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Analysis of Spacecraft Cabin Carbon Dioxide Capture via Deposition

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Extended manned missions through deep space present a number of unique challenges yet to be solved before said missions are feasible. One pertinent challenge is the CO_2 removal system, as the current state-of-the-art requires repeated, costly maintenance. Multiple alternative CO_2 removal systems are currently being evaluated as potential successors, including solid and liquid sorbents. An alternative to sorption techniques entirely is deposition of CO_2 from the cabin atmosphere onto a cold surface. Deposition provides numerous benefits, including multiple methods of generating a cold surface. Cryogenic coolers and thermal radiators are two methods that are both highly reliable. Another benefit is the ability to provide humidity and trace contaminant control, as well as CO_2 storage and compression, in addition to CO_2 capture. Cryogenic coolers, specifically Stirling coolers, are currently being tested for use in Martian atmosphere CO_2 capture, but the work described in this paper is one of the first examinations into the application of spacecraft cabin atmosphere. After the Stirling cooler CO_2 deposition system was built, a test matrix of varying inlet flow rates, CO_2 concentrations, and temperature set points was completed to evaluate the system. In addition, one set of parameters was selected to ensure repeatability and determine a working cycle time. A decaying increase of CO_2 removal rate with decreasing temperature was observed at all tested inlet flow rates and concentrations. Also, CO_2 removal rate decayed with system run time. The data gleaned from this initial study will be used to inform a more efficient, cycling CO_2 deposition system design.

Nomenclature

AES	=	Advanced Exploration Systems
ARC	=	Ames Research Center
C	=	concentration
CDep	=	CO_2 Deposition
CDRA	=	Carbon Dioxide Removal Assembly
CO_2	=	carbon dioxide
HX	=	Heat Exchanger
ISRU	=	In-Situ Resource Utilization
ISS	=	International Space Station
KF	=	Klein Flange
KSC	=	Kennedy Space Center
MFC	=	Mass Flow Controller
N_2	=	nitrogen
NASA	=	National Aeronautics and Space Administration
NIKS	=	NASA Innovation Kick Start

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O_2	=	oxygen
r	=	rate
r_{max}	=	maximum rate
SC	=	Stirling Cooler
T	=	temperature
t	=	time
TC	=	Thermocouple
TSA	=	Temperature Swing Adsorption

I. Introduction

THE goal of the National Aeronautics and Space Administration (NASA) is to return humans to the surface of the moon, then journey to Mars and even beyond. In order to accomplish this ambitious goal, robust life support systems are required to operate without reliance on a resupply. The current air revitalization system on the International Space Station (ISS), the Carbon Dioxide Removal Assembly (CDRA), utilizes sorbent-based, temperature-swing adsorption (TSA) technology.[1] An array of alternative CO_2 removal systems are currently being evaluated as potential successors, including solid and liquid sorbent-based systems.[1] An attractive new solution is different from sorption techniques entirely: forcing a phase change of CO_2 from the cabin atmosphere by solidifying it onto a cold surface. Generating a cold surface can be accomplished via multiple methods, including cryogenic coolers and thermal radiators to deep space.

CO_2 deposition, or CDep, is highly reliable as it has no expendable materials, no vacuum is required, and needs minimal moving parts. CDep also potentially eliminates the need for a separate storage system to deliver pressurized, pure CO_2 to an O_2 generation system, such as the Sabatier processor currently on the ISS. A deposition system can also be designed to remove residual humidity in addition to CO_2 via a multi-stage process, and may even aid in trace contaminant control.

CO_2 deposition technologies are currently being explored to scrub CO_2 from flue gas in power plants,[2] and cryogenic Stirling coolers have been utilized in these processes as well.[3] In terms of space technologies, Stirling coolers are in use on satellites flying today in order to cool electronics, and have also been evaluated for in-situ resource utilization (ISRU) in the Martian atmosphere.[4,5] However, deposition methods for CO_2 capture have only been evaluated in substantially higher CO_2 partial pressures than what is present in a cabin atmosphere. This lack of life support-focused research is starting to be rectified, including the modeling of system parameters under required operating conditions,[6] as well as some initial trials in the use of a piston cooler,[7] and Stirling cooler.[4] However, these trials were merely for storage of CO_2 or did not test in the required partial pressure range to determine its viability as an effective cabin CO_2 removal technology.

The work described herein was performed at Ames Research Center (ARC) and evaluates the performance of a Stirling cooler to deposit CO_2 from simulated cabin air. CO_2 removal efficiency, cycle time, and sensitivity to input parameters were included in the evaluation.

II. Theoretical Background

The basis of the phase change method of CO_2 capture utilizes the condensation and deposition temperature differences between N_2, O_2, and CO_2 to selectively remove CO_2 from the air stream. The process involves flowing cabin air across a cold surface in a chamber that is below the deposition temperature of CO_2, but above the condensation points of N_2 and O_2, and allowing the CO_2 to deposit. The CO_2-free air then re-enters the cabin. Once the cold surface is considered saturated with solid CO_2, the system switches to a parallel chamber. The solid CO_2 in the first chamber then sublimes and is stored in a pressure vessel for delivery to Sabatier or other process for O_2 regeneration.

The ISS is currently maintained at an average of 3.0 mmHg, but an even lower partial pressure of 2.0 mmHg, or approximately 2600 ppm assuming atmospheric pressure, will be required to maintain crew health on future missions.[8,9] Also, for a 4-crew mission, the CO_2 removal system must remove 4.16 kg of CO_2 per day.[8]

The first operating parameter that dictates the deposition system design is temperature. Utilizing the Clausius-Clapeyron equation and known conditions at the triple point, the deposition temperature can be estimated for any CO_2 partial pressure. At a partial pressure of 2.0 mmHg, the deposition temperature of CO_2 is about 142K. If a lower partial pressure is desired, then the deposition temperature also decreases. Therefore, the operating temperature of the cold surface must be below this deposition temperature in order to both reduce the CO_2 partial pressure as well as overcome heat transfer effects to allow CO_2 to deposit. When using a Stirling cooler, the surface temperature is dictated by the cooling power. A Stirling cooler operates by using a piston and displacer to repeatedly compress and expand a working

fluid, typically helium, across two heat exchangers and a regenerator. This cycle generates a temperature gradient, therefore producing a cold surface. As the desired operating temperature increases, so does the amount of cooling power generated (at the same input power).

The second parameter that affects the system design is pressure drop. As the mass of solid CO_2 accumulates onto the cold surface, the pressure drop across the chamber should increase slowly, until a limit is reached, then increases exponentially. This change in rate of pressure drop increase may dictate the cycle time.[6]

The final operating parameter to consider is cabin air inlet flow rate. The higher the inlet flow rate, the more CO_2 is exposed to the cold surface, but the more cooling power is required to deposit a sufficient amount of CO_2.

III. Experimental Methods

A. Test System

A previously discussed mass and energy balance shows that a Stirling cooler with approximately 20W of cooling power at the desired operation temperature, or about 117K, can theoretically remove the majority of CO_2 from an air stream up to 5 slpm.[10] The cold tip of the Stirling cooler, a Janis SC-10, is enclosed in a chamber via Klein Flange (KF) fittings. The chamber is outfitted with inlet and outlet ports (both with an attached pressure transducer), 5 psi pressure safety valve, thermocouple (TC) feedthroughs, low and high range CO_2 meters (Sable CA-10 and co2meter.com iSense, respectively), and a viewport, as seen in figure 1a. The outlet port is plumbed to a fume hood, and the chamber is insulated. The inlet line is controlled by a 0-5 slpm mass flow controller (MFC) and is plumbed to a gas cylinder containing the desired inlet components. The Stirling cooler and MFC are controlled by LabVIEW, and the data from the pressure sensors, TCs, and CO_2 meters are recorded using LabVIEW as well.

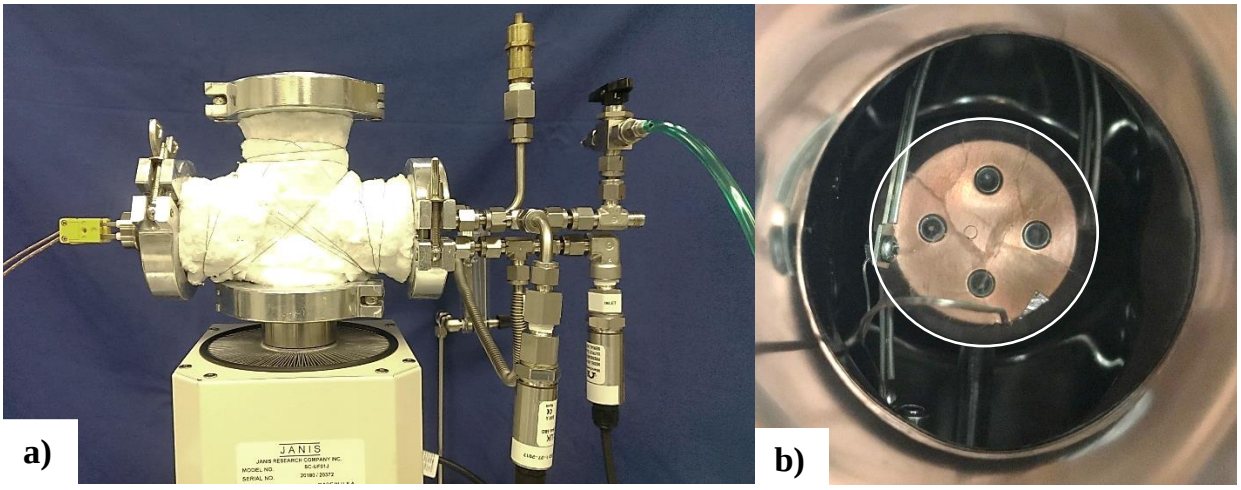

Figure 1. Janis SC-10 Stirling Cooler: a) side view of attached chamber with inlet/outlet ports and instrumentation; b) top view through viewport showing CO_2 ice (encircled in white) on copper cold tip.

The procedure used for each trial is the following: after initiating LabVIEW, the cooler is set to the desired power level and allowed to reach a steady state temperature (phase I). Next, the gas inlet valve is opened and the MFC is set to the desired flow rate (phase II). CO_2 is allowed to deposit for a set amount of time; typically for 1 hour. Outlet CO_2 concentration is constantly monitored. If the CO_2 accumulation is visually deemed about to clog the inlet port, then the trial is halted prematurely. Then, the MFC flow is halted, CO_2 gas inlet valve closed, and the cooler turned off. Accumulated solid CO_2 is allowed to sublime and is measured by flowing past the outlet CO_2 meter (phase III). Lastly, the cooler tip is allowed to reach room temperature before the trial is complete (phase IV). The time to complete each phase of operation: cool down, deposit, sublime, and warm up, is then recorded. The preliminary trial of flowing pure CO_2 at a flow rate of 1 slpm, with cooler power at 100%, quickly saturated the cold tip with CO_2 ice as seen in figure 1b. CO_2 ice was observed in further trials, but the buildup was far less significant and not quantifiable. No significant change in differential pressure was observed in any trial performed.

B. Test Matrix and Temperature Profile

After the preliminary trial with pure CO_2 to confirm operability, a test matrix of varying CO_2 partial pressures with a balance of N_2 were tested, as well as varied inlet flow rates and cooler power levels, as laid out in table 1. The different flow rates were chosen to provide a range within the calculated capability of the Stirling cooler operation. The CO_2 partial pressures tested Earth-like, spacecraft nominal, and high-concentration atmosphere levels. Lastly, the cooler power levels were selected to test various cold tip temperatures in order to determine the performance range of the system.

Table 1. Test Matrix.

Flow Rate	Cooler Power					
CO_2 Conc.	50%	60%	70%	80%	90%	100%
500 ppm	1 slpm	1, 2.5 slpm	1, 2.5 slpm	1, 2.5 slpm		
2600 ppm	1 slpm	1, 2.5, 5 slpm	1, 2.5, 5 slpm	1, 2.5, 5 slpm	2.5, 5 slpm	5 slpm
5000 ppm		2.5 slpm	2.5 slpm	2.5 slpm		

Not all partial pressures and flow rates were tested at each power level due to them being outside the temperature range of CO_2 capture at that concentration, or to prevent unnecessary stress on the cooler or MFC. In addition to the trials listed in the test matrix, the chosen test case of 2600 ppm, 2.5 slpm, and 80% cooler power was repeated twice in order to measure precision, test a zero-air balance rather than N_2, and test extended-cycle CO_2 capture performance.

A typical temperature profile of each trial completed is shown in figure 2, with the 4 operational phases highlighted. The shift from phase to phase is evident due to the sudden rise in temperature.

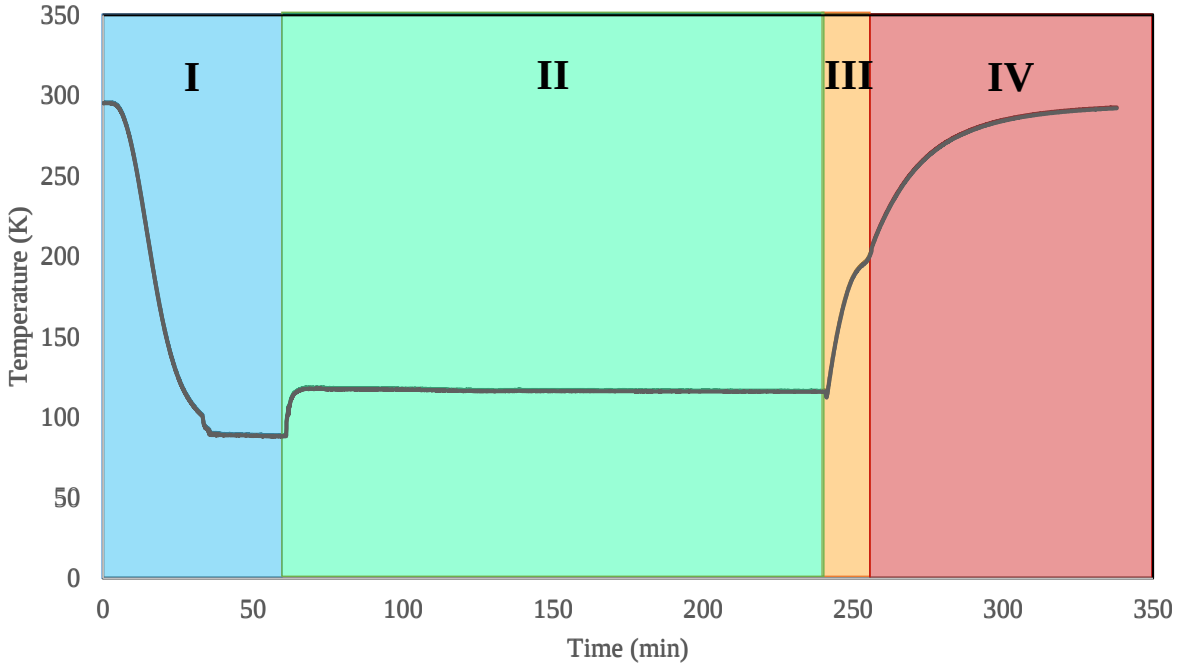

Figure 2. Graph of temperature changes over the 4 phases of CO_2 removal operation: I. cool down, II. deposit, III. sublime, and IV. warm up. This particular trial's conditions were 5000 ppm CO_2, 2.5 slpm, 80% power.

As the graph shows, after reaching steady state in phase I and initiating flow in phase II, a new, higher temperature steady state was reached due to the thermal loading of cooling the flowing gas. Phase III marks where the cooler and flow was shut down, the cold surface warmed to 196K, and held until all CO_2 sublimed. Finally, phase IV continued warming to room temperature. If the system was allowed to reach room temperature, the warm up time was significantly longer than the cool down time. Fortunately, the system would not need to warm above 200K before restarting the phases in an operating system, thereby shortening required transition time.

The 2 trials performed that intentionally did not follow this temperature profile were the initial, pure CO_2 test and the 2600ppm test at 5 slpm flow rate and 100% power. In these cases, gas was flowed during the cool down phase as well, rather than begin at the deposition phase, in order to prevent thermal shock to the cooler operating at max power.

IV. Results and Discussion

After obtaining the raw data from each trial, the average tip temperature was calculated by averaging the cold tip TC data from phase II: deposition. The percent CO_2 captured was calculated by taking the difference of the average CO_2 outlet concentration and the inlet concentration during the deposition phase, then dividing by the inlet concentration. Plotting these results for the various partial pressures and flow rates tested reveal a repeating trend of ability to capture CO_2, as shown in in figure 3.

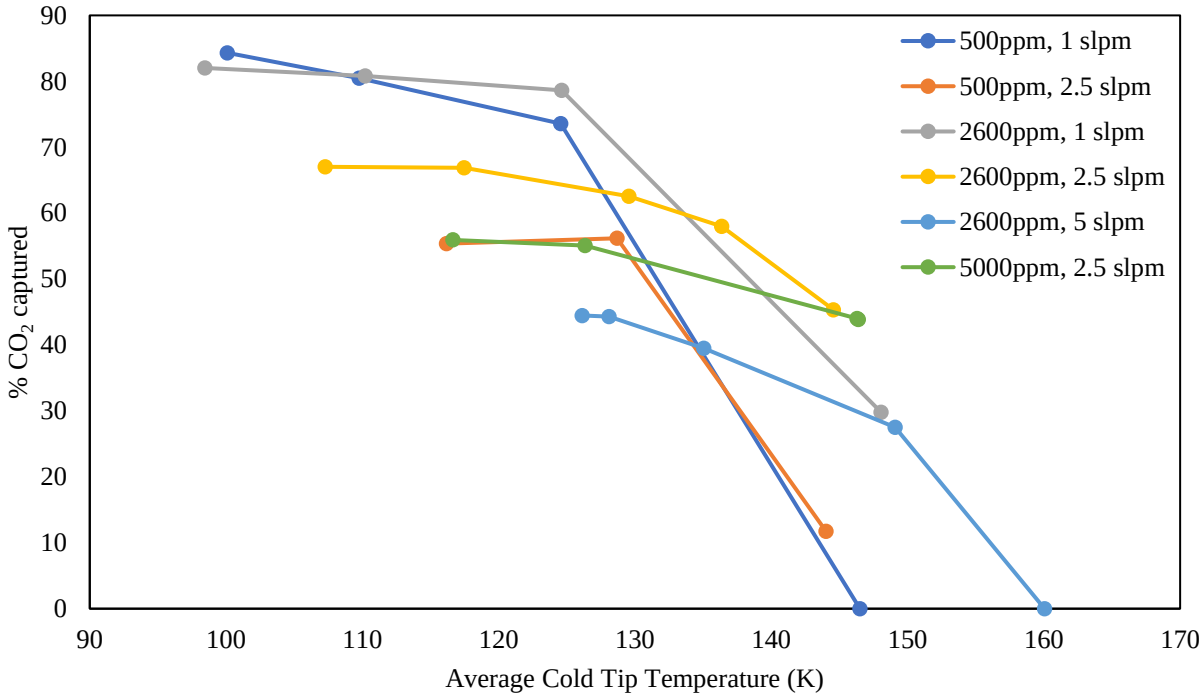

Figure 3. Average percentage of CO_2 captured vs. steady state cold tip temperature measured during the deposition phase.

Regardless of inlet concentration or flow rate, as the average cold tip temperature decreases, the percent CO_2 captured at first greatly improves, then approaches a maximum capture ability asymptotically. Interestingly, each flow rate and inlet concentration begin the asymptotic behavior at approximately 125K. At cold tip temperatures warmer than 125K, trials with the same inlet concentration fall on the same line, but at temperatures colder than 125K, trials with the same flow rate fall on the same line instead. In general, this data shows that in any inlet conditions, a limit is reached where increasing input power will no longer significantly increase amount of CO_2 captured.

The 1 slpm data shows the highest percent CO_2 captured, which concurs with heat transfer predictions as a slower flow allows more contact time for cooling the inlet gas. Percent CO_2 captured over 80% was obtained, which is better than expected as no system optimization was performed to improve performance. The setup is simply a tube directed towards a cold surface, with no pre-cooling, and inlet gas is able to freely flow within the chamber.

When examining overall CO_2 removal efficiency, in terms of total amount of CO_2 removed per amount of cooling power required, the 5000 ppm trials are the most efficient. This result is logical because the higher partial pressure allows for a larger difference between input and output CO_2 concentration, and therefore total mass removed. An increase in flow rate also allows for more total CO_2 capture, but the increase in efficiency is not as severe, due to overcoming heat transfer effects from increased flow.

Also interesting to note, when using the average cold tip temperature as the deposition temperature to determine CO_2 partial pressure via the Clausius-Clapeyron equation, there were multiple instances when the inlet CO_2 concentration was lower, meaning that no CO_2 should be captured. But, a significant amount of CO_2 capture was still

observed. One example is the case of 2600 ppm, 2.5 slpm, 60% power, which captured 45% of inlet CO_2, even though the cold tip temperature was 145K. The reason for this phenomenon is unknown. One idea was potential monolayer formation due to CO_2 adsorption onto the copper surface, but this would not account for a significant percentage of the mass of CO_2 captured. If this phenomenon proves to be repeatable, it is potentially beneficial in an operational standpoint as the system would still capture a partial amount of CO_2 even if not running at desired conditions.

Next, the raw data from the deposition phase was used to calculate the average CO_2 removal rate for each trial. This was done by taking the area under the curve of the outlet CO_2 concentration to calculate total mass of CO_2 captured, then dividing by the total time of deposition phase operation. This calculated rate was plotted against the average cold tip temperatures, and then curve fitted in order to better predict CO_2 removal rates at different set conditions. The equation determined to fit each set of data is shown in equation 1:

$$r = r_{max}(1 - ae^{bT}) \tag{1}$$

Where r is the CO_2 removal rate in kg/day, T is the average cold tip temperature in K, r_{max} is the experimentally determined maximum CO_2 removal rate, and a and b are unknown fitting factors, currently determined iteratively. The fits for all of the 2600 ppm input cases are shown in figure 4, and the corresponding values of r_{max}, a, and b are shown in table 2.

Table 2. Best fit parameters for 2600 ppm inlet concentration.

	r_{max} (g CO_2/day)	a	b
1 slpm	0.0061	$2x10^{-7}$	0.101
2.5 slpm	0.0125	$1x10^{-6}$	0.088
5 slpm	0.0164	$1.2x10^{-7}$	0.1001

The fits to the raw data have an r squared value of 0.995 or better, showing excellent agreement. These curves may change in future systems with different architecture and deposition surface areas. But, they can be used to provide an initial guess for system settings, and after being recalculated for new system configuration, optimize system efficiency.

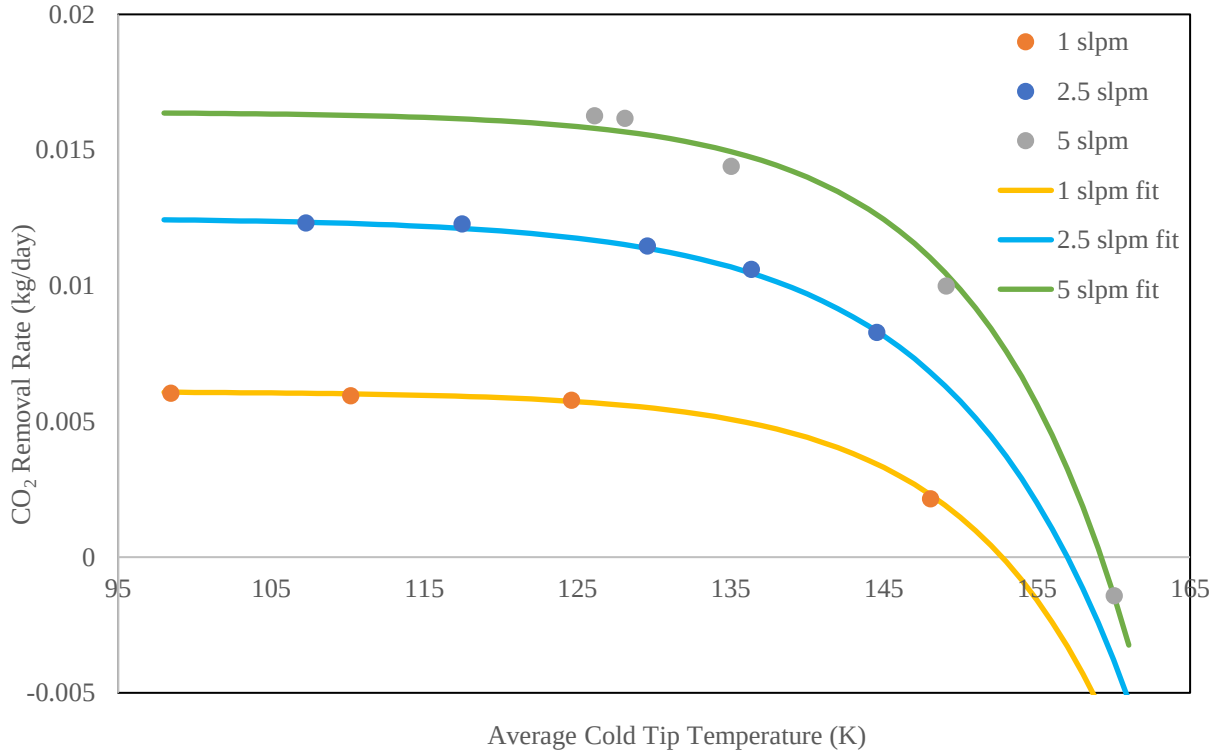

Figure 4. Best fit curves of average CO_2 removal rate vs. average cold tip temperature for the 2600 ppm inlet condition.

Next, the 2600 ppm, 2.5 slpm, 80% power case was repeated, and the deposition phase was maintained for 8 hours instead of 1 hour. The total amount of CO_2 captured increased from 0.5g to 3.3g. Although the total amount increased, the average CO_2 removal rate decreased. Looking at the CO_2 outlet concentration, shown in figure 5, the gradual degradation of CO_2 capture is apparent. The trend is logarithmic, and the fit is given in equation 2:

$$C = 0.0325 \ln t - 0.0594 \quad (2)$$

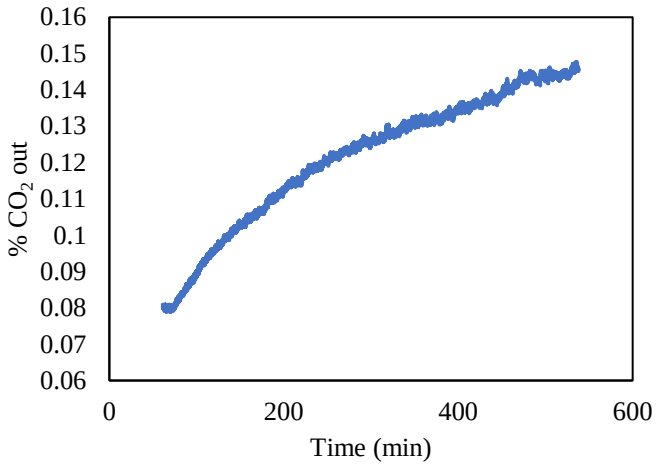

Figure 5. Outlet CO_2 concentration of cooler during deposition phase for the inlet conditions of 2600 ppm, 2.5 slpm, 80% power.

Where C is the outlet CO_2 concentration in percent CO_2 and t is time in minutes. The r squared value for this fit is 0.996, showing excellent agreement. As the trend shows, the performance of the system decays over time, and would eventually reach a CO_2 outlet partial pressure that is no longer acceptable. The reason behind this observed trend is theorized to be the buildup of CO_2 ice on the cold tip. Since CO_2 has a significantly lower thermal conductivity than copper, it would behave as an insulator and slowly increase the temperature that the inlet flow is exposed to. One way to mitigate this trend is to increase the surface area of the cold surface, and the cycle time of future systems will likely be dictated by the decay in removal rate instead of pressure drop.

Lastly, the 2600 ppm, 2.5 slpm, 80% power case was repeated again, but with a zero-air (79% N_2, 21% O_2) balance instead of N_2 balance, and a deposition phase duration of 1 hour. The results of the trial showed excellent precision, with the temperature profile and CO_2 outlet concentration overlapping with the prior test cases at these conditions, as seen in figure 6. When directly comparing with the 1-hour deposition phase trial, the average cold tip temperatures were within 0.04K of each other, and the percent CO_2 captured were only 0.1% different. This high precision not only shows good repeatability of the system, but also that the inclusion of O_2 in the inlet does not alter performance. Further repeatability tests were not performed before beginning work on the next-generation CO_2 removal system.

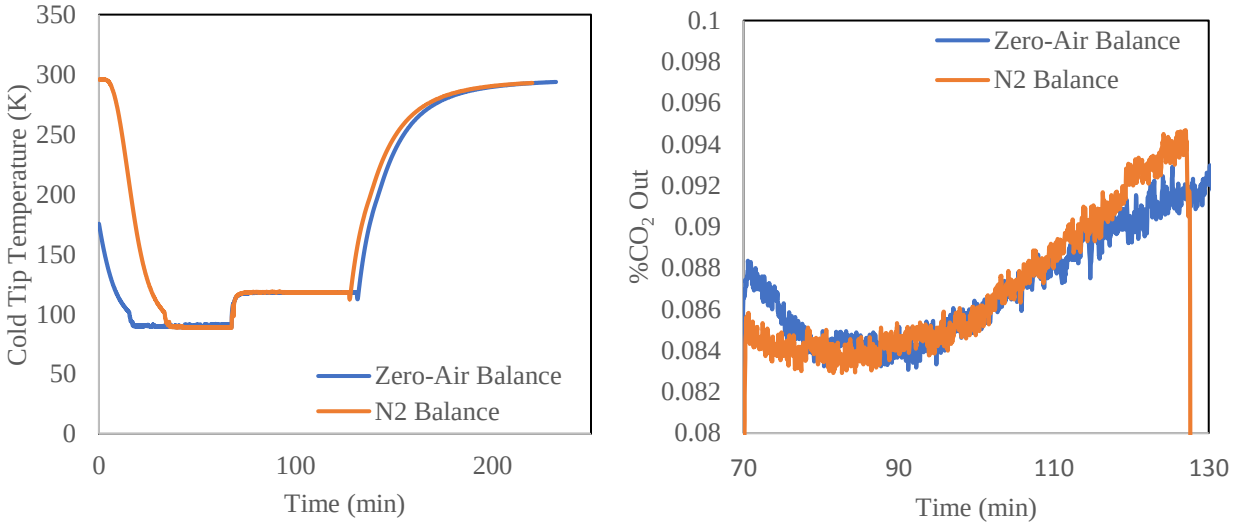

Figure 6. Comparison of zero-air and N_2 balance for the inlet conditions of 2600 ppm, 2.5 slpm, 80% power: a) 4-phase temperature profile; b) outlet CO_2 concentration during deposition phase.

V. Future Work

The design and build of a next-generation, fully-cycling Stirling cooler CO_2 deposition system is currently in process at ARC. This system will be built at the scale of 1 astronaut, and the design will interpret the conceptual schematic of full-scale operation previously described.[10] Lessons learned from this work, as well as complementary work currently being performed for ISRU applications at Kennedy Space Center (KSC), will be incorporated into the design and operation.[5] Work on the next-generation system is already underway, so evaluating advanced testing conditions using the existing system will not be performed. These conditions include allowing up to 40% relative humidity to observe parasitic water loading as well as adding trace contaminants to measure any capture. The current hypotheses are that water will freeze out easily, but as the humidity increases, the thermal loading will diminish the ability to remove CO_2. Also, all trace contaminants, except for hydrogen, carbon monoxide, and methane, could freeze onto the cold surface prior to or along with the CO_2. These hypotheses will be tested on the new system once it is operational. Electrical power input will also be measured on the new system so that total energy required for a full-scale operation system can be estimated.

VI. Conclusion

A Stirling cooler was utilized to evaluate CO_2 deposition as a potential method for CO_2 removal in a spacecraft cabin atmosphere. A test matrix was followed to obtain data on varied inlet concentrations, flow rates, and cooler power levels. The data showed diminishing return on increasing input power, as well as decay in amount of CO_2 captured with extended operation. These trends will dictate the initial parameters and cycle time to test in future iterations of the system. Repeatability was excellent, and CO_2 was removed at temperatures warmer than expected. These results inspire favorable expectations for the sub-scale, cycling test system currently being designed. In general, the condensation and deposition temperature differences between air components can successfully be leveraged to selectively remove CO_2 from cabin atmospheres, and this technology should be further evaluated for use on future missions.

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References

[1]Knox, J., et. al. "Development of Carbon Dioxide Removal Systems for Advanced Exploration Systems 2015-2016." *46th International Conference on Environmental Systems Proceedings*, July 2016, pp 418-426.

[2]Song, C., Kitamura, Y., Li, S., and Jiang, W. "Parametric Analysis of a Novel Cryogenic CO_2 Capture System Based on Stirling Coolers." *Environmental Science and Technology*, Vol. 46, 2012, pp. 12735−12741.

[3]Jensen, M., et al. "Prediction and Validation of External Cooling Loop Cryogenic Carbon Capture (CCC-ECL) for Full-Scale Coal-Fired Power Plant Retrofit." *International Journal of Greenhouse Gas Control*, Vol. 42, 2015, pp. 200-212.

[4]Paredes-Garcia, J., et al. "CO_2 and Trace Contaminant Removal System for Manned Missions beyond LEO." *46th International Conference on Environmental Systems Proceedings*, July 2016, pp 3050-3057.

[5]Muscatello, A., et. al. "Testing and Modeling of the Mars Atmospheric Processing Module." *AIAA SPACE and Astronautics Forum and Exposition Proceedings*, September 2017.

[6]Chambliss, J., Sweterlitsch, J., and Swickrath, M. "Potential Uses of Deep-Space Cooling for Exploration Missions," *42nd International Conference on Environmental Systems*, American Institute of Aeronautics and Astronautics, July 2012.

[7]Anderson, M. and Curley, S., "Evaluation of Cryofreezer Technology through Simulation and Testing," *35th International Conference on Environmental Systems*, American Institute of Aeronautics and Astronautics, 2005.

[8]"Evaluation Criteria for CO_2 Removal System Technological Assessment (FY17)," NASA. https://nspires.nasaprs.com/external/viewrepositorydocument/cmdocumentid=565739/solicitationId=%7B21E0270C-BC1F-EFC4-3D87-30713B5FF373%7D/viewSolicitationDocument=1/CO2%20Removal%20System%20Technological%20Assessment%20Requirements.pdf [cited 25 April 2017].

[9]James, J., Meyers, V., Sipes, W., Scully, R., and Matty, C. "Crew Health and Performance Improvements with Reduced Carbon Dioxide Levels and the Resource Impact to Accomplish Those Reductions." *41st International Conference on Environmental Systems*, American Institute of Aeronautics and Astronautics, July 2011.

[10]Belancik, G., et. al. "Characterizing Cryogenic Carbon Dioxide Capture for Life Support Systems." *47th International Conference on Environmental Systems Proceedings*, July 2017.