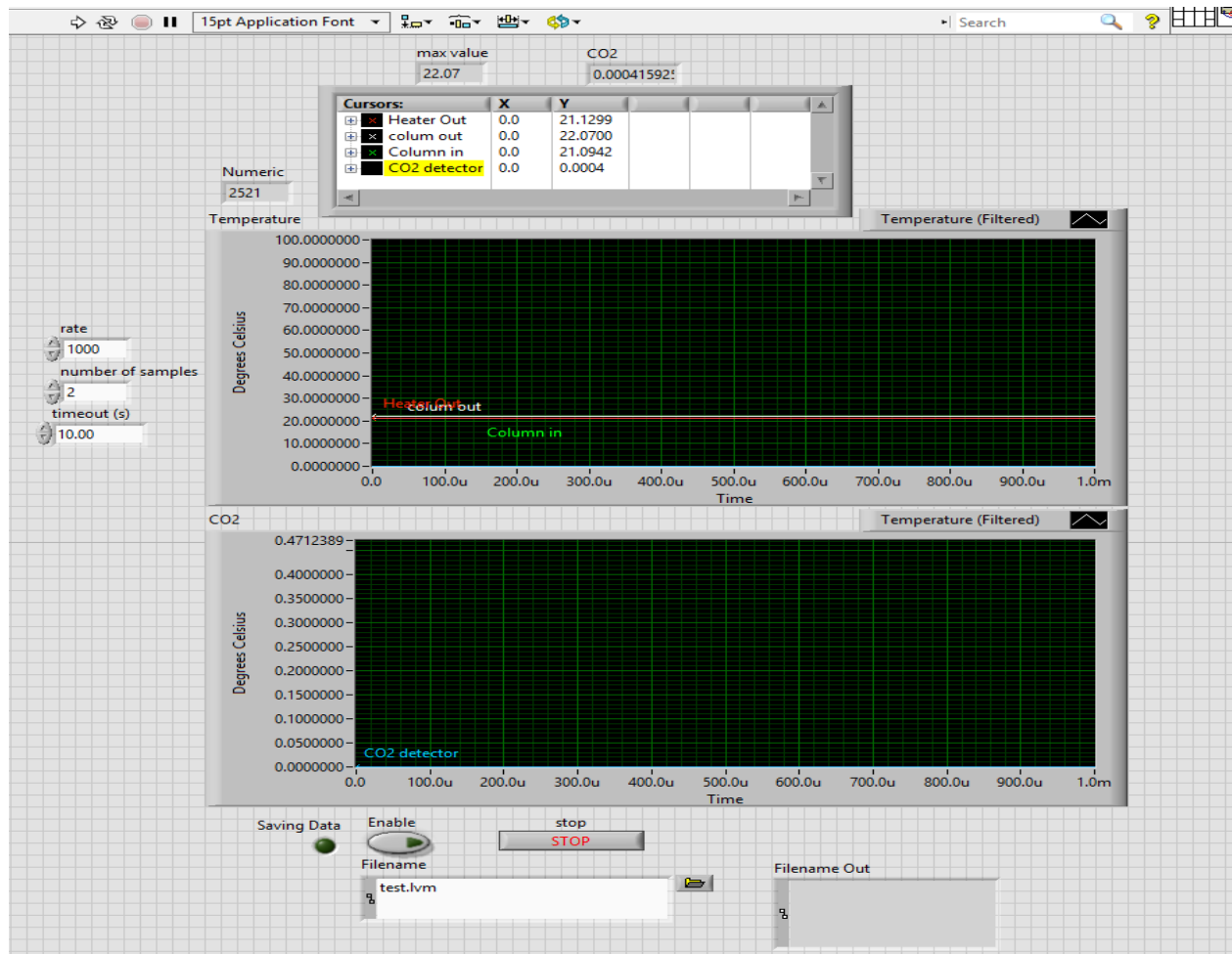


**Figure 5.** LabVIEW Graphical user interface for the NASA X-Hab CO2 absorption system.
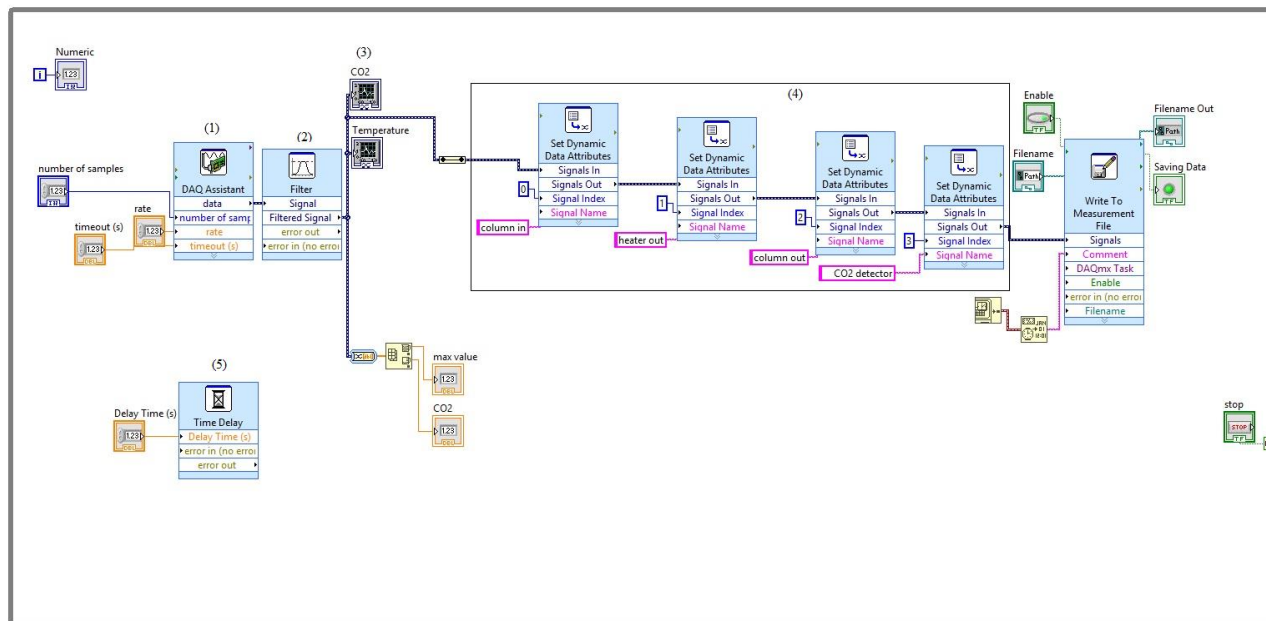
**Figure 6.** Image 6. LabVIEW Data Acquisition program.

ionic liquid and $CO_2$. Experiments were conducted to determine the amount of liquid flow that was best suited for this apparatus and it was determined that a liquid flow rate must be kept below 0.4 GPM or the column will flood and restrict gas flow. It was determined experimentally that the column can operate at the maximum desired gas flow-rate of 3 L/min when the liquid flow-rate is kept below 0.3 GPM.

**Results**

In total 4 experiments were conducted, and each showed the ionic liquid was able to reduce the $CO_2$ partial pressure to between 0.11 and 0.21 torr depending on the $CO_2$ feed concentration. Each of the three tests were conducted with different $CO_2$ concentrations with the first test conducted at a $CO_2$ input of 9.8 torr, the second at 3.8 torr, the third at 5.4 torr, and the last test conducted at 50% by volume $CO_2$. More tests are needed to confirm these results and to operate the system at longer times. In the experiments below the system was operated for no more than 2 hours. For each of the following experiments the following conditions were used:

| | |
|---|---|
| TMN mass in adsorber: | 718.9994 g |
| H2O mass in adsorber: | 179.50 g |
| Concentrations: | 80 wt% TMW |
| | 20 wt% H2O |

The specific run conditions of experiments 1 are shown below and the effluent $CO_2$ concentration versus time is shown in Table 1:

Experiment #1: Input

| | | |
|---|---|---|
| CO$_2$ Flow: | 14.2 | mL/min |
| N$_2$ Flow: | 1122 | mL/min |
| Total Flow: | 1136 | mL/min |
| CO$_2$ volume %: | 1.293 | |
| CO$_2$ Partial Pressure: | 9.827 | torr |
| Chiller: | 0 | ℃ |
| Heater: | 74 | ℃ |

Experiment #1: Output "Breathable Air"

| | | |
|---|---|---|
| CO$_2$ Flow: | 0.33 | mL/min |
| N$_2$ Flow: | 1122 | mL/min |
| Total Flow: | 1123 | mL/min |
| CO$_2$ Partial Pressure: | 0.114 | torr |

| Time | Total Flow rate [mL/min] | CO$_2$ Partial Pressure - Effluent [torr] |
|---|---|---|
| 11:15 | 1129.5 | 0.0684 |
| 11:19 | 1115.3 | 0.0456 |
| 11:21 | 1058 | 0.0912 |
| 11:22 | 1063.7 | 0.0988 |
| 11:24 | 1056.3 | 0.0912 |
| 11:27 | 1045.9 | 0.0988 |
| 11:30 | 1060.5 | 0.0988 |
| 11:32 | 1103.1 | 0.0988 |
| 11:34 | 1096.7 | 0.0684 |
| 11:36 | 1084.6 | 0.1140 |
| 11:41 | 1023.1 | 0.1140 |
| 11:42 | 1031.1 | 0.1140 |
| 11:43 | 1024.7 | 0.1064 |
| 11:45 | 1057.5 | 0.1140 |

**Table 1.** Results from experiment 1.

The results in Table 1 show a nearly complete removal of the CO$_2$ in the feed gas. However, this experiment was only conducted for approximately 30 mins making it difficult to use the data to evaluate long term steady-state behavior.

The second experiment was conducted at the following initial conditions:

Experiment #2: Input

| | | |
|---|---|---|
| CO$_2$ Flow: | 11.5 | mL/min |
| N$_2$ Flow: | 2298.5 | mL/min |
| Total Flow: | 2310.0 | mL/min |
| CO$_2$ volume %: | 0.4952 | |

Experiment #2: Output "Breathable Air"

| | | |
|---|---|---|
| CO$_2$ Flow: | 0.33 | mL/min |
| N$_2$ Flow: | 2298.5 | mL/min |
| Total Flow: | 2298.8 | mL/min |
| CO$_2$ Partial Pressure: | 0.116 | torr |

CO₂ Partial Pressure: 3.8     torr
Chiller:             13     ºC
Heater:           64     ºC

In the second experiment a problem was found with the gas supply system. Near the end of the test there was a leak somewhere in the system which is reflected in the data below. While the leak is evident as shown by the change in flow rate in Figure 7, the $CO_2$ volume % readings of the $CO_2$ detector in the output stream remained constant. The data from this experiment are tabulated in Table 2. Figure 7 displays the total volumetric flow-rate in blue with its axis on the right. The partial pressure of the $CO_2$ [torr] is reflected on the left axis. The green horizontal line near the bottom of the graph represents the partial pressure of the $CO_2$ [torr] normally present in the atmosphere. The spikes in the graph represent the verification of input conditions by bypassing the gas flow to the column and redirecting the total flow directly through the flowmeter and the CO2 detector. The gas leak was located after this experiment and corrected.

| Time | Total Flow rate [mL/min] | CO₂ Partial Pressure - Effluent [torr] |
|---|---|---|
| 12:01 | - | 0.0684 |
| 12:02 | 2123.2 | 0.0456 |
| 12:04 | 2114.3 | 0.0912 |
| 12:05 | 2114.6 | 0.0988 |
| 12:10 | 2114.2 | 0.0912 |
| 12:13 | 2114.8 | 0.0988 |
| 12:15 | 2114.8 | 0.0988 |
| 12:16 | 2114.6 | 0.0988 |
| 12:17 | 2117.4 | 0.0684 |
| 12:20 | 2112.7 | 0.1140 |
| 12:22 | 2112.7 | 0.1140 |
| 12:23 | 2112.9 | 0.1140 |
| 12.24 | 2113.3 | 0.1064 |
| 12:26 | 2113.7 | 0.1140 |

**Table 2.** Results from experiment 1. This table shows only data at later times in the experiment.
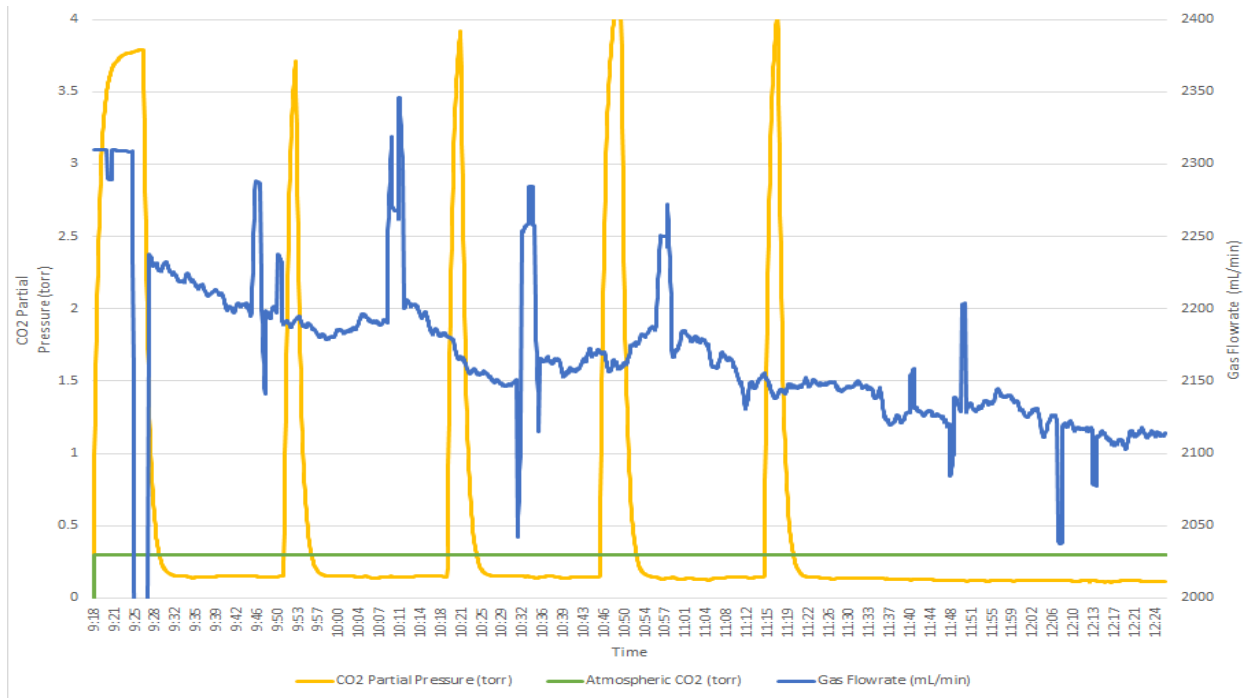
**Figure 7.** Results from experiment 2 showing a leak in gas stream via a decreasing flow rate.

Conditions for Experiment 3 are shown below, the tabulated data is shown in Table 3, and the results are plotted in Figure 8.

Experiment #3: Input                                    Experiment #3: Output "Breathable Air"

$CO_2$ Flow:              17      mL/min        $CO_2$ Flow:              0.63    mL/min
$N_2$ Flow:               2358   mL/min        $N_2$ Flow:               2358  mL/min
$CO_2$ volume %:       0.7160              $CO_2$ Partial Pressure:  0.21    torr
$CO_2$ Partial Pressure: 5.4      torr
Chiller:              13      ºC
Heater:               64      ºC
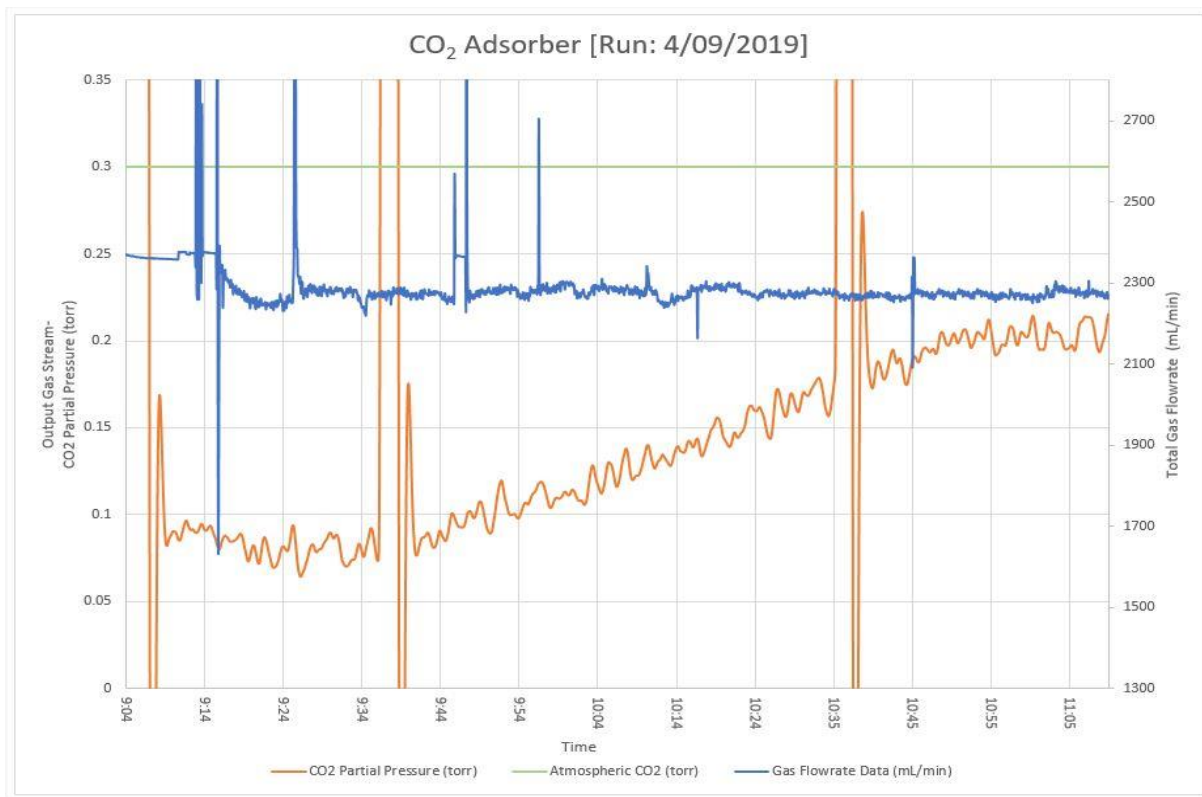
**Figure 8.** Results from experiment 3.

| Time | Total Flow rate [mL/min] | $CO_2$ Partial Pressure - Effluent [torr] |
|---|---|---|
| 9:05 | 2365 | 5.468 |
| 9:10 | 2359 | 0.089 |
| 9:15 | 2374 | 0.092 |
| 9:20 | 2237 | 0.076 |
| 9:25 | 2263 | 0.084 |
| 9:30 | 2281 | 0.087 |
| 9:35 | 2266 | 0.083 |
| 9:40 | 2266 | 0.116 |
| 9:45 | 2275 | 0.085 |
| 9:50 | 2273 | 0.099 |
| 9:55 | 2278 | 0.104 |
| 10:00 | 2297 | 0.111 |
| 10:05 | 2287 | 0.112 |
| 10:10 | 2276 | 0.124 |
| 10:15 | 2265 | 0.138 |
| 10:20 | 2291 | 0.156 |
| 10:25 | 2266 | 0.160 |
| 10:30 | 2265 | 0.161 |
| 10:35 | 2275 | 0.180 |
| 10:40 | 2277 | 0.176 |
| 10:45 | 2364 | 0.191 |
| 10:50 | 2269 | 0.203 |
| 10:55 | 2267 | 0.207 |
| 11:00 | 2260 | 0.207 |
| 11:05 | 2277 | 0.196 |
| 11:10 | 2270 | 0.215 |

**Table 2.** Results from experiment 3.

The graph above shows that the ionic liquid has a loading phase prior to coming to what appears to be a steady state (more experiments are needed to confirm the approach of steady state). However, the last 10 minutes of the run did have a consistent concentration of $CO_2$ absorption. The cause of $CO_2$ spike at 10:40 is unknown. The cause of $CO_2$ spike at 9:40 is a test of the input stream. With each of the three experiments showing near complete removal of the $CO_2$ from the feed steam, even at CO2 concentrations as high as 5.4 torr, the next experiment sought to determine the upper limit of CO2 feed gas concentration that could be processed by the absorber.

Experiment #4: IL Capacity

The purpose of this experiment was to determine how much $CO_2$ the IL could adsorb before needing to be regenerated. Stoichiometric calculations yielded a maximum of ~90 hour run time at an inlet CO2 concentration of 5 torr before the IL would be loaded. To reduce the time required to saturate the IL, a gas stream of 50 vol% $CO_2$ was utilized. Using this concentration of $CO_2$ yielded unexpected results. A $CO_2$-taurinate complex precipitated within 2 minutes and had to be dissolved by increasing the temperature of the IL to 70°C and circulating the fluid for ~1.5 hours. Once dissolved, the system was shut down and allowed to cool down. Crystals formed as the IL cooled and deposited in multiple parts of the system as seen below. A more detailed explanation of this behavior is provided in the "Instructors Addendum."
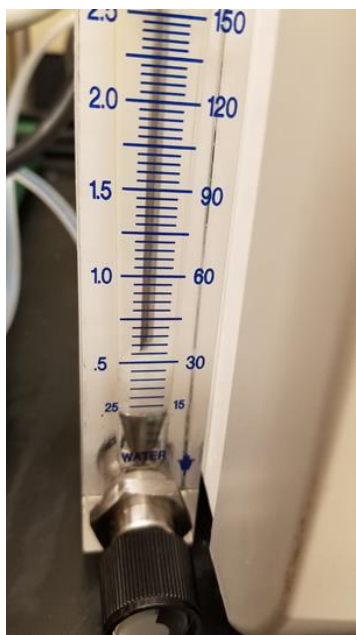


**Figure 9.** Bottom of absorber flask.



**Figure 10.** Crystals deposited in the flowmeter.

The formation of crystals throughout the apparatus and close to the end of the project prevented further experiments, but this experiment provided key insight into the screening of ionic liquids for closed environments at low $CO_2$ partial pressure. Specifically, with the majority of the ionic liquid literature focused on flue gas capture, it is likely that leading ionic liquid candidates for flue gas capture may not be ideal candidates for low concentration $CO_2$ removal and that some ideal low concentration $CO_2$ removal candidates will likely be rejected (due to changes in viscosity or formation of precipitates) if the ionic liquid is only being examined at high $CO_2$ concentrations. New experiments now need to be conducted evaluating this behavior and its impact on $CO_2$ life support systems.



**Figure 11.** Crystals deposited in the heat exchanger.



**Figure 12.** Looking into the adsorber flask from above.

**Conclusions**

The results presented show that it is possible to utilize a commercial absorber column and a task specific ionic liquid to remove $CO_2$ from feed gas streams at concentrations relevant to closed air revitalization. Analyzing the data from the experiment with $CO_2$ inlet partial pressures of 5.47 Torr, the ionic liquid absorbed 96.26% of the $CO_2$ in this experiment. The partial pressure of $CO_2$ in the purified outlet stream (0.21 Torr) is lower than the atmospheric $CO_2$ level (0.3 Torr). This indicates that the ionic liquid successfully removes $CO_2$ from the gas inlet stream and exceeds NASA's requirements

Going forward, more experiments are needed to develop a complete understanding of the behavior of the system. Specifically, longer $CO_2$ absorption runs are required to ensure that the system is at steady-state. More experiments are also needed to optimize and confirm the regeneration conditions used in the heat exchangers. Detailed phase equilibrium data also need to be collected to understand when precipitation occurs.

From a systems perspective, to further enhance the results of this experiment, the system controls need to be completely automated to reduce human error. The rotameters can be replaced with mass flow controllers for more accurate supply conditions. Automating the ionic liquid delivery system will prevent accumulation in both the regeneration flask as well as the round

bottom flask at the bottom of the column by synchronizing the pumps. Lastly, adding a secondary volumetric flow meter at the outlet of the regeneration flask, humidity sensors to both gas outlets, and an extra $CO_2$ detector will increase manipulability of the entire system. Use of a 79% nitrogen 21% oxygen stream would be a necessary variable to observe if the addition of oxygen affects the performance of the liquid. Similarly, the addition of water vapor at varying partial pressures would offer insight into how the carbon dioxide removal system would behave in conditions comparable to those on existing closed air environments. Physical property testing would give more insight to optimize the process of the carbon dioxide capture and the energy required to regenerate the ionic liquid. Addition of ultrasonic flowmeters would allow more accurate measurements of the IL flow and allow for more control and a more detailed analysis of the IL. A conductivity sensor placed in the bottom of the absorber flask would allow for the constant monitoring of the concentration of the IL. Condensation traps on the regeneration flask and the absorber outlet would significantly reduce water loss from the system. A volumetric flow meter on the outlet of the regeneration flask would allow for direct measurement of the $CO_2$ released and it would not be necessary to determine the IL loading phase by calculation. Humidity sensors on both outlets would allow for final assessment of the gas leaving the system. The addition of a new $CO_2$ analyzer would help verify the data already collected and would allow for future runs to be more accurate.

References
[1] El sherif, D., & Knox, J. C.. International Space Station Carbon Dioxide Removal Assembly (ISS CDRA) Concepts and Advancements. 1-5. Retrieved March 25, 2019.

Appendix
A1. Equipment
Equipment List

| | | Item | Part # | Vendor |
|---|---|---|---|---|
| 1 | | Absorber | CG-1830-10 | ChemGlass |
| 2 | | Rotameter - CO2 | FLDC3305ST | Omega |
| 3 | | Rotameter - N2 | FLDN3301ST | Omega |
| 4 | | Brooks Variable Area Mechanical Flowmeter | 4UN03 | Grainger |
| 5 | | Condenser- Graham | CG-1830-30 | Chemglass |
| 6 | | Round Bottom Flask, 3L, 3-Neck | CG-1523-V-04 | Chemglass |
| 7 | | NiDAQ board | USB-6003 | National Instruments |
| 8 | | DryCal Flow meter | 200-520-M Defender | MesaLabs |
| 9 | | K-type Thermocouple | TJ36-CASS-18U-5 | Omega |
| 10 | | Across International C20-7 Ai C20-(20°C to 99°C) 7L Chiller | 13-874-182 | Fisher |
| 11 | | Polypropylene Diaphragm Pump | 2P795 | Grainger |
| 12 | | Horiba CO2 Detector | VIA-510 | Horiba |
| 13 | | CO2-Bone Dry (99.9% CO2) | | NexAir |
| 14 | | Nitrogen - Ultra Pure | | NexAir |

A2. Budget
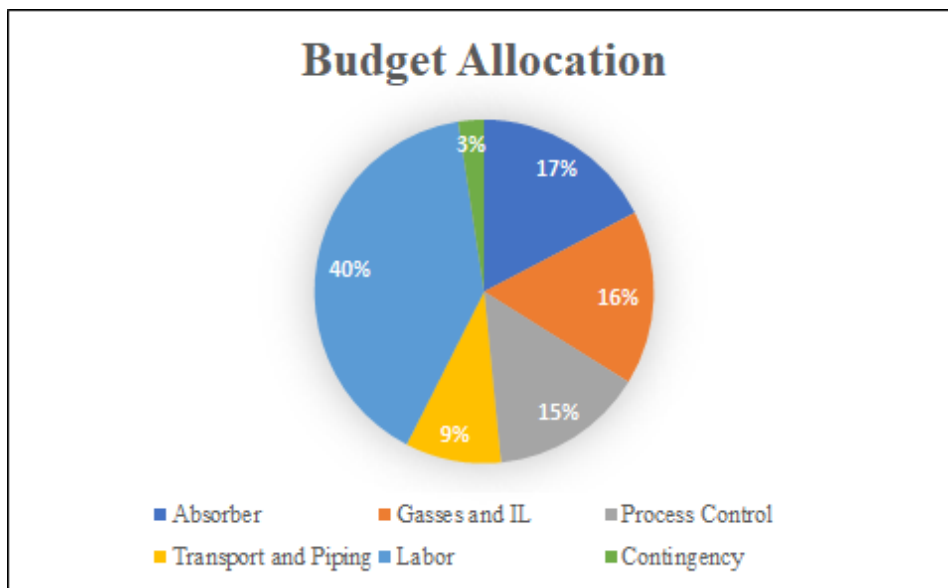
A3.  System Operating Procedure
Revised: April 30, 2019

System Start-up (Part 1: Gas)

1.      Turn on the powerstrip above the water baths.
2.      Turn on $CO_2$ detector.
3.      Turn on DryCal flow meter.
4.      Turn on both water baths.
        a.      Thermofisher: Power button on the front of the control panel.
        b.      Allied International: Flip the breaker on the back of the control panel up to turn
                on.  Hold the "Run" button on the screen until the pump and cooler start.
5.      Start the LabView software.
        a.      Change "Enable" to off and ensure the "Saving Data" indicator is dark.
        b.      Start the program by clicking the arrow at the top left of the menu bar.
6.      Start DryCal Pro software.
        a.      Go to Setup Tab.
        b.      Select "DryCal Software" in "Communication Control" box.
        c.      Select "Continuous" in "Data Acquisition Mode".
        d.      Select "COM1" in the dropdown menu and click "Test".
        e.      A window should pop up that shows "Communication Successful".
        f.      Return to the "Data" tab and select "Get Flow".
7.      Open bench  $N_2$ valve completely.
        a.      Adjust the bench pressure regulator until it reads 5 psig.
        b.      Open the  $N_2$ rotameter until flow rate is above 1.5 L/min.
8.      DryCal should start collecting data
9.      Allow the gas flow to stabilize while the system is heating up.
10.     Let $CO_2$ detect warm up for 1 Hour.

$CO_2$ Detector Calibration

1.      Turn on the vacuum pump behind the $CO_2$ detector.
2.      Open the rotameter at the front of the $CO_2$ detector until the sample gauge in the $CO_2$
        detector measures 100 m L.
3.      On $CO_2$ detector make sure "Range" is set to "5.000%".  Operating Manual PDF for the
        $CO_2$ detector is on the computer desktop.
4.      When the measurements have stabilized, press "Zero" in the "CAL" box on the detector.
5.      Record the voltage measured from LabView.
6.      Open Excel Spreadsheet "Calculations" on Desktop
7.      Desired Conditions

       a.      Enter desired $CO_2$ partial pressure in "Desired Conditions"

       b.      Enter a proportionally large desired $CO_2$ approximately flow rate in "Desired Conditions" section.

8.      Under the "Supply Conditions" section

       a.      Enter actual $N_2$ flow rate into "Supply Conditions"

       b.      Adjust the "Total" flow rate until "Desired $CO_2$" flow is similar to that in "Desire Conditions" section.

       c.      Adjust the $CO_2$ rotameter and use the total flow rate measurement from the DryCal as the guide for flow rate.  The rotameter is inaccurate.

9.      Once the flowrate has stabilized, enter the stabilized value into the "Actual Total" in the "Supply Conditions" section.

10.     Use the value in the "Actual Vol. %" field to calibrate the $CO_2$ detector using the steps in the Operating Manual.

11.     Record the voltage measured in LabView.

12.     Divide the partial pressure calculated in Excel with the voltage reading measured in step 11 to obtain the "K value" to be entered into LabView.  This value is the slope of the line between the zero point and the calibration point.  The "K value" will convert the data reported by LabView into the actual partial pressure of $CO_2$ in the output stream.

## Gas Flow Verification

1.      Turn the bypass valve on the gas supply line to bypass the absorber and feed gas directly to the DryCal.  Close the isolation valve at the gas input at the absorber  column.

2.      Allow the gas flow to the DryCal to stabilize and record the flow rate.

3.      Open the isolation valve at the absorber and turn the bypass valve on the gas supply line to allow gas to flow to the adsorber.

## System Start-up (Part 2: Liquid)

1.      Open the gas isolation valve at the absorber.

2.      Turn the gas bypass valve to start supplying the absorber with gas.

3.      Turn the switch on the Variac to 120V and set the dial to 30 Volts as measured by the digital readout.

4.      Ensure the ionic liquid flowmeter is completely open.

5.      Allow fluid to transfer into the regeneration flask until it is above the ring support at a minimum.

6.      Start the pump at the regeneration flask and set the voltage to 30 volts.

7.      Adjust the  voltage of the bottom pump until it is slightly faster than the adsorber supply pump and the  regeneration flask remains full.

Data Acquisition

1.      DryCal
     a.      During the run: Click "Copy" to copy the data to the clipboard and paste the data into an excel sheet.
     b.      At the end of the run: Either use the method above or select "Save Data" from the File menu.
2.      LabView
     a.      Stop the program by pressing "Stop" below the graphs.
     b.      Name the file to "Data [time-month-day-year]"
     c.      Change "Enable" to on and ensure the "Saving Data" indicator is green.
     d.      Start the program by clicking the arrow at the top left of the menu bar.

System Shutdown

1.      Stop the LabView software.
2.      Copy the data file in the LabView Data folder to the folder on the desktop labeled "Data."
3.      Stop DryCal Pro software.
     a.      Select "Copy" above the data field.
     b.      Paste the data into an Excel spreadsheet.
     c.      Save the file to the "Data" folder on the desktop.
     c.      Name the file to "Data [time-month-day-year]"
4.      Turn off the vacuum pump at the $CO_2$ detector.
5.      Turn off the $CO_2$ detector
6.      Close the $N_2$ and $CO_2$ bench pressure regulator until it reads 0 psig.
7.      Close bench $N_2$ and $CO_2$ supply valves fully.
8.      Turn off both water baths.
     a.      Thermofisher: Power button on the front of the control panel.
     b.      Allied International: Hold the "Run" button on the screen and wait for the pump and cooler stop. Flip the breaker on the back of the control panel down to turn off.
9.      Remove a stopper on the adsorber flask.
10.      Turn off the ionic liquid pump at the absorber.
11.      Allow the pump at the regeneration flask to pump all remaining ionic liquid back through the absorber
12.      Turn off the pump at the regeneration flask by pressing the "Standby" button above the control dial.
13.      Replace the stopper on the absorber flask.
14.      Turn off the power strip above the waterbaths

# Process and Instrumentation Diagram

## Process Flow Diagram
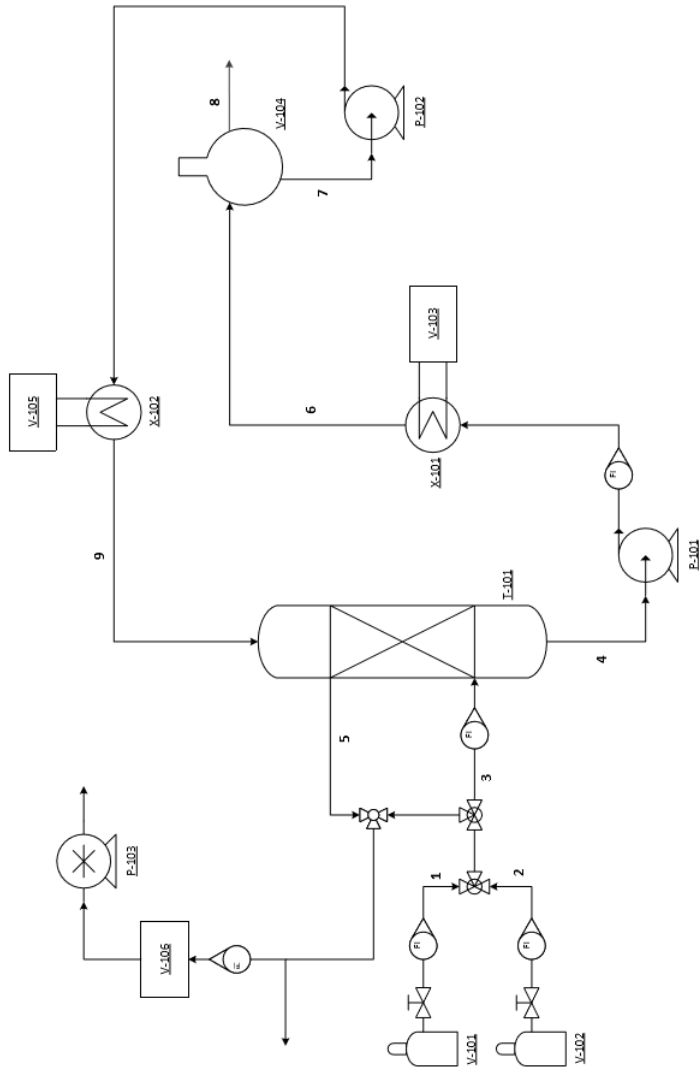


| Line | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|---|---|---|
| N₂ | 2298.5 | - | 2298.5 | - | 2298.5 | - | - | - | - |
| CO₂ | - | 11.5 | 11.5 | 10.974 | 0.33 | 10.974 | - | 10.974 | - |
| IL | - | 11.5 | - | 378.5 | - | 378.5 | 378.5 | 10.974 | 378.5 |
| Total Flow (mL/min) | 2298.5 | 11.5 | 2310 | 389.515 | 2298.8 | 389.515 | 378.5 | 10.974 | 378.5 |
| Temperature (°C) | 20 | 20 | 20 | 36 | 25 | 45 | 40 | 40 | 34 |
| Pressure (atm) | 1 | 1 | 1 | 1 | 1 | 1.01 | 1 | 1 | 1.01 |
| Density (g/L) | 1.25 | 1.96 | 1.2535 | 3177 | 1.2501 | 3177 | 3270 | 1.96 | 3270 |
| Viscosity (Pa-s) | 1.76E-5 | 1.47E-5 | 1.7586E-5 | - | 1.75998E-5 | - | >8.9E-4 | 1.47E-5 | >8.9E-4 |

## Instructors Addendum

Of note is the precipitation that the students observed when exposing the solution to a stream of 100% $CO_2$ at ~1 atm. The purpose of this experiment was to gauge the total capacity for $CO_2$ capture, as it was evident that the system was not being saturated through contact with a model air recycle steam. However, after contact with the pure $CO_2$ stream, a solid formed that was previously not observed. This was not wholly unexpected as explained below.

The parent salt is tetramethyl ammonium taurinate, shown below; however only the anion (taurinate) is involved in $CO_2$ capture.

Tetramethylammonium
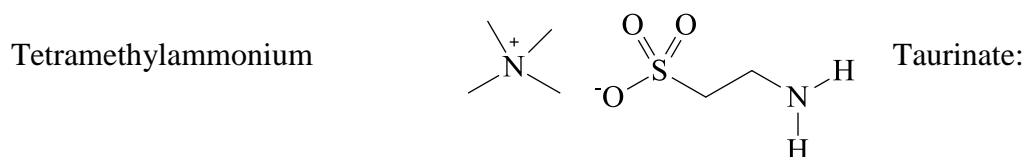
Taurinate:

When $CO_2$ dissolves into the aqueous solution, $CO_2$ may react with water to form carbonic acid, however, the amine on the taurine in a stronger nucleophile and equilibrium reaction with the amine will dominate. The reaction forms a zwitterionic anion (with two formal negative charges and one formal positive charge.) This zwitterion can undergo a proton transfer to formally form the carbamic acid anion. The relative position of this latter equilibrium is determined by a number of factors such as the ionic strength of the solution and pH.

zwitterionic anion

carbamic acid anion
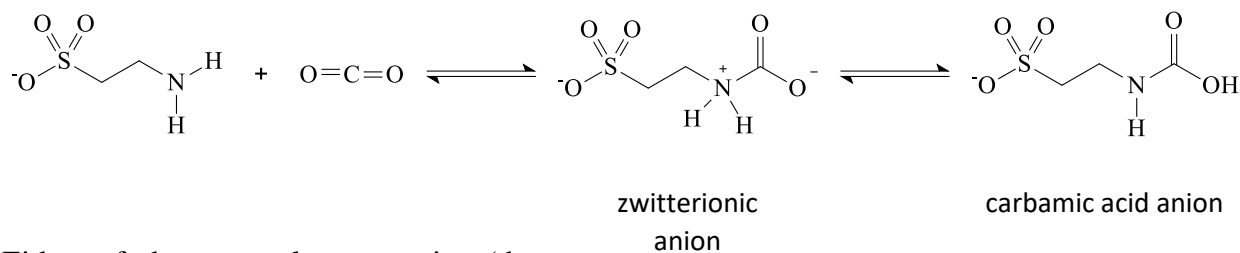
Either of these two latter species (the zwitterionic anion or the carbamic acid anion) may act as an acid to protonate an unreacted taurinate (although only reaction of the carbamic acid anion is shown below.)
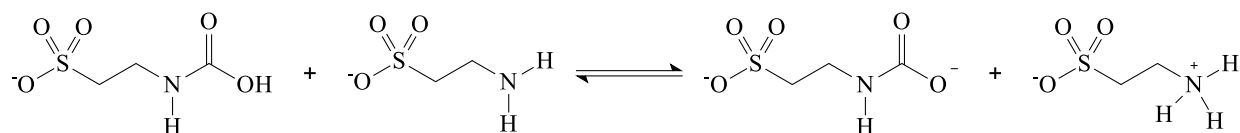
It is likely that all of these reactions are taking place during the $CO_2$ capture process to some extent. However, under low $CO_2$ partial pressures, the amount of these secondary ions is low, likely well below any solubility limit. When contacted with gas streams with higher $CO_2$ partial pressures, the concentrations of these species will increase and a solid will precipitate. Although we are not confident yet about the actual identity of the precipitate, heating will drive the equilibrium in reverse by liberating the $CO_2$ in the initial step. Again, we note that this precipitate was only observed during very high $CO_2$ partial pressures, and not under conditions representative of air revitalization.