Closed Environment Air Revitalization System
Based on Metal Organic Framework Adsorbents

eXploration Habitat (X-Hab) 2014 - Final Report

T. Grant Glover – University of South Alabama

Abstract

This project utilized a systems engineering methodology to develop a vacuum swing adsorption system with full Labview automated control. The project was successful and provided students with an introduction to systems engineering and air revitalization. Specifically, two stainless steel adsorption beds were custom designed and manufactured and a sequence of computer controlled valves were used to deliver CO_2 laden, humid air, to the adsorbent where the CO_2 was removed from the air stream. Runs were completed using 13X zeolite and bed timing and switching was controlled by the computer based on the data output of a CO_2 detector.

Adsorption runs using the MOF have not been completed upon the writing of this report; however, the MOF material is currently being synthesized and the runs will be completed upon receipt of the material. A follow up meeting with NASA has been tentatively planned to discuss the output of these experiments. Consistent with systems engineering practice, an end of project assessment of the class was conducted with the students and several items were realized. Specifically, the short period of performance of this grant makes it necessary to maintain a narrowly focused scope on the project such that multiple experiments after systems development (T&E) need to be limited to ensure timely completion of the proposed tasks. Also, procurement of parts may need to be moved forward in time to allow for delivery delays, and it may be necessary to request SDR, PDR, and CDR dates from NASA that are ahead of the NASA anticipated schedule. These types of lessons provided valuable to both the PI and the students and ultimately illustrate the necessity of proper systems engineering schedule risk assessment.

The class met the objectives of the project and provided an introduction to systems engineering to undergraduate students. As a metric of that success, the lead engineer of the undergraduate design team acquired a job with an aerospace defense contractor, which he attributed to his knowledge of systems engineering concepts that were acquired via the X-Hab class.

Report Contents

Contained in this report is a poster that was developed by the design team and presented at their capstone design symposium (pdf page 2). Participation in the symposium is required and allows students to present their capstone designs to the entire University of South Alabama (USA) Chemical Engineering faculty as well as members of the USA Chemical Engineering industrial advisory board, and other chemical engineers working in engineering roles in the local chemical industry. The symposium requires both a poster presentation and a 20 oral presentation, the slides from the presentation are included in this report and start on pdf page 30. Also included in this document is the written report developed by the students detailing the work that was done over the course of the project (pdf page 3).

Novel Adsorbent Air Revitalization for Closed Environments

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Abstract

Recently, NASA has turned its attention to making long-term space travel feasible for humans, which requires maximization of resource recycling. As competitors in NASA's Exploration Habitat (X-Hab) Challenge, this design team has proposed and designed a system for the testing of an air purifying system containing a novel adsorbent (UiO-66). This adsorbent will capture carbon dioxide from cabin air with the goal of maintaining a hospitable environment for space travelers. Using the systems engineering approach, the system was designed to be low maintenance, have automatic operation, and have minimal energy requirements. With a budget of $20,000, this team has designed and constructed a two-bed system for continuous air regeneration and data collection. Tests were recently performed with zeolite 13X. UiO-66 will be compared to this traditional adsorbent.

Current CO_2 Removal Technology

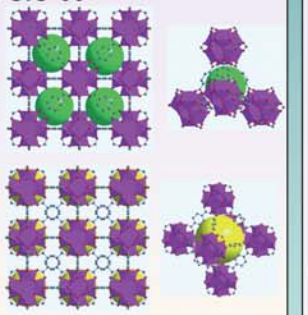
- Liquid Amine Scrubbing
  - Well-established method for CO_2 capture
  - Major health concerns: amines and degradation products could limit use in closed environments
- Zeolites
  - Resistant to damage from high pressures and temperatures
  - Strong selectivity for CO_2, water competitively adsorbs
  - 13X Zeolite acquired for comparison

Metal Organic Framework (MOF)

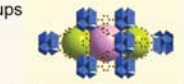
- MOFs are 3D frameworks comprised of metal clusters connected by organic ligands
- Ligands are molecules that bond to a central metal atom or ion
- MOFs are good adsorbents because of high porosity
- Unfortunately, they have traditionally exhibited weak chemical, thermal and mechanical stability

Novel MOF: UiO-66

- UiO-66 exhibits greater stability due to 12-fold connections between zirconium-based octahedra ($Zr_6O_4(OH)_4$) by 1,4-benzene-dicarboxylate ligands
- 3-D octahedral/tetrahedral structure maintained after adsorption & desorption
- UiO-66 exhibits CO_2 selectivity & can be tuned with different functional groups



UiO-66 – Green spheres are tetrahedral spaces, yellow spheres are octahedral spaces.[1]



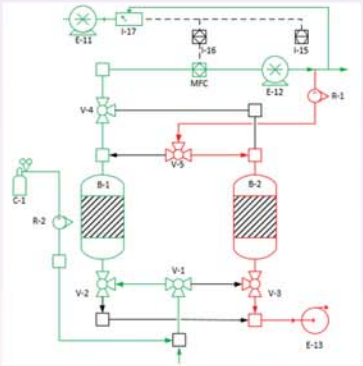
Combined tetrahedra and octahedron

Color key: dark purple/blue=zirconium; gray=carbon; red=oxygen; large spheres=pores

System Setup

- UiO-66 beds with outer jackets made of 304 stainless steel
- Bed/jacket unit allows for optional heat tracing to aid desorption and creates annulus for optional cooling water during adsorption
- Outlet air samples fed to CO_2 detector. LabVIEW executes valve actuation based on detector signals.

System Operation

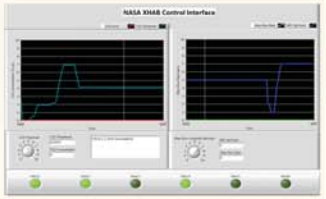


- System operates by VSA: Vacuum pumps pull air through the beds
- Green is path of adsorption; Red is path of desorption
- Green and red paths change after each cycle
- New cycle: outlet CO_2 = 0.7%

LabVIEW used for GUI

Left graph: real time CO_2 level

Right graph: real time mass flow rate

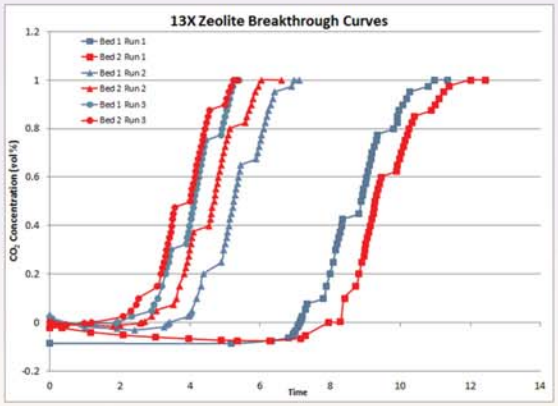


Conclusions & Future Work

- Zeolite cannot purify humid air for extended times
  - We expect necessary dehumidifcation/humidification sequences or high-energy desorption processes to be bypassed if UiO-66 is tuned for CO_2 selectivity and low water affinity
- Perform UiO-66 testing in Summer / Fall of 2014
- Used for graduate thesis in coming semesters

Zeolite 13X Testing

- Zeolite is tested first, as UiO-66 synthesis was delayed
- Testing occurred with ambient air containing 1% CO_2



- Y-axis is % CO_2 in air leaving the beds. X-axis is time in minutes.
- Breakthrough is the time it takes for CO_2 to be detectable in the outlet stream

Zeolite 13X Results

Run	Breakthrough Time (min)
1	7
2	2 to 3
3	3 to 4

  - Complete desorption of H_2O & CO_2 does not occur during bed regeneration
  - Thus less and less sites are available for adsorption with each new cycle
- We expect better regeneration of UiO-66 under the same conditions

References & Acknowledgements

1. Biswas, S. & Van Der Voort, P. A General Strategy for the Synthesis of Functionalised UiO-66 Frameworks: Characterisation, Stability and CO2 Adsorption Properties. *Eur. J. Inorg. Chem.* **2013,** 2154–2160 (2013).

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Abstract

Space exploration has long been a priority for the United States and a fascination for the world. The research and engineering behind such endeavors as NASA's missions required countless hours of modeling, testing, and fabricating, in addition to ample creativity and ingenuity. Recently, NASA has turned its attention to making long-term space travel feasible for humans, which requires maximization of resource recycling. As competitors in NASA's Exploration Habitat (X-Hab) Challenge, this design team has proposed, designed, and tested a novel adsorbent for the capture of carbon dioxide from cabin air with the goal of maintaining a hospitable environment for space travelers. Using the systems engineering approach, the design phase enabled many of the typical hurdles to be planned for and avoided. By investing in the design phase, multiple configurations and ideas were proposed and each thoroughly evaluated before acceptance or rejection. As with many projects, procurement proved to be challenging and consumed a large portion of time that was planned to be used for testing and evaluation. Although this phase of the project was shortened, the system was tested to show the proof of concept of the project. However at the time of this report, data had not yet been collected.

1. Introduction

NASA has traditionally used replaceable lithium hydroxide canisters as a means of air-regeneration in their space missions. These systems were implemented in several missions, including Mercury, Gemini and Apollo where they were the sole source of carbon dioxide removal, and Space Shuttle and International Space Station missions where they are a secondary method of carbon dioxide removal[1]. Recently, a research challenge was issued to Universities across the country in which funds were to be allocated to highly innovative propositions for the long-term maintenance for design, fabrication and testing. This proposal uses a novel metal organic framework (MOF) in a pressure-swing adsorption (PSA) and vacuum-swing adsorption (VSA) system to remove carbon dioxide and regenerate the adsorbent in order to provide a long-term, sustainable system to effectively revitalize cabin air.

2. Traditional Materials for CO_2 Capture

2.1. Liquid Amines

A well-established method for carbon dioxide capture is amine scrubbing.[2] This process involves contacting carbon dioxide in an absorber with a liquid amine solution, such as 20% monoethanolamine in water. Regeneration of the amine is then achieved via stripping with water vapors. This method has been implemented to remove carbon dioxide from submarines and coal-fired flue gases in power plants.[2,3] While this method has proved effective, a major drawback is the degree of toxicity of the amines.[4] Because the air-regeneration system will have direct access to cabin air, as well as being in close proximity to living quarters, it is essential that the process be as inherently safe as possible. In addition to toxicity, the stripping process for MEA regeneration would involve the production of steam for the stripper.[2]

2.2. Zeolites

One class of molecular sieve commonly used for gas adsorption is zeolite, which is composed of a three-dimensional crystalline aluminosilicate framework.[5] These materials exhibit high selectivity to carbon dioxide due to an affinity for polar species. In addition, they have uniform pore size, allowing only molecules of a certain size to pass through. Also, they are very resistive to damage from high pressures and temperatures. However, a problem arises when using these zeolites in the presence of moisture. While carbon dioxide has a strong affinity to the zeolite structure, unfortunately, water has even stronger affinity because it is more polar. Consequently, enough energy must be imparted to the adsorbent to prevent water from collecting on sites used for CO_2 adsorption.[5]

3. Metal Organic Frameworks

A Metal Organic Framework (MOF) is a three-dimensional framework comprised of metal clusters connected by organic ligands. These structures have high pore volumes and are thus suitable for adsorption processes, such as those involved in separation of gases.[6]

3.1. Stability

To date MOFs have exhibited weak thermal, chemical, and mechanical stability, hindering their use in large scale applications. However, UiO-66 is a zirconium-based MOF composed of Zr_6O_4-$(OH)_4$ clusters linked by terephthalate anions leading to a 3-dimensional arrangement of micro pores with each centric octahedral cage surrounded by eight corner tetrahedral cages[7]. It has shown to retain its crystalline structure upon adsorption and desorption cycles and has a high water and thermal stability (>773 K)[7,8]. Powder X-ray diffraction (PXRD) indicates that the UIO-66 retains its crystallinity when exposed to water. Figure 1 shows comparisons of the PXRD patterns for modified UIO-66 before and after exposure to water. In all cases the peak positions and peak height ratios remain virtually unchanged indicating no change in crystillinity[9].

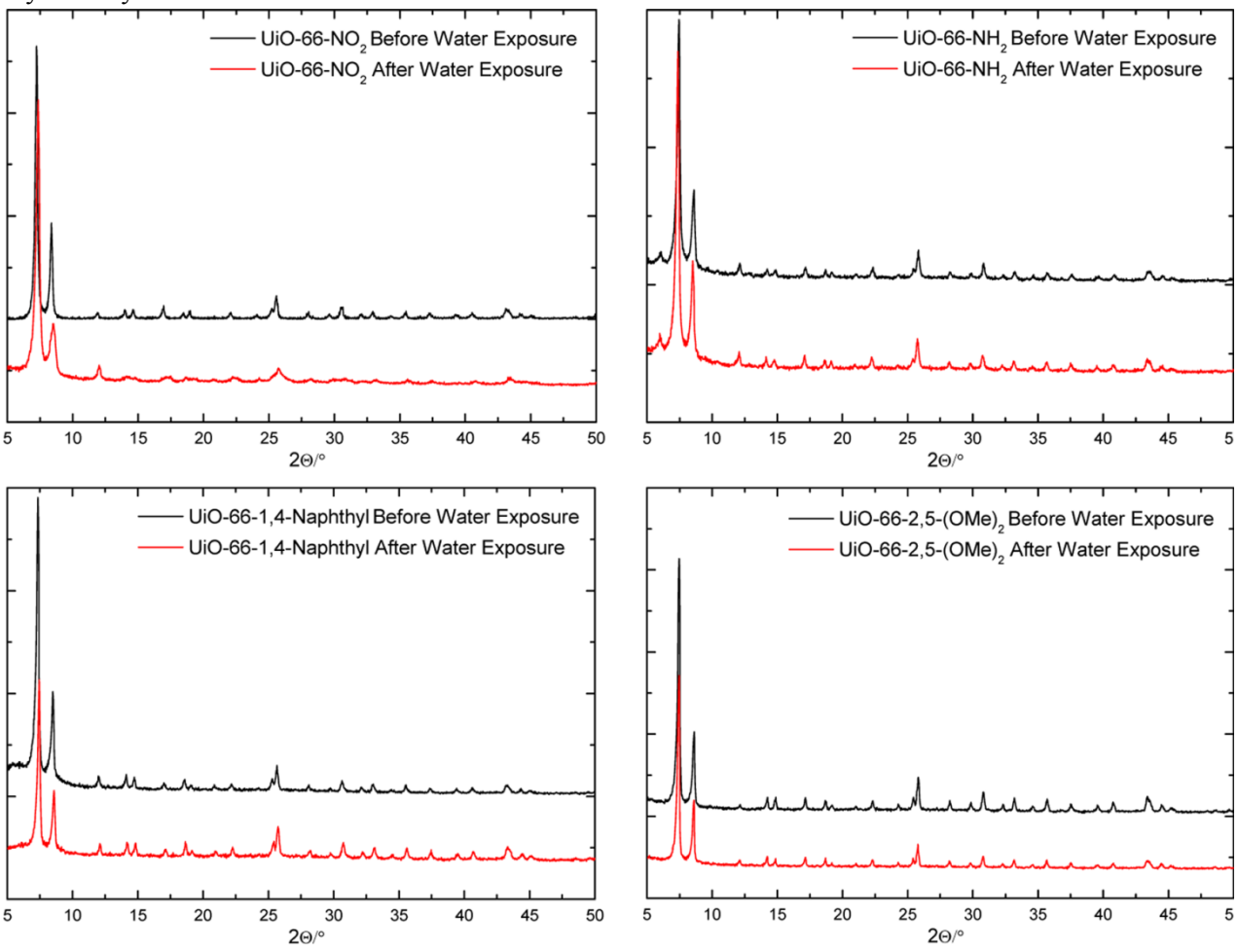

Figure 1. PXRD patterns before and after exposure to water vapor and subsequent reactivation.

3.2 Efficiency

The major complication for gas adsorption with MOFs is their sensitivity to water vapor. The water vapor competes for sites with the CO_2 decreasing the efficiency of CO_2 adsorption. Humidity plays a paramount role in water vapor adsorption. At humidity levels lower than 20% water uptake is roughly 3.5 mol/kg[9]. At levels higher than 20% the efficiency of CO_2 adsorption decreases due to the significant increase in water uptake as shown in Figure 2[9].

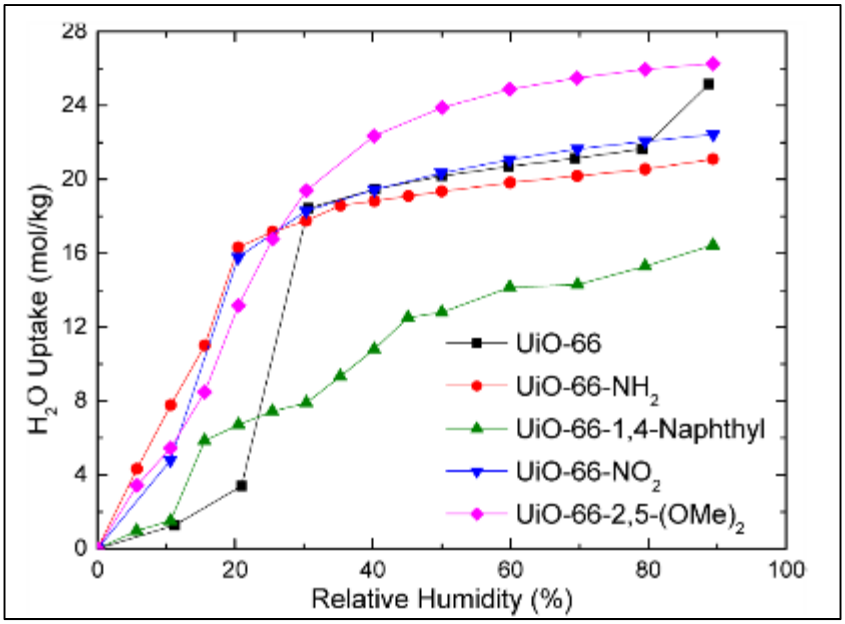

Figure 2. Water vapor adsorption as a function of relative humidity at 298 K and 1bar.

Uptake of water derives complications in the desorption phase. Since desorption is fundamentally a phase change the energy required to regenerate the MOF is 40.71 kJ/mol_{H2O}.

4. Operating Conditions

4.1. Pressure Swing Adsorption

Gas separation can be performed via several pathways; one of these being pressure swing adsorption. PSA operates by pressurizing a packed bed of adsorbent particles by passing a multicomponent gas stream over the packed bed. One or more of the compounds within the stream will adsorb to the packed bed particles and all non-adsorbing compounds will pass over the packed bed. The non-adsorbed molecules are released from the pressurizing packed bed, and subsequently the packed bed is de-pressurized. This depressurization creates a driving force that allows the adsorbed molecules to break away from the adsorbent. The depressurization step also utilizes a counter current purge stream to move the desorbed gases away from the adsorption particles and out of the adsorption beds. PSA systems are operated via the [modified] Skarstrom Cycle and are designed to operate with a minimum of two adsorption beds. The utilization of two beds produces a continuous supply of separated material. The two (or more) adsorption beds operate out of phase. This means that while one adsorption bed(s) is performing the required separation, the other bed(s) is performing a regeneration step to remove any residual adsorbed molecules. This allows the entire system to reach a cyclic steady state; at which time the amounts adsorbed and desorbed are equal. One drawback of PSA is the energy consumption required to pressurize the adsorption beds.

4.2. Temperature Swing Adsorption

Another type of gas separation is Temperature Swing Adsorption (TSA) which uses heat to depressurize a saturated adsorption bed. TSA can be utilized in sequence with a PSA system. This operates by de-pressuring and heating the adsorption bed simultaneously. A TSA system requires additional piping and instrumentation to regulate and monitor the temperature variations within the beds.

4.3. Vacuum Swing Adsorption

Vacuum Swing Adsorption operates along the same pathway as a PSA system; however, the adsorption beds operate under vacuum pressure instead of positive pressure. A VSA system utilizes a minimum of two vacuum pumps; one to move the gas stream through the adsorption beds and another to operate the countercurrent purge step to remove desorbed gases from the adsorption beds.

Thus this team will utilize the MOF UiO-66within a combined TSA/VSA system and report its adsorption characteristics and overall suitability for this application.

5. Design Process

For the entire design process of this system, a Systems Engineering approach was utilized, in which a series of definitions of increasing complexity are outlined to control every aspect of a project. This helps to organize the design process and facilitate a smooth transition from broad scope goals to detailed requirements, all while minimizing errors in time management as well as reducing misallocation of resources.[10]

This section, Design Process, is largely comprised of three chronological reviews: a System Definition Review (SDR), a Preliminary Design Review (PDR), and a Critical Design Review (CDR). Combined, these illustrate all steps taken from initial concepts to close-out, including all projections and goals at the time and their subsequent revisions. Therefore, in each review discussed below, original content is left in place and changes are noted in succeeding reviews.

5.1 SDR (System Definition Review) and PDR (Preliminary Design Review)

The design of this system begins with the SDR. The SDR was produced near start-up of the project (September 23rd through October 2nd of 2013) and was intended to as a tentative framework from which to coordinate all aspects of design. As the design process continued into procurement and assembly phase, the team produced an updated design review on November 18th, 2013. This next review, the Preliminary Design Review (PDR), is based upon the System Design Review, but includes important changes and greater detail on the status of the project. In the following paragraphs, all changes and details made will be discussed, with the understanding that any undiscussed topics remain unchanged from the SDR.

Overall Goals

Within the SDR, the mission, goals and objectives of the project are first defined. The basic goal of the entire project was to design and construct a fully operational demonstration of a NASA habitat air

revitalization system. Further objectives to be met were automated control, utilization of novel molecular framework adsorbent, and minimal energy requirements.

Concept of Operation

Next, the Concept of Operation was developed (ConOps), which outlines how all the systems within the process will work together, independent of any one scenario.[10] In this ConOp, carbon dioxide laden air is delivered to an alternating two-bed arrangement, in which carbon dioxide is selectivity adsorbed and desorbed on a Metal-Organic Framework (MOF), a process which is driven by equilibrium.[11] The air will be purified in the beds using VSA with automated feedback to control valve actuation. Purification will occur continuously, resulting in a sustainable yield of breathable air.

Requirements Definition

The preferred system solution is a low maintenance system that can last for long durations with little supervision by the crew. Preliminary functional requirements are to produce ten liters of carbon dioxide free air per minute, to have LabVIEW communicate with the gas chromatograph, and to have real-time, automatic sampling.

Originally, the system had been conceptualized to operate on PSA, where air was to be pressurized into the beds at over 2 atm and let out of the beds at atmospheric pressure. However, NASA representatives determined the PSA method originally presented in the SDR to be unnecessarily wasteful of energy. Suggestions were made to reduce energy consumption by decreasing the loading/regenerating pressure difference and incorporating temperature swing adsorption to compensate for the decrease. Consequently, the team chose to reduce the loading pressure and use VSA by pulling a vacuum on the exit lines to the bed to draw air at atmospheric pressure through the MOF. Also, the option of TSA was planned for if the need arose for additional desorption energy.

The system design proposed to meet all these requirements can be seen in Figure 3.

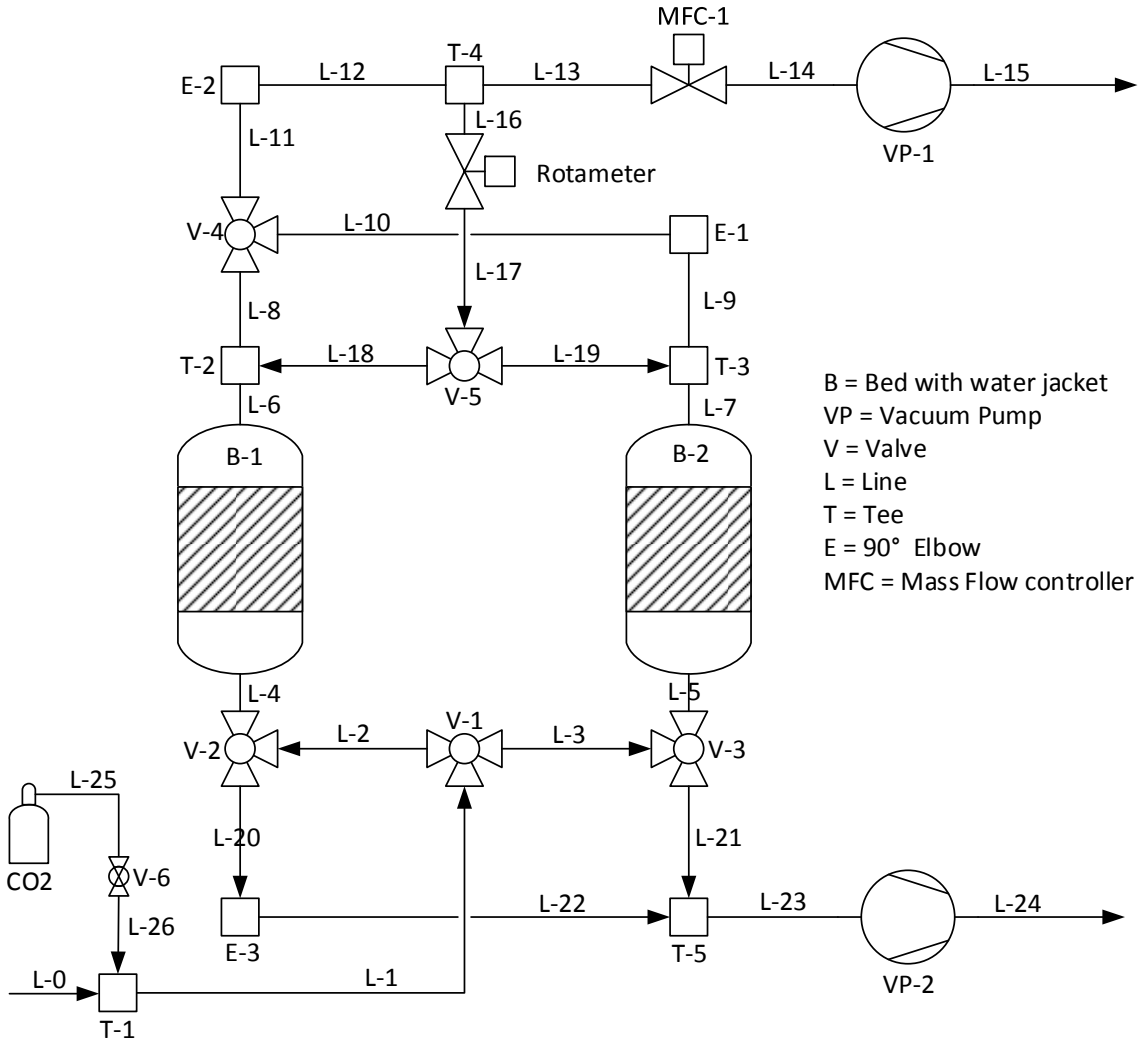

Figure 3. Preliminary functional block diagram from the SDR.

In Figure 3, taken from the SDR, carbon dioxide and air meet at a tee fitting and enter into a three-way valve that diverts flow to one of the two beds. Air is drawn through one bed at a time by a vacuum pump placed at the end of the product stream line. While air is being purified in one bed, a fraction of the filtered air is diverted for the regeneration of the adjacent bed. This air is pulled counter-currently through the bed by another vacuum pump, placed at the effluent exit. After the SDR was presented, changes were made regarding the gas delivery system to the beds. A new diagram was then produced, which can be seen in Figure 4.

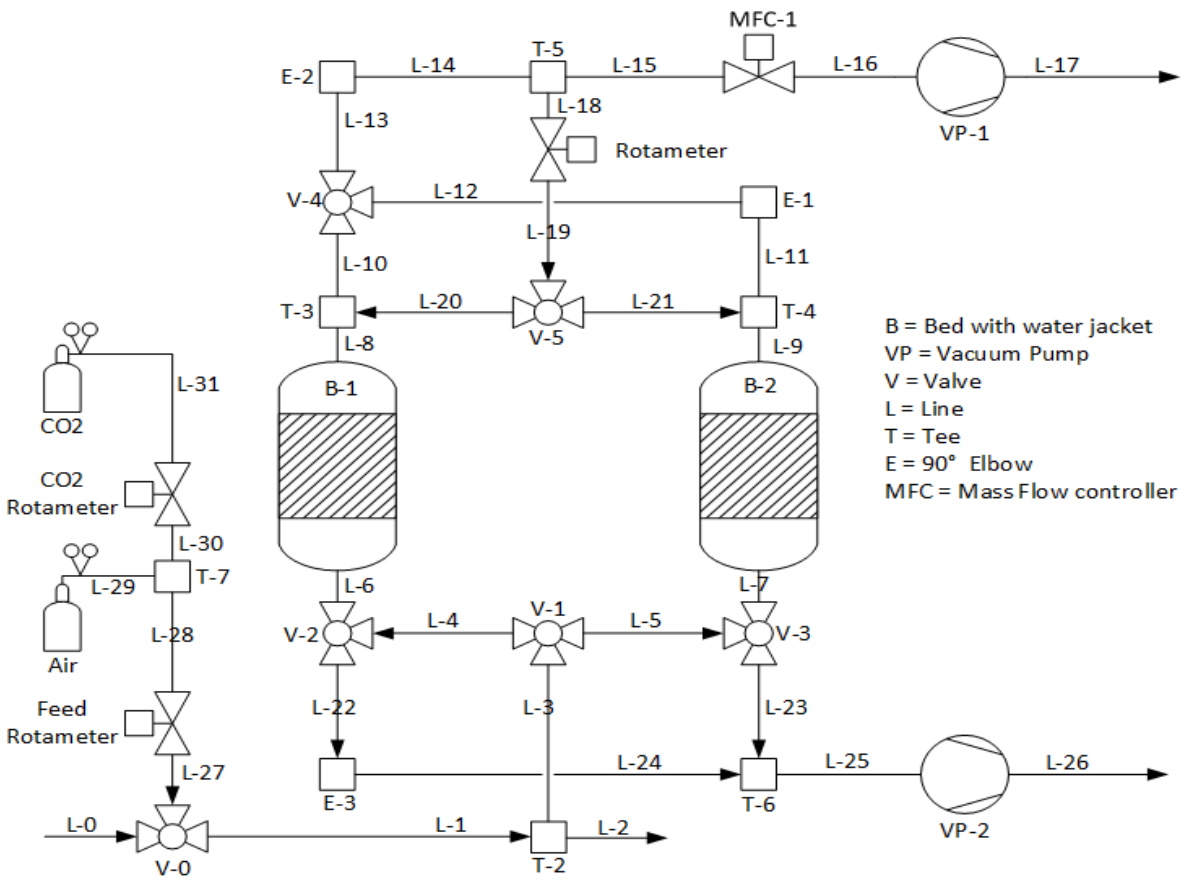

Figure 4. Shown above is the second block flow diagram presented to NASA in the PDR.

As reflected in Figure 4, the gas delivery system was expanded to include a dry air feed to mix with the carbon dioxide. This involved the addition of a tee fitting (T-7), an air tank, and a control valve. This configuration was the basis for how the system was to be assembled throughout the PDR and into the CDR. However, upon further evaluation from the project adviser, it was discovered that the location of the feed line for regeneration air would present an issue regarding air flow. Diverting air from the main line at T-5 would result in very low counter-current flow through the beds due to both pumps simultaneously drawing on this line in opposite directions. Consequently, the P&ID was revised for a second time, this time relocating T-5 to the exit side of VP-1. Such a configuration allows adequate air flow to be diverted through the beds for regeneration, as the pumps will no longer be competing. After the final design was accepted, a P&ID was constructed to show the analytic equipment, electric-solenoid controlled valves, computer with LabVIEW, controller and updated pumps. Figure 5 shows the as-built conditions of the system in the P&ID.

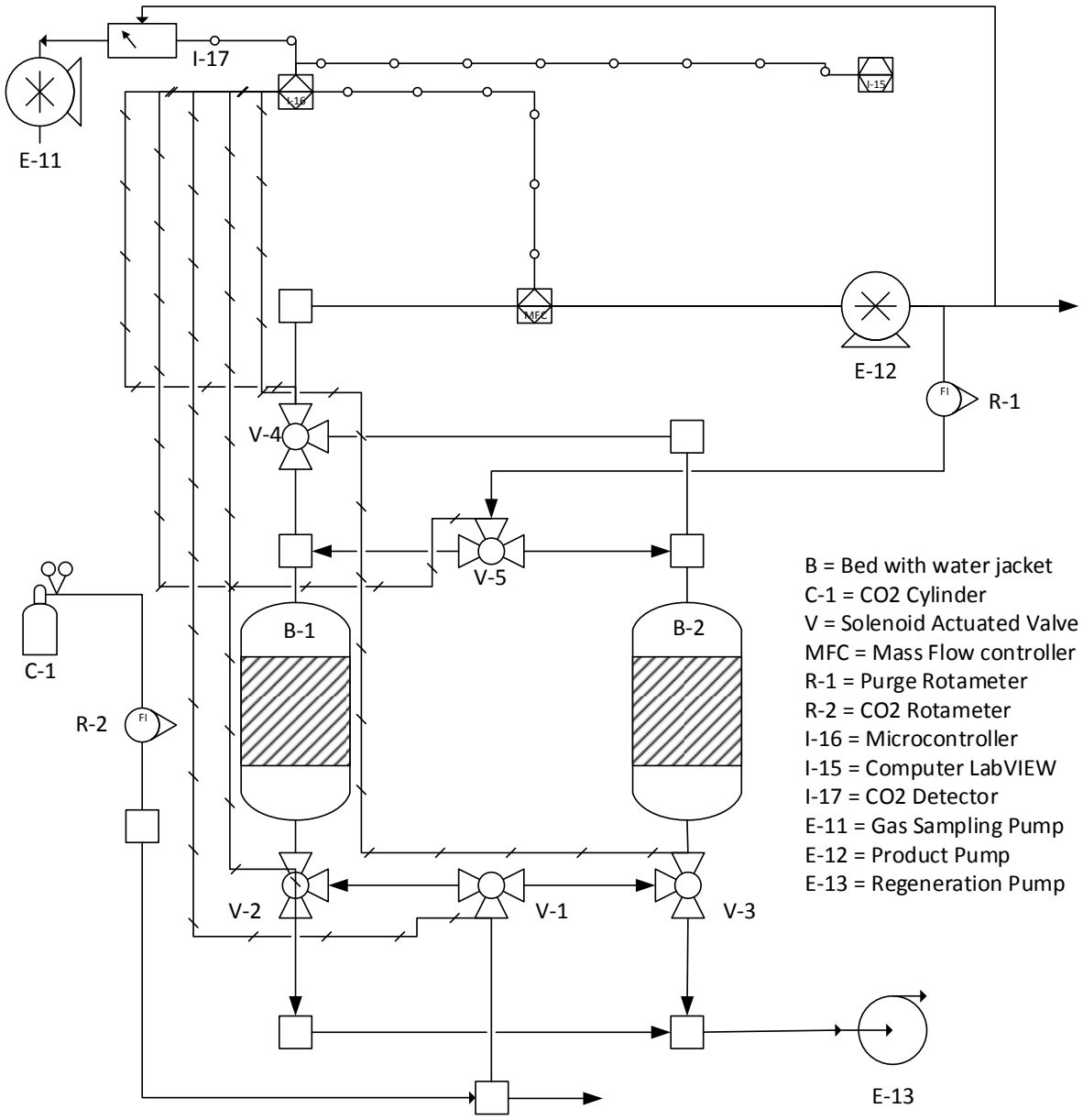

Figure 5. Displayed above is the as-built P&ID for the system.

Work Breakdown Structure

Once all objectives and overall processes are defined, the System Architecture must be outlined. Within this step are the system definition, concept, and layout. A flow sheet of the System Architecture can be viewed in Figure 6. In this flow sheet, it can be seen that the operation of NAARCE is dependent upon four different sub-sections: Automation and Instrumentation, Gas Delivery, Beds, and Analytics. Within Automation and Instrumentation is the requirement of a software control system, which itself possesses readout, valve control, and data logging capabilities. This will allow for communication between the analytical and gas delivery sub-systems, resulting in automated control of air flow through the beds based upon CO_2 content and experimentally determined breakthrough times. As for the Gas Delivery regime, it

consists of mass flow and pressure control mechanisms, as well as associated fittings. For the beds, they will contain adsorbent and packing, and the specific adsorbent will be a UiO-66 MOF, as mentioned previously. Lastly, under analytics, a carbon dioxide detection apparatus is required, and incorporated into Automation and Instrumentation to provide automatic operation.

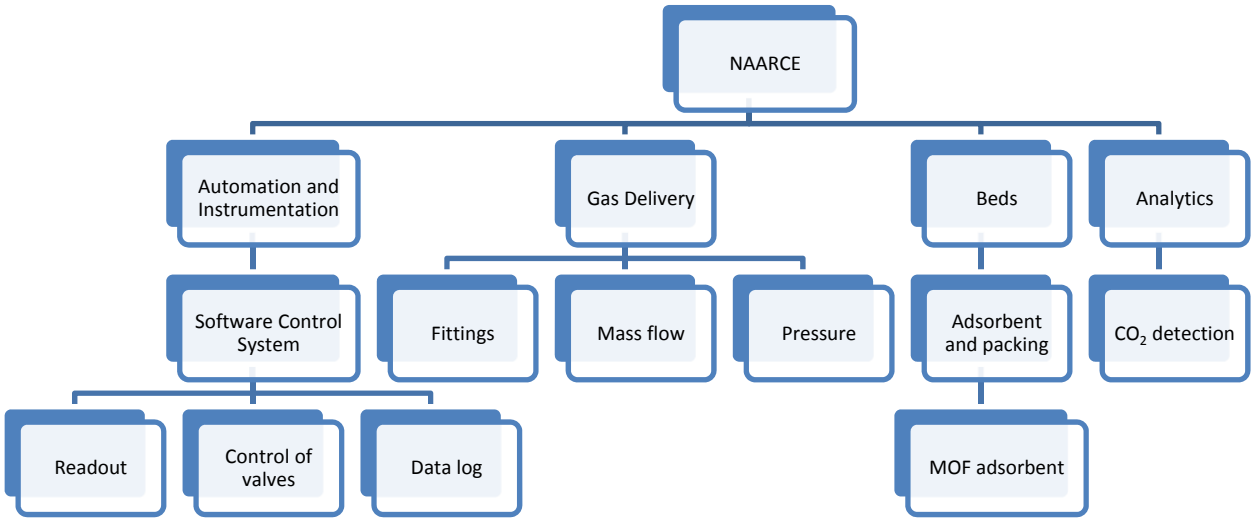

Figure 6. Shown above is a flowchart of the system architecture.

Next, Level 1 Systems Requirements are defined. The overarching system requirement is operated with vacuum-temperature swing adsorption. A more detailed breakdown of requirements between adsorption and desorption can be seen in Figure 7 and Figure 8, respectively.

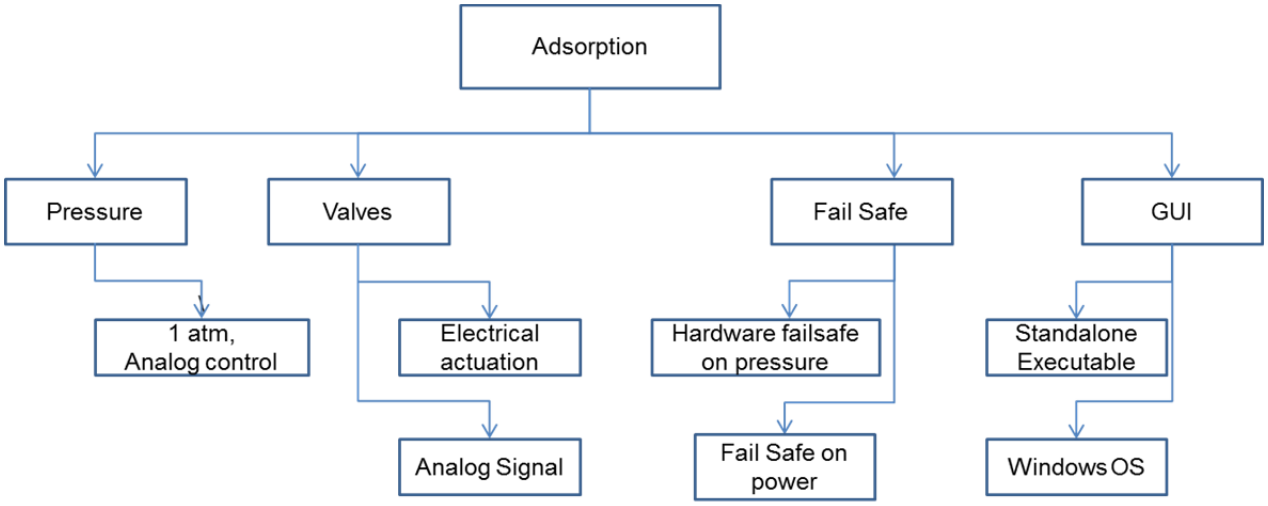

Figure 7. Level 1 system requirements for adsorption.

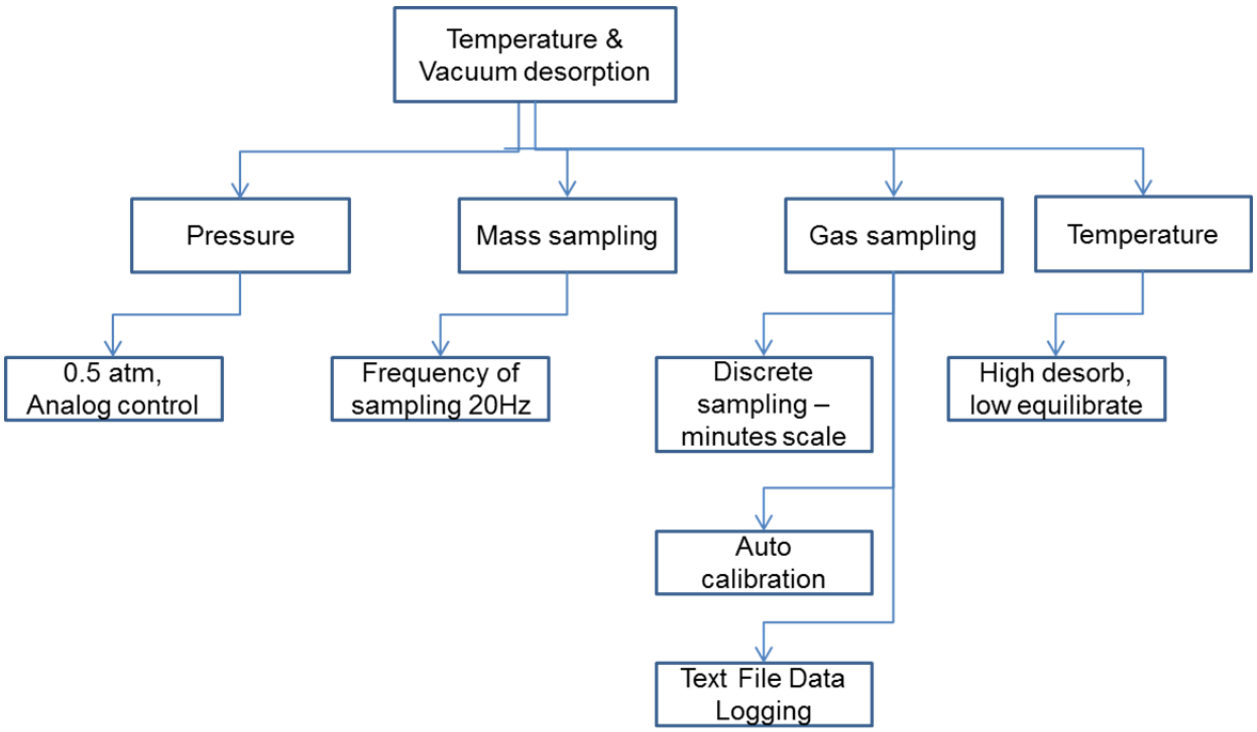

Figure 8. Level 1 system requirements for desorption.

After this, the Work Breakdown Structure (WBS) is formulated. The first subsystem level can be seen in Figure 9. Within this WBS, the entire plan for executing the project from start to finish is broken into seven phases.

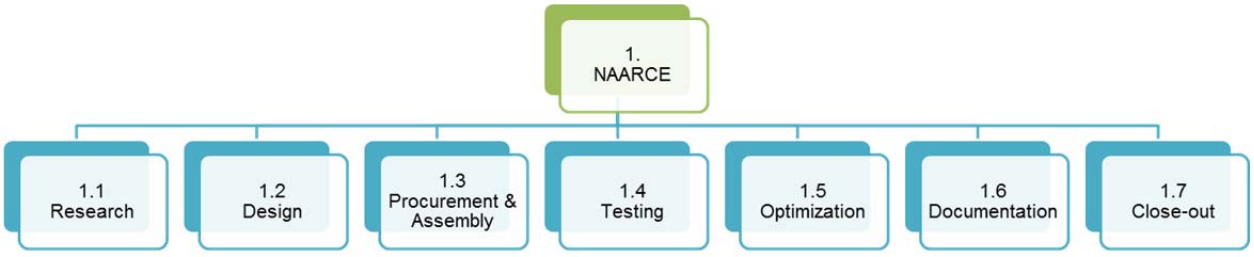

Figure 9. Shown above is the first set of subsystems in the WBS for NAARCE.

Shown in Figure 10 is the first phase of the project, which involves extensive research. The first sub-phase of research, 1.1.1. Adsorbent, involves studying carbon dioxide selectivity of the MOF, along with effects of pressure and temperature variations on its structural stability. This step involved extensive literature review which was summarized previously. Next is the Process Control Instrumentation sub-phase. Within this section is the investigation of appropriate pressure and mass flow controllers. It was during this phase that a pressure controller was removed from the design and mass-flow controllers were researched and prices obtained so that the project requirements and budget could be met. For sub-phase 1.1.3., Analytic

Instrumentation, research of a suitable gas chromatograph and further research of automatic sampling, calibration, and standard operating procedure was necessary. Lastly, under sub-section 1.1.4., automation, is the investigation of appropriate electric actuation and Graphical User Interface. For this phase, assistance from Aaron Anderson from the Department of Electrical Engineering was requested.

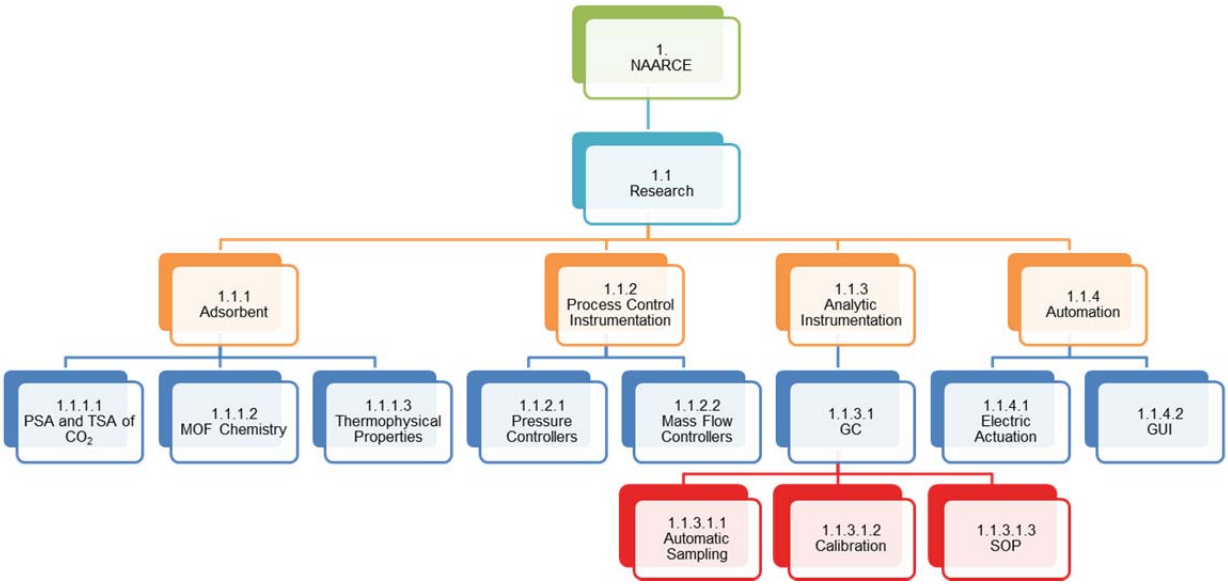

Figure 10. Displayed above is the hierarchical diagram for set one of the WBS.

The next phase is Design, which is also composed of four sub-phases. The first design sub-phase is System Configuration. Types of valves, tubing, and process control instrumentation must be selected. Under the valves category, the proper placement of valves must be determined, and they must be constructed for electrical actuation. As for process control instrumentation, it was decided that a mass flow controller, manufactured by Brooks Instrument would be used. The second sub-set of Design is MOF beds, for which cycle times and exact pressure and temperature swings must be specified. Also, as previously mentioned, the MOF beds are designed as a pair to allow for continuous operation. The next design category is for analytics. For analytics, the aforementioned gas chromatograph was to be used, the exact means of detection being a thermal conductivity detector. This instrument will be used for automatic sampling and calibration and will output composition data to the graphical user interface (GUI), the last sub-phase, which will be composed of LabVIEW. A hierarchical diagram showing this whole phase can be seen in Figure 11.

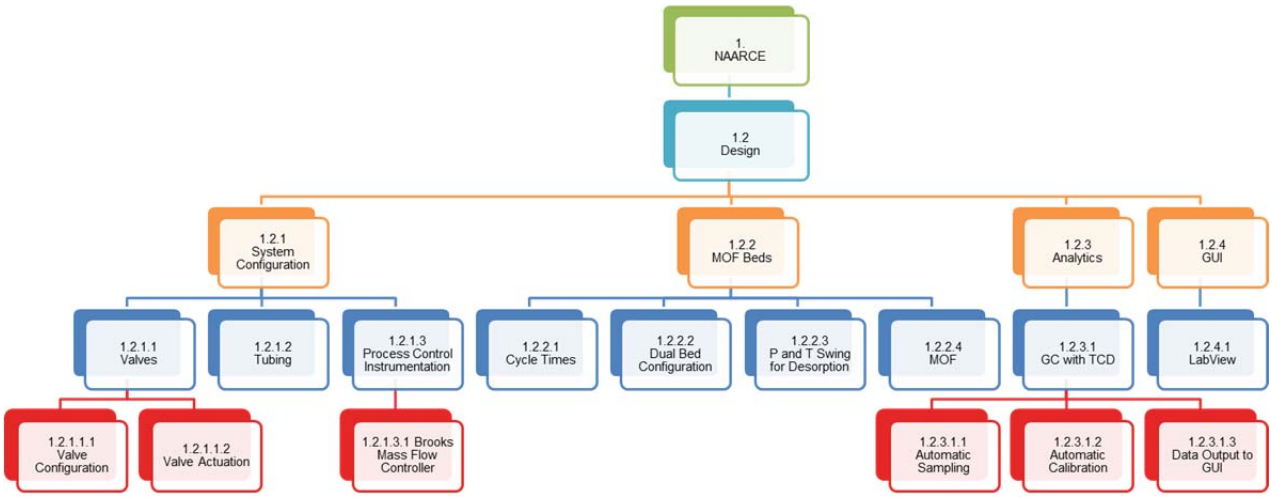

Figure 11. Shown above for the second set of the WBS.

Next is the Procurement and Assembly phase. The first step in this phase is to acquire all pieces of equipment and materials specified in the aforementioned design phase. Under 1.3.1 System Configuration is procurement of valves, tubing, beds, and process control instrumentation. It was decided that Swagelok was to be the source of all valves and associated actuators. Teflon tubing was decided to be used because it is chemically inert, flexible and allows ease of construction. The MOF beds were assembled by Evonik using 316L stainless steel, and process control instrumentation, comprised of a mass flow controller, was purchased from Brooks Instrument. In section 1.3.2, MOF beds, the MOFs were synthesized at the Georgia Institute of Technology using NASA funds. This MOF was delivered along with proper water-resistant binding, which imparts uniform particle size to the material, which reduces dusting and pressure drop across the beds. In step 1.3.3, Analytics, the HP 5890 Series II Gas Chromatograph was replaced by the Horiba VIA-510 CO_2 Analyzer. This piece of analytic equipment gave faster feedback of the process stream and simplified the calibration process. Lastly, under the GUI section, LabVIEW software was provided by National Instrument. A diagram summarizing this phase at the time of the SDR can be seen in Figure 12.

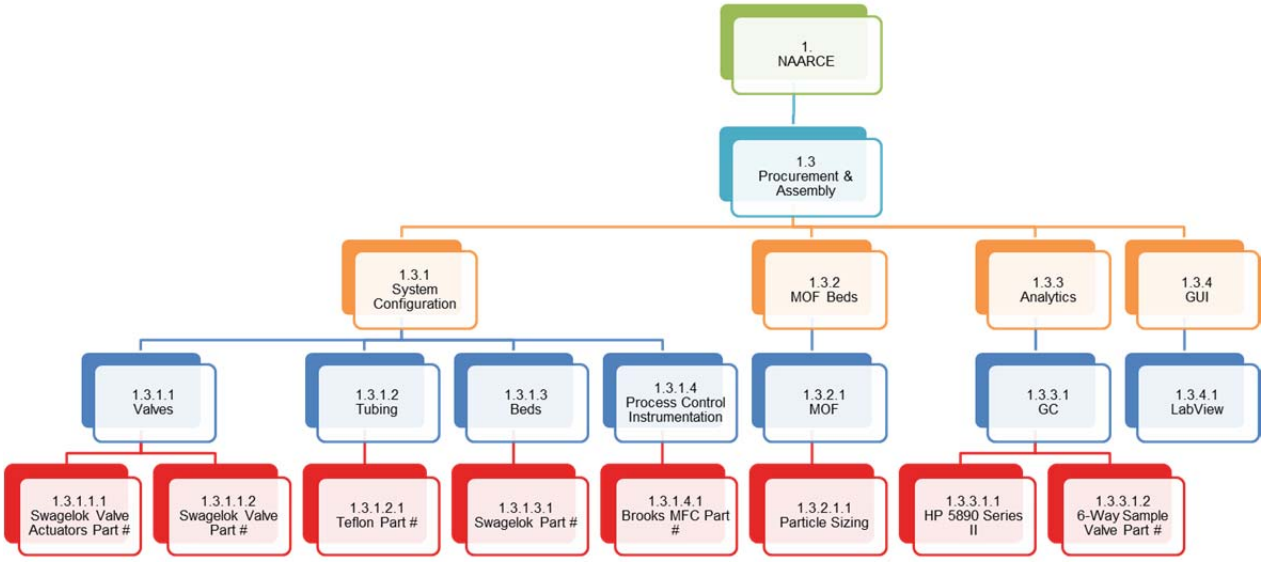

Figure 12. Displayed above is the third phase of the WBS from the SDR.

For the PDR, the Procurement and Assembly phase was further specified, as seen in Figure 13.

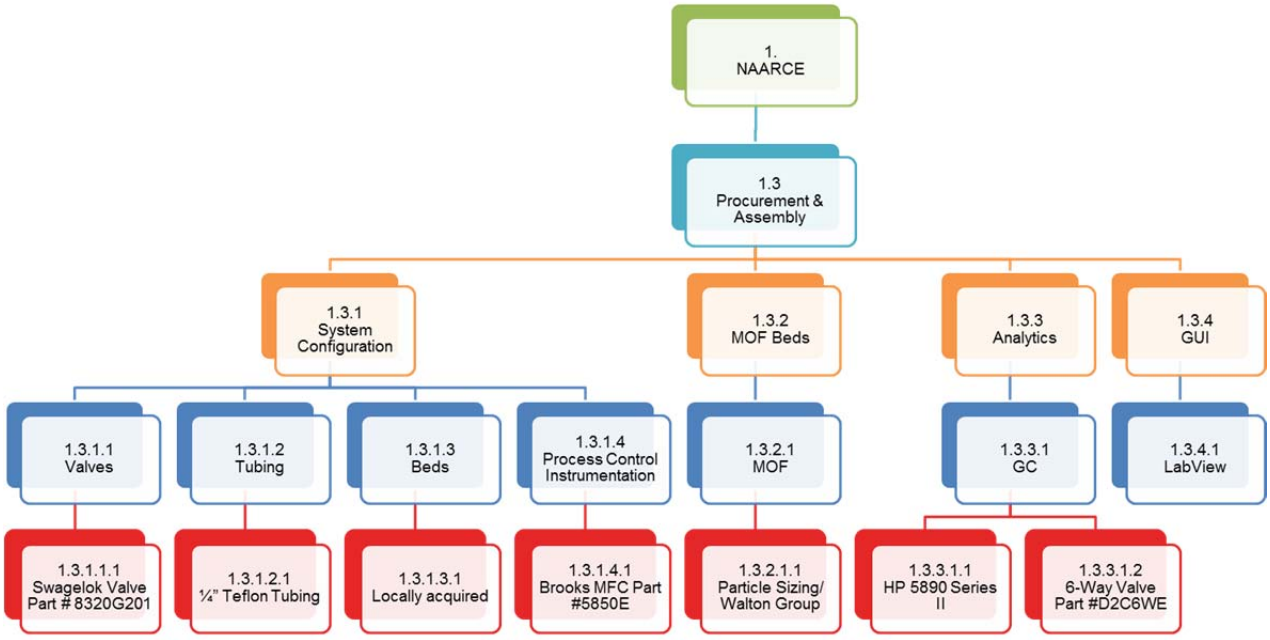

Figure 13. Shown above is the Procurement and Assembly WBS from the PDR.

After procurement and assembly of all materials and equipment, LabVIEW was programmed to coordinate valve actuations in proper sequence to allow for bed regeneration. Upon completion of this, the fourth phase of the project, Testing, began. The first set of deliverables under this phase is to calibrate the Horiba VIA-510 to report accurate values of carbon dioxide in the product stream. Carbon dioxide levels will be monitored in this way to provide efficiency information on the beds. The next and most important step within Testing is to research the system stability. Within this step, information must be collected regarding regeneration cycle count, water adsorption, energy requirements, and equilibration time requirements, which all have a drastic effect upon the long-term performance and life of the MOF. Lastly is testing for total product volume produced during the life of the MOF. Due to time constraints, the system stability and total product volume were not tested, but will be further examined in the future.

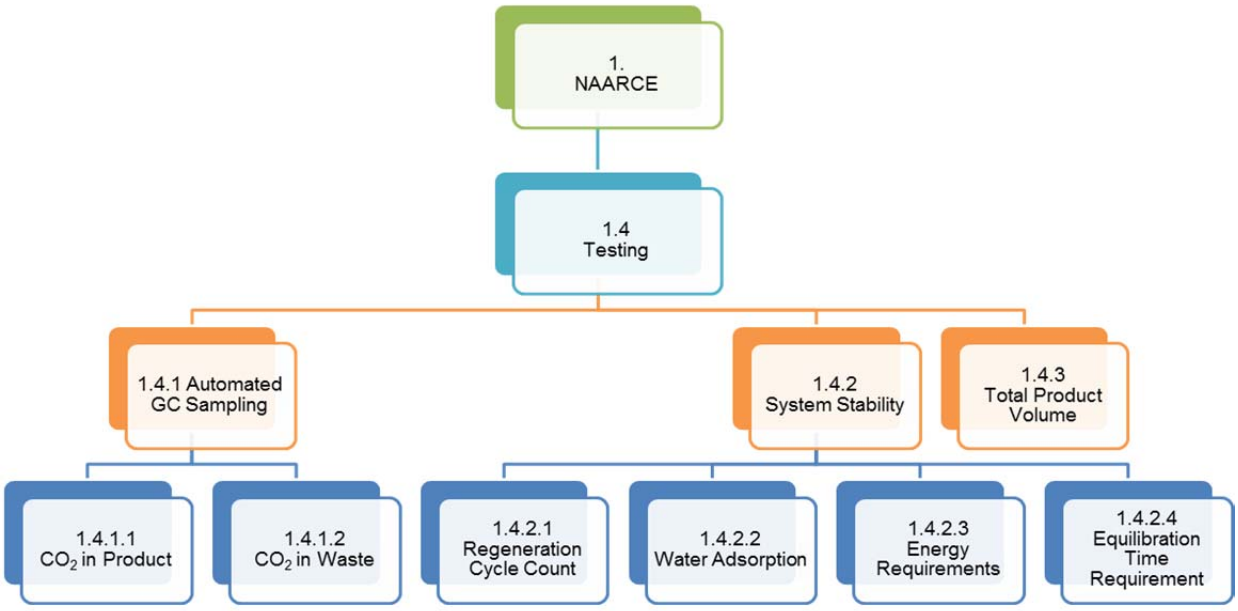

Figure 14. Shown above is the fourth phase of the WBS used in the SDR.

Figure 15. The diagram above shows the fourth phase of the WBS from the PDR.

The next phase of the project is to optimize the system, sub-phase 1.5. Here, special optimization effort must be allocated to maximize carbon dioxide adsorption, minimize water adsorption, and maximize efficiency of each cycle time. Maximizing cycle efficiency can be done by finding a balance between reduction of breakthrough time and maximization of product volume.

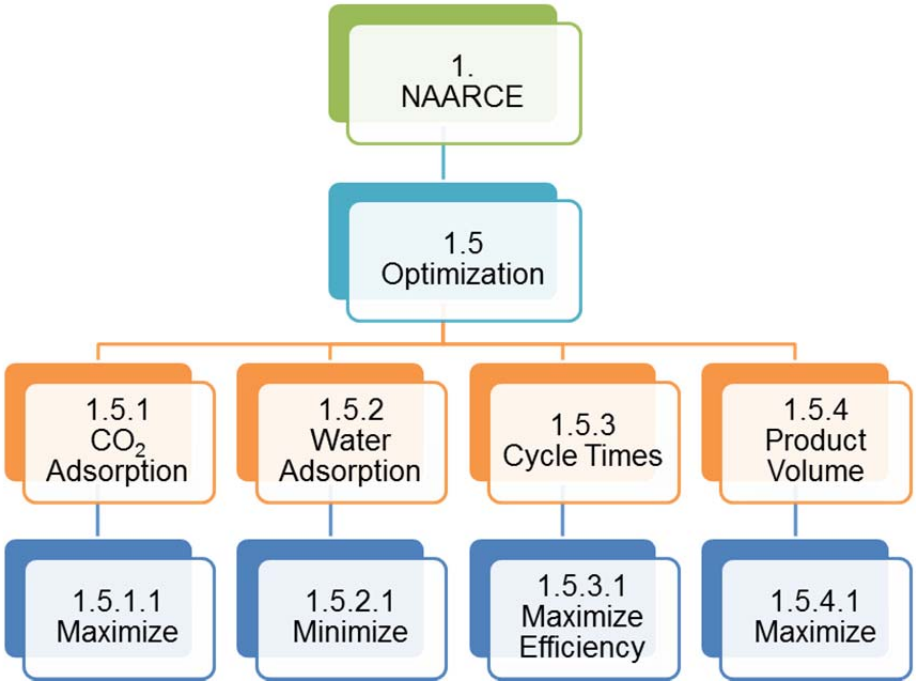

Figure 16. The fifth phase of the WBS is shown above.

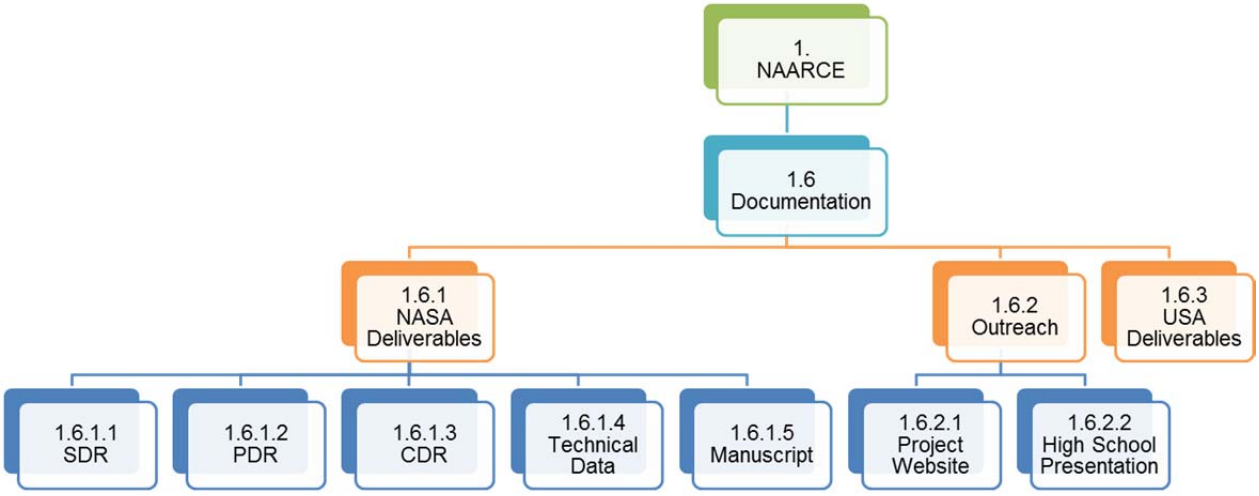

Figure 17. The sixth phase of the WBS is displayed above.

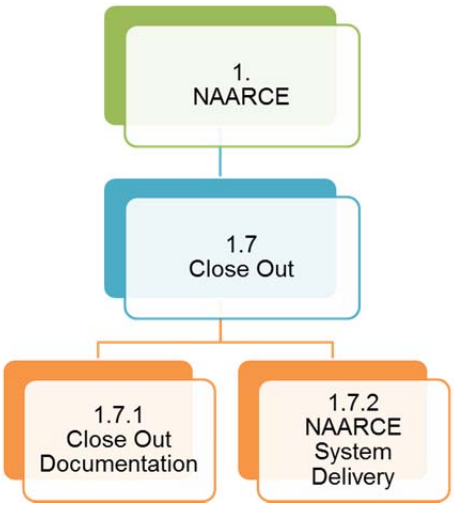

Figure 18. The last phase, phase 1.7, of the WBS is displayed above.

5.2. Risk Assessment and Mitigations

Risk Management combines both risk assessment and risk mitigation. Risk assessment is the planning for, and prioritization of, risk in a project. Risk mitigation involves the handling and monitoring of project risk. As shown in Figures 19 and 20, a risk was first listed, and then a numerical value from one to five was assigned, based on an agreed impact and likelihood of occurrence. Once these Impact and Likelihood values were established, the risks were plotted on the 5x5 Risk Cube (Figure 20) and assigned an overall rating, dependent upon their position in the cube. The priority was assigned as a final step as a visual clue

to help manage and maintain the importance of a particular risk. In the Risk Cube, the numbers shown in each compartment represent the number of the individual risk on the Risk Matrix, (i.e. number 1 is the "project goes over schedule" line item and corresponds with the "1" shown on the cube). This method of quantification allows for identification of risk that can have a small likelihood of occurrence, yet a high impact to the project so that such events can be avoided altogether, if the impact is high enough. If an event has a high likelihood and low impact, the prudent choice may be to avoid that as well to avoid unnecessary delays or problems.[10]

Impact	Likelihood	Overall	Risk	Priority
2	3	Low	1. Project goes over schedule	2
4	4	Low	2. System cannot deliver required volume	7
4	4	Low	3. Delay in Parts	8
2	3	Medium	4. Insufficient funding	1
3	4	Low	5. MOF delayed	6
4	3	Low	6. Large pressure drop across beds	4
2	5	Low	7. System Leak	5
3	3	Medium	8. Bed Procurement	3

Figure 19 Risk matrix produced and used to manage project risk

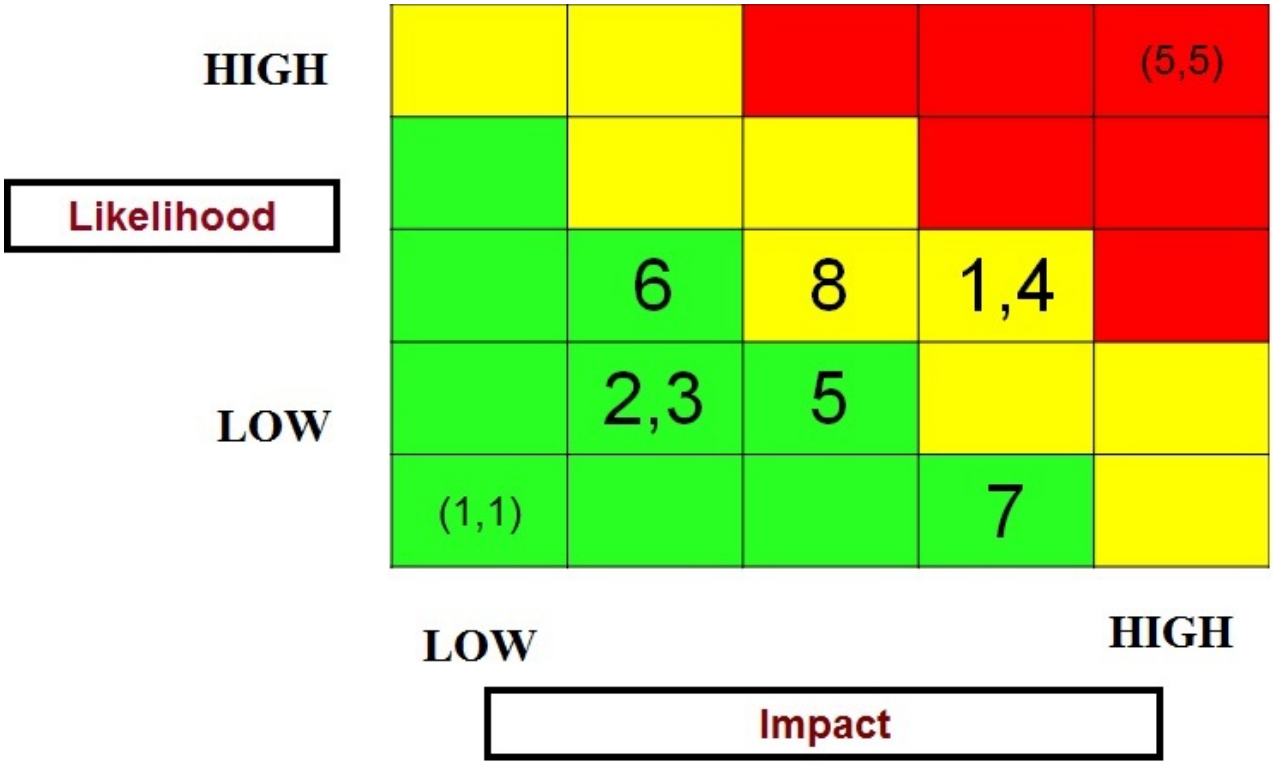

Figure 20. Shown above is the 5x5 Risk Cube.

5.3. Cost and Schedule Data

Cost and schedule constraints are integral in each project and must also be managed. Owners and stakeholders do not want to pay more for than necessary nor wait longer than necessary for equipment. As projects continue past the anticipated completion date, they can become more costly. By carefully managing the schedule and budget, the risks of the project going over-budget and beyond turnover can be successfully mitigated and managed. Figure 18 shows the Gantt Chart that was used to plan and schedule milestones for the project.

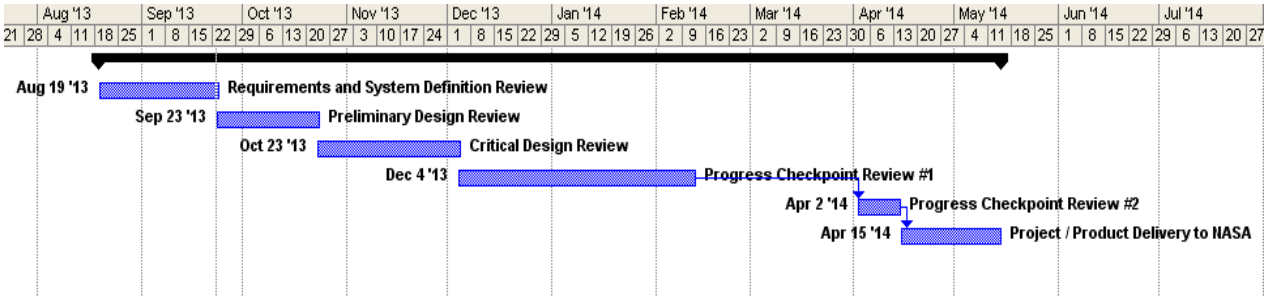

Figure 21. Displayed above is the NAARCE Gantt Chart for scheduling.

Update of Progress

At the time of the PDR production, the exact MOF bed design was being specified by Scott Sedlacek. The original design was a glass bed and jacket so that it would be more visually appealing. After much research, no commercial off the shelf (COTS) product could be located to meet this specification. The design then shifted to one in which 304 stainless steel would be used for bed and jacket construction. This was done in collaboration with Evonik Industries. The materials were purchased by the University of South Alabama, and Evonik Industries provided the fabrication labor and expertise. A detailed layout of the beds can be seen in Figure 22 and Figure 23. In this design, the bed was structured to allow for TSA. For this, an outer jacket composed of stainless steel was designed to encase the MOF beds and openings were cut to allow heat tracing to be run along the inner beds. With this configuration, heat tracing imparts energy to the beds, aiding in the desorption process, while water cools the beds back down to allow for adequate adsorption to take place.

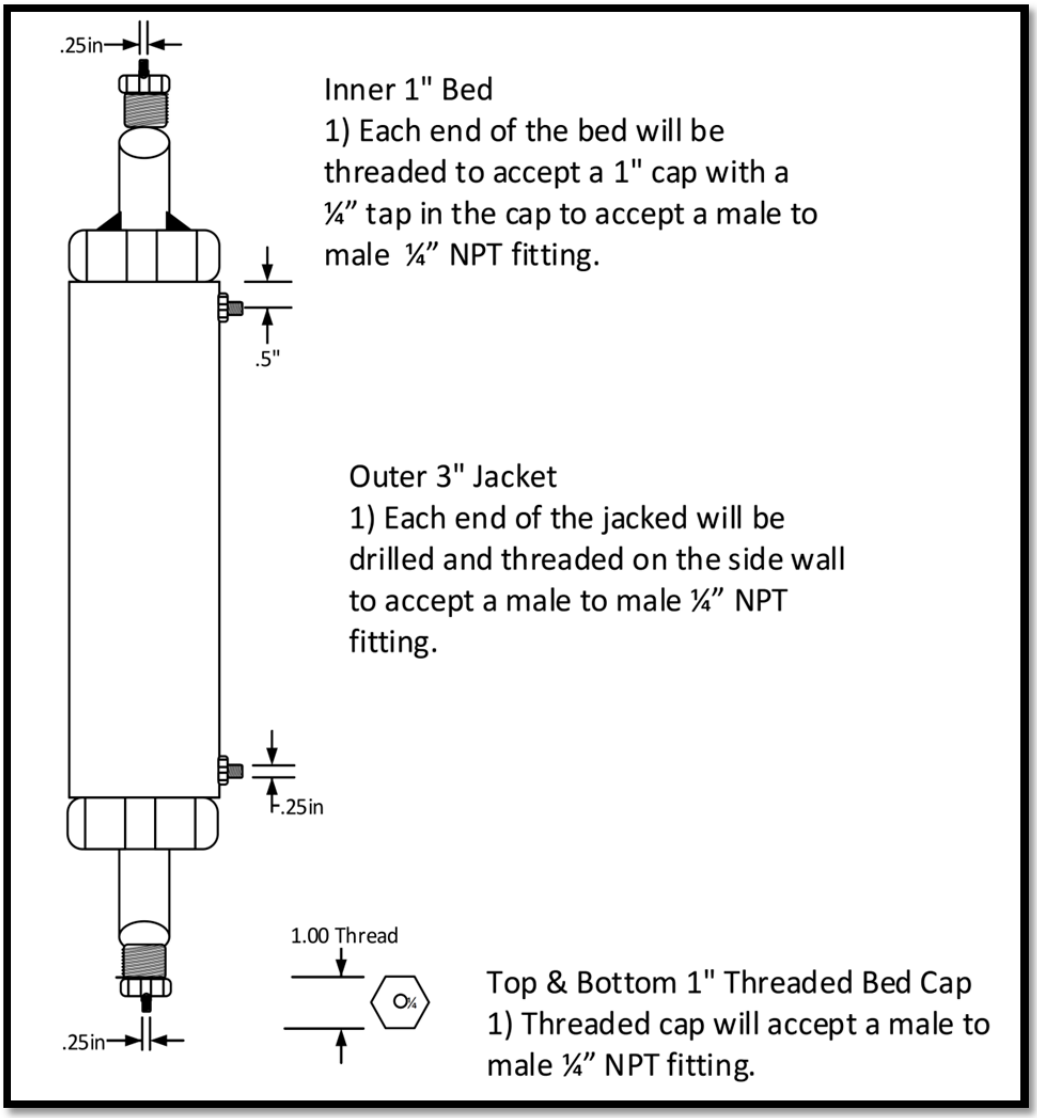

Figure 22. Shown above is a diagram specifying the design details of the MOF beds.

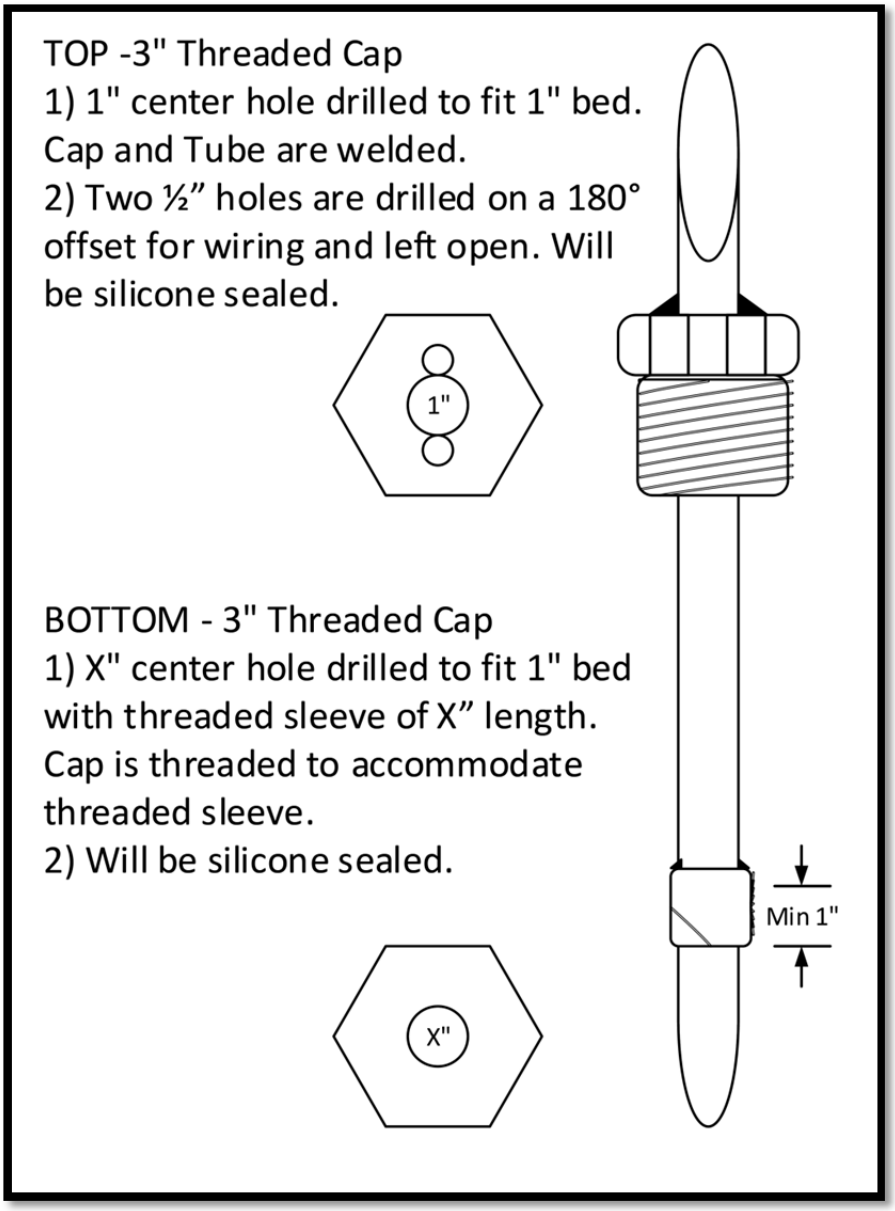

Figure 23. Shown above is a diagram with further details on the MOF bed fittings.

After presenting this design concept to fabricators at Evonik, the fabricators advised against the use of threaded caps to hold the MOF bed and outer TSA jacket in place due to the possibility of galling the threads. Consequently, the bed setup was reconfigured with bolted flanges and gaskets to secure the beds. **Error! Reference source not found.** and Figure 25 present the shop drawings produced by Evonik Industries and the Change Analysis or Management of Change.

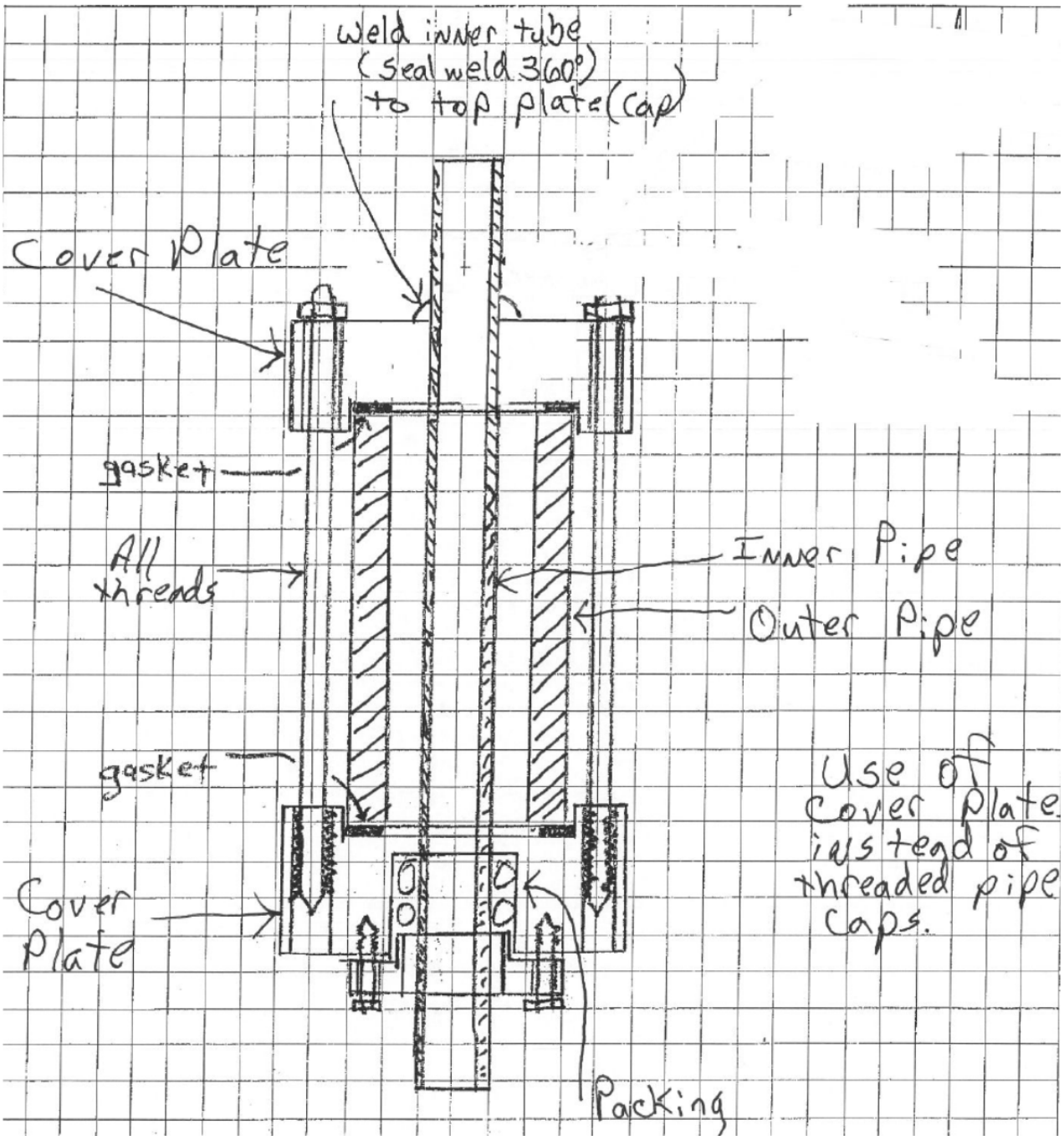

Figure 24. The drawing above shows shop drawings of proposed modifications to the adsorbent design.

Modifications- use of cover plates rather than threaded pipe caps	Pros	Neutral	Cons
Associated Cost		Cost would most likely be lower, or at worst, not increase. We will use surplus materials in shop and machining times are equal.	
Safety	Threaded pipe caps will be more difficult to seal than gaskets with end plates. Pipe threads traditionally develop small burrs and metal slivers from assy/disassy.		Use of cover flanges would increase weight. Assembled unit would still be manageable by one person.
Assemble/Maintain	Threaded pipe threads have a higher tendency to seize from assy/disassy. Centering of all components will be more precise. Extra gasket can easily/economically be provided.		Overall Diameter of assembled unit would increase from around 4" to 5". Overall length may shorten, but no more than 1" overall. All would still be centered

Figure 25. Shown above is the Management of Change applied to the changed bed design.

5.4 CDR (Critical Design Review)

The third Design Review, known as a Critical Design Review, occurred on February 3rd, 2014 and further built upon the previous two reviews.

5.4.1 Subsequent Alterations

Alterations due to time limitations

The heat tracing and water delivery to the MOF beds were abandoned due to time limitations. Because of the nature of the project and the ability for continued research, the heat tracing and water delivery were carried through the manufacturing phase, but were not connected to the system. Integration will occur at a later date.

Alterations due to Budget Limits

Unforeseen expenses were the cause of an additional alteration to the operation of the system. This was the case with the dry air supply, as repairs necessary to fix the nitrogen generator were outside the boundaries of the budget, and long term use of compressed nitrogen gas cylinders was not economically practical. As such, it was decided that testing would not involve running the system with dry air, and that ambient air mixed with carbon dioxide would comprise the feed to the system. The addition of a Horiba VIA-510, stand-alone carbon dioxide detector simplified the analytic portion of the project. The concern of water interference with the detection of CO_2 was alleviated when the detector was calibrated using dry gas cylinders and the same results were obtained when using an ambient air stream injected with bottled CO_2.

5.4.2 Procurement Issues

After the procurement phase of the WBS, delays in arrival of a few major pieces of equipment and materials resulted in setbacks to the final assembly. Because of time constraints, it was necessary to find ways to bypass some of these delays by using alternative equipment or modifying the system. This was the case with the primary vacuum pump, as delivery of the Edwards pump was delayed by several weeks. Consequently, a lower quality Fisher Scientific pump was chosen as a temporary substitute to allow for testing to be carried out. However, delays in procurement of the jacketed beds, as well as UiO-66, reduced the amount of time originally allocated for testing and optimization.

5.4.3 Construction and Interface Programming

The first steps in assembly involved constructing the cart and attaching the ¼ inch aluminum plate provided by Evonik along the back. Next, the approximate positions of the valves, mass flow controller, rotameters, and teflon tubing were determined. This was done by placing the valves, MFC and rotameters on the upper shelf of the cart and drawing lines representative of tubing in between them. Holes were then drilled into the shelf, the items were bolted into place, and the tubing was attached. It was determined that the pumps and control box would reside on the bottom shelf. Next, the MOF beds and outer jackets were assembled and the 75 micron MOF screens were installed. Both units were mounted onto the aluminum plate and tubing was connected. Once all equipment was mounted to the cart, a NEMA enclosure containing the microcontroller, relays, and terminal blocks for the system was constructed. LabVIEW was then programmed by Aaron Anderson to allow for automated control of valve actuation.

6. Experiments and Optimization

Delivery of UiO-66 was delayed by four weeks due to solvent contamination in the synthesis laboratory at Georgia Tech. As a consequence, experimentation using the novel MOF adsorbent had to be delayed, and data points were collected using zeolite.

7. Conclusions and Recommendations

A major hindrance in the progress of this project was caused by delays in equipment arrival. To account for this in future design projects, it is recommended that additional procurement time (if applicable) be factored into the schedule from the beginning. Assuming that procurement delays will occur should allow a more accurate timeline of deliverables to be formulated. Likely, this would result in equipment and materials being ordered as soon as possible so as to leave adequate time for assembly and testing.

Another oversight was the bed design. While the design was very well thought out and planned, the weight of the beds was not taken into account. Due to this, weight from mounting the beds was more than expected and caused a tipping hazard of the cart. If the weight of the beds were accounted for, the cart would have been more appropriately sized and/or the water jackets of the beds could have been manufactured from a lighter material, reducing the tendency of the cart to tip.

The synthesis of MOF UiO-66 was also taken for granted. The manufacturer received a batch of poor quality solvent, preventing prompt synthesis of the adsorbent. Although beyond the control of the project

administration, this was a set-back in the success of the project. During the planning phase of this project, this risk was identified and mitigated by the acquisition of a zeolite 13X as a preliminary solution to this problem.

Although problems surfaced that could have been avoided, the Systems Engineering approach helped to identify many problems before they were encountered so that plans could be made to work around them, without detrimental losses to the project. As mentioned above, the zeolite was acquired to mitigate the MOF delay. The front-end-heavy design phase prevented unnecessary spending of parts that were not needed. The various reviews that were performed before monies were spent were invaluable to help find errors and mistakes and to make sure that every component in the system was necessary and specified appropriately. The methodical line of reasoning used to make decisions and implement changes allows for continuous improvement of projects. This project is a success because of the lessons learned from the Systems Engineering approach.

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Novel Adsorbent Air Revitalization for Closed Environments

NAARCE

Team Members:

Trey Davis

Kimson Do

Rachel Sweat

Jeffrey Kalagian

Spencer Blindauer

Scott Sedlacek

NASA eXploration Habitat Academic Challenge

- NASA funded academic challenge
- Deep Space Habitat system development
- Teaches systems engineering used for NASA procurement
- NAARCE utilizes novel adsorbent
  - Provides fundamental research in field of gas adsorption

- Customer Needs
  - CO_2 removal system for inhabiting closed environments
  - $ budget from NASA NSGF grant
  - System reviews prior to procurement and construction
    - Systems Definition Review (SDR)
    - Preliminary Design Review (PDR)
    - Critical Design Review (CDR)

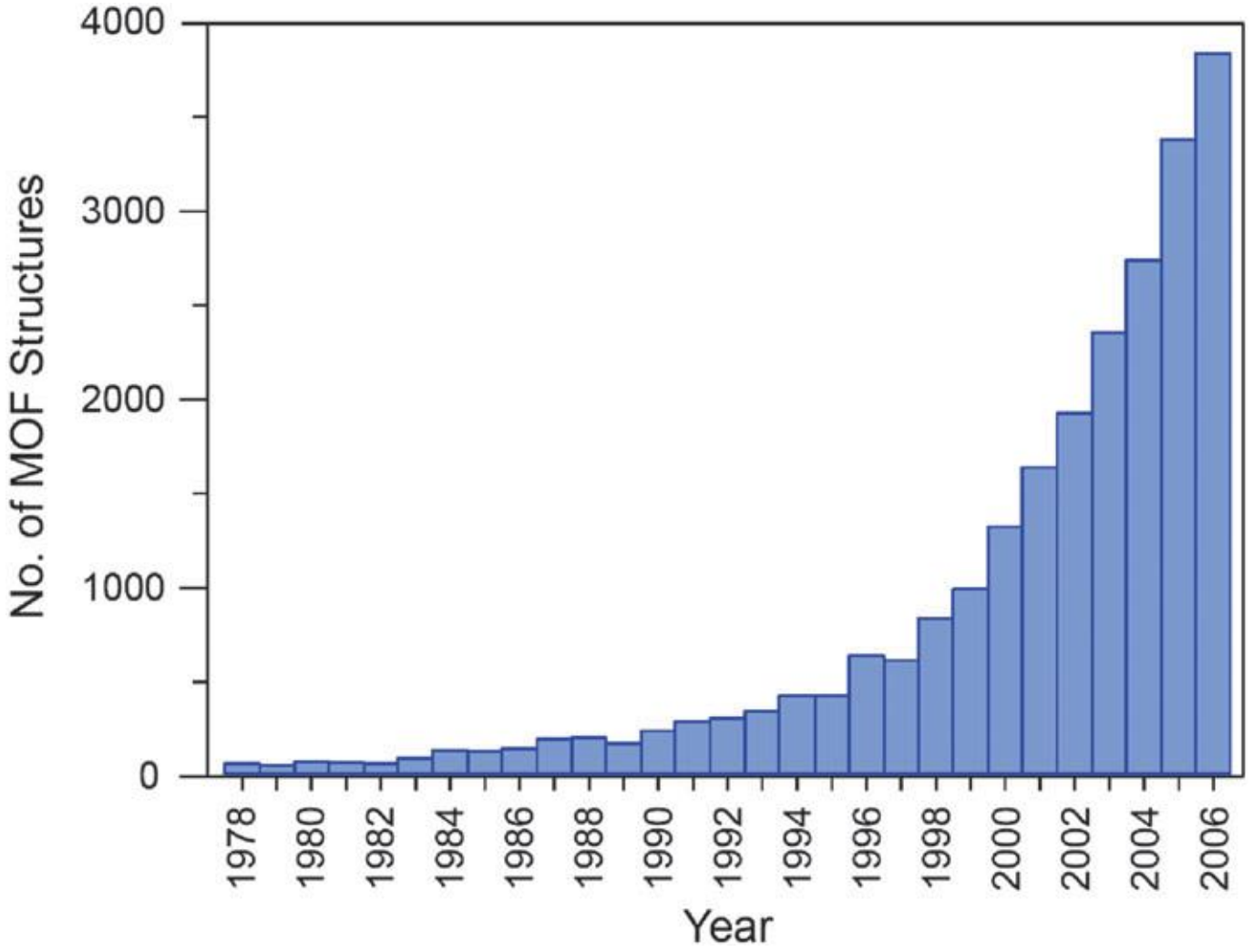
Current CO_2 Removal Technology

- Liquid Amine Scrubbing
  - Well-established method for CO_2 capture
  - Major health concerns with amines and degradation products could limit use in closed environments
- Zeolites
  - Resistant to damage from high pressures and temperatures
  - Strong selectivity for CO_2, water competitively adsorbs
  - 13X Zeolite acquired for contingency plan

Metal-Organic Frameworks

- 3D frameworks comprised of metal clusters connected by organic ligands
- Ligands are molecules that bond to a central metal atom or ion
- Gas adsorption processes benefit from high pore volumes in these MOFs
- Large-scale use limited due to low stability
- Thermal, chemical, and mechanical stabilities are weak

No. of New MOFs Created per Year

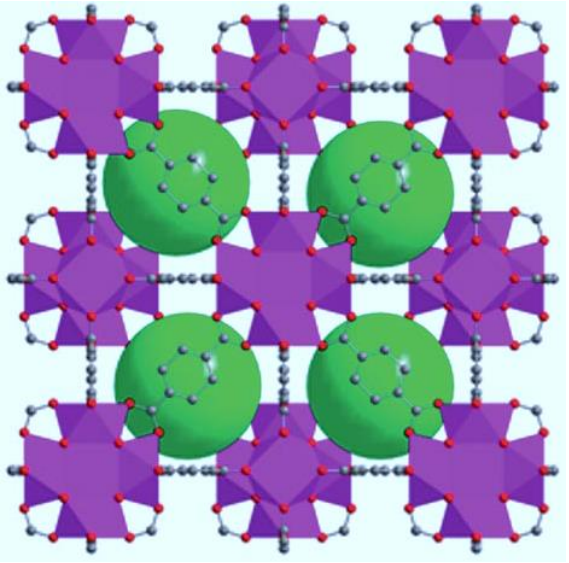


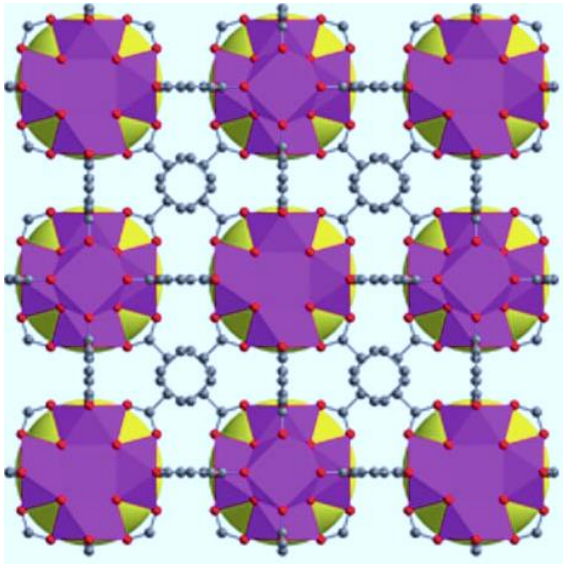
Long, J. R. & Yaghi, O. M. The pervasive chemistry of metal-organic frameworks. *Chem Soc Rev* **38,** 1213–1214 (2009).

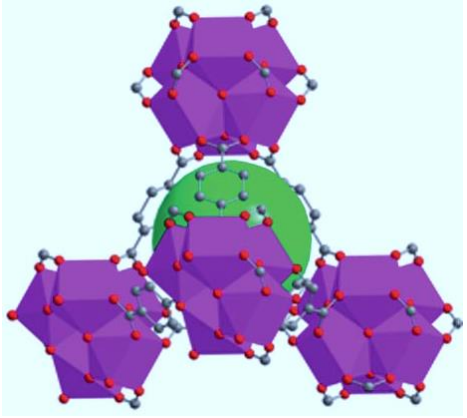
UiO-66 MOF

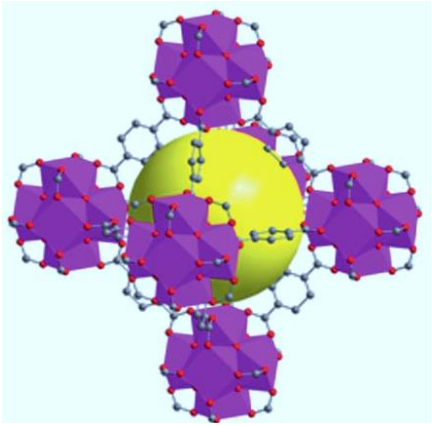
- More stability due to 12-fold connections between zirconium structures
- Shown to retain structure through adsorption and desorption cycles
- Has high water and thermal stability
- PXRD indicates little to no change in structure after exposure to water

UiO-66 Structure



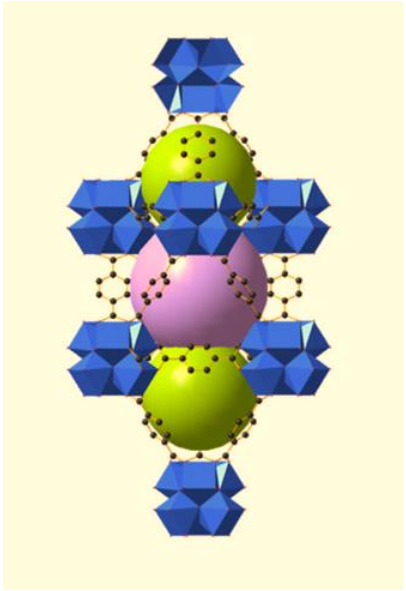






Metal clusters: $Zr_6O_4(OH)_4$

Ligands:
1,4-benzene-dicarboxylate



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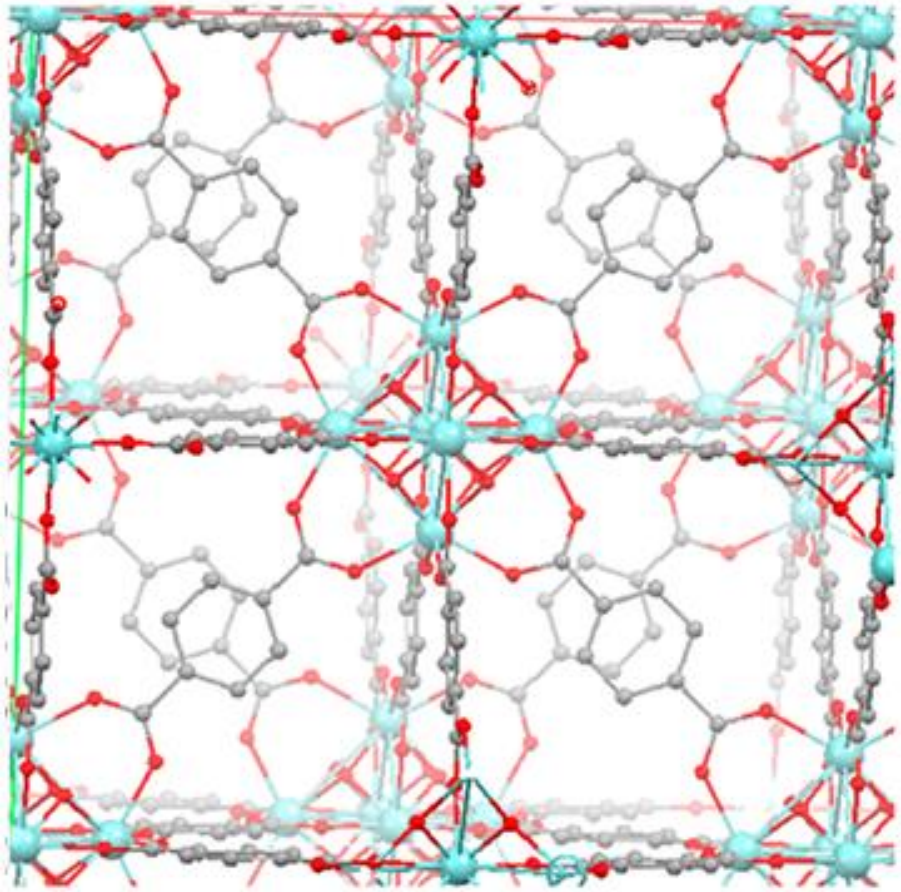
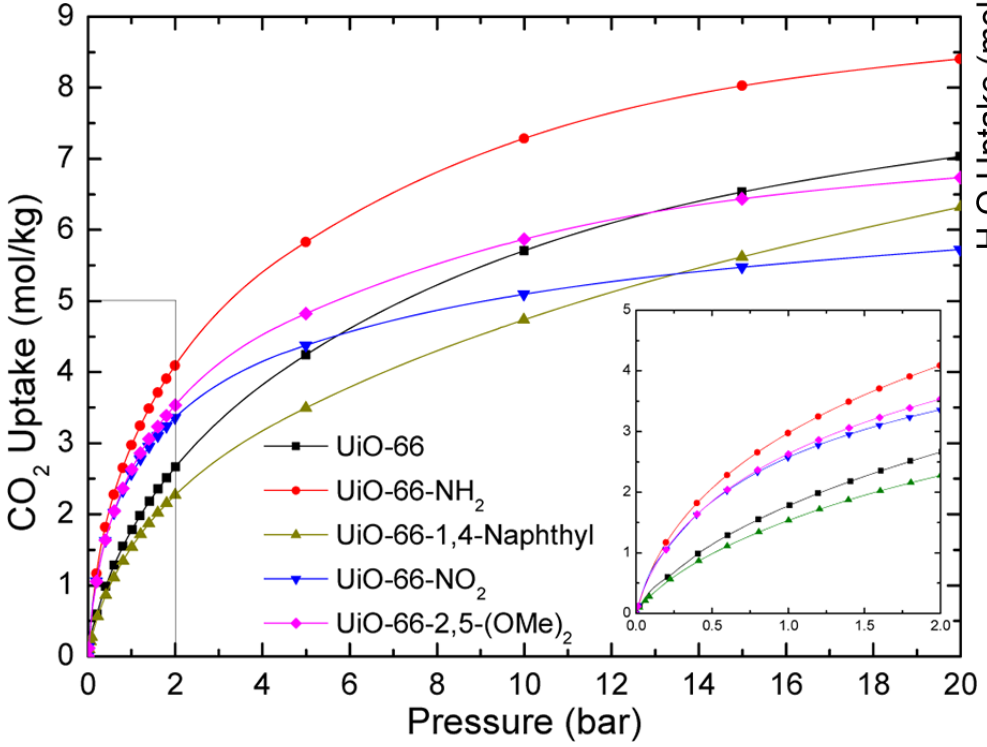
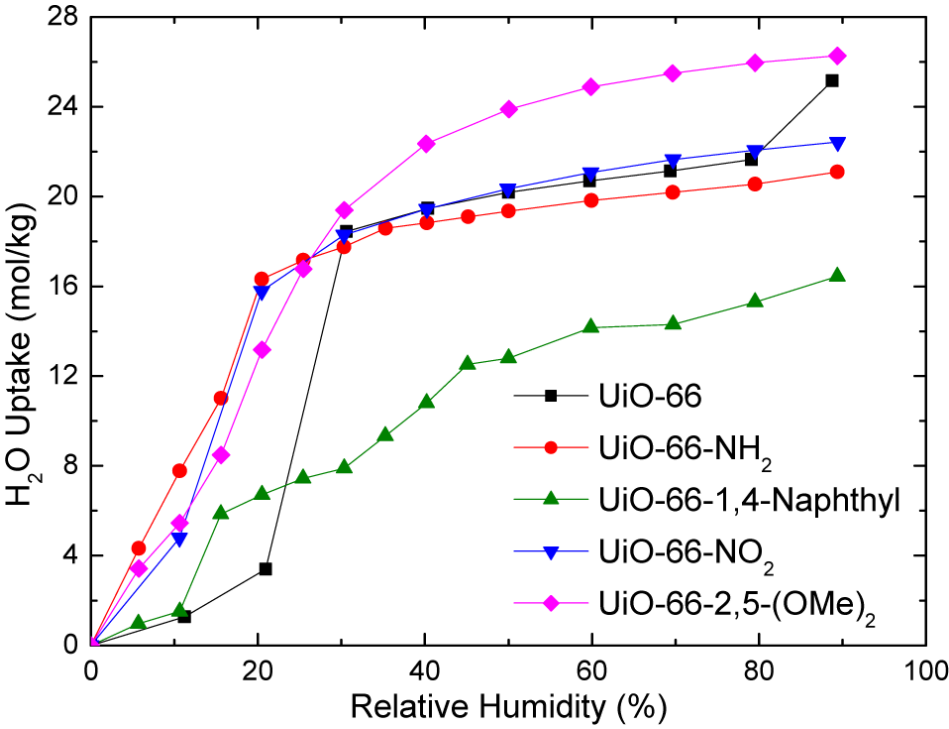
UiO-66 Structure



Cmarik, G. E., Kim, M., Cohen, S. M. & Walton, K. S. Tuning the Adsorption Properties of UiO-66 via Ligand Functionalization. *Langmuir* **28,** 15606–15613 (2012).

UiO-66 MOF Efficiency





Cmarik, G., Kim, M., Cohen, S. & Walton, K. Tuning the Adsorption Properties of UiO-66 via Ligand Functionalization. *Langmuir* **28,** 15606–15613 (2012).

Systems Engineering

Guide the engineering of complex systems [1]

1. Focused on the system as a whole
2. Lead the formative stage of a new system development
3. Bridges the traditional engineering disciplines

[1] Kossiakoff, Alexander; Sweet, W. N.; Seymour, S. J.; Biemer, S. M. In *Systems Engineering Principles and Practice,* 2nd Ed.; Sage, A. P. Ed.; Wiley Series in Systems Engineering and Management; John Wiley & Sons: Hoboken, NJ, 2010.

Application of Systems Engineering

- Customer Needs
  - CO_2 removal via Vacuum Swing Adsorption (VSA)
  - Systems Engineering exposure
- Initial design
  - 4 subsystems
    - Gas Delivery: piping, valves, gas cylinders
    - Analytics: CO_2 detection
    - Beds: adsorbent and adsorption beds
    - Automation and Instrumentation: software control system
  - Outside Assistance: AutoCAD, LabVIEW

System Modeling

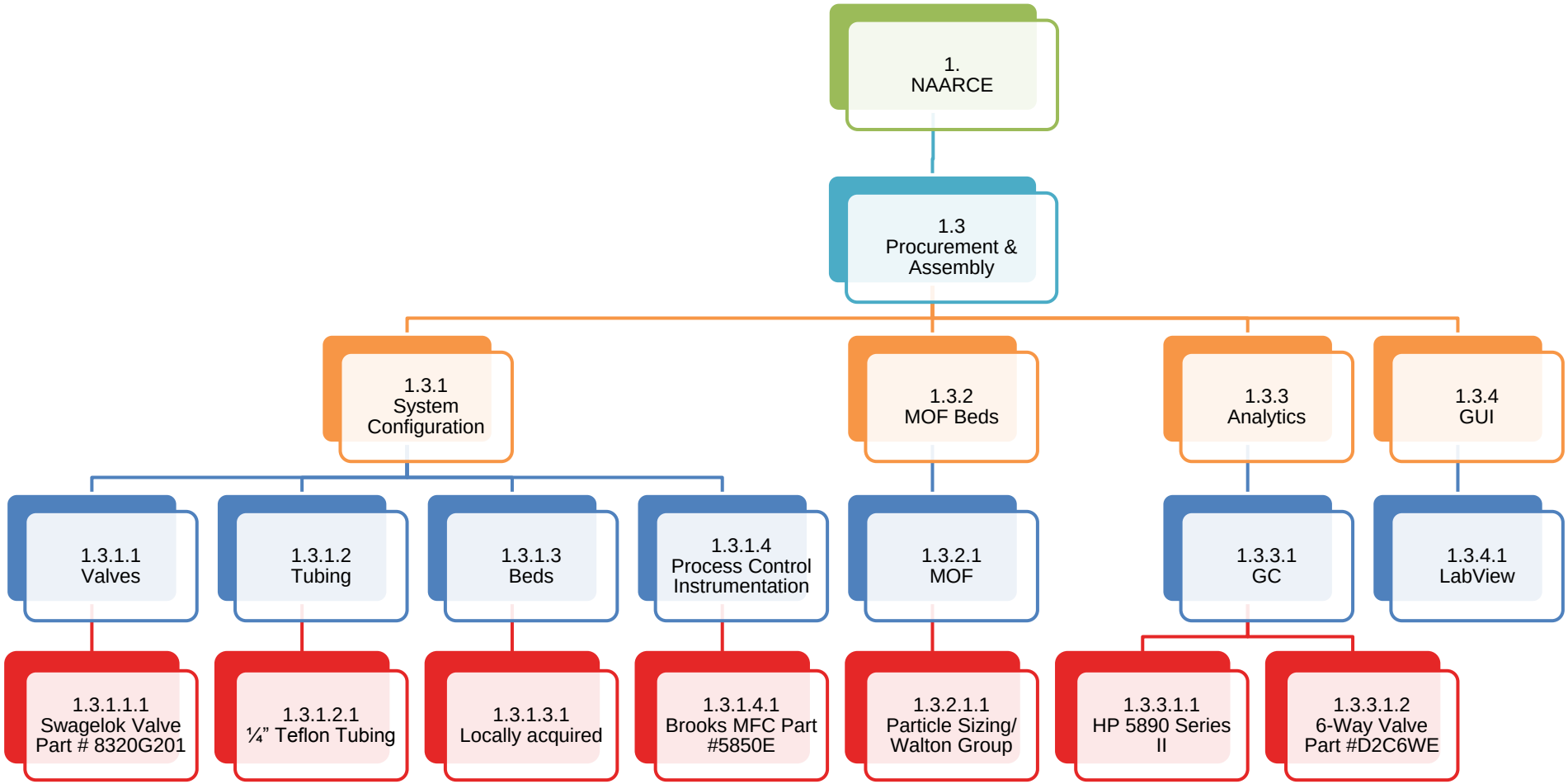
- CO_2 Set Point Mass Balance
  - 35 mL/min CO_2 flow for 5 L/min system flow = 0.7% CO_2
- Estimated Breakthrough Time
  - 0.26 pound zeolite/bed @ 1 mol/kg = 50 minute breakthrough time
- Partial Differential Equations
  - Adsorbed phase and fluid phase components
  - Need quantified mass transfer data
  - Quantified multi-component isotherm data for CO_2 and water
  - Solve series of PDE's numerically

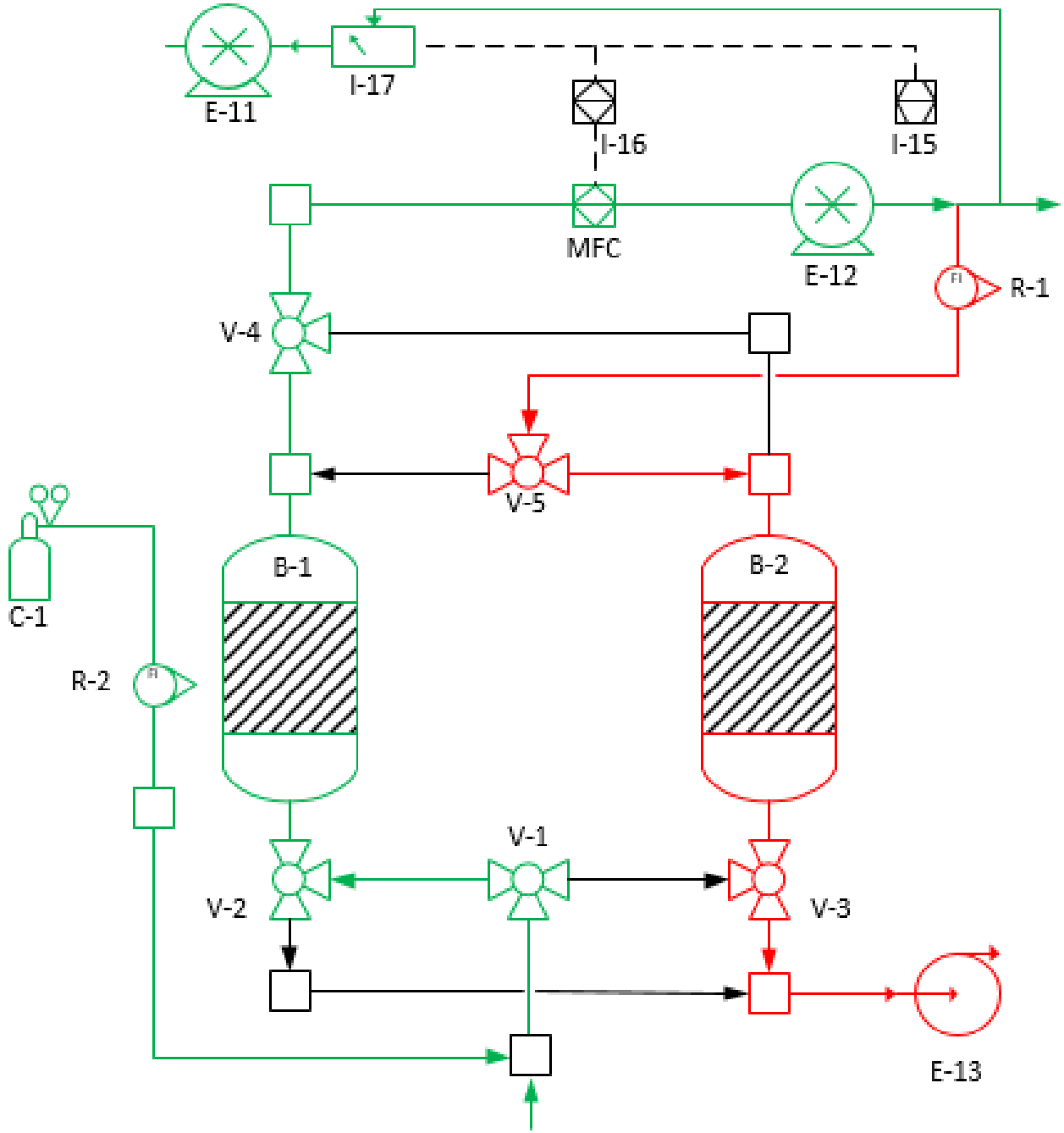
[1] Kossiakoff, Alexander; Sweet, W. N.; Seymour, S. J.; Biemer, S. M. In *Systems Engineering Principles and Practice,* 2nd Ed.; Sage, A. P. Ed.; Wiley Series in Systems Engineering and Management; John Wiley & Sons: Hoboken, NJ, 2010.

NAARCE System

- VSA / TSA System
  - Heating/Cooling System
- Two Bed Design
- Vacuum Regeneration Pump with Countercurrent Purge Stream
- CO_2 Analyzer Analytical System
- LabVIEW Controls and Interface

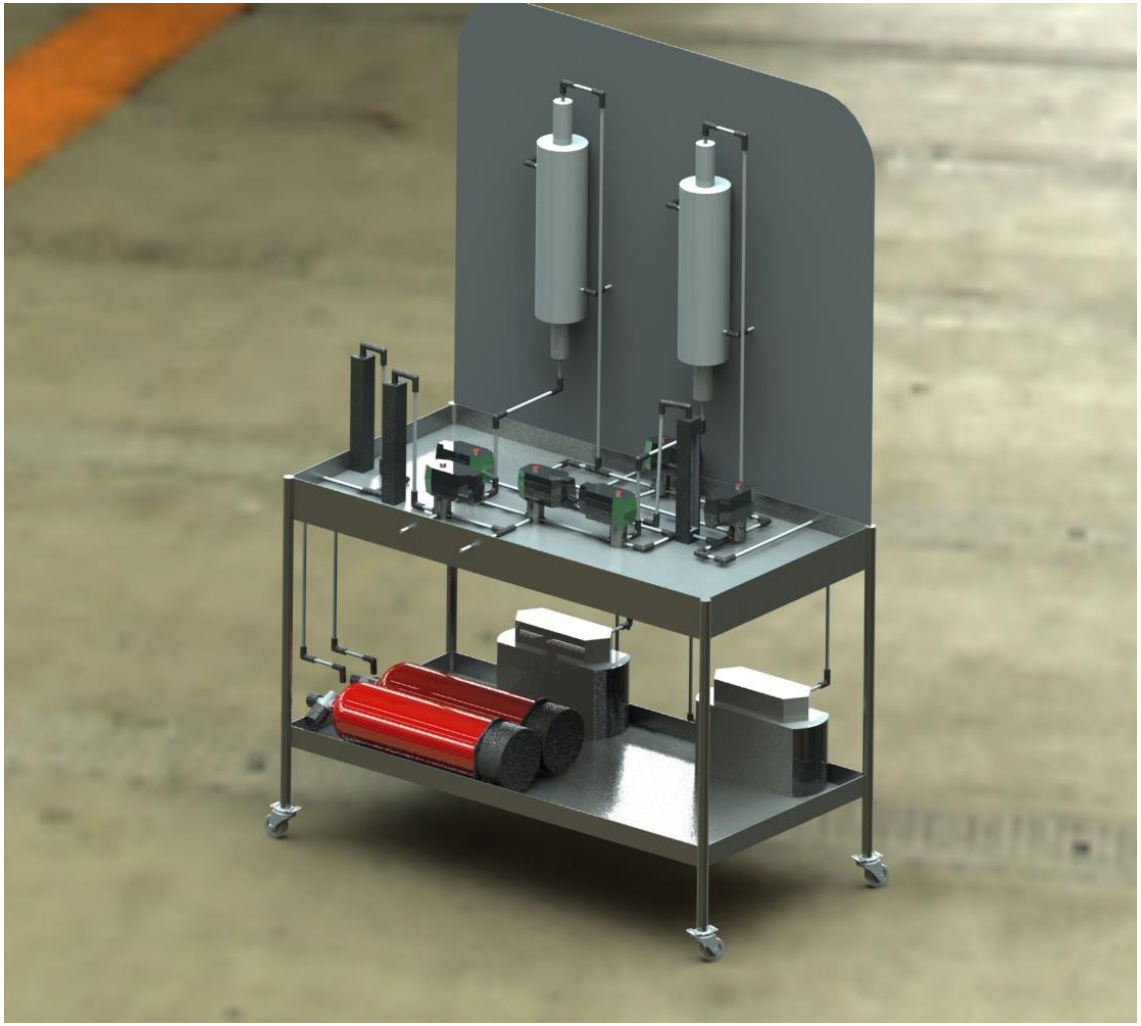
Work Breakdown Structure




E-11
I-17
I-16
I-15
MFC
E-12
R-1
V-4
V-5
B-1
B-2
C-1
R-2
V-1
V-2
V-3
E-13

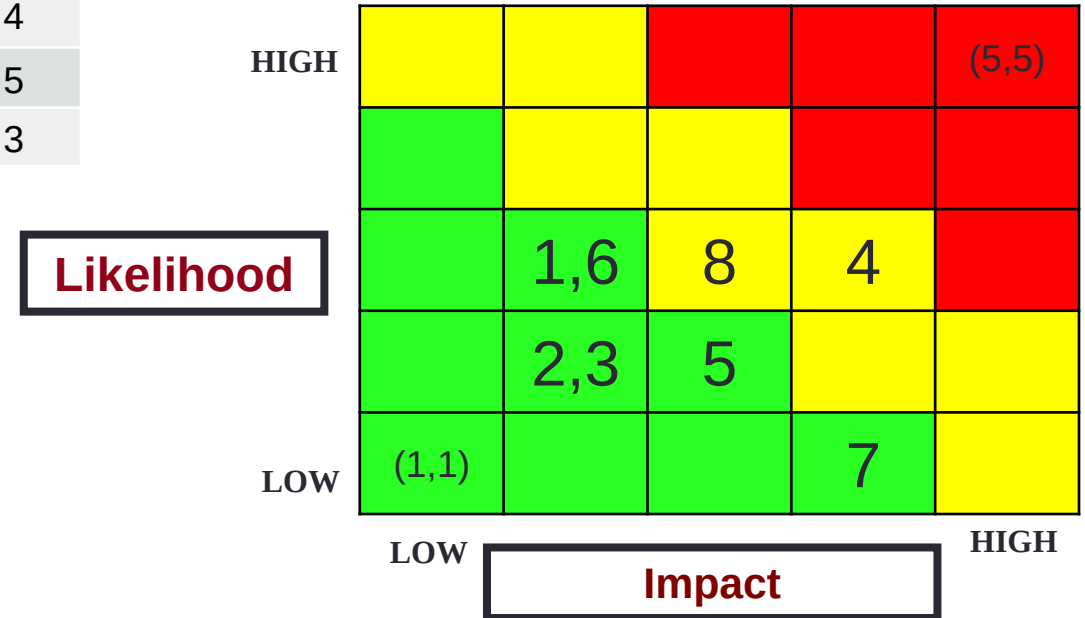
Ideal System Model

- CDR required AutoCAD drawing and design



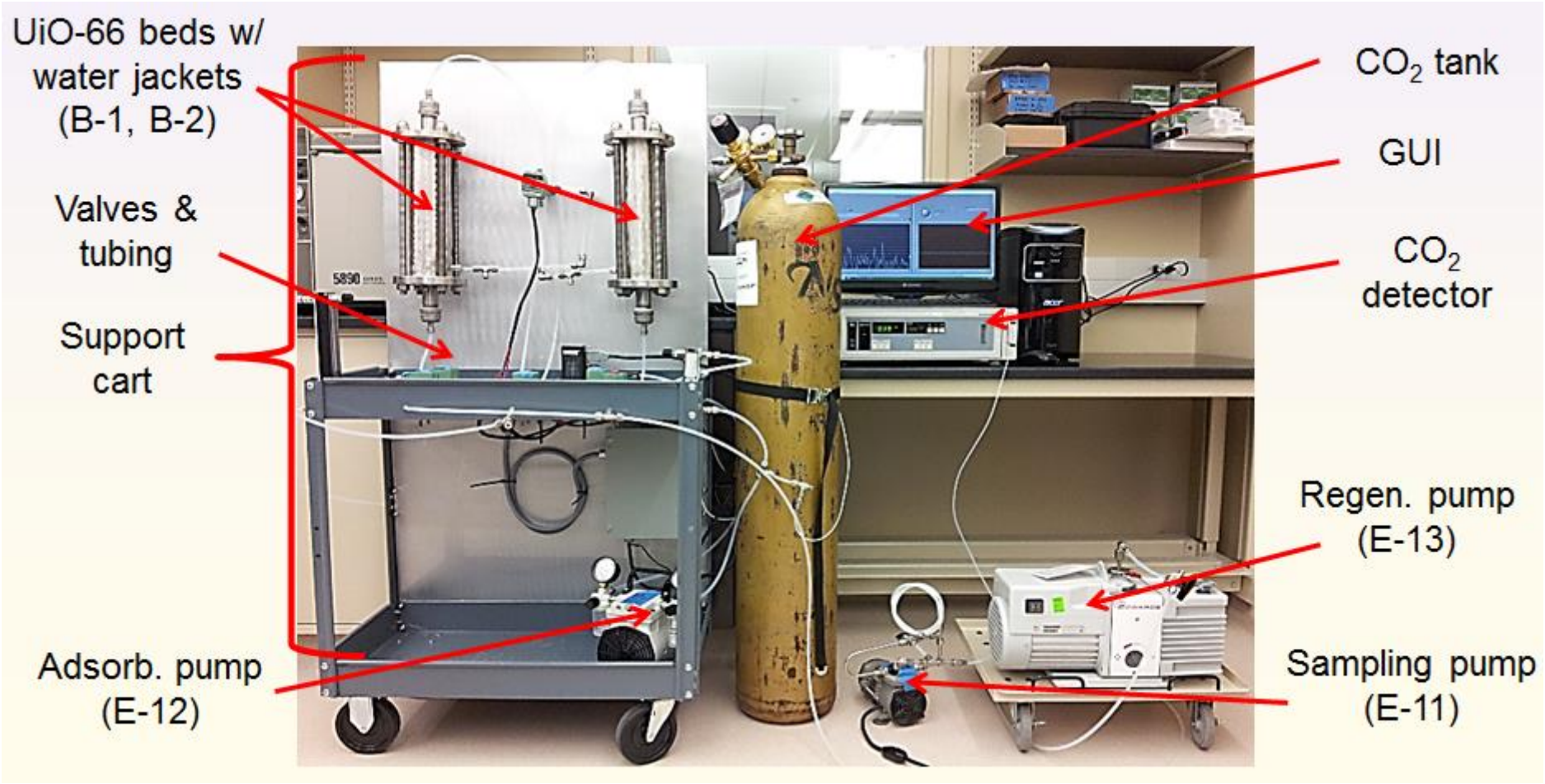
Risk Assessment

Risk	Priority
1. Project goes over schedule	2
2. System cannot deliver required volume	7
3. Delay in Parts	8
4. Insufficient funding	1
5. MOF delayed	6
6. Large pressure drop across beds	4
7. System Leak	5
8. Bed Procurement	3



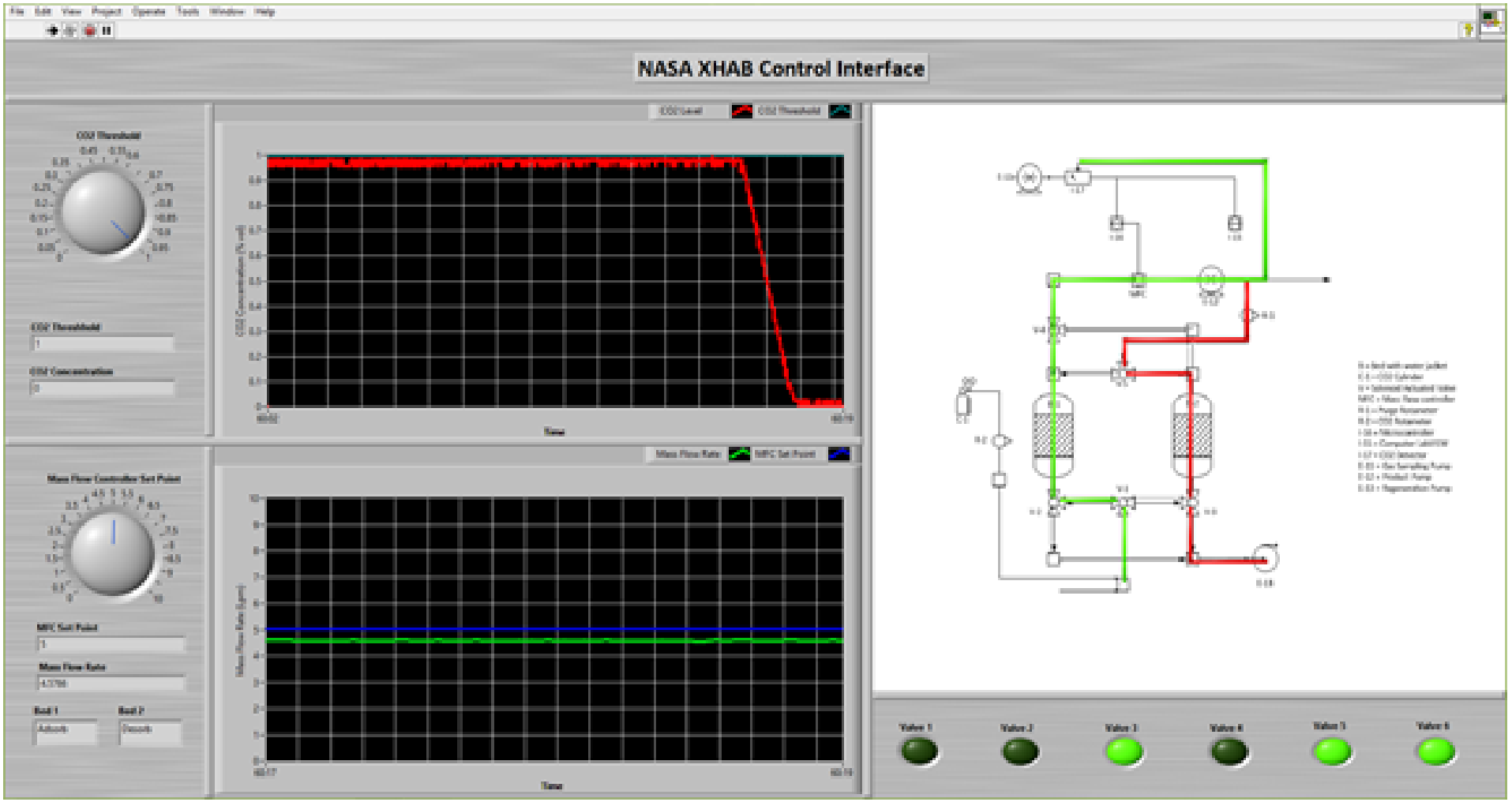
System Assembly

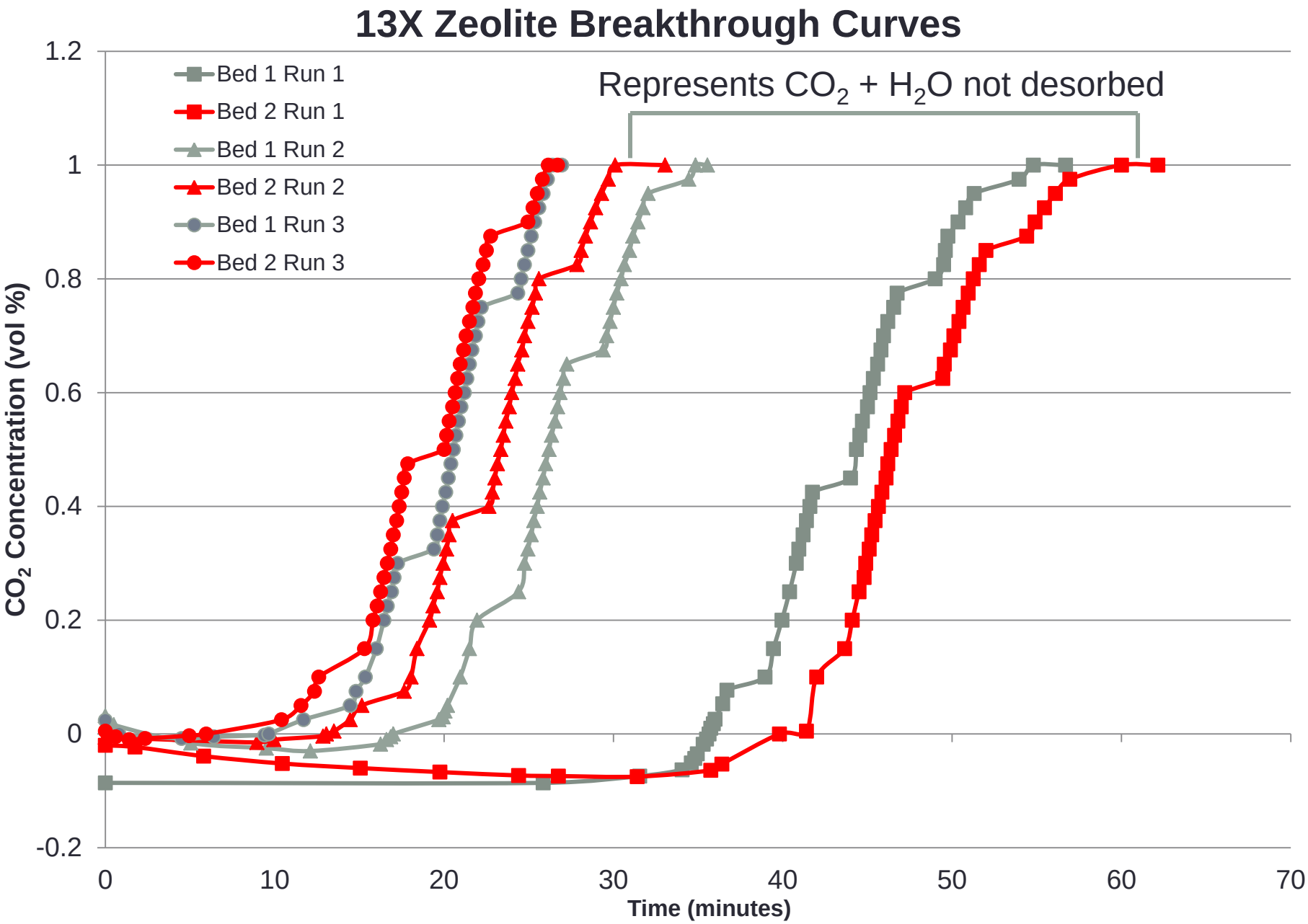
- Evonik Industries sponsored bed fabrication
  - Special thank you to Kerry Hill and Tim Harrison
- Mounted valves and connected tubing
- Mounted beds after fabrication
- Wired valves and controlling system
- Calibrated analytical system
- Pressure tested system and control ability


UiO-66 beds w/ water jackets (B-1, B-2)
Valves & tubing
Support cart
Adsorb. pump (E-12)
CO_2 tank
GUI
CO_2 detector
Regen. pump (E-13)
Sampling pump (E-11)

System Interface with User

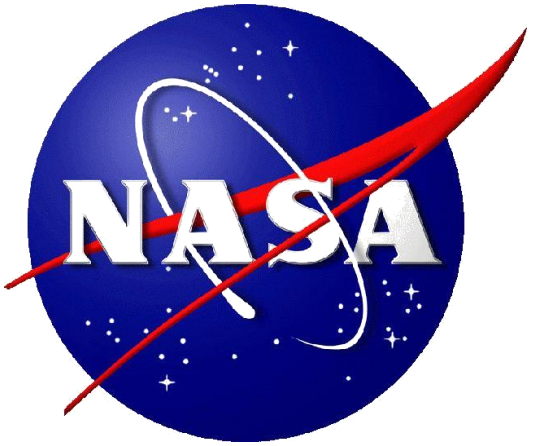
- LabVIEW used to automate system




13X Zeolite Breakthrough Curves
Represents CO_2 + H_2O not desorbed
Bed 1 Run 1
Bed 2 Run 1
Bed 1 Run 2
Bed 2 Run 2
Bed 1 Run 3
Bed 2 Run 3
CO_2 Concentration (vol %)
1.2
1
0.8
0.6
0.4
0.2
0
-0.2
0
10
20
30
40
50
60
70
Time (minutes)

Future Work and Lessons Learned

- System Optimization
- Perform MOF run in Summer / Fall of 2014
- Used for graduate thesis in coming semesters

- Project Delays / Oversights
  - Parts procurement
  - MOF synthesis
  - Load distribution of system

Acknowledgements