

# Efficacy of FTIR Analysis in Determining CO<sub>2</sub> Loading on Diglycolamine

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In support of advanced air revitalization technologies to enable human spaceflight beyond low earth orbit, performance studies have been conducted using a liquid amine, Diglycolamine (DGA) between teams at NASA's Johnson Spaceflight Center (JSC) and Ames Research Center (ARC). Liquid amines have been used in regenerable earth-based systems to remove CO<sub>2</sub> from industrial systems as well as for closed-environment air revitalization because they can be regenerated at lower temperatures than solid sorbent systems. As an additional advantage to solid sorbent-based systems, liquid sorbents can be cycled between an adsorbing contactor and degassing chamber, thereby reducing system complexity by operation in a continuous loop. In an effort to inform a regeneration system design for micro-gravity applications, ARC has performed a number of tests to characterize the degas mechanics of DGA. In order to accurately measure the amount of CO<sub>2</sub> captured or released by the amine, methods such as gravimetric weighing and chemical desorption are reasonable, however the first iteration test setup for a scaled down degas system required analysis on small sample sizes. Fourier-transform infrared spectroscopy (FTIR) analysis was experimentally evaluated to analyze CO<sub>2</sub> concentration because it can produce measurements with sample sizes on the order of 100's of  $\mu$ L. Calibration against chemical desorption showed relatively good correlation and test data showed reasonable adherence to expected trends, however more extensive testing should be conducted to fully validate the usage of FTIR to determine CO<sub>2</sub> loading on DGA.

## Nomenclature

<i>ARC</i>	=	NASA Ames Research Center
<i>CO<sub>2</sub></i>	=	Carbon Dioxide
<i>DGA</i>	=	Diglycolamine
<i>FTIR</i>	=	Fourier-transform infrared spectroscopy
<i>H<sub>2</sub>S</i>	=	Hydrogen Sulfide
<i>JSC</i>	=	NASA Johnson Space Center
<i>MEA</i>	=	Monoethanolamine
<i>N<sub>2</sub></i>	=	Nitrogen
<i>ZnSe</i>	=	Zinc Selenide

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## I. Introduction and Technical Background

CARBON dioxide capture technologies are currently being investigated for potential future flight systems to support human space exploration. In an effort to aid in the design of a liquid amine sorbent system led by NASA Johnson Space Center (JSC), NASA Ames Research Center (ARC) has begun the work in characterizing the desorption kinetics of Diglycolamine (DGA), a liquid amine that was down-selected for usage in the proposed system.<sup>1</sup> A baseline design for a degassing unit was developed by JSC that relied on capillary flow to allow for direct liquid-to-air contact while maintaining liquid flow control.<sup>2</sup> This degassing unit was proposed to utilize a multitude of “V” shaped channels, hereby referred to as “V-channels,” to take advantage of capillary flow. The work done at ARC was built upon this initial design, and the regeneration characteristics reported in this paper pertain to this specific configuration. Given the complexity of building a multi-channel system and the restraint of performing characterization in a 1-g environment, designs were made at ARC to build a single V-channel degasser with the goal of characterizing the degas mechanics at a fractional scale of the proposed system. Also, due to the scale of the benchtop system and instrumentation limitations, measuring the CO<sub>2</sub> released by the DGA would be a challenge itself. Due to the high temperature of the degas environment, it was impossible to use an immersion-based CO<sub>2</sub> probe. The vapor pressure of the DGA also proved to be problematic if trying to use a CO<sub>2</sub> probe in a closed circulated gas loop, since initial regeneration efforts revealed that DGA had a significant evaporation rate and would likely contaminate a probe.

Efforts to characterize CO<sub>2</sub> loading on DGA included measuring the liquid pH, viscosity, Raman spectroscopy, chemical desorption, and Fourier Transform Infrared spectroscopy (FTIR). Measurement efforts using pH and Raman spectroscopy failed to produce discernable results. Viscosity measurements yielded good results, since DGA viscosity increases with increasing CO<sub>2</sub> loading, however one of the design considerations was to be able to dilute the DGA in a water solution. This would not be a problem for adsorption characterization, but since the regeneration process requires heat, the solution would lose a significant amount of water to evaporation/boiling, thereby skewing viscosity results. Chemical desorption has been described as a viable method of recapturing and measuring CO<sub>2</sub> loading from a DGA solution<sup>1</sup>, and initial verification at ARC agreed with previous assessments. This method of mixing a strong acid into a solution of amine loaded with CO<sub>2</sub> lowers the pH of the solution, which releases the CO<sub>2</sub> from the amine. This process will hereby be referred to as “pH desorption”. While pH desorption can be depended on to provide an accurate measurement of CO<sub>2</sub> loading on DGA, the sample amount required to provide discernable data is approximately 1mL. For the proposed benchtop experimental scaled degasser, a 1mL sample size removed intermittently from the starting solution raised concerns that the accuracy of the degas rate measurements would be negatively affected. FTIR was proposed as a potential measurement method that could use a smaller sample size to determine CO<sub>2</sub> loading, as sample sizes could be reduced to the order of 100’s of  $\mu$ L. FTIR analyses to measure CO<sub>2</sub> loading on amines have also been performed in the past to reasonable success with monoethanolamine (MEA).<sup>3</sup> Another benefit of FTIR was that the CO<sub>2</sub> loading measurement should not be affected by water loading since the wavenumber peaks for OH do not interfere with those of the carbonyl region. For the remainder of this paper, language pertaining to “percent loading” of CO<sub>2</sub> shall refer to mass percent loading. For example, if a 1g solution of DGA has 7% CO<sub>2</sub> loading, that means that it contains 0.07g CO<sub>2</sub>.

## II. Historical Background

The usage of liquid amines to remove CO<sub>2</sub> from an air stream has heritage in various Earth-based systems. This process, also known as amine gas treating or gas sweetening, utilizes aqueous solutions of amines to remove acid gases like hydrogen sulfide (H<sub>2</sub>S) as well as CO<sub>2</sub> from hydrocarbon processing industrial plants.<sup>4,5</sup> This prior history using amine-based CO<sub>2</sub> scrubbing systems in industrial systems made this technology attractive to the US Navy for usage in a human-in-the-loop system during the advent and design of nuclear-powered submarines, which required an air-revitalization system capable of maintaining low CO<sub>2</sub> partial pressures. As a result, all US Navy submarines were outfitted with monoethanolamine (MEA) scrubbers.<sup>6</sup> A general system diagram is shown in Figure 1.

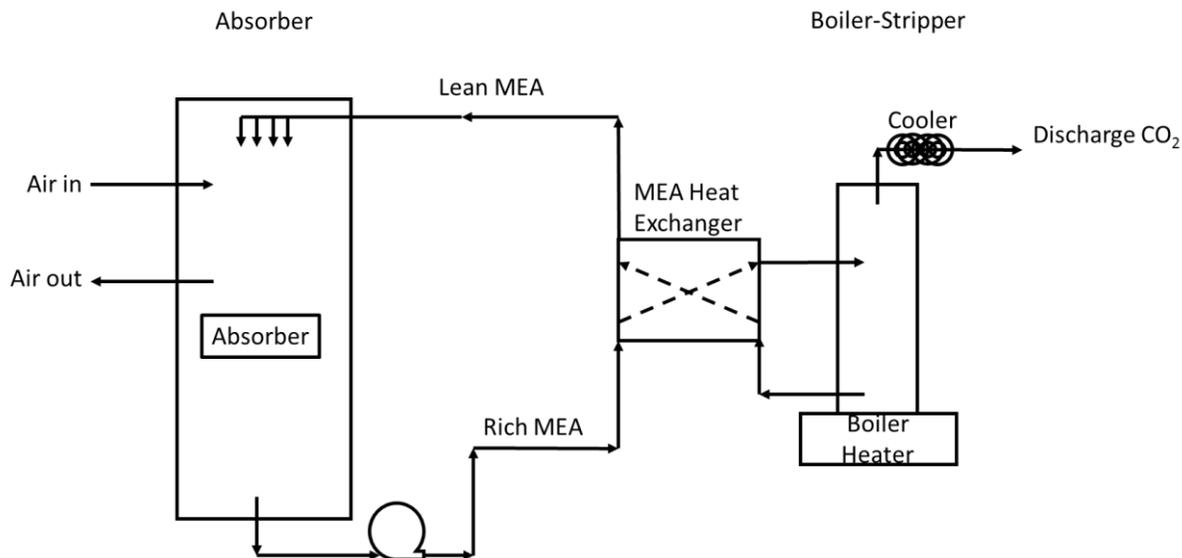


Figure 1. MEA CO<sub>2</sub> scrubber schematic adapted from Carey, 1983<sup>6</sup>

JSC conducted a study evaluating the characteristics of various commercially available liquid amines including MEA, methyl diethanolamine (MDEA), DGA, and others. The conclusion of this study was a recommendation that DGA be used for future evaluation and system design for a liquid amine CO<sub>2</sub> scrubber.<sup>1</sup>

### III. Methodology

#### A. Baseline Sample Generation

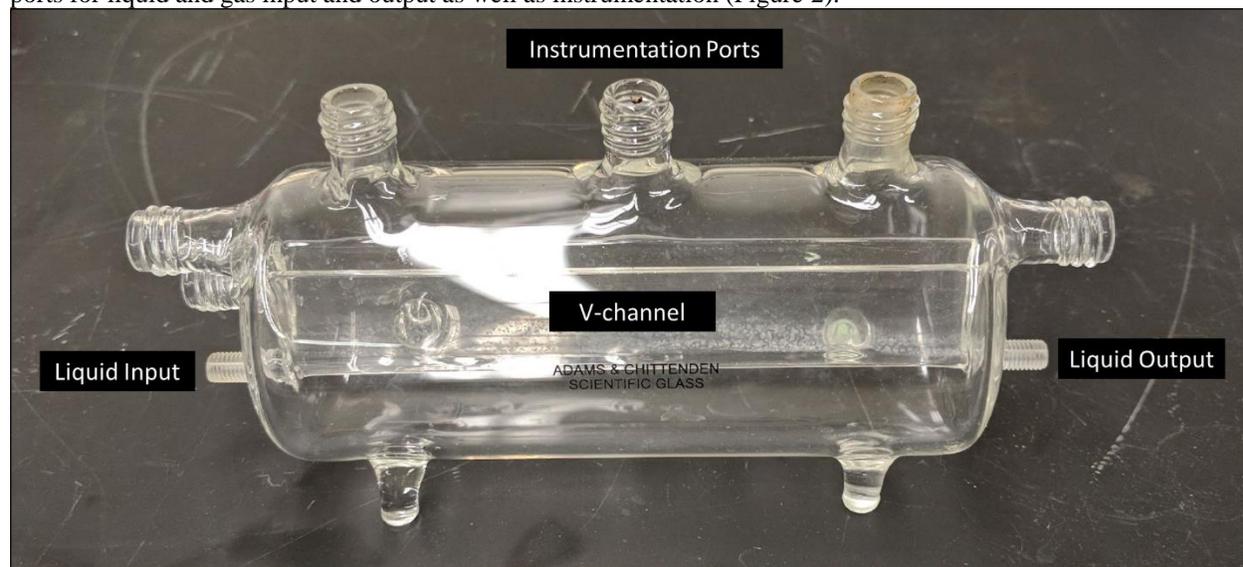
In order to create consistent samples from which to draw pre-loaded DGA for degassing kinetics experimentation, CO<sub>2</sub> was loaded onto 200mL batches of DGA. Three different loading concentrations were achieved by varying the amount of time each batch was exposed to CO<sub>2</sub>. To load CO<sub>2</sub> into these batches of DGA, a 0.5 micron stainless steel sparger was used to disperse 600mL/min ultra-high purity grade CO<sub>2</sub> (Matheson Gas). Three batches of DGA were loaded for 5, 10, and 15 minutes, respectively. This process was again repeated for a volumetric mix of 35% deionized water and 65% DGA. These six batches were then used as standards to characterize the FTIR analysis in relation to pH desorption and used as preloaded samples from which to perform the investigation of DGA degas kinetics.

#### B. Degas Kinetics Experimentation

To characterize the desorption kinetics of DGA, a test matrix was developed to address various system parameters. The parameters of interest reported in this study were:

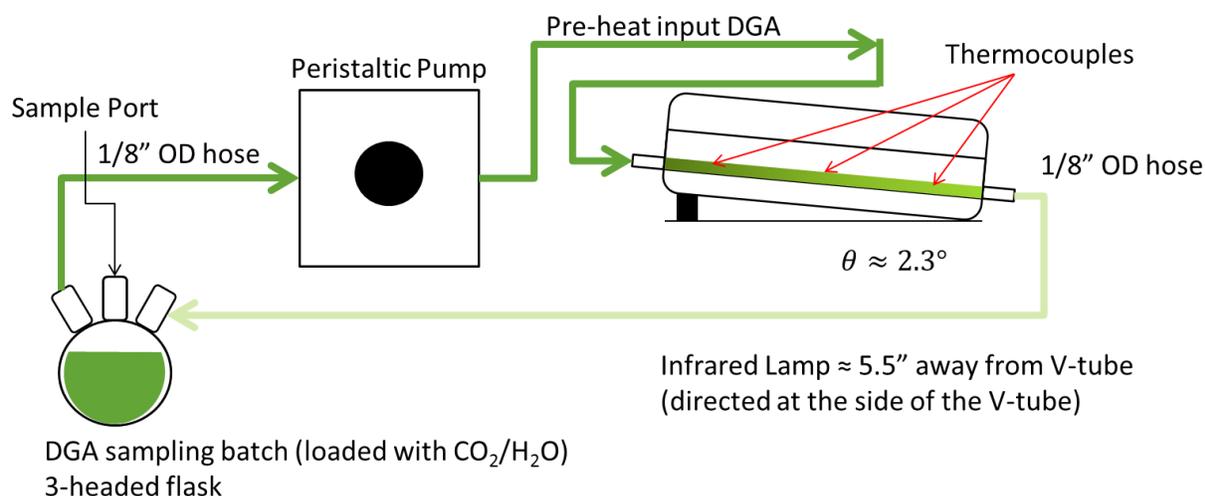
1. Degas temperature
2. Liquid flowrate (contact time)
3. Presence of sweep gas
4. Water concentration

In order to separate and individually observe the effects of changing each of these parameters, an experimental glass contactor, hereby referred to as a “V-tube,” was custom-built and procured through Adams & Chittenden Scientific Glass. This glass V-tube was constructed with a single V-channel encased by a glass tube with various ports for liquid and gas input and output as well as instrumentation (Figure 2).



**Figure 2. Glass V-tube constructed by Adams & Chittenden Scientific Glass**

The experimental setup and process and instrumentation diagram has been provided in Figure 3. First, 10mL of preloaded DGA (prepared via the procedure in Baseline Sample Generation) is introduced to the DGA source and sampling flask. The peristaltic pump draws the liquid from the flask and pumps it through a 1/8” OD silicon hose into a preheat loop to bring the liquid up to the desired degas temperature and into the input port of the V-tube. The liquid then travels through the V-channel and is drawn back into the flask by the peristaltic pump. Since a single pump is used and the reactor is sealed, the input and output flowrates should be consistent. Samples are drawn from the initial preloaded DGA source and sampling flask and intermittently through the duration of the test. Heat is provided to the system via an infrared lamp (500W).



**Figure 3. V-tube experimental setup**

**C. pH Desorption:**

The method of pH desorption was used to release the bonded CO<sub>2</sub> from Diglycolamine solutions. In this procedure described by Rogers, 2017<sup>4</sup>, approximately 96-98% of the adsorbed CO<sub>2</sub> can be recovered from solution

in gaseous form. The pH desorption setup is depicted in Figure 4. Specifically, this procedure consisted of the following steps:

1. Measure the mass of an empty flask with stir bar
2. Introduce approximately 1mL of DGA solution to the flask and record new mass
3. Dilute the solution in the flask with deionized water
4. Seal flask and turn on stirrer (vigorous)
5. Evacuate the inverted graduated cylinder volume of approximately 200mL air and record starting volume
6. Inject acid with purge air through acid line and record total volume injected into system
7. Allow 3 minutes for desorption to occur
8. Record final volume from inverted flask

Then, knowing the initial mass of the solution and the volumetric CO<sub>2</sub> evolved from the reaction, one can then calculate the mass percent loading of CO<sub>2</sub> in the initial solution.

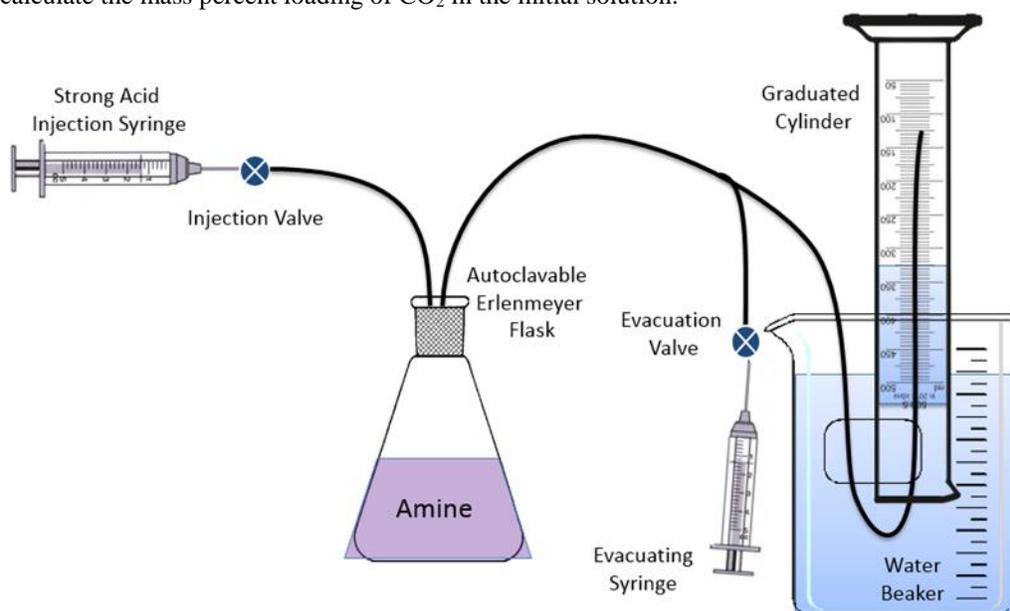
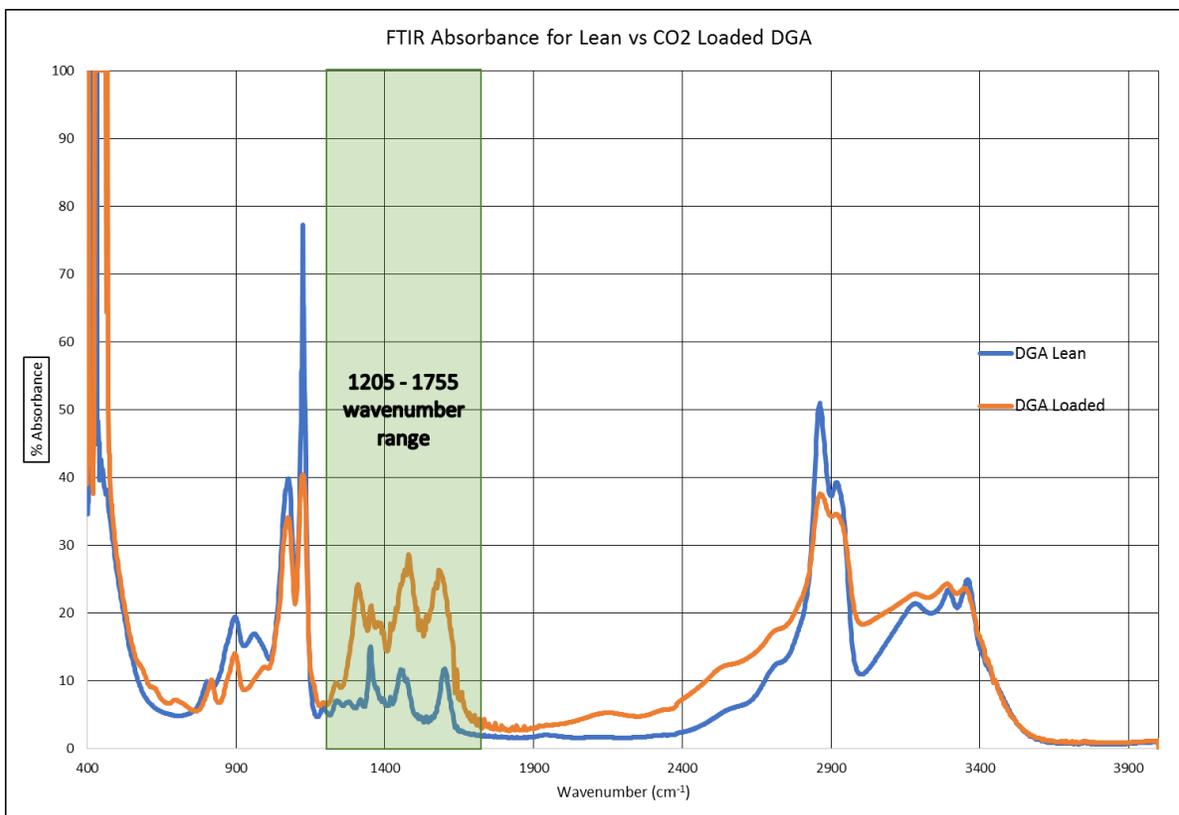


Figure 4. pH desorption setup<sup>1</sup>

#### D. Fourier Transform Infrared Spectroscopy:

The three batch solutions of DGA loaded with CO<sub>2</sub> described in section A were used as standards to calculate CO<sub>2</sub> loading. A 4-point calibration curve was prepared by determining CO<sub>2</sub> percent loading of the standards via the pH desorption method described above. To calibrate the FTIR, samples from the standards were loaded into a demountable IR window liquid cell (Buck Scientific p/n 6500C) with 4mm thick ZnSe crystal windows and a 0.015mm sample spacer. Samples were loaded using a luer lock gastight syringe and the entire apparatus was disassembled and washed with first pure water, then isopropanol in between each sample analysis. FTIR analysis was performed on a Mattson Galaxy 6020 FTIR using WinFIRST v2.10. Transmittance data was collected at 10kHz from wavenumbers 400 to 4000cm<sup>-1</sup> with a resolution of 4. Data analysis was performed using Spectragryph V1.1.0. Baselines were normalized for samples and standards together as a batch by first using the “sample baseline” feature built into Spectragryph using the range of wavenumbers from 3800-4000cm<sup>-1</sup>, then the “normalize peak” function was used on peak 895cm<sup>-1</sup> to set all 895cm<sup>-1</sup> peaks to the same height. This peak was chosen because it was a peak from DGA that remained consistent in all samples. Peak area was obtained from wavenumbers 1205 to 1755cm<sup>-1</sup> which is the observed bound carbonyl region in DGA (Figure 5). A calibration curve was made using peak area vs percent CO<sub>2</sub> loaded, and then percent CO<sub>2</sub> was determined for each sample. It is worth noting that with this normalization method, standard samples did not need to be physically run with each test sample for the FTIR-calculated CO<sub>2</sub> loading level to be within 10% of the expected value from the pH desorption test as long as the standard data was processed and normalized with the test samples.

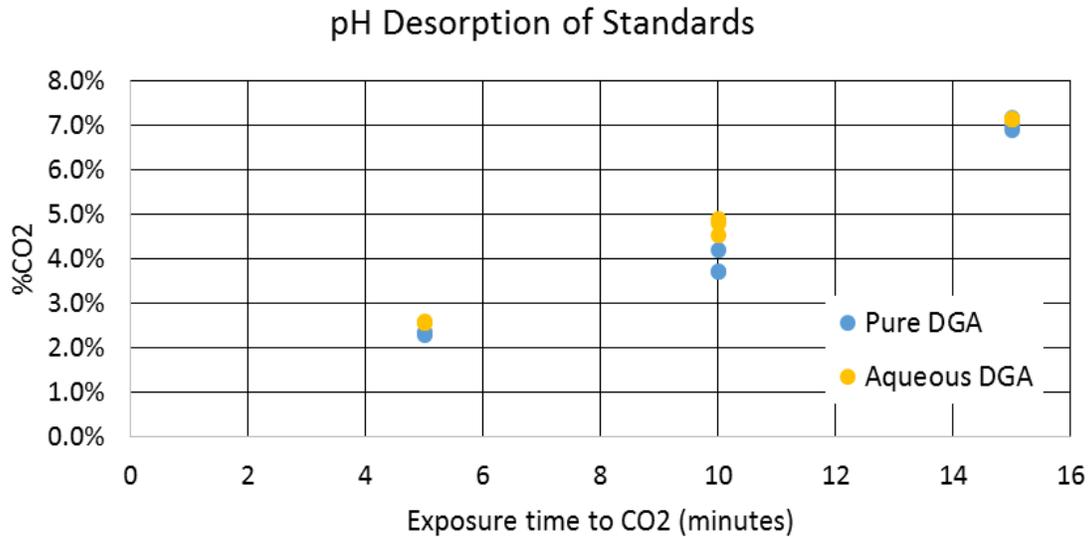


**Figure 5. FTIR absorbance plot for DGA, lean and CO<sub>2</sub> loaded**

#### **IV. Experimental Data**

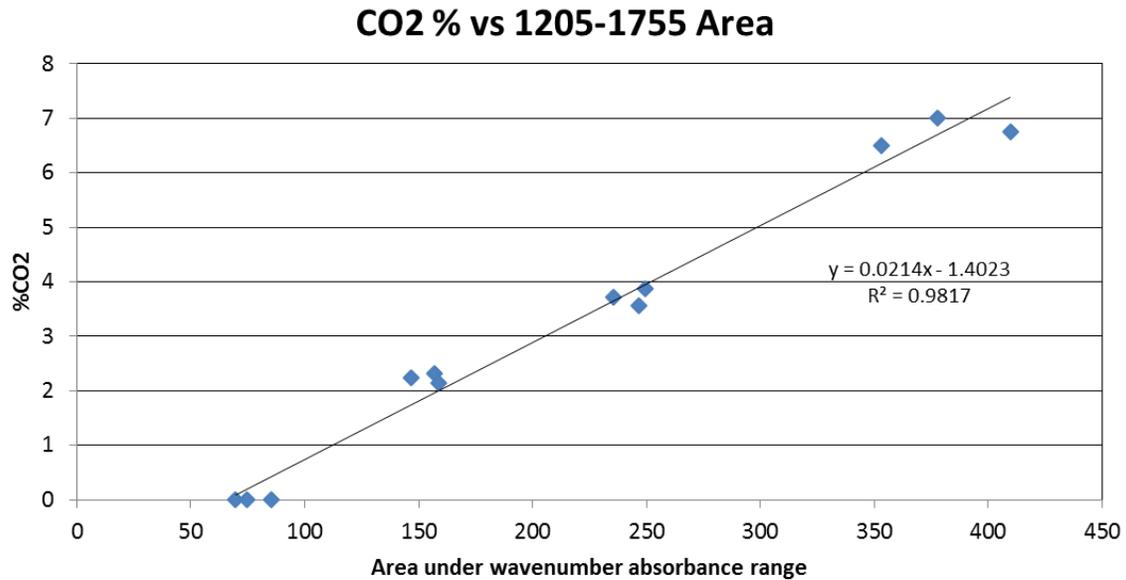
##### **A. Preloading and FTIR calibration samples**

Following the methodology described above, three volumes of pure DGA were loaded with CO<sub>2</sub> for 5, 10, and 15 minutes respectively, and pH desorption was performed on each of the samples in triplicate. This process was again repeated for a volumetric mix of 35% deionized water and 65% pure DGA. pH desorption results are shown in Figure 6. Variance and deviation between samples can be attributed mainly to the resolution of the graduated cylinder, as previously described.<sup>1</sup> It is an interesting coincidence that the CO<sub>2</sub> loading levels in the 35% water diluted samples are comparable to the loading levels in the pure DGA samples.



**Figure 6. pH desorption to calculate CO<sub>2</sub> preloading on aqueous and non-aqueous DGA solutions**

To calibrate the FTIR readings, 500 $\mu$ L samples were analyzed by the FTIR methodology described in section IIID. Peak area in the wavenumber range from 1205 to 1755 $\text{cm}^{-1}$  was calculated for each sample and results are shown in Figure 7. These results show that the FTIR results could be used with relative success in determining CO<sub>2</sub> loading on the preloaded DGA samples.

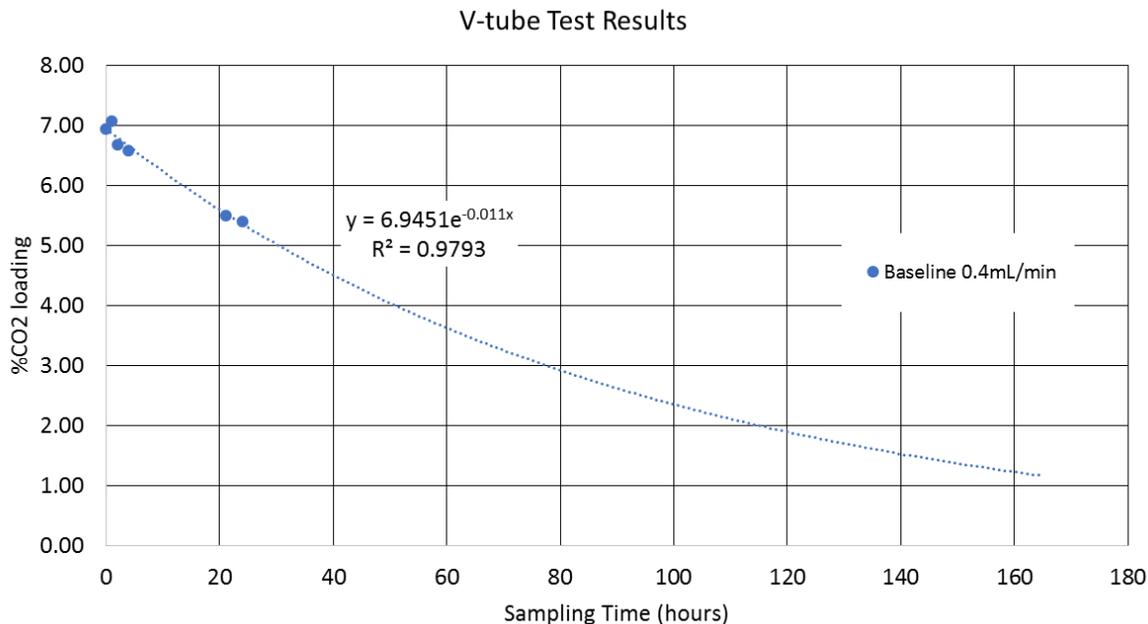


**Figure 7. FTIR calibration against pH desorption**

#### B. Experimental Test Cases

A baseline test case was established based on initial design parameters provided by JSC. For this test, the V-tube was set to run at a target degas temperature of 85 $^{\circ}$ C with a flowrate of 0.4mL/min. The input solution was the 15-minute preloaded pure DGA sample, and there was no sweep gas present during the test. Samples were taken at the initiation of the test, then at 1, 2, 3, and 4 hours into the test, and then again at 21 and 24 hours into the test. It was observed that the solution was slightly discolored at the end of the test. FTIR results from this test are shown in

Figure 8. As discolored DGA has been a known characteristic result when the solution is heated in the presence of oxygen, FTIR analysis was performed on clear and various discolored samples and the wavenumber range pertaining to CO<sub>2</sub> loading were not affected. Therefore, FTIR analysis to determine CO<sub>2</sub> loading on discolored samples was still considered to be viable.

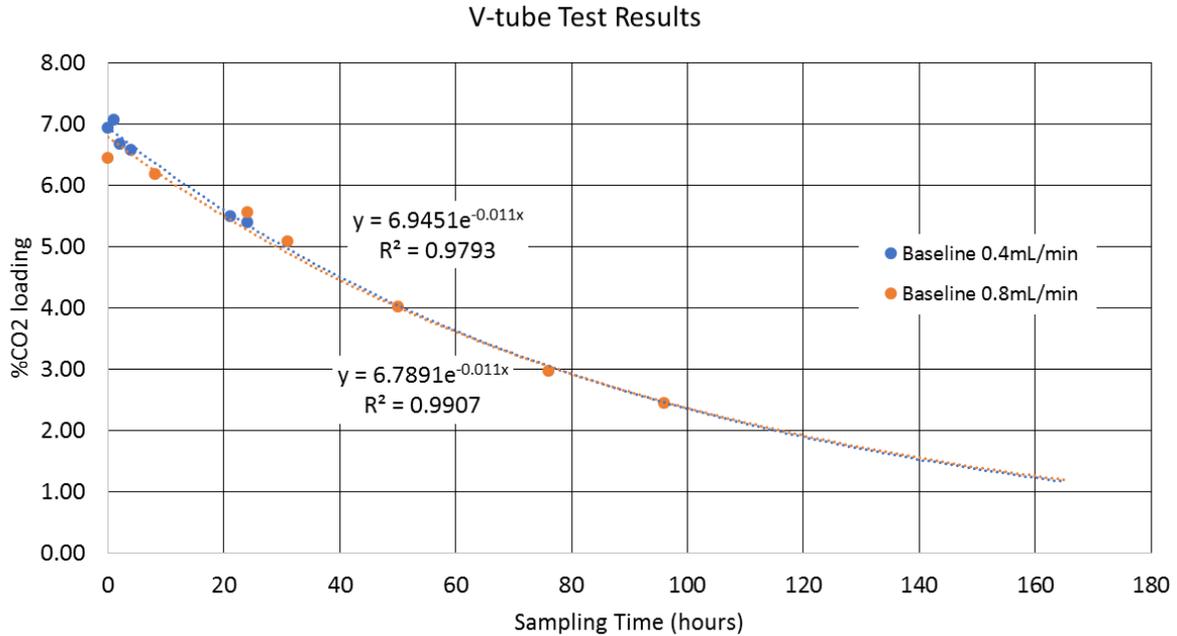


**Figure 8. Baseline V-tube run CO<sub>2</sub> loading**

From these results, it was determined that the test would need to be extended well past 24 hours to see more CO<sub>2</sub> unloading from the solution. The same test parameters were attempted three more times, but each time failure occurred because the peristaltic pump could not consistently operate at 0.4mL/min for extended periods of time. The baseline test case was then revised to flow at a higher target flow rate of 0.8mL/min while keeping all other parameters the same. Under the new parameters, the baseline test was run for a total of 96 hours, with samples taken intermittently. It was observed that discoloration occurred gradually through the duration of the test, and evaporated DGA recondensed inside the V-tube above the liquid level in the V-channel (Figure 9). FTIR results for CO<sub>2</sub> loading are added to the plot and shown in Figure 10. An exponential trendline has been imposed on the data and seems to fit reasonably ( $R^2 > 0.99$ ).

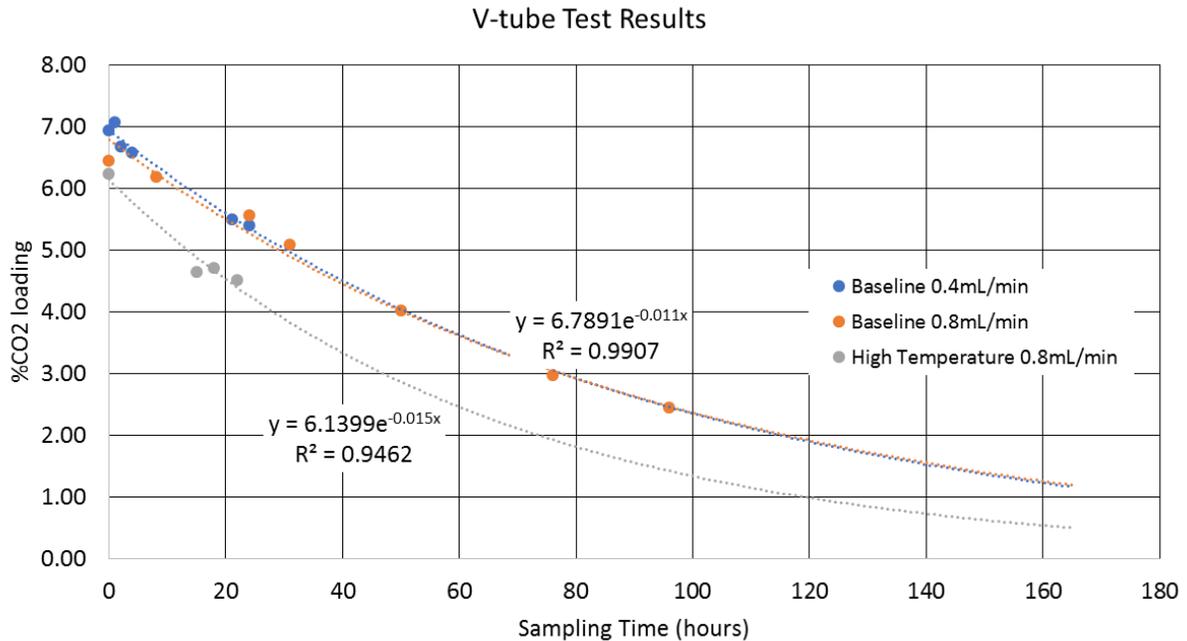


**Figure 9. End of V-tube run showing sever discoloration of the DGA as well as condensing DGA inside V-tube**



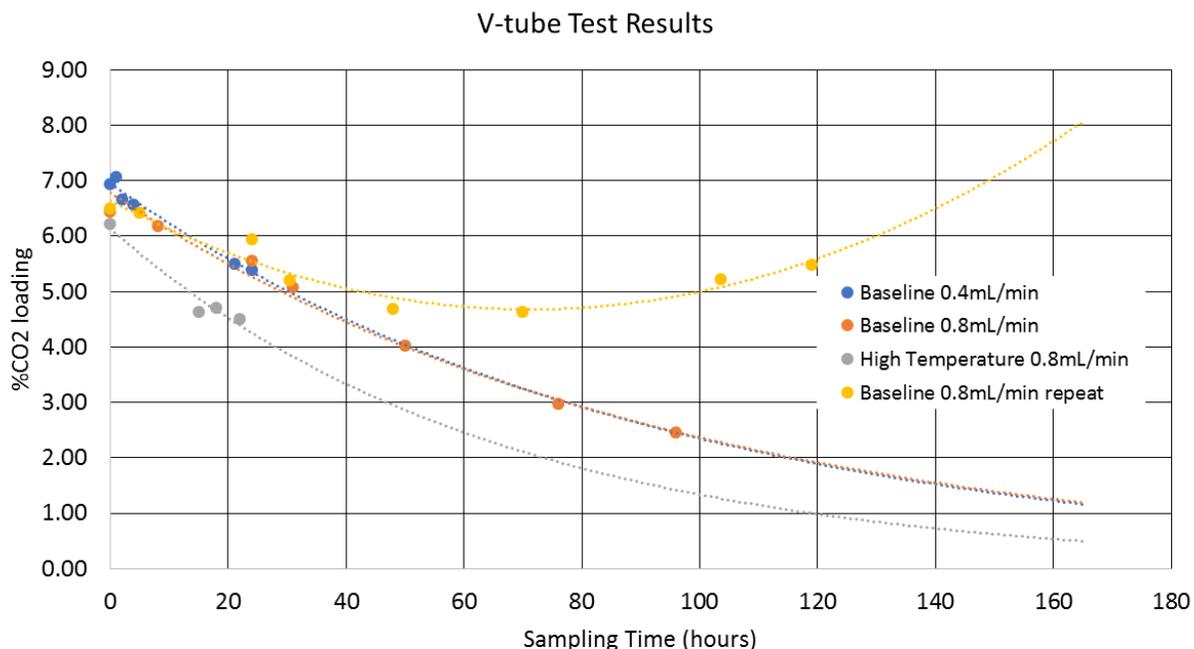
**Figure 10. Baseline and Revised Baseline V-tube runs**

In the next test case, the V-tube was set to target a degas temperature of 105°C. The input solution was once again the 15-minute preloaded pure DGA sample flowing at 0.8mL/min without sweep gas present. Discoloration and evaporation occurred much more rapidly during this test, and as a result, the test was terminated at 24 hours. The discoloration observed at 24 hours runtime during this test was comparable to the discoloration observed in the baseline test at 96 hours runtime. Cumulative FTIR results from the baseline tests and the high temperature test are shown in Figure 11. The results suggest that the higher temperature causes the DGA to release CO<sub>2</sub> at a higher rate, which is expected.



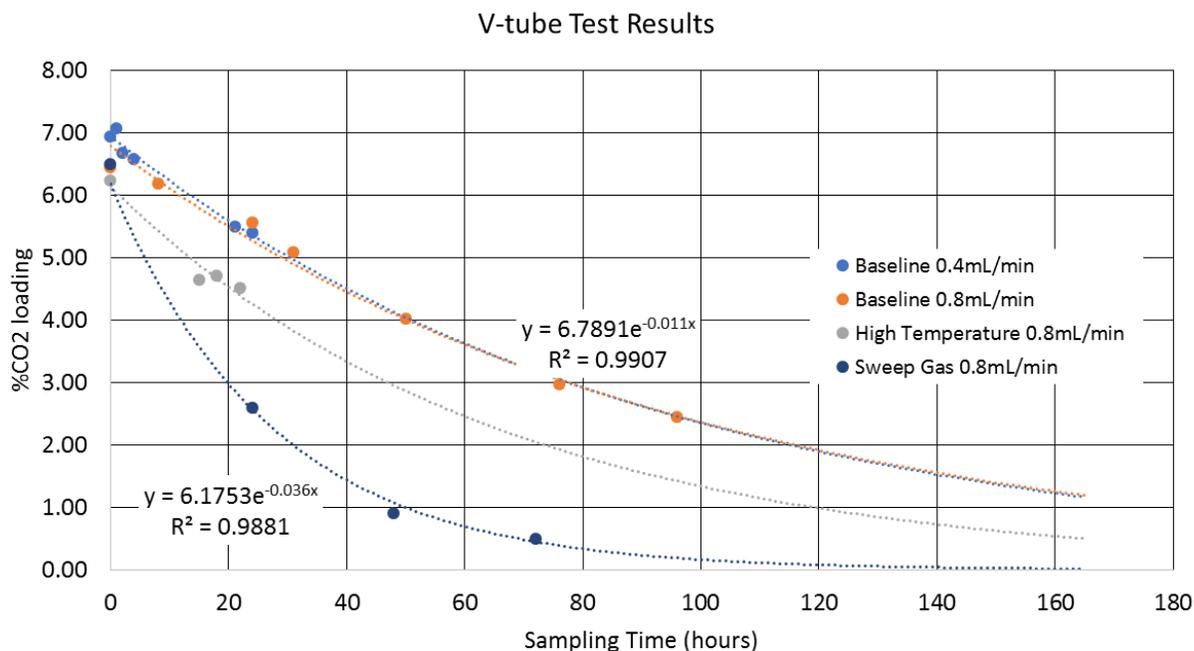
**Figure 11. High temperature V-tube run compared with baseline**

At this point the team decided it would be prudent to run a repeat of the baseline test to gain confidence in the repeatability of results. Cumulative FTIR results are shown in Figure 12. It is observed that for the first four sampling points, the CO<sub>2</sub> loading follows comparably with the initial baseline evaluation, however it deviates as the runtime increases. Very oddly, the CO<sub>2</sub> loading appears to increase at the end of the test. At this point, the cause of this apparent increase in CO<sub>2</sub> loading is unknown. A fault in the FTIR calibration was suspected, however verification samples were analyzed and returned positive results.



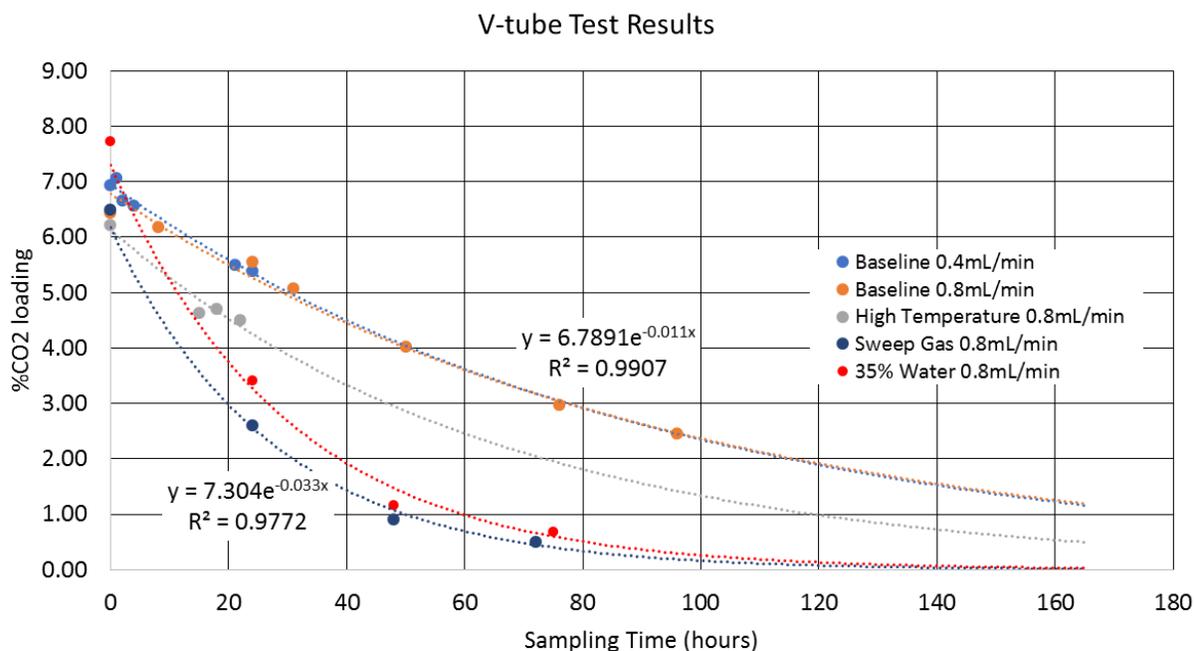
**Figure 12. Repeated Baseline run shows poor results**

In the next test case, N<sub>2</sub> sweep gas (UHP, Matheson Gas), was plumbed into the headspace of the V-tube and set at a flowrate of 400mL/min. The target degas temperature was 85°C and the input DGA was the 15-minute preloaded sample at 0.8mL/min. The test was allowed to run for 72 hours and the cumulative FTIR results from the initial baseline, the high temperature run, and the sweep gas run are shown in Figure 13. It was noted that during the sweep gas run, discoloration was not observed, which was expected since oxidation is the suspected cause of amine discoloration.



**Figure 13. V-tube run with N<sub>2</sub> sweep gas at 400mL/min**

In the final test case, the 35% water/65% DGA mixed solution was used as the initial preloaded sample. As before, the 15-minute CO<sub>2</sub> preload was used with the target degas temperature of 85°C, 0.8mL/min liquid flowrate, and no sweep gas. Cumulative FTIR results are shown in Figure 14. Total runtime was 75 hours and discoloration was observed. The results from this test show that an aqueous DGA solution will more readily release captured CO<sub>2</sub>, and the rate is comparable to using a sweep gas during regeneration.



**Figure 14. Aqueous DGA solution (35% water) V-tube run**

## V. Comparisons, Conclusions, and Future Work

CO<sub>2</sub> degassing characteristics were explored under varying parameters in this study. Using a benchtop-scale, custom-built V-tube, varied degassing system design parameters of temperature, flowrate, water dilution, and sweep gas were compared to a baseline set of parameters. In order to measure the CO<sub>2</sub> content in a given DGA solution, Fourier Transform Infrared Spectroscopy was calibrated against a known method of pH desorption. Experimental samples of DGA solution were then analyzed using FTIR and CO<sub>2</sub> loading levels were interpolated based on the calibration set. The usage of FTIR to analyze CO<sub>2</sub> loading seemed to work reasonably well, however more extensive method testing would be necessary to fully verify results and improve repeatability. Given the time requirement and the limited sample size of the solution in these experiments, it was not feasible to verify each FTIR reading with a parallel pH desorption volumetric CO<sub>2</sub> measurement.

Of the test cases, using a starting solution of 35% water and 65% DGA is the most promising option because it showed similar degas rates to using a sweep N<sub>2</sub> gas in a system with a starting solution of pure DGA. This is a promising result because using a sweep gas to increase the rate of CO<sub>2</sub> reclamation would be impractical in a spaceflight system, as the whole purpose of a CO<sub>2</sub> scrubber is gas separation.

Moving forward with the design of a degassing system, the teams at JSC and ARC are fully characterizing the aqueous 35% water/65% DGA solution in terms of uptake and regeneration. Currently, work is underway at ARC to characterize single pass regeneration data at elevated temperatures (115°C) as well as to investigate the effect of adding custom synthesized carbonic anhydrase to the solution on CO<sub>2</sub> capture and release rates.

### Acknowledgments

The authors would like to thank Tanya Rogers and Giraldo Alvarez for their insights and inputs throughout the experimental testing.

### References

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