

Continued Development of Advanced Sorbents for Improved RCA Performance

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NASA has a strong interest in improving the method to control carbon dioxide (CO2) and humidity in the Exploration Extravehicular Mobility Unit (xEMU). Historically, the Metox has been used to remove CO2 from the Extravehicular Mobility Unit (EMU). However, this unit utilizes a solid silver oxide sorbent which has a finite capacity and requires maintenance for thermal regeneration between extravehicular activity (EVA) missions. The technology currently planned to replace the Metox in the xEMU is the Rapid Cycle Amine (RCA). This device utilizes a regenerable, pressure swing adsorption system which consists of two beds that alternate between adsorption of CO2 and H2O and desorption of said compounds through exposure to space vacuum. The RCA currently utilizes an amine-based sorbent to perform this function designated as SA9T. While this sorbent has significant reversible CO2 uptakes, an increase in these uptake capacities would enable the reduction of the RCA mass, volume, and power consumption while also enabling lower CO2 levels in the xEMU. In addition, the current sorbent emits low levels of ammonia which must be removed from the suit using a separate technology, and a reduction of these emission levels is desirable.

In an ongoing SBIR Phase II project, Reaction Systems developed new sorbents that have the potential to improve the performance of the RCA. Reaction Systems used a rapid screening testing method along with its expertise in the development of CO_2 sorbents to identify several materials that have potential to outperform SA9T. In this project, Reaction Systems tested the performance of the sorbents under realistic conditions using a twin bed CO_2 control module in a full-scale ventilation loop simulator and characterized the sorbent cycle times as a function of CO_2 partial pressure. The ammonia off gassing characteristics of these sorbents were also characterized and they were found to emit less ammonia than a sorbent that has a similar composition as SA9T.

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Nomenclature

Acfm	=	actual cubic feet per minute
°C	=	degrees Celsius
°F	=	degrees Fahrenheit

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Btu/h	=	British thermal units per hour
cm^3	=	*cubic centimeters*
CO_2	=	carbon dioxide
EMU	=	Extravehicular Mobility Unit
xEMU	=	Exploration Extravehicular Mobility Unit
EVA	=	extra vehicular activity
ft^3	=	cubic feet
g/h	=	grams per hour
h	=	hour
H_2O	=	water
in	=	inch
L	=	liter
mg	=	milligram
mm	=	millimeters
mm Hg	=	millimeters of mercury
NDIR	=	non-dispersive infared
N_2	=	nitrogen
OD	=	outer diameter
Pa	=	Pascal
PLSS	=	Portable Life Support System
$ppCO_2$	=	Partial pressure of CO_2
psia	=	pounds per square inch absolute
RCA	=	Rapid Cycle Amine
RH	=	relative humidity
s	=	second
sccm	=	*standard cubic centimeters per minute*
slpm	=	standard liters per minute
wt%	=	weight percent

I. Introduction

Nasa had a strong need to develop technology to control CO_2 and humidity in the Exploration Extravehicular Mobility Unit (xEMU) as it seeks to meet the objectives of the Artemis program. These objectives include landing humans on the surface of the Moon and eventually Mars[1]. Moreover, NASA has set the CO_2 partial pressure limit at 2.2 mm Hg at a metabolic rate that produces 2.44 g/min of CO_2. While the Metox, which contains a solid silver oxide sorbent, has performed well to control CO_2 from the suit it has a finite capacity and must be removed and regenerated at elevated temperature between extravehicular activity (EVA) missions. However, longer mission times are needed and therefore the Rapid Cycle Amine (RCA) is being developed. The RCA utilizes two beds that alternate between being on line to remove CO_2 and H_2O and off-line for regeneration by exposure to space vacuum. Although this is an attractive configuration, the beds cycling requires power consumption and causes O_2 losses. Both of these scale with cycling frequency. Overall, however, this approach offers the benefit of smaller adsorption beds and facilitates longer EVA durations than the previous Metox technology.

The baseline sorbent used in the development of the RCA is designated as SA9T. Although the sorbent has performed well, developing higher capacity sorbents would reduce the bed cycle frequency with which the RCA operates. The current SA9T sorbent also emits low concentrations of ammonia and therefore another objective for a new sorbent would be reduced ammonia emissions.

In SBIR Phase I and an ongoing Phase II project, Reaction Systems has developed new sorbents that have the potential to perform as well or better than SA9T and also shown lower ammonia emissions [2]. Reaction Systems accomplished this by identifying compounds that have structures that are likely to reversibly absorb CO_2 and screening candidate compounds in a way that uses the same performance criteria as the RCA. Reaction Systems has demonstrated expertise in the development of advanced sorbents for CO_2 control in both EVA and cabin applications [3,4]. Thus, unlike total CO_2 uptake measurements, or cyclic uptake measurements using fixed cycle times, the results from these tests will identify sorbents that will exhibit superior performance in full scale tests when loaded into the RCA.

II. Experimental Procedures

A. Preparation of Candidate Sorbents

All previous iterations of the RCA, including RCA-1, RCA-2 and RCA-3, have used SA9T[19] and many reports are available that describes the overall performance of the sorbent in terms of cycle time as a function of exposure pressure. However, screening data obtained under the conditions that were used in this project have not been published and therefore, a similar sorbent was prepared and tested to produce baseline performance values. The preparation of this sorbent, which is described in a US patent by Birbara, et al.[5], includes a process where tetraethyleneamineacrylonitrile (TEPAN) was prepared by mixing tetraethylenepentamine (TEPA) with acrylonitrile (ACN) in what is known as a Michael-Addition reaction and is shown in Figure 1.[6] Other candidate sorbents were identified based on their structures and their potential to have high cyclic CO_2 capacities. The sorbents described were then were impregnated on a high surface area polymethyl methacrylate (PMMA) support, in the form of beads approximately 0.5 mm in diameter. After impregnation, the candidate sorbents were dried at 75°C for 16 hr. and then stored in air-tight vials. All sorbents flowed freely and did not agglomerate.

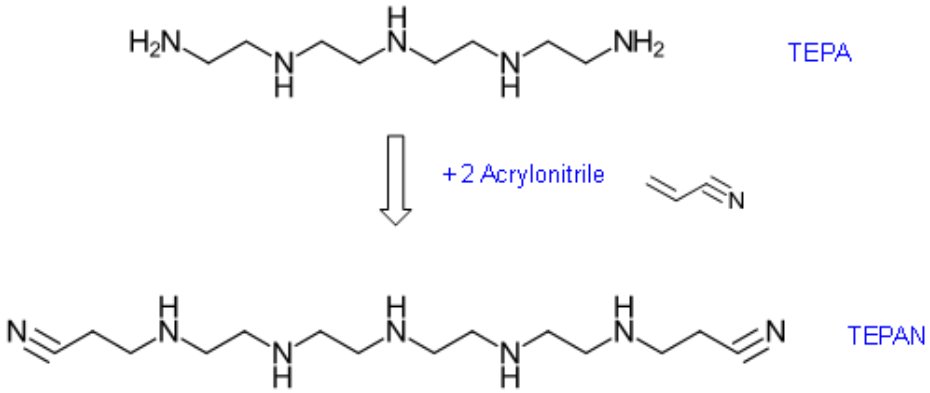

Figure 1. Preparation of TEPAN.

B. Sorbent Evaluation

1. Description of Test Rig

A schematic of this test rig is shown in Figure 2 and was described in detail previously[2]. Briefly a gas handling manifold is used to generate the desired gas mixture, and a saturator is used for humidity. After the flows are combined, a Vaisala RH sensor was used to measure the RH before the flow contacted the sorbent. A sample weight of 0.5 grams was used in a packed bed, contained in a ¼-in OD SS tube. A Lauda circulating chiller was used to control the temperature of the sorbent bed, which was measured with a 1/16th-in. thermocouple which was inserted into the sorbent bed. Typically, the bed temperature and the circulating chiller temperatures were within 1°C of each other during testing. The flow exiting the sorbent bed was directed into a CO_2 NDIR analyzer which measured the CO_2 concentration exiting the bed. In this configuration, the difference between calculated CO_2 concentration entering the bed and the measured concentration exiting the bed were used to calculate the uptake capacity of CO_2. Similarly, the concentration of CO_2 exiting the bed during the desorption cycle was used to calculate the quantity desorbed. Additional equipment was added to the test rig since the previous description[2] which enabled vacuum desorption capabilities. This equipment is depicted in Figure 2 and includes a vacuum scroll pump, a vacuum chamber, vacuum compatible bellows valves, and a needle valve used to vent the vacuum chamber in order to control the quality of vacuum applied.

2. Test Method

The sorbent screening tests were carried out using the CO_2 concentration exiting the bed to stop the adsorption cycle and switch to the desorption step. The test rig software monitored the CO_2 concentration being measured by the NDIR analyzer and switched the cycle from adsorption to desorption based on a CO_2 limit preset into the software. In the Phase I and beginning part of the Phase II effort, the desorption step was enacted with a nitrogen sweep flow. Although this method did not reduce the total pressure in the desorption step as is the case in the RCA, it did reduce

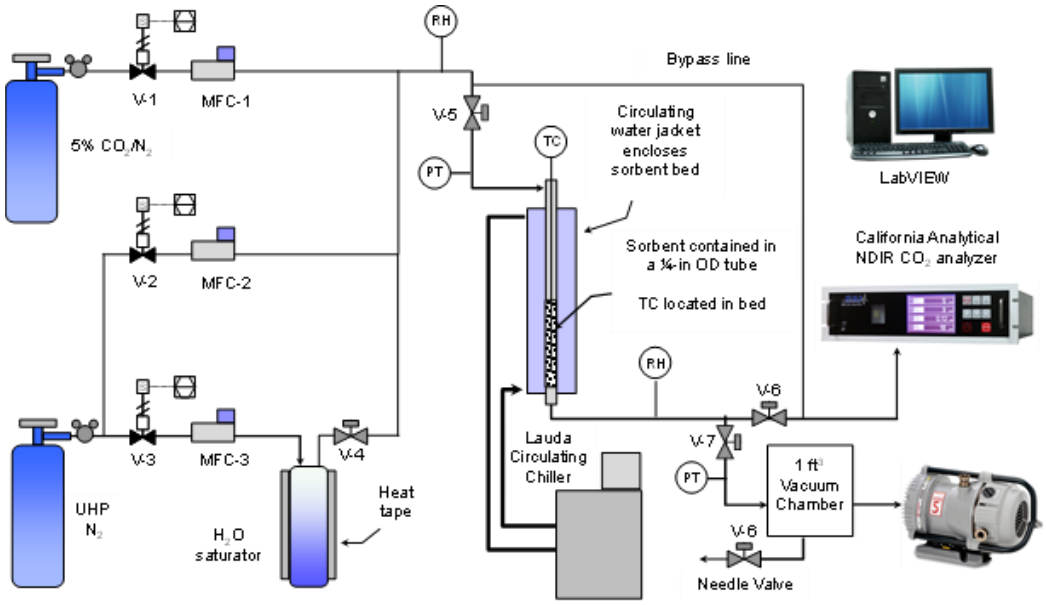

Figure 2. Reaction Systems' test rig for cyclic CO_2 uptake measurements.

the CO_2 partial pressure to zero, which is an important parameter in a pressure swing system. However, it was then discovered that quantity of the sweep flow strongly influenced the performance and cycle times of the candidate sorbents[2]. Thus, the vacuum equipment just discussed was installed which allowed for the desorption step to be enacted through exposure to vacuum, similar to the actual operation of the RCA.

In both desorption configurations, the limit that triggered the end of the adsorption step was 0.5 vol%, which is equivalent to a partial pressure of 3 mm Hg at the facility laboratory located in Golden, CO which has an average atmospheric pressure of 615 mm Hg. After the software switched the flow, the desorption time was set to be equal to the time it took to reach the CO_2 limit in the last adsorption cycle. This is representative of how the RCA would operate under steady state conditions with both beds performing equal ½ cycle times.

After loading the sample in the cell, the sorbent was first degassed by heating the bed to 50°C in a flow of 125 sccm N_2 for 30 minutes or until the CO_2 level being read by the analyzer was less than 0.01%. The sample was then cooled to 25°C and then the analyzer was calibrated by flowing a mixture of CO_2 and N_2 that produced a concentration of 1.0% as the flow was directed though the bed bypass line. After calibration, the flow was switched to the sorbent bed and the flows were set to the first exposure pressure and the system was operated for 10 adsorption/desorption cycles. This process was repeated until data had been obtained at all preprogrammed CO_2 exposure pressures.

In these tests, the relative gas flow wass 125 sccm per 1 cm^3 of sorbent. This is commensurate to the flow in the RCA. For example, in the RCA, a flow of 6 acfm at 4.3 psia is equivalent to 2.9 scfm or 82.8 slpm. Each bed contains approximately 715 cm^3 of sorbent and therefore the relative flow is 115 sccm per cm^3 of sorbent. Moreover, Chullen et al.[7,8] correlate CO_2 flow with metabolic rate and report a value of 0.774 sccm per Btu/hr in the RCA. Normalized for the bed volume the value is 1.08E-3 sccm/Btu/hr/cm^3. At the atmospheric pressure of Golden, CO, a partial pressure of 6.0 mm Hg corresponds to a concentration of 0.98% CO_2 or a net CO_2 flow of 1.23 sccm given the total of 125 sccm for the 1 cm^3 bed volume. This partial pressure corresponds to a metabolic rate of 1,000 btu/hr, and thus, the CO_2 flow is 1.23E-3 sccm/Btu/hr/cm^3. The lower setting of 4.8 mm Hg correlates to a metabolic rate of 703 Btu/h. Tests were carried out at a relative humidity (RH) of 40%.

3. Evaluation Methods

A detailed rationale for the screening method used in these tests has been presented previously[2]. Briefly, methods measuring total uptake and even those measuring cyclic uptake with predetermined cycle times are not representative of the way the RCA functions. Therefore, in these screening tests, a method simulating the RCA function was used to evaluate sorbents. Once the CO_2 flow was started, the adsorption cycle switched from adsorption to desorption when the CO_2 concentration exiting the bed reached a preselected value. The desorption period was then set to be equal to the most recent adsorption period. In this case, the data may be shown as ½ cycle time as a function of $ppCO_2$. In this case, the CO_2 adsorption profile is a key parameter. In particular, the efficiency of the adsorption step as a function of the sorbent loading will determine the cycle time. If the efficiency drops off quickly with loading, then

the CO_2 concentration exiting the sorbent bed will rise more rapidly during the adsorption step, and reach the threshold set point that trips the cycle. On the other hand, if the efficiency remains high as the sorbent loads, then it will take longer to reach the threshold value, which will result in longer cycle times and higher weight loadings.

C. Full Scale Test Rig

Tests were also carried out for larger batches of sorbent with a test rig that simulates the flow in the full-scale ventilation loop. A drawing of the test rig is shown in Figure 3. The system is constructed of vacuum compatible components and operates at full scale representative pressures and flow rates. The system has in-line Vaisala GMP-252 probe CO_2 sensors and Vaisala HMT-334 humidity sensors at the entrance and exit of the test article, depicted as the RCA 1.0 in Figure 3. Omega PX509 pressure transducers and Omega HKQ316SS probe thermocouples are also installed on the inlet and exit lines. A hermetically sealed Airtech 3BA1002 – AB22 model vacuum regenerative blower is used to circulate the flow through the test article and the rest of the loop. The blower is designed for vacuum operation and has a variable speed DC control. It is capable of producing flows from 2 acfm up to 9 acfm with the expected system pressure loss. The actual flow is monitored by a mass flowmeter. Porter 601 CV Series II mass flow controllers are used to introduce N_2 and CO_2 into the system and a custom designed water injection system is used for H_2O injection in order to reach desired humidity levels in the loop. Finally, an Edwards XDS 35 and E2M80 vacuum pump are used to reduce the pressure of the system and for applying vacuum for sorbent regeneration. The system also can be fit with an FTIR unit that can be used to characterize trace contaminants in the flow in tests with carbon sorbents.

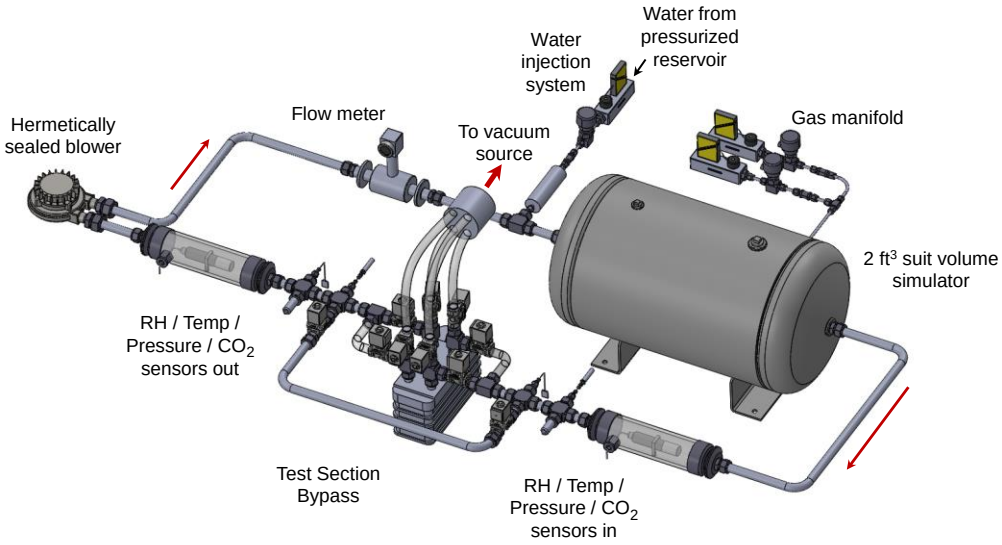

Figure 3. Reaction Systems' full scale test rig.

III. Experimental Results

A. Screening Results

In this body of work, over 175 candidate sorbents were synthesized and screened for their cyclic uptake capacity in the rapid screening apparatus depicted in Figure 2. Detailed data from the results of tests was presented in depth in the previous report on this work[2], including as mentioned, the implementation of vacuum desorption for the realistic screening of small quantities of sorbents. The cyclic uptake results for some of the most promising candidate sorbents synthesized are depicted in Figure 4 as measured ½ cycle time as a function of CO_2 partial pressure condition. The ½ cycle times of the sorbent synthesized with TEPAN on PMMA are also depicted for comparison. As has been mentioned at length previously, the ½ cycle of these candidate sorbents is representative of their cyclic uptake capacity and the determining factor in their potential performance.

The sorbents that are depicted in comparison to TEPAN/PMMA are RSI-1, RSI-4, RSI-8, RSI-9 (the labeling and formulations of these sorbents is not consistent with what has been previously published[2]). RSI-8 and RSI-9 were of the last ten sorbents to be synthesized during this body of work, and they exhibited some of the highest cycle times of

all candidate sorbents. The ½ cycle times that they exhibited were longer than TEPAN/PMMA at all of the partial pressure conditions, including the lowest condition of 4.1 mm Hg. While multiple other candidate sorbents exhibited longer ½ cycle times than TEPAN/PMMA at the higher partial pressure conditions, including RSI-1 and RSI-4, these were the first candidate sorbent that exhibited a higher uptake capacity than TEPAN/PMMA at all six of the CO_2 partial pressure testing conditions. The ½ cycle times for RSI-9 were 17.38 min, 8.56 min, 6.24 min, 4.31 min, 3.01 min, and 2.10 min for CO_2 partial pressure conditions of 4.1 mm Hg, 6 mm Hg, 7 mm Hg, 8.6 mm Hg, 10 mm Hg, and 12.4 mm Hg, respectively. This is in comparison to those measured for TEPAN/PMMA in the same partial pressure condition order at 13.95 min, 7.16 min, 5.25 min, 3.61 min, 2.47 min, 1.66 min. In the same order of partial pressure conditions, RSI-8 exhibited ½ cycle times of 15.89 min, 8.74 min, 6.75 min, 4.92 min, 3.53 min, and 2.44 min. As is apparent, RSI-8 exhibited the longest ½ cycle times witnessed at all partial pressure conditions except for the lowest which RSI-8 exhibited the longest time witness.

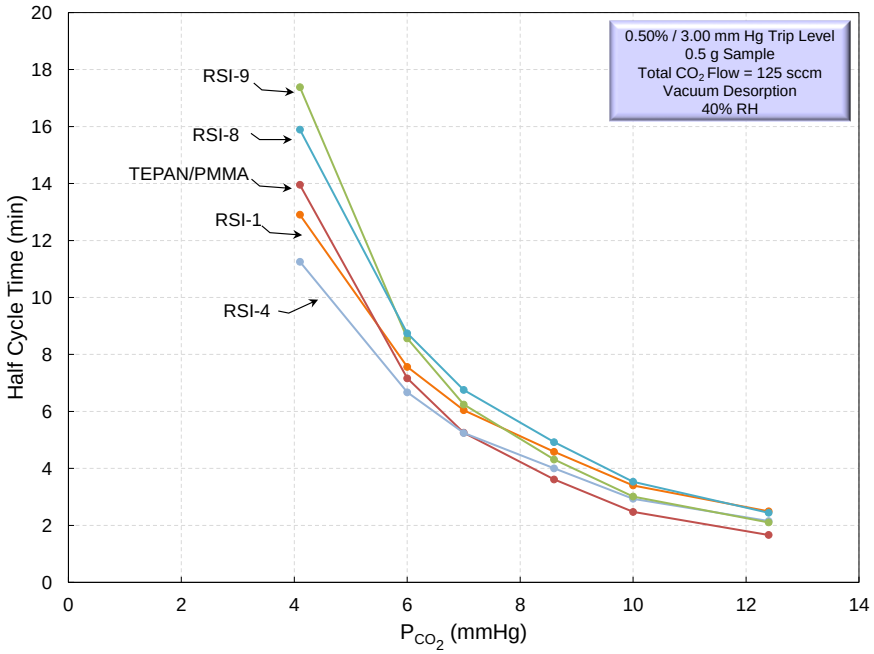

Figure 4. ½ cycle times for TEPAN/PMMA, RSI-1, RSI-4, RSI-8, and RSI-9.

In addition, RSI-1, exhibited very promising uptake results at the four highest partial pressures. As has been discussed previously[2], high cyclic capacity at the highest partial pressures provides a significant advantage for candidate sorbents as a result of the short ½ cycle times and high number of cycles required to operate at these conditions. Its ½ cycle times were longer than TEPAN/PMMA at all of the conditions except for the lowest of 4.1 mm Hg; its times were comparable to TEPAN/PMMA at the 6 mm Hg condition but notably longer at the highest four partial pressures. The times measured for RSI-1 in the same condition order as previously written were 12.9 min, 7.56 min, 6.04 min, 4.58 min, 3.4 min, and 2.49 min.

The results from candidate sorbents synthesized with RSI-4 are also seen in Figure 4. RSI-4 had longer cycle times than TEPAN/PMMA at the three highest partial pressure conditions and an equivalent ½ cycle time to TEPAN/PMMA at the 7 mm Hg partial pressure. It's ½ cycle times at the three highest partial pressure conditions were equitable to those of RSI-2. The ½ cycle times of RSI-4 were measured at 11.25 min, 6.67 min, 5.24 min, 4.0 min, 2.93 min, and 2.15 min, again, in the same partial pressure condition order as previous.

B. Analysis of Cycles over an EVA

Meginnis et al.[9] listed metabolic rates as a function of time for several different EVA scenarios. In the profile that was described as "Standard" only about 25% of the time is spent at metabolic rates less than 1000 Btu/h. In addition, the average metabolic rate over this eight-hour period is 1250 Btu/h, which corresponds to a CO_2 partial pressure of 7.02 mm Hg. As shown in Figure 4, the half cycle times for all four RSI sorbents obtained during this body of work are greater than those of TEPAN/PMMA at CO_2 partial pressures higher than 6 mm Hg. If it is assumed that the performance of the TEPAN/PMMA sorbent is representative of SA9T, this result suggests that the overall number of cycles that occur over the course of an EVA would be lower with not only RSI-8 and RSI-9, which have longer cycle times at all conditions, but also with RSI-1 and RSI-4.

An analysis was carried out the using half cycle times calculated for TEPAN/PMMA at the metabolic rates in the "Standard" based on a correlation by Meginnis et al. [9] The number of half cycle times that would be expected with the RSI sorbents sorbent were then calculated based on the relative differences in half cycle times between the TEPAN/PMMA sorbent and RSI sorbents shown in Figure 4. Finally, the half cycle times for each sorbent and the

duration at each point in the EVA mission were used to calculate the number of cycles that would occur with each sorbent at each condition in the EVA profile.

The analysis shows that the relative differences in cycle time at the highest met rates have the biggest impact on total cycles. For example, at the lowest met rate, the half cycle time for the TEPAN/PMMA is 2.7 min longer than the RSI-4 sorbent. Over the duration of this condition, 7 half cycles occur with the TEPAN/PMMA sorbent, whereas 8.5 half cycles would be expected with the RSI-4 sorbent. Therefore, the difference in half cycles at this metabolic rate is only 2.5. On the other hand, at the two highest metabolic rates, the number of cycles estimated for the RSI-4 sorbent is 32, whereas the number estimated for TEPAN/PMMA is 39. Thus, even with the short time at these metabolic rates, the use of the RSI-4 sorbent would reduce the number of half cycles by 7.

The cumulative numbers of half cycles for each sorbent over the duration of the mission were also calculated, and they are depicted in Figure 5. The results indicate that the number of half cycles expected over the duration of the mission with the RSI-1 sorbent is 128, and for RSI-4, RSI-8, and RSI-9, they are 147, 120, and 131 cycles, respectively. This is compared to 164 half cycles that would be required with the TEPAN/PMMA sorbent. For the best performing sorbent, RSI-8, this represents a reduction of 44 cycles versus TEPAN/PMMA. For RSI-9, the reduction is less, at 33 cycles; yet it is still significant. Considering RSI-9 has the longest ½ cycle time at the lowest partial pressure, the difference in performance between RSI-8 and RSI-9 versus TEPAN/PMMA emphasizes the beneficial effect that longer cycle times at higher CO_2 partial pressures has on the mission. Reducing the total number of cycles reduces power consumption and O_2 losses that occur during regeneration.

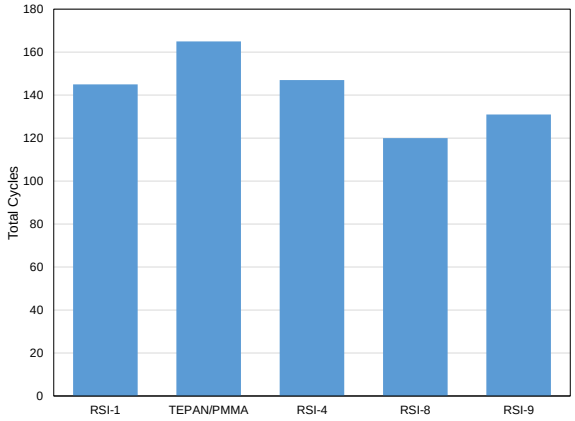

Figure 5. Total cycles for TEPAN/PMMA, RSI-1, RSI-4, RSI-8, and RSI-9.

C. Ammonia Emissions

1. Thermal Ammonia Emissions

Tests were carried out to investigate the ammonia emission characteristics of candidate sorbents as well. Approximately 0.5 grams of sorbent were placed in the test cell in the CO_2 uptake test rig, and the flow exiting the test section was directed into a MAX Fourier Transform Infra-Red (FTIR) gas analyzer for ammonia analysis. After the sorbent was loaded into the test cell, a flow of N_2 was directed through the bed at a rate of 125 sccm. Baseline data were obtained prior to loading the sample into the cell to verify that any ammonia measured during the test with the sample was emitted from the sorbent itself. After starting the N_2 flow, the sorbent temperature was maintained at 25°C for 20 minutes and then the temperature was raised at a rate of 1.5°C per minute until a final temperature of 50°C was reached; this temperature was maintained for one hour. The total quantity of ammonia emitted was then calculated given the measured ammonia concentration, flow rate, and duration of test.

The results for the TEPAN/PMMA sorbent are depicted in Figure 6. As can be seen, there is an initial spike in concentration followed by an elevated and stable concentration once temperature was increased to 50°C. The concentration measured during tests with RSI sorbents followed a similar pattern, however, the concentration reached by the RSI sorbents at temperature was lower than that of TEPAN/PMMA. As can be seen, the concentration that the TEPAN/PMMA sorbent yielded during elevated temperature was approximately 0.2 ppm, and the concentration that was measured for the RSI sorbents

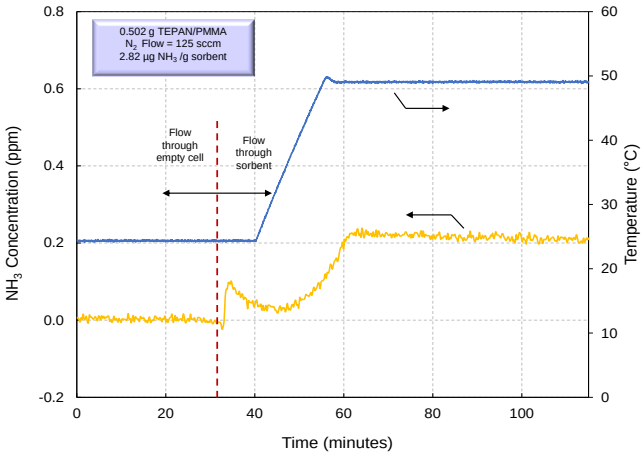

Figure 6. Thermal ammonia emission test results for TEPAN/PMMA.

were lower and, and sometimes significantly so. The concentration reached by RSI-4 was only 0.04 ppm once it reached temperature. As a result, the total ammonia emitted for all of the RSI sorbents was lower than that of TEPAN/PMMA.

Figure 7 depicted the results of the thermal ammonia emissions plotted again the total number of cycles that would be conducted during the standard EVA profile. This was done because of the importance of both metrics for candidate sorbents, and the total cycles were calculated according to the measured ½ cycle times of the candidate and the method described above. The results of sorbents RSI-1, RSI-2, RSI-4, RSI-5, RSI-6, and TEPAN/PMMA are shown in Figure 7. The ½ cycle times of RSI-2, RSI-5, and RSI-6 were not shown previously in Figure 4 in order to ensure clarity of the figure and results. Additionally, emissions testing for both RSI-8 and RSI-9 had not been completed at the time of this report.

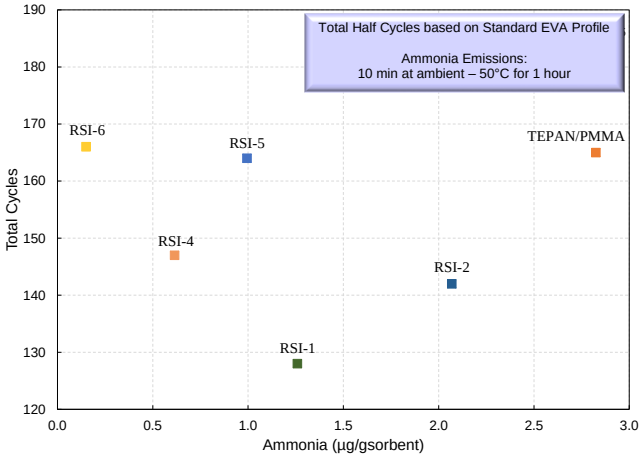

Figure 7. Thermal ammonia emissions vs total cycles in standard PLSS EVA profile.

In Figure 7, TEPAN/PMMA is represented in top right corner with the highest level of ammonia emissions and 164 total cycles. To the left of TEPAN/PMMA, candidate sorbents with RSI-6 and RSI-5 are plotted, with RSI-6 exhibiting the lowest quantity of ammonia at 0.15 µg NH_3 / g sorbent and a similar total number cycles to TEPAN/PMMA at 166 cycles. The RSI-5 combination exhibited close to averaged behavior between TEPAN/PMMA and RSI-6 with emissions of 0.99 µg NH_3 / g and total cycles of 164. RSI-1 is represented in the bottom of the plot with lowest total cycles at 128 and thermal ammonia emissions of 1.26 µg NH_3 / g. RSI-4 is similar to RSI-6 in that it also exhibits uptake capacity and emissions representative of an average between its two constituents with emissions of 0.62 µg NH_3 / g and a total number of cycles of 147. RSI-2, which was thermally treated RSI-1, exhibited a similar total number of cycles to RSI-1 at 142 but emitted more ammonia at 2.07 µg NH_3 / g.

2. Ammonia Emissions During Cyclic Testing

While the thermal emission testing can offer insight on the degradation nature of sorbents and act as an accelerated lifetime test, monitoring the ammonia emissions of the sorbents during cyclic testing when exposed to CO_2 and humidity provides information about their ammonia production levels during testing under conditions more representative of their actual potential use. Candidate sorbents were subjected to cyclic testing at 4.1 mm Hg CO_2 partial pressure, and in addition, the FTIR analyzer was installed at the outlet of the NDIR CO_2 analyzer to monitor the ammonia concentration. The desorption cycle was conducted with 800 sccm nitrogen sweep flow so that the ammonia concentration could be monitored during both adsorption and desorption cycle. Testing was conducted for 64 hours with an increased sorbent bed temperature of 30°C in order to potentially promote higher emissions and ½ cycle time reduction.

Cyclic emission testing was conducted for TEPAN/PMMA, RSI-1, and RSI-4. The results of the test with RSI-4 are pictured in Figure 8 with the ammonia concentration represented by the blue curve plotted on the left axis and the inlet and measured outlet CO_2 concentrations represented by the grey and yellow curves, respectively, plotted on the right

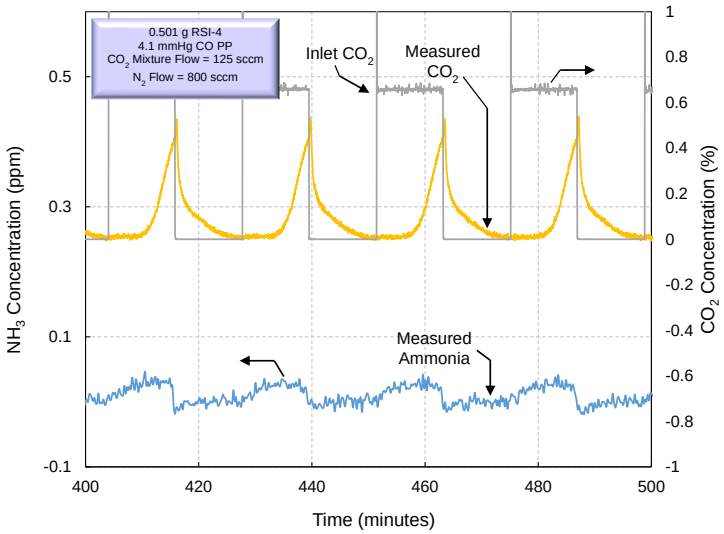

Figure 8. Cyclic ammonia emission test for RSI-4.

axis. The adsorption cycle is indicated by the non-zero inlet CO_2 concentration and the desorption cycle occurs when it is reduced to zero. The measured outlet CO_2 concentration rises during the adsorption cycle and falls during the desorption cycle which is consistent with previous cyclic testing when sweep nitrogen was used for desorption.

The ammonia concentration fluctuated during testing in a very interesting, periodic manner. During the adsorption cycle, the ammonia concentration rose to a level of 0.04 ppm and remained there, and once the desorption cycle started, the ammonia concentration dropped immediately to 0 ppm for its duration. The total flow during the adsorption cycle was 125 sccm compared to 800 sccm during the desorption cycle so it would be expected for the ammonia concentration to be reduced regardless of other factors as a result of dilution. However, testing was also conducted with 125 sccm nitrogen desorption flow to eliminate this factor, and the net results were the same. Initially, the reduced, equivalent desorption flow was conducted with the same procedure, trip limit, and equivalent adsorption/desorption times and the ammonia concentration increased and decreased at the same interval of time as the ½ cycles but didn't decrease to zero during testing. This was likely a result of residual ammonia in the sorbent bed not being flushed quick enough with only 125 sccm during the desorption cycle. Subsequent testing was conducted with the equivalent desorption flow and same trip limit from adsorption to desorption, but the desorption cycle was extended longer than the adsorption cycle to allow for sufficient purging of any residual ammonia. During it, the concentration decreased to 0 ppm during the desorption cycle and increased during the adsorption cycle in the same manner as depicted in Figure 8. These results indicate ammonia emissions during cyclic testing are induced by the presence of CO_2 and/or humidity during the adsorption cycle.

For the test with TEPAN/PMMA, the ammonia concentration followed a similar trend as is seen in the TEPAN/PMMA data where it rises during the adsorption step and remains at zero during the desorption step. However, the increase in concentration during the adsorption was greater than it was for RSI-4, and it rose to approximately 0.09 ppm. Similar to the thermal emission testing previously discussed, the ammonia concentration curve was integrated, and the total quantity of ammonia emitted was calculated for each test. Over 66 hours of testing, TEPAN/PMMA emitted a total of 10.62 µg NH_3 per gram of sorbent, and over 67 hours of testing, the total ammonia emitted for the RSI-4 sorbent was only 2.24 µg NH_3 per gram of sorbent, a level substantially lower than TEPAN/PMMA.

The ammonia data from the RSI-1 test followed the same trend as it did with TEPAN/PMMA and RSI-4. The concentration rose to a similar level as it did with TEPAN/PMMA during the adsorption cycle, and the total ammonia emitted for RSI-1 over 66 hours of testing was 11.14 µg NH_3 per gram of sorbent. This result was surprising considering the significantly lower emissions produced from RSI-1 compared to TEPAN/PMMA during the thermal emission testing discussed in the previous section.

These results are significant because they suggest different mechanisms for ammonia emissions from candidate sorbents which aren't consistent or proportionate in quantity from sorbent to sorbent and from mechanism to mechanism. RSI-1 exhibited significantly lower emissions than TEPAN/PMMA during the thermal emission testing but exhibited very similar emissions during cycling testing. RSI-4, however, yielded significantly lower emissions than TEPAN/PMMA in the thermal emissions testing. This emphasizes the stability of RSI-4 in both thermal and cyclic testing environments, and this is important because both circumstances would likely have an impact on the overall lifetime of candidate sorbents when used in their intended applications.

In Figure 9, TEPAN/PMMA, RSI-1, and RSI-4 and denoted with their same cycle numbers as previous compared to ammonia emitted during the cyclic emissions testing. Again, TEPAN/PMMA is in the top right of the plot with the highest number of cycles and the high ammonia emissions, and again, RSI-4 is lower left of it with a significant reduction in ammonia emissions and fewer cycles. RSI-1, however, displays a different relation to TEPAN/PMMA and RSI-4 with the same reduction in cycles but slightly higher ammonia emissions than TEPAN/PMMA. These plots emphasize the comprehensive comparative performance between candidate sorbents with a visual representation, and it is promising that the RSI-4 sorbent maintains its lower ammonia emission

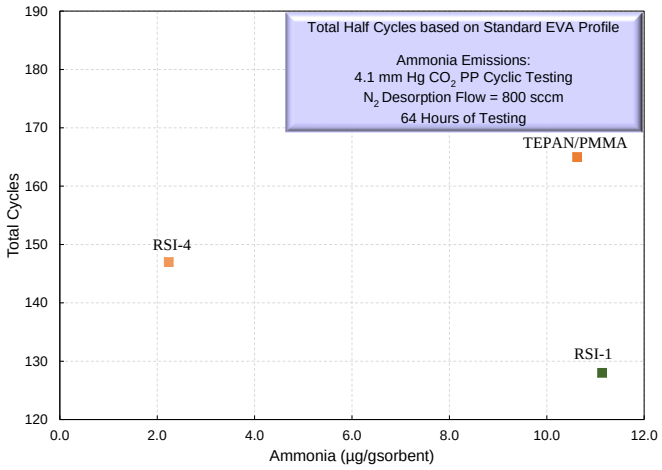

Figure 9. Cyclic ammonia emissions vs total cycles in standard PLSS EVA profile.

and total cycle metrics compared to TEPAN/PMMA in both situations.

D. Thermal Aging Tests

During this body of work, accelerated aging tests were carried out on three different candidate sorbents in order to quantify the effect of the potential degradation process during extended lifetime use. To do this, samples of TEPAN/PMMA, RSI-1, and RSI-4 were synthesized at the same time and then placed inside an oven heated to 50° C. The samples were placed in sample vials with their top removed so that the sorbents were exposed to the laboratory air during the heating process. Prior to heating, all three sorbents were screened in the rapid screening testing apparatus to quantify their initial cyclic uptake capacity prior to the heating process. The samples were then tested in the same manner after heating intervals of 1 month, 2 months, 3 months, and 6 months. The weights of the samples of were also recorded throughout the process.

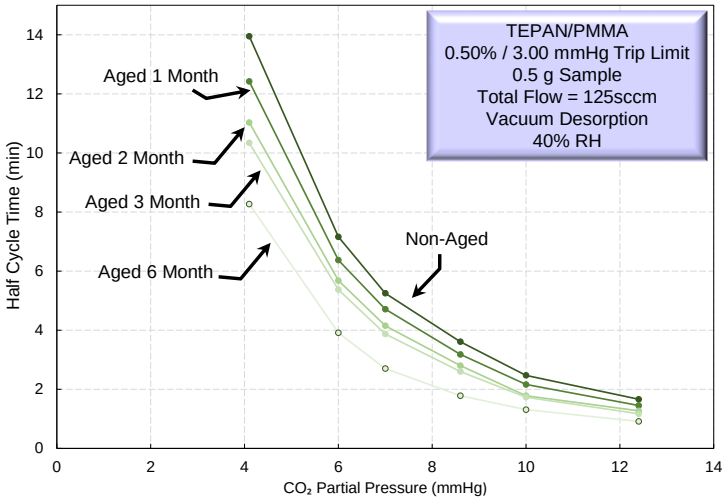

Figure 10. 1/2 Cycle Times of TEPAN/PMMA during aging tests.

The results of the tests after each time interval for TEPAN/PMMA are depicted in Figure 10, and as can be seen and as would be expected, the heating process decreases the uptake capacity of the sorbent. After each heating interval, with perhaps the exception from 2 months to 3 months, the ½ cycle times at all of the partial pressure conditions were decreased a significant amount. Prior to again, the ½ cycle times were for TEPAN/PMMA, which were previously listed in this report, were 13.95 min, 7.16 min, 5.25 min, 3.61 min, 2.47 min, and 1.66 min. After 6 month's of aging, the times were reduced to 8.27 min, 3.91 min, 2.70 min, 1.75 min, 1.31 min and 0.91 min at the same respective partial pressure conditions of 4.1, 6, 7, 8.6, 10, 12.4 mmHg.

As mentioned, this test was conducted for RSI-1 and RSI-4 after the same heating intervals as well. Figure 11 depicts the final comparative half cycle times for the three candidate sorbents before aging and after 6 months of aging. As can be seen, prior to aging, RSI-1 and RSI-4 exhibit longer ½ cycle times than TEPAN/PMMA at the higher partial pressure conditions. RSI-1 exhibits longer ½ cycle times at the four highest conditions of 7, 8.6, 10, and 12.4 mmHg PP_{CO2}. At the 6 mm Hg condition, TEPAN/PMMA and RSI-1 have essentially equivalent times, and TEPAN/PMMA only exhibits a longer ½ cycle time at the lowest condition of 4.1 mm Hg. RSI-4 exhibits a similar advantage and has longer ½ cycle times than TEPAN/PMMA at the 8.6, 10, and 12.4 mm Hg conditions. After aging,

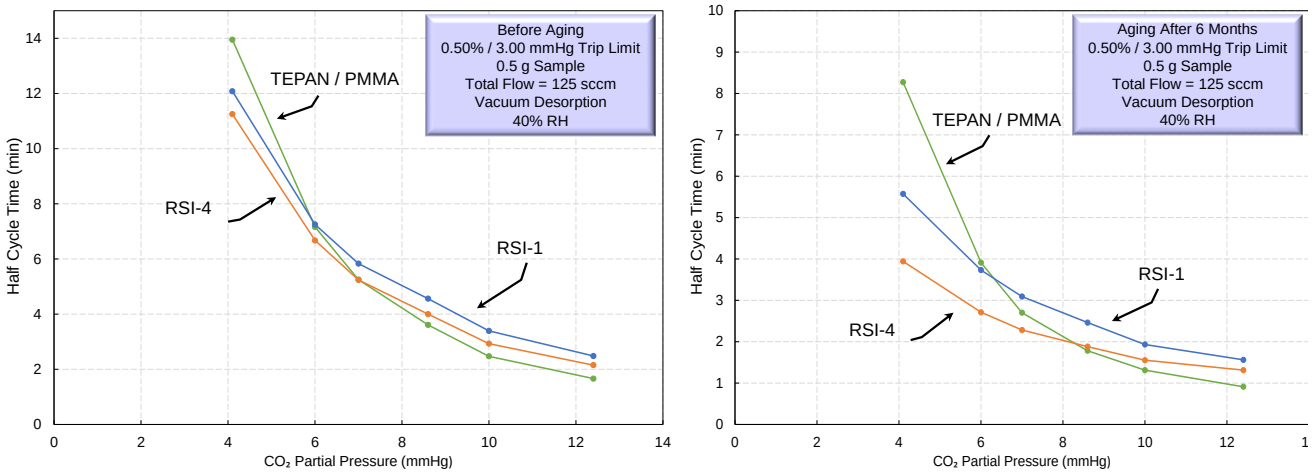

Figure 11. ½ Cycle Times for RSI-1, RSI-4, TEPAN/PMMA before aging and after six months of aging.

the same observations can be seen on the right side of Figure 11. RSI-1 exhibits longer ½ cycle times than TEPAN/PMMA at the four highest partial pressure conditions, and RSI-4 exhibits longer times at the three highest partial pressure conditions.

As has been discussed previously, this advantage has a significant effect on the total number of cycles that would potentially be enacted by an RCA utilizing the candidate sorbents as a result of the total number of cycles required at the higher partial pressure conditions. Using the method discussed earlier in this report, the total number of cycles were calculated for the candidate sorbents before and after aging. TEPAN/PMMA prior to aging was assumed to be the baseline sorbent from which the other ½ cycle times were ratioed in order to calculate total number of ½ cycle times, and it would require 164 total cycles to operate during the standard profile. An RCA utilizing TEPAN/PMMA after six months of aging would require 310 cycles, and an RCA utilizing 6 month aged RSI-1 and RSI-4 would require 234 and 302 cycles, respectively. This is a significant difference. For reference, an RCA utilizing non aged RSI-1 and RSI-4 would require 130 and 147 cycles, respectively. Prior to aging, RSI-1 exhibited a total cycle advantage of 34 cycles, and RSI-4 did 17 cycles. After aging, RSI-1 demonstrates an even higher total cycle advantage of 70 cycles, and RSI-4 exhibits an advantage of 8 less total cycles. These results demonstrate that the candidate sorbent RSI-1 has the potential to exhibit higher stability and a longer lifetime than TEPAN/PMMA.

E. One Third Scale Module Tests

1. One Third Scale Module

Tests were also carried out in a mid-scale CO_2 control module that was additively manufactured from aluminum AlSi10Mg. The module contains two thermally connected beds which contain the hexagonal lattice that is shown in Figure 12. Each bed has screens on both inlet and outlet ports to contain sorbent particles. The inlet and outlet ports of each bed were drilled and tapped to accommodate ½" NPT threads and ½" MNPT x KF16 fittings were installed. Each bed contains two fill ports on the top surface; they were drilled and tapped with ¼" MNPT threads, and fit with ¼" MNPT to Swagelok plugs.

The internal lattice was also additively manufactured, resulting in a reproducible, well-controlled structure that can be thermally modeled. Figure 13 includes several views of the lattice structure and illustrates the fit of the CO_2 sorbent beads within the pore structure of the lattice. The overall dimensions of each bed are 6.35-inx 3.59-inx 0.84-in, resulting in an overall volume of 19.09 cubic inches. The total aluminum volume of the lattice within each bed is 2.66 cubic inches, which translates to a relative density of 13.95%. The surface area of the metal lattice on an overall per unit volume basis is 19.96 square inches per cubic inch, and the total metal surface area within each bed is 380.97 square inches.

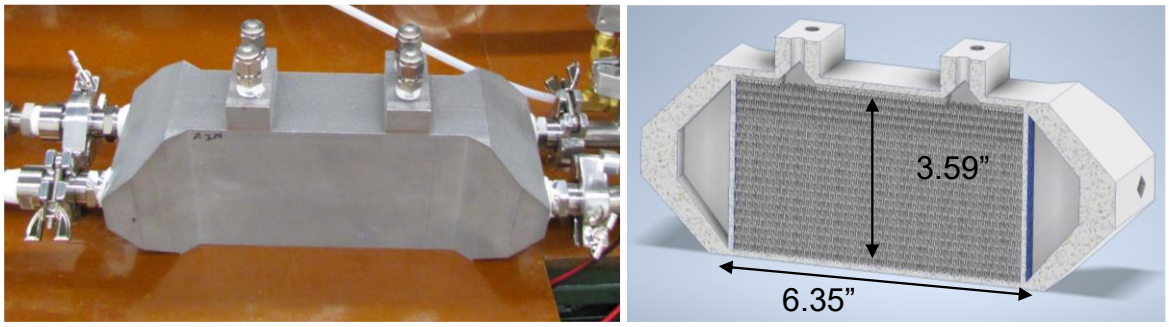

Figure 12. DMLS Aluminum 1/3 Scale CO_2 control module.

2. Module Test Results

Tests were carried out with two sorbents, TEPAN on PMMA beads and RSI – 9. In both cases, 239 grams of sorbent were loaded into the beds. The sorbents were loaded equally into both beds using the fill ports on the top of the module and a vibration table to distribute the maximum amount of sorbent evenly within each bed. This mass of sorbent corresponds to a total volume of 478 cm^3, which is 30% of the sorbent that is utilized in the RCA-3.

A picture of the mid scale module installed in the loop is shown in Figure 14. The ventilation loop flow is split and directed into the inlet of each bed on the left side of the figure. The outlet line of each bed contains a tee, one end of which leads to a vacuum desorption line and the other to the ventilation loop outlet line. The inlet, outlet, and vacuum line of each bed are regulated by vacuum compatible bellows valves which are pneumatically actuated. At the inlet and outlet of the module, there is a CO_2 sensor, humidity sensors, pressure transducer, and thermocouple.

The photograph on the right side of the figure shows the vacuum system that consists of a 30 gallon tank and an Edwards E2M80 pump, which has a maximum displacement of 57 CFM and ultimate vacuum of 0.01 Pa. An oil mist filter was also installed at the outlet of the 30 gal tank to prevent any potential oil mist from backflowing into the ventilation loop.

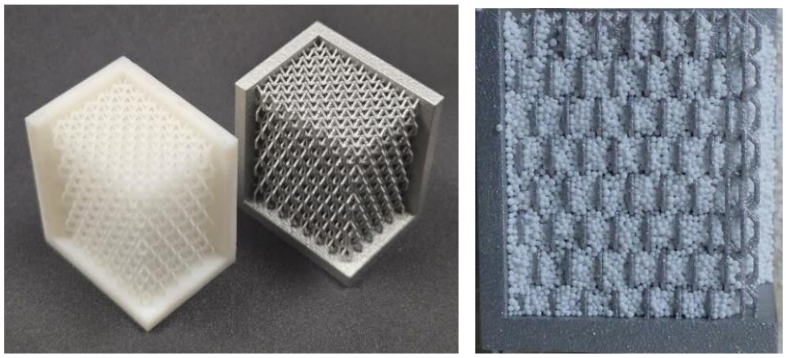

Figure 13. a) Printed sample lattice pieces (left); b) Sample lattice with TEPAN/PMMA (right).

The procedure that was used for the operation of the ventilation loop is as follows. Initially, both sorbent beds are exposed to vacuum for approximately 30 minutes in order to desorb residual CO_2 and water. Then, the entire loop is evacuated and backfilled with nitrogen to 4.5 psia. Circulating flow is started and controlled to approximately 1 acfm, and the module is initially operated with 1:30 timed cycles. Nitrogen flow is initiated to replace the ullage volume lost during cycling in order to maintain a constant pressure within the system. Humidity is injected and maintained until a steady state level is reached at approximately 40-60% at the inlet of the module. Because of the sorbents' high affinity for water, the requires approximately 1-2 hours before it reaches a steady state adsorption and desorption rate. Once achieved, CO_2 injection is started and nitrogen flow is decreased to compensate. The timed cycles are then stopped and the module is switched to CO_2 limit activation switching where the beds are switched according to the module outlet CO_2 partial pressure. This is carried out until the cycle time reaches a steady state value which requires approximately 10 full cycles per bed or 20 bed switches.

Metabolic rates of 500 btu/hr, 1000 btu/hr, 1600 btu/hr, 1800 btu/hr, and 2000 btu/hr were simulated. The metabolic rates were based on CO_2 injection rate in the ventilation loop and the quantity of sorbent loaded in the mid-scale module. Assuming the CO_2 adsorption and desorption rate, and thus CO_2 removal capacity of the sorbent are proportionate to the volume of sorbent, the mass injection of CO_2 was scaled according to the ratio of sorbent in the mid-scale module to that in the full-scale RCA 3.0. Met rate versus CO_2 production for full scale conditions is listed in Papale et al., and 30% of the sorbent in the RCA 3.0 was loaded into the mid-scale module. Thus 30% of the listed flows were used.

In tests with TEPAN/PMMA, the system was unable to reduce the outlet CO_2 concentration below 3 mm Hg at all metabolic rates and therefore obtaining steady state cycle times was not possible. On the other hand, in tests with the RSI sorbent, the system reached s steady state conditions at all metabolic rates. However, in order to carry out a back-to-back comparison of sorbent performance, tests were carried out with both sorbents where the trip limits were varied

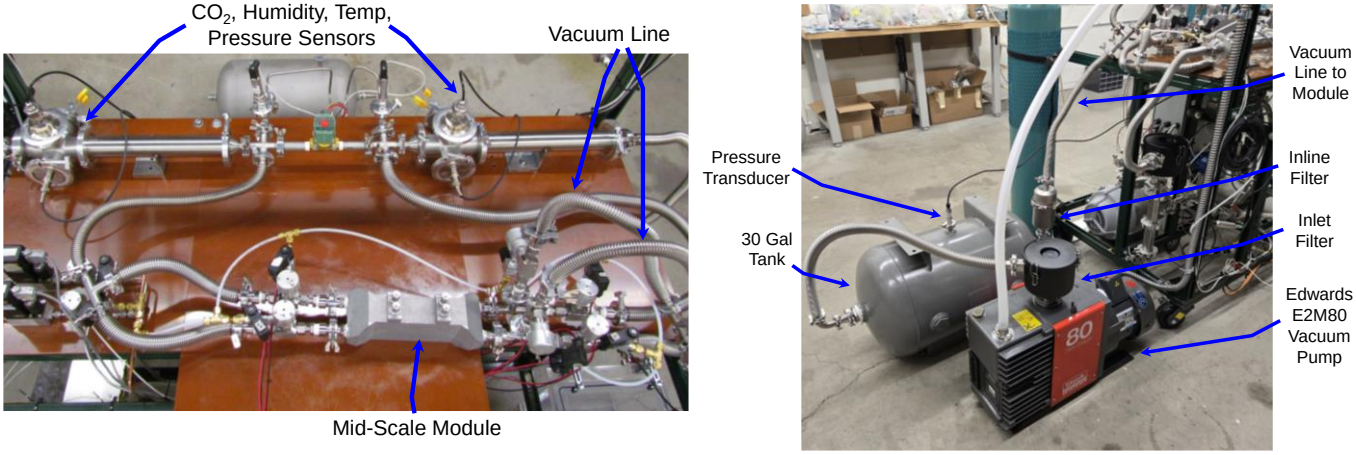

Figure 14. a) AM 1/3 Scale twin bed CO_2 control module installed in Reaction Systems' ventilation loop; b) Vacuum system of ventilation loop (right).

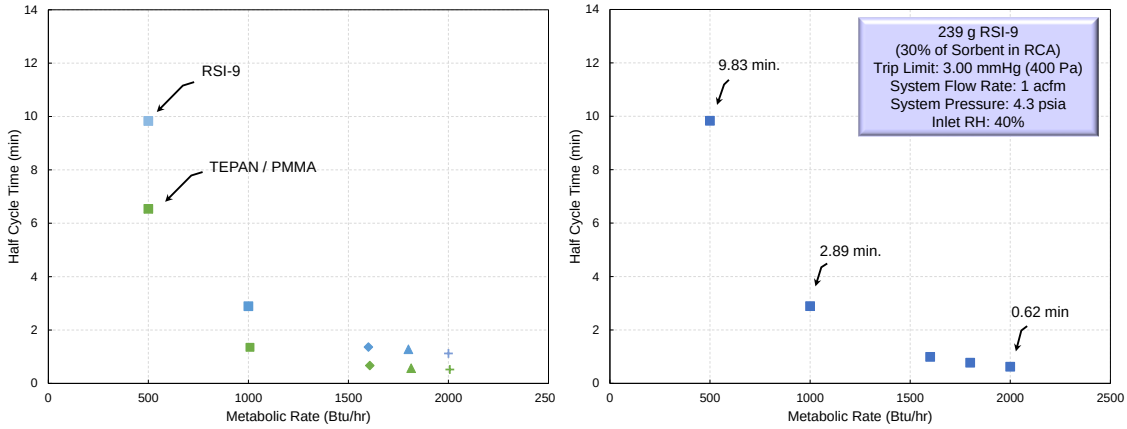

Figure 15. Summary of steady state ½ cycle times measured on the mid-scale module. a) TEPAN/PMMA and RSI-9 with trip limits of: 3.0 mmHg at 500 and 1000 btu/hr, 3.75 mmHg at 1600 btu/hr, 4.0 mmHg at 1800 btu/hr, and 4.5 mmHg at 2000 btu/hr (left);b) ½ cycle times for RSI-3 at a trip limit of 3 mm Hg at all metabolic rates (right).

so that both sorbents could be compared on the same basis. The results of these tests are included in in the left chart in Figure 15. The results with RSI-9 are shown in the blue symbols whereas the results with TEPAN/PMMA are shown in the green symbols. These results show that in all cases, the ½ cycle times for RSI-9 are significantly greater than those obtained for TEPAN/PMMA sorbent. The results obtained for the RSI-9 at the 3 mm Hg trip level are shown in the chart on the right side of Figure 15. The results show that the ½ cycle times vary from 9.83 min at a metabolic rate of 500 Btu/hr to 0.62 minute at the highest rate of 2000 Btu/hr. These values are all consistent with previous results reported in tests with RCA-1.0 and RCA 2.0 [8].

In Figure 16, the inlet and outlet PP_{CO2} for the tests simulating metabolic rates of 500 btu/hr for RSI-9 and TEPAN / PMMA are shown on the left and right, respectively. The testing conditions, including ½ cycle times, had reached steady state values for both data sets, and as indicated by the time measured between outlet PP_{CO2} peaks, the ½ cycle times were 9.83 min for RSI-9 and 6.54 min for TEPAN/PMMA. The pattern of the outlet concentrations for both sorbents was consistent and expected for the 400 Pa trip limit. For both sorbents, once the module switches beds, the outlet concentration drops rapidly and then begins rises until it reaches the limit of 400 Pa. Once it reaches 400 Pa, the beds are switched again and pattern repeats itself. The inlet concentration follows a similar relative pattern as the outlet concentration as a result of the longer cycle times and the varying partial pressure within the entire loop. Data from the other metabolic conditions followed these patterns and demonstrated the operational ability of the mid-scale module to maintain a steady state gas composition within the ventilation loop and provide an effective method for comparison of candidate sorbents at relevant, circulating conditions.

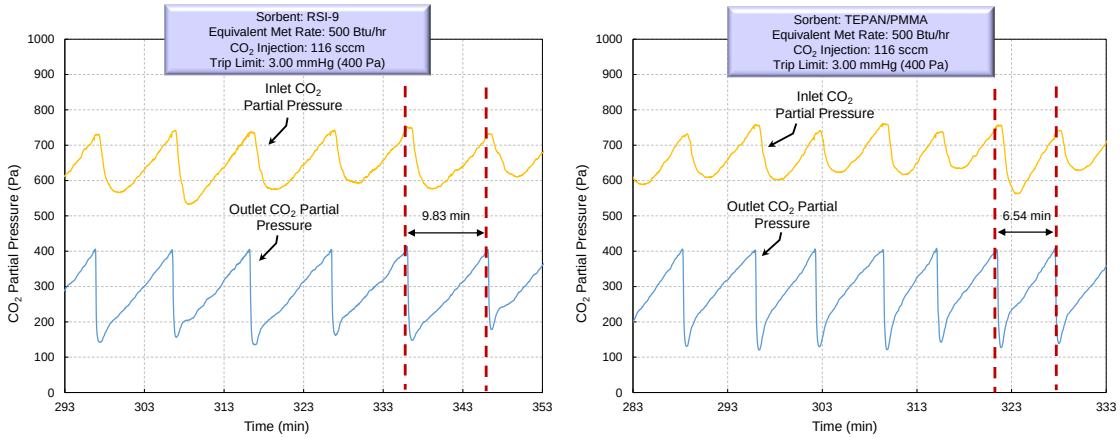

Figure 16. Inlet and outlet CO_2 partial pressures for 500 btu/hr metabolic rate. a) RSI-9 (left); b) TEPAN / PMMA (right).

F. Full Scale Module Design

In addition to the mid scale module previously discussed, a full scale test module was designed for testing of the developed sorbents. It is a dual bed module, and is capable of containing 788 cm^3 of sorbent per bed, the same quantity of sorbent that the RCA 3.0 does[8]. It will be used in future work to test candidate sorbents at the full scale conditions of the xEMU ventilation loop, including circulating flow and CO_2 injection rates. It will utilize the same ordered, internal lattice as previously described for the mid scale module, and it will also be additive manufactured out of aluminum. The orientation of the sorbent beds was altered to reduce pressure drop in order to accommodate the full scale circulating flow, and the sorbent bed inlet and outlet manifolds were designed to promote uniform static pressure throughout the sorbent bed inlet and outlet in order to produce uniform flow distribution through the beds. The sorbent fill ports and inlet/outlet flow ports orifices will be welded with KF, vacuum compatible fittings. The model of the full scale module is shown in Figure 17.

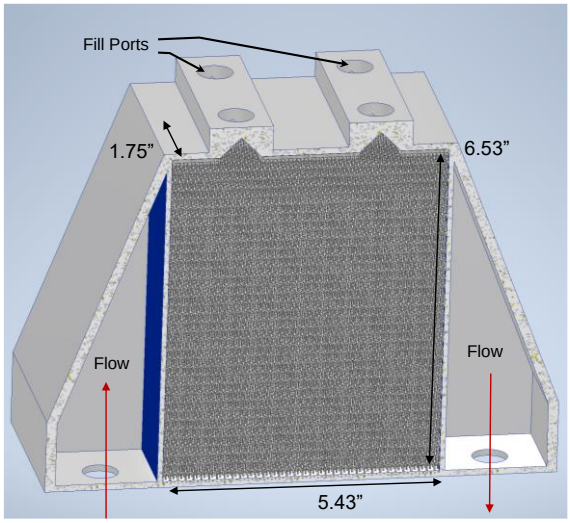

Figure 17. Model of full scale module

IV. Conclusions

In this work, candidate sorbents for use in the RCA were screened in a test rig that simulated the CO_2 partial pressures expected in the xEMU ventilation loop. The test rig relied on the CO_2 concentration in the flow exiting the packed bed to trip the adsorption cycle, and it set the duration of the subsequent regeneration cycle to be equal to the last adsorption cycle, simulating the relative times that would be expected in the RCA during use. Sorbents were screened under realistic conditions, and in this work, several sorbents have been identified that have the potential to outperform SA9T. Two sorbents exhibited longer ½ cycle times at all partial pressure conditions than a sorbent composed of TEPAN on PMMA, and several other sorbents exhibited longer ½ cycles times than TEPAN on PMMA at the highest three partial pressure conditions. All of these sorbents have the potential to reduce the number of half cycles required in an EVA mission, and/or reduce the baseline CO_2 partial pressure in the suit.

In addition, the ammonia emission characteristics of the sorbents were investigated, and they exhibited the potential to emit less quantities of ammonia than SA9T. The off gassing characteristics of sorbents were investigated under thermal degradation conditions as well during cyclic uptake testing with CO_2 and humidity. The results were compared to the performance of the TEPAN/PMMA sorbent and all of the screened sorbents exhibited lesser ammonia than TEPAN/PMMA under the thermal test. One of the sorbents emitted significantly less ammonia than TEPAN/PMMA during the cyclic adsorption off gas test and one of the candidate sorbents exhibited comparable performance. These candidate sorbents were also subjected to an accelerated lifetime test in which they were stored for a period of 6 months at an elevated temperature and screened for their cyclic uptake capacity at time intervals. The superior uptake capacity that the candidate sorbents exhibited over the TEPAN/PMMA sorbent prior to the aging process was retained through the again process.

A large batch of one of the most promising sorbents was synthesized and testing in an additive manufactured CO_2 control module. The module was produced with DMLS out of aluminum and was sized to contain 30% of the sorbent that is contained in the xEMU RCA 3.0 design. The module was tested in Reaction Systems' full scale ventilation loop at conditions commensurate to the quantity of sorbent contained within it. The sorbent was tested at the same CO_2 partial pressure conditions as in the rapid screening apparatus, the steady state ½ cycle times were measured and compared with the results of the same test conducted with TEPAN/PMMA in the mid scale module. Similar to the rapid screening test, the candidate sorbent, RSI-9, exhibited longer ½ cycle times than the TEPAN/PMMA sorbent at all of the partial pressure conditions. A full scale module was also designed, and in upcoming work, full scale batches of candidate sorbents and TEPAN/PMMA will be synthesized and tested under the full scale conditions existent in the xEMU ventilation loop.

Acknowledgments

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