Creare

Innovative Technology and Product Development

March 10, 2021

U.S. Army Contracting Command
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Subject: Final Report
Contract No. W911QY-20-P-0277

Dear Ms. McGraw:

Enclosed is the Final Report for the above-referenced SBIR Phase I project titled "Compact, Low-Power Water Harvester."

Please contact me (603-640-2405; mgizenson@creare.com) if you have any questions.

Sincerely,

Michael G. Izenson
Principal Investigator

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Submitted by email

Final Report (Data Item B001)

COMPACT, LOW-POWER WATER HARVESTER

SBIR Phase I Contract No. W911QY-20-P-0277
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14. ABSTRACT
Creare is developing a compact, lightweight system for extracting water vapor from the atmosphere and producing high-quality drinking water. Our microchannel water extractor (MWX) system uses Creare's innovative, additive manufacturing techniques and high-capacity MOF sorbents to build an extremely compact heat and mass exchanger for efficient sorption of water vapor from air. We proved feasibility in Phase I by demonstrating MOF coatings that integrate with compact heat & mass exchange structures; measuring the cyclic sorption capacity of the coatings; and producing a concept design for an atmospheric water extraction system. In the Option phase, we plan to demonstrate production of potable water compliant with TBMED-577.

15. SUBJECT TERMS
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1 INTRODUCTION

1.1 BACKGROUND

Warfighters require over three gallons of drinking water per day for sustainment. Reducing the logistical burden of supplying this water is a priority for the Army. To meet this need, Creare is developing a compact, efficient device that will enable individual warfighters to produce drinking water by harvesting it from ambient humidity. Our Microchannel Water Extractor (MWX) is an innovative device that promises breakthrough performance by combining three innovative technologies:

1. Creare's proven technology for low-cost fabrication of microchannel heat and mass exchangers using proprietary hybrid additive manufacturing (HAM) technology (Figure 1). This technology has been well established for use in compact heat exchangers and will provide an excellent basis for a compact sorbent bed based on water sorption in nanocrystal metal-oxide framework (MOF) materials.
2. RTI International's innovative, high-volume MOF materials (Figure 2). These high-performance sorbent materials and RTI's fabrication methods are well suited to provide thin coatings of MOF sorbent on the microchannel surfaces.
3. A rapid-cycle, dual-bed sorption system that efficiently uses heat generated by a small combustor to drive water sorption/desorption from two beds operating 180° out of phase.

Preliminary sizing calculations show that the MWX sorbent beds should be extremely compact and lightweight (< 2 kg total mass of sorbent beds) and efficient (about 50 g fuel per kg of water produced).

Figure 1. Microchannel Heat Exchanger Produced Using Creare's HAM Technology. Highly uniform array of microchannels enable high surface area density. Efficient coupling of MOF sorbents with process streams yields very rapid kinetics. Module in photo is 9 in. long.

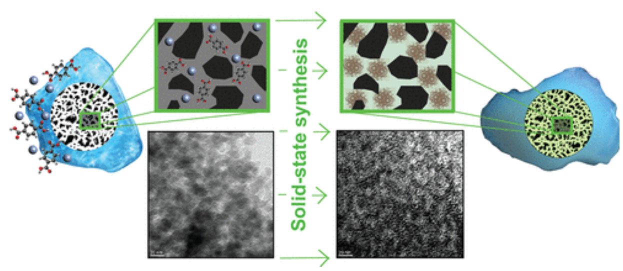


Figure 2. Nanocrystalline MOF Materials Produced by RTI. The MOF is well dispersed within mesoporous materials via novel "solid-state" synthesis. The mesoporous supports can be produced in thin layers on HXA surfaces.

1.2 SCOPE

In Phase I, we are demonstrating MOF coating and fabrication methods for microchannel sorbent beds, measuring cyclic water sorption performance, and producing a concept design and performance estimates for the MWX system. In the Option phase, we will test the water produced by the MOF sorbent for compliance with TBMED-577, formulate a detailed analysis and produce a final thermal/fluid design of the microchannel sorbent bed, select the main components in the MWX system, and produce a system layout design.

1.3 RESULTS TO DATE

Testing and evaluation of sorbent performance demonstrates the feasibility of developing a microchannel water extractor that meets the Army's requirements. Key results from Phase I are as follows:

1. *MOF coating development*. RTI developed methods to apply thin (100 µm) coatings of MOF-801 material to metal plates. The coatings use a thermo-curing polymer binder and a thin, acrylic protective layer. These coatings comprised approximately 50% MOF and 50% binder and demonstrated excellent adhesion to MWX sample components provided by Creare.
2. *MOF-coated samples for sorption testing*: RTI coated several flat plate samples provided by Creare. These plates were relatively thick and designed for use in the Phase I sorption test rig.
3. *MOF-coated samples for MWX demonstration*: Creare produced a set of thin-foil sample plates with features that are prototypical for the MWX water sorption cores. We sent these plates to RTI, where they were coated with RTI's final MOF formulation.
4. *MWX fabrication trials*: We tested the suitability of the coated sample plates for assembly by HAM. These fabrication trials showed that the MWX assembly process is compatible with the MOF coatings, and that the MOF coatings have no significant effect on the coatings or their adhesion to the plates.
5. *Sorption test rig*: We built a small test rig that enabled us to measure the water scavenging performance of RTI's MOF coating formulation in the MWX configuration. The rig enables us to measure water sorption and desorption from a coated plate under well-controlled experimental conditions.
6. *Sorption performance*: We completed measurements of the water scavenging performance of the sorption test sample prepared by RTI. The test rig clearly demonstrates the ability of the MOF-coated MWX to adsorb water from ambient moisture at low temperature and then desorb water when heated to moderate temperatures (nominally 90°C). We demonstrated operation consistent with a water production rate of 86 mg/s per m^2 of coating.
7. *System concept design*: We have updated our system concept design based on the results of the Phase I tests. Although the water scavenging performance measured in our proof-of-concept tests is not yet optimized and is smaller than our projections, we still believe that the system will meet the Army's requirements if we appropriately modify the system design and operating parameters. Our current design concept will produce 14 L of water per day and have a total system mass of 5.4 kg (11.9 lb_m).

1.4 NEED FOR A COMPACT WATER HARVESTER

Water harvesting technology must overcome considerable technical challenges before a compact device will be attractive for use in the field. Existing sorption technology is too inefficient to enable a compact system that meets the Army's requirements.

1.4.1 Technical Challenges

Warfighters need a great deal of drinking water—over three gallons (roughly 30 lb_m) per day for sustainment. Carrying this much water on extended patrols or sorties is a significant burden. A small device that can harvest water from the atmosphere and produce drinking water would be a significant benefit. However, state-of-the-art technology for water extraction faces significant challenges.

One problem is that water vapor in the atmosphere has a very low concentration, particularly in cooler environments. Under the conditions specified in Topic A20-062 (20°F to 125°F, 40% RH), the absolute humidity can range from 35 g H_2O/kg dry air at high temperature to only 0.86 g H_2O/kg of dry air at the lowest temperature. As a result, the quantity of air that must be harvested to meet sustainment requirement varies tremendously depending on ambient conditions. Figure 3 shows the volume of air corresponding to the topic requirement of 14 L per day. While these volumes are manageable for higher temperatures (747 m3 at 100°F/40% RH), the volumes are enormous at the low end of the operating range (12,300 m3 at 20°F/40% RH). As a result, the device will require large throughput of air to meet requirements under all conditions, and high mass transfer efficiency is essential.

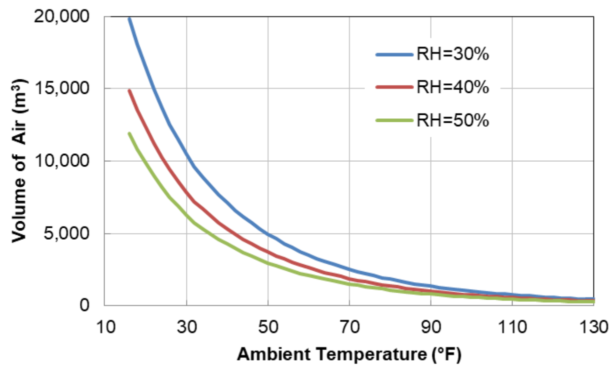


Figure 3. Volume of Air That Contains Enough Water Vapor to Meet Daily Sustainment Requirement for an Individual Warfighter.

Secondly, sorption and desorption of water are energy intensive. A sorption bed releases energy during sorption (roughly equivalent to water's heat of condensation) and requires the same amount of heat addition during desorption. The heat transfer needed to maintain stable temperatures during these parts of the cycle must occur as efficiently as the mass transfer of water vapor into and out from the sorbent material. To enable rapid cycling, the sorbent bed must be assembled with features that enable extremely effective heat and mass transfer. State-of-the-art systems are based on relatively crude sorbent supports and large flow channels, both of which limit the rates of heat and mass transfer. This increases the time needed to cycle the bed and implies the need for larger beds to meet the Army's water production requirement.

1.4.2 Requirements

The basic requirements for the water harvester were detailed in Topic A20-012 and listed in Table 1. In addition to these quantitative requirements, the design must be intrinsically safe (possess anti-microbial features, capable of being sanitized and/or disposable) and provide hygienic functionality and convenience.

Table 1. Requirements for Water Harvester		
Water production rate	L/day	14
Ambient relative humidity		40%
Max fuel consumption	kg/day	0.5
System weight	lb_m	< 20
Operating temperature range	°F	25 to 125
Production cost	$	< 100

1.4.3 State of the Art

Existing technology cannot meet the Army's goals because cycle time is too slow, sorbent materials cannot be integrated with compact and efficient sorbent bed structures, and power consumption is high due to inefficient design of balance-of-plant subsystems.

Atmospheric water extraction is moving away from traditional dehumidification techniques such as fog harvesting and direct condensation (which are prohibitively expensive outside of humid environments) and toward novel application of sorbent materials.[1] Researchers have demonstrated feasibility of water harvesting by using a temperature swing bed approach, exposing air at different conditions (ranging from controlled laboratory settings to desert environments) to beds of sorbent material at low temperature, allowing the material to saturate with water, then heating the bed to release trapped water.[2,3] Although functional for atmospheric water extraction, most sorbent-based approaches today struggle to exceed ~1 liter of water per kilogram of sorbent per day, significantly less than that required for the technology to trade well against alternatives. Key limitations in existing approaches include the following:

- Adsorption/desorption cycle times on the order of several hours, driven by kinetics and dictated by sorbent bed geometry.
- Sorbent materials structured as pellets or powder, which are difficult to integrate efficiently into heat exchangers.
- High power consumption due to inefficient design of supporting systems for heat and mass transfer.

[1] Tu, Y., Wang, R., Zhang, Y. and Wang, J., "Progress and Expectation of Atmospheric Water Harvesting," *Joule*, Vol. 2, No. 8, 2018, pp. 1452–1475.
[2] Kim, H., Rao, S.R., Kapustin, E. A., Zhao, L., Yang, S., Yaghi, O. M. and Wang, E. N., "Adsorption-Based Atmospheric Water Harvesting Device for Arid Climates," *Nature Communications*, Vol. 9, No. 1, 2018, pp. 1–8.
[3] Hanikel, N., Prevot, M. S., Fathieh, F., Kapustin, E. A., Lyu, H., Wang, H., Diercks, N. J., Grant Glover, T. and Yaghi, O. M., "Rapid Cycling and Exceptional Yield in a Metal-Organic Framework Water Harvester," *ACS Central Science*, Vol. 5, No. 10, 2019, pp. 1699–1706.

1.5 MICROCHANNEL WATER HARVESTER

We propose to meet the Army's requirements by developing microchannel sorbent beds for nanocrystal MOF materials. We will use these sorbent beds to build an innovative, simple system that provides rapid sorption cycling and continuous water production from a dual-bed, temperature swing system.

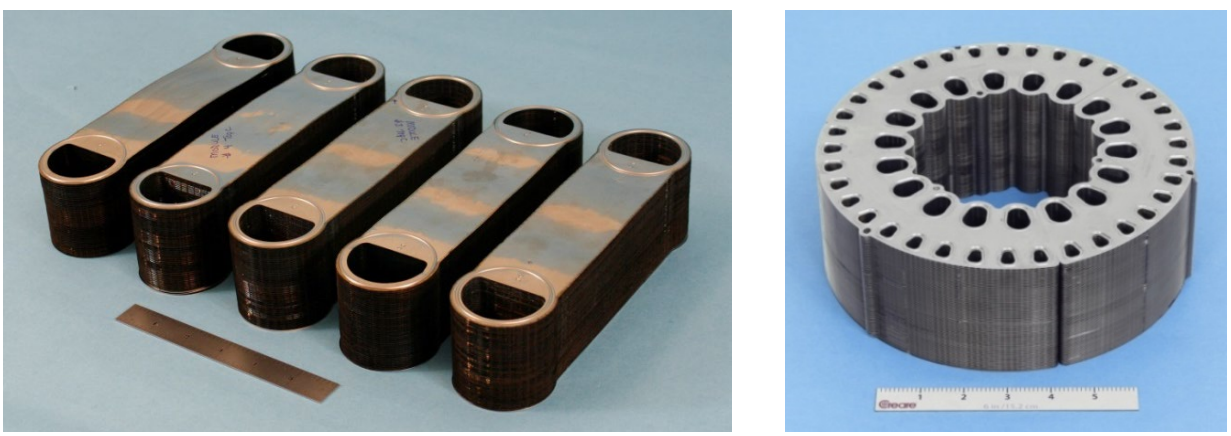
1.5.1 Compact, Efficient Water Extraction System

The design concept for Creare's microchannel water harvesting system is proprietary and is described in the Phase I proposal and in separate reports to the Army. The overall architecture is a two-bed temperature swing system with heat for desorption provided by a small combustor and cooling for sorption and condensation provided by the flow of ambient air through the system. While one bed is heated to desorb water, the other is cooled to adsorb water from the atmosphere and condense water from the desorbing air stream.

1.5.2 Microchannel Sorbent Beds

Creare's HAM technology enables us to produce high-performance, compact microchannel heat and mass exchange structures at low cost using methods that are ideally suited for integration with MOF materials. We propose to use this approach to produce microchannel sorbent beds for high-efficiency water harvesting.

We have used HAM successfully to build compact, high-performance heat exchangers for heat recuperation in small gas turbine engines (Figure 4). Details of the HAM process are proprietary and have been described to the Army in other documents.



(a) Five 100-Plate Modules From the Recuperator of the Rolls-Royce 700-hp M250 Gas Turbine Engine

(b) Recuperator for UAV Turbines 50 hp UTP-50R Turboprop Engine

Figure 4. Microchannel Heat Exchangers Produced by Creare

1.5.3 Innovative Nanocrystalline MOF Materials

RTI has developed nanocrystalline Zr-fcu-MOF-801, which has demonstrated good water sorption under constant humidified airflow at 10% RH and 25°C and good desorption at different temperature and 10% RH as well (Figure 5). Using isoreticular chemistry (computational modeling), RTI will design and construct novel MOFs with fcu and xhh topologies and with a suitable aperture size for water sorption.

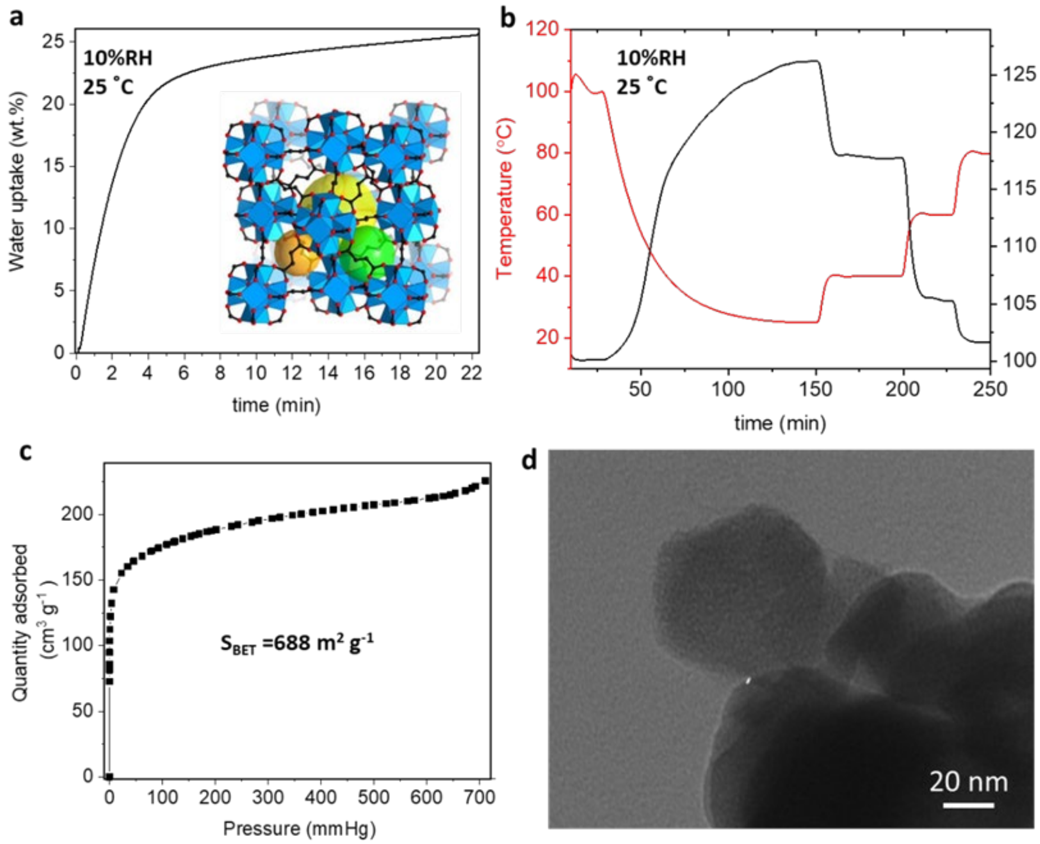


Figure 5. Water Sorption Properties of Zr-fcu-MOF-801. (a) Dynamic vapor sorption properties of Zr-fcu-MOF-801. (b) Dynamic vapor sorption properties of Zr-fcu-MOF-801: adsorption at 25°C and 10% RH and subsequent desorption at 40°C, 60°C, and 80°C and 10% RH. (c) Surface area of Zr-fcu-MOF-801. (d) TEM picture of Zr-fcu-MOF-801 nanocrystalline.

RTI has developed methods for applying coatings of MOF materials to metal substrates. The current state of the art is to use mesoporous polymer carriers, which can be applied in layers as thin as 250 µm. More advanced methods would grow MOF directly on the metal substrates following etching with HF. In the Base phase of Phase I, RTI is applying MOF sorbents to sample substrates using the polymer approach. In the Option phase, we will explore the direct growth approach, which promises to reduce mass transfer resistance and enable more rapid cycling.

1.6 Scoping Design of MWX System

To estimate the overall weight and airflow requirements of our MWX concept, we performed scoping calculations based on a projection of the state of the technology at the conclusion of Phase II of this program. The estimated size and performance depends on the amount of water that can be absorbed in the MOF and how efficiently the MOF can be applied in thin layers to the surface of the heat and mass exchanger beds. Details of the projected sorbent layers are proprietary and were described in the Phase I proposal. We focus our scoping efforts on the mass of the exchanger beds, as these will make up most of the system weight (additional system mass will come from fans, combustor, fuel bottle, water reservoir, and tubing as well as filtration/purification if needed). Table 2 shows the parameters used and the results of this scoping analysis. Based on ambient conditions of 30°C and 40% RH, we conclude that the swing beds in a 14 L/day system would have a dry weight of 2.04 kg. To perform at this level for these ambient conditions, the beds would require 52.1 ft3/min of airflow, a relatively small amount easily supplied by a small computer cooling fan.

Table 2. System Scoping Design

Ambient Temperature	°C	30
Ambient Relative Humidity		40%
Water Production Rate	L/day	14
Estimated Total Mass of Beds	kg	2.04
Estimated Total System Mass	kg	4.5
Airflow needed	ft^3/min	52.1

Regarding consumables for the system, fuel consumption needed to condense 14 L/day of water from the air requires approximately 0.7 kg of fuel (assuming a net heat of combustion of JP-8 at 43,200 kJ/kg), assuming no external heat sources are available,. With a water latent heat of 2,200 kJ/kg, this means that 0.051 kg of fuel is needed per kg of water produced. Limiting the system to producing 10 L of water per day results in a minimum of 0.5 kg of fuel required.

2 PHASE I TECHNICAL OBJECTIVES

We have successfully achieved all the objectives for the Base phase of Phase I. Table 3 summarizes the Base phase results, and the following sections of this report provide more detail.

This Phase I feasibility study is part of a larger program, which has the objective of enabling individual warfighters to produce their own drinking water in the field by harvesting it from air. The approach is to develop a compact, lightweight water harvesting system using Creare's MWX system and RTI's nanocrystalline MOF sorbents. The goal of Phase I is to prove feasibility through fabrication demonstrations, sorbent cycling measurements, water quality testing, analysis, and design. The specific technical objectives for Phase I are as follows:

- Demonstrate sorbent bed fabrication approach. We will show by test that we can assemble an MWX sorbent bed using HAM without affecting the MOF coating (Base phase).
- Demonstrate MOF coating approach. RTI will show that thin (250 µm or less) polymer coatings of Zr-fcu-MOF-801 can be produced on prototypical MWX sorbent bed structures (Base phase). RTI will show that MOF materials can be grown directly on etched sorbent bed structures (Option phase).
- Measure MOF water harvesting performance. We will measure the water recovery from temperature-swing sorption/desorption cycling using prototypical MOF and substrate materials (Base phase).
- Measure quality of harvested water. In the Option phase, Cascade Designs will measure the quality of water harvested using Zr-fcu-MOF-801 and compare results with TBMED-577 requirements (Option phase).
- Show a compact, low-power, inexpensive implementation. In the Option phase, we will produce a detailed design of the MWX sorbent beds and scoping-level system layout design (Base phase). We will specify all major components in the system and refine the system layout design (Option phase). In both phases, we will estimate the size, weight, and power consumption of the MWX system.

Table 3. Phase I Objectives and Status

Phase I Objective	Status
Demonstrate Sorbent Bed Fabrication Approach	• Successfully demonstrated joining of coated plates.
Demonstrate MOF Coating Approach	• Coating process developed for 100 µm thick layers of Zr-fcu-MOF-801 comprising 50% MOF and 50% binder • These MOF coatings demonstrated excellent adhesion to MWX sample plates
Demonstrate MOF Water Harvesting Performance	• Test rig assembled. • Test rig proven capable of measuring water harvesting performance of MOF coatings. • Demonstrated harvesting water at a rate of 86 mg H_2O/s per m^2 of MOF coating under simulated MWX operating conditions.

Phase I Objective	Status
Measure Quality of Harvested Water	Planned for Option phase
Show a Compact, Low-Power, Inexpensive Implementation	Planned for Option phase

3 PHASE I RESULTS

Results from the Base phase of Phase I are as follows:

- RTI identified a MOF coating formulation that adhered well to sample water extractor plates.
- RTI applied MOF coatings to two sets of samples provided by Creare. One set of samples had characteristics that are prototypical for elements of the sorbent beds in an MWX system. The other set was designed for use in our test rig to measure sorption performance of the MOF coating.
- We used the coated samples that had prototypical MWX bed features to demonstrate the key assembly steps of the MWX beds.
- We assembled a test rig to enable measurement of the water harvesting performance of the second set of coated samples.
- We measured the water harvesting performance.
- We used results of these tests to update our concept design for the MWX.

3.1 COATING TRIALS

RTI prepared MOF-801 materials and developed techniques for applying MOF coatings to samples provided by Creare. At Creare, we evaluated the coatings for adhesion and compatibility with our HAM process.

3.1.1 MOF Coating Development

The RTI team synthesized up to 50 grams of Zr-fcu-MOF-801 that was used for the development of the MOF coating. The resulting MOF materials were thoroughly characterized to confirm the formation of the right crystalline structure exhibiting excellent properties for water adsorption from air. The water uptake for the resulting MOF material was evaluated by thermogravimetric analysis (TGA). Under air stream containing 80%RH, the MOF material demonstrated excellent adsorption capacity up to 35 wt.% of H_2O uptake at 25°C after regeneration at 100°C. This confirms the feasibility of the MOF to capture water from air (Figure 6).

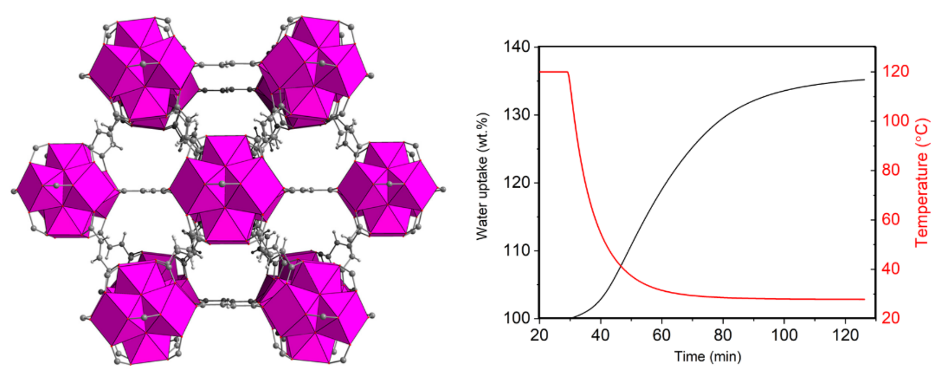


Figure 6. MOF-801 Structure and Water Uptake Measured by TGA Using Air Stream Containing 80%RH

The next step consisted in the identification of the right coating formulation. In fact, to determine the best MOF/polymer ink that can be casted onto the microchannel sorbent bed plates provided by Creare, different parameters were evaluated to obtain a uniform coating that preserves the water adsorption properties of the MOF, such as solvent, polymer binders, solvent:MOF mass ratios, MOF:polymer mass ratios, thicknesses, and curing temperature/time.

Solvent Screen. The initial test consisted of evaluating different alcoholic solvents with pure MOF at different solvent:MOF mass ratios. Methanol, ethanol, and isopropanol (iPrOH) were evaluated at 10:1 solvent:MOF mass ratio. Isopropanol with higher boiling point, and thus slower evaporation, resulted in more homogeneous coating. Thin MOF layers were formed on glass substrate upon dropping the MOF ink and leaving it to spread by gravity. This solvent was selected for the rest of the tests. The resulting MOF coatings were removed from the glass easily because they did not have any polymeric binder.

Solvent:MOF Mass Ratio Screen. After varying different iPrOH:MOF mass ratios, 8:1 was found to be the optimal ratio, as lower ratios (i.e., 10:1) led to very liquid ink that did not form a continuous MOF coating (MOF aggregation), and higher ratios (i.e., 5:1) led to cracking and automatic peeling off the MOF coating. The optimal 8:1 ratio resulted in continuous and uniform MOF coating.

Polymer Binder Screening.

1. *Polyvinyl Butyral*. The first approach consisted of using a well-known polymer for coatings such as polyvinyl butyral (PVB). The use of 10 wt.% of PVB in the coating formulation resulted in nice MOF coatings on glass substrate, but the resulting MOF layer was easily detachable due the high loading of MOF. Higher concentrations of PVB led to significant reduction of the ability to adsorb water from the atmosphere without further improving coating integrity. Therefore, we moved on with another polymeric binder.
2. *UV-Curing Polymer Binder*. The use of UV-curing polymer resulted in better adhesion to the substrate (e.g., glass). Using only 10 wt.% of this polymer precursor in the MOF coating formulation resulted in a uniform coating upon quick exposure to UV lamps (few minutes). Due to this promising result obtained with UV-curing polymer binder on glass substrate, we decided to apply the coating on Creare's dimpled plates. Different loadings of MOF + polymer coating formulations were added on the concave side of the plates (dimple up), and the formulation was spread by gravity. We found that approximately 400 to 450 mg is the maximum amount of coating formulation that we could use, as higher loading resulted in cracking and peeling of the MOF coating once the iPrOH is evaporated. The resulting MOF coatings obtained after UV curing showed good uniformity and relatively good mechanical resistance; nevertheless, the reproducibility of the preparation was challenging because MOF layer did sometimes crack and peel off when dried and/or UV cured. An example of successful coating using UV-curing polymer additive is shown in Figure 7. Another drawback of UV curing acrylic polymer was the partial blockage of the water adsorption performance.

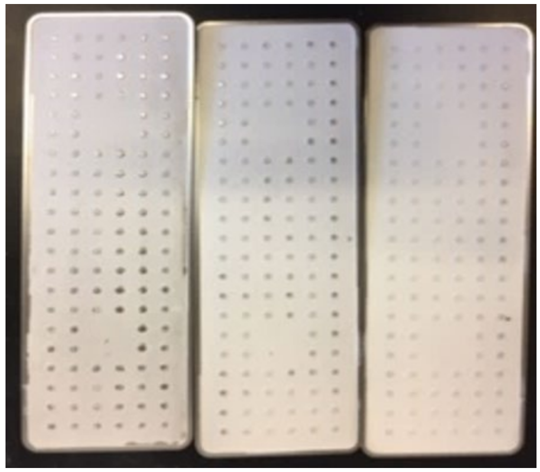


Figure 7. MOF Coatings Containing UV-Curing Polymer Binder

3. *Thermo-Curing Polymer Binder*. The reproducibility challenges of UV-curing binders encouraged us to explore other curing polymer additives that could provide more reliable uniform coatings upon solvent evaporation. The use of new polymer additives led to more reproducible and uniform MOF coatings upon the evaporation of iPrOH. This polymer binder precursor allows for more material flexibility during the solvent evaporating step that avoids the formation of cracks. The same formulation can be applied in larger surfaces (see Figure 8) with similar good results. Apparently, polymer binders did not block the water adsorption performance of the MOF coating, which confirms that is the best additive, so far, to apply uniform coating layers (see Figure 8). In addition, the formulation of the polymer precursor can be easily tuned to allow for more porosity and more hydrophilicity upon curing, which will rule the water adsorption kinetics of the resulting MOF-coated plates. We propose the optimization of the formulation during the next stage of the project.

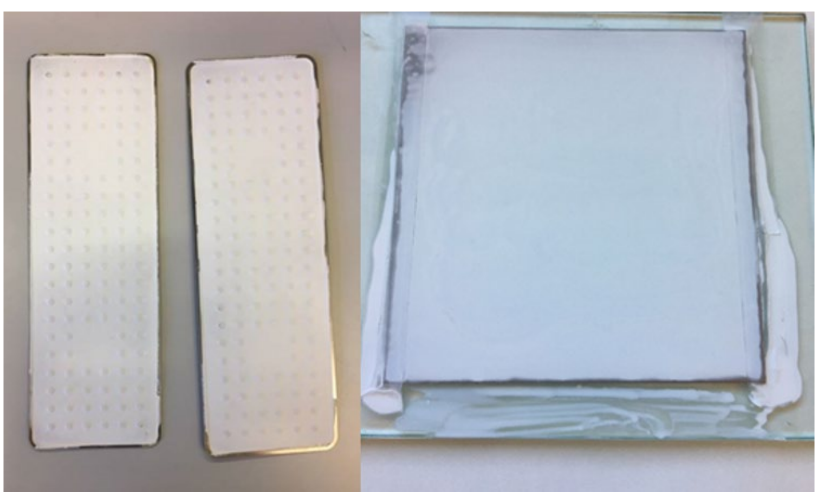


Figure 8. MOF Coatings Containing Thermo-Curing Polymer Binder

3.1.2 Fabrication Trials Using MOF-Coated Sample Plates

RTI's thermo-cure polymer binder sample plate coating yielded a 100-µm-thick coating on the plate surface. The coating is approximately 50% MOF and 50% adhesive material and protective surface layer. Figure 9 shows a sample plate of the weldable substrate. The configuration of these weldable plates makes them suitable for the fabrication trials discussed below. RTI also coated flat plate substrates for use in the performance testing (also discussed below).

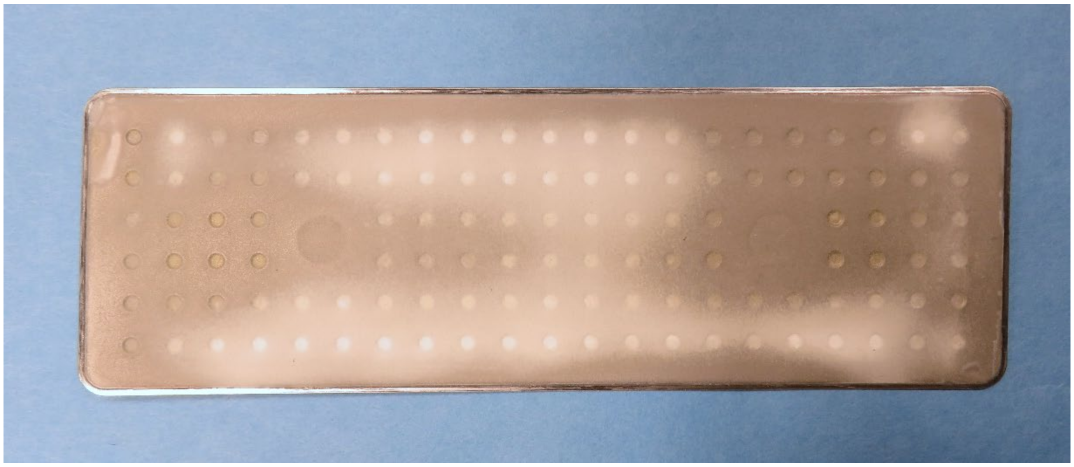


Figure 9. MOF-Coated Sample Plate

We were primarily interested in three key aspects of the coating as produced by this trial:

1. Quantity of adhesive be used in the coating. The goal is to maximize the MOF material present.
2. Thickness of the coating. Thinner coatings have lower resistances to mass and heat transfer.
3. Adhesion of the coating to the substrate.

Once RTI finished coating the samples, we conducted adhesion trials with the samples. Figure 10 shows simple stick test results of the coating trial. RTI masked these sample plates on the to-be-welded perimeter to ensure the weld joint remained free of MOF material. The coating appears to have good mechanical stability, showing little to no debonding of material in the simple stick test. The tape test captured only minor flecks of material from the coating edges abutting the masked portion of the sample plate.

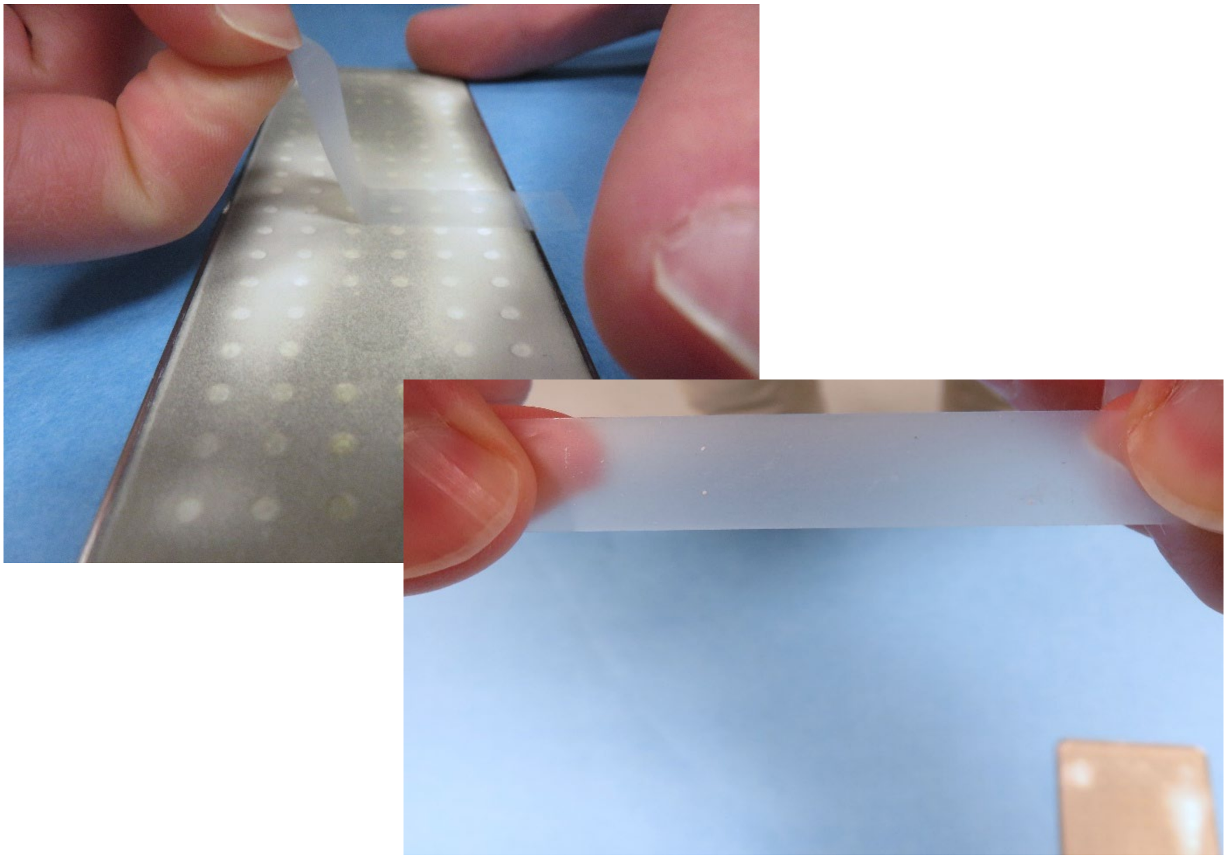


Figure 10. Initial Coating Adhesion Trial Results of a Weldable Sample (left) and a Flat Plate Sample (right).

3.2 WELDING AND ASSEMBLY

We demonstrated the key fabrication processes that will be needed to construct the MOF-coated heat and mass exchanger portion of the MWX system. This demonstration focused on the key HAM steps needed to produce the microchannel sorbent bed core.

We first conducted tests to determine welding parameters to be used to seal together the mating halves of the exchanger plates. This was done prior to coating the plates such that the same parameters could be applied to the coated plates to determine if the coating interfered with the weld process and vice versa. This precoated weld trial also helped to define a perimeter to mask during MOF coating. Figure 11 shows an image of the weld trial. The perimeter shown includes a sequence of different welding parameters. The rightmost bead on the lower edge represents the best identified welding parameters for this material. Figure 12 shows a closeup of this portion of the bead.

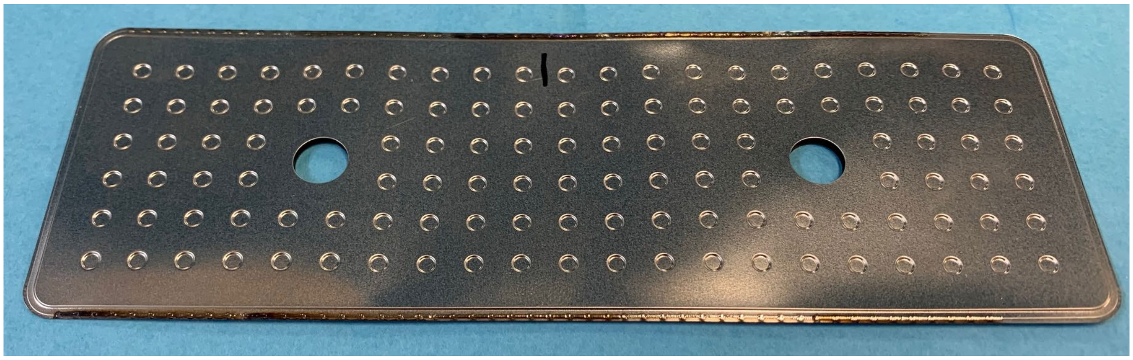


Figure 11. Test Coupon Used for Weld Parameter Investigation

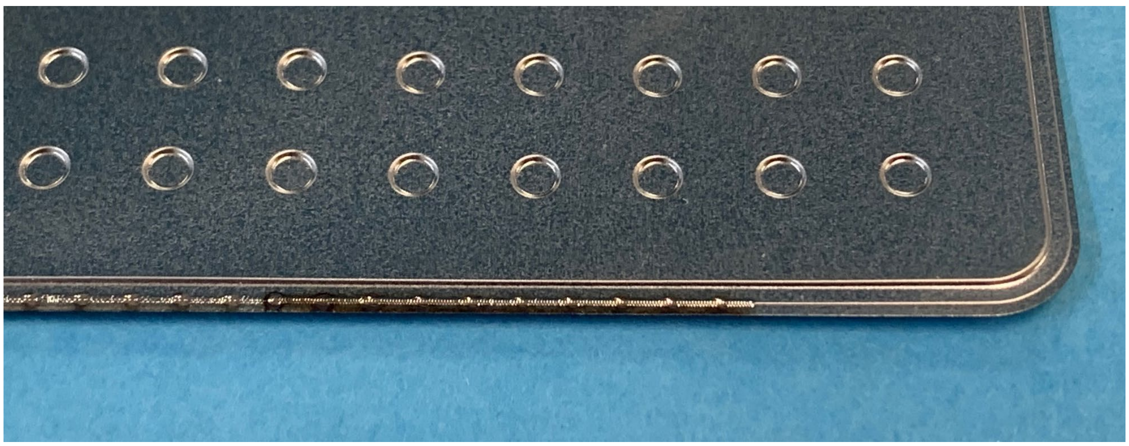


Figure 12. Close-Up of Perimeter Weld Achieved With Best Identified Welding Parameters

We conducted weld trials using the coated samples. Our initial trial did not include any attempt to clean up the area surrounding the weld, since we were interested in learning whether any special treatment of this region would be necessary for successful joining. Figure 13 shows the sample before and after the weld process. Figure 14 shows a closeup of the weld joint for this same sample. As the MOF surface adhesion was already compromised, we were not concerned with any material loosened by contact with the weld fixture at this stage. We primarily paid attention to the condition of the MOF near the weld joint. We did not notice any apparent change to the MOF near the weld joint that would suggest overheating as anticipated. However, we did see that in select regions of the weld, we were not able to achieve good bonding. The state of the weld suggests that the weld region contained some contaminants that interfered with the process. As made obvious by the closeups, the MOF material itself is not intruding on the immediate area of the weld joint. It is likely that some other residue from the coating process or associated plate handling led to the failure. Thus, we concluded that cleaning of the pre-weld joint is needed to ensure adequate exchanger plate bonding.

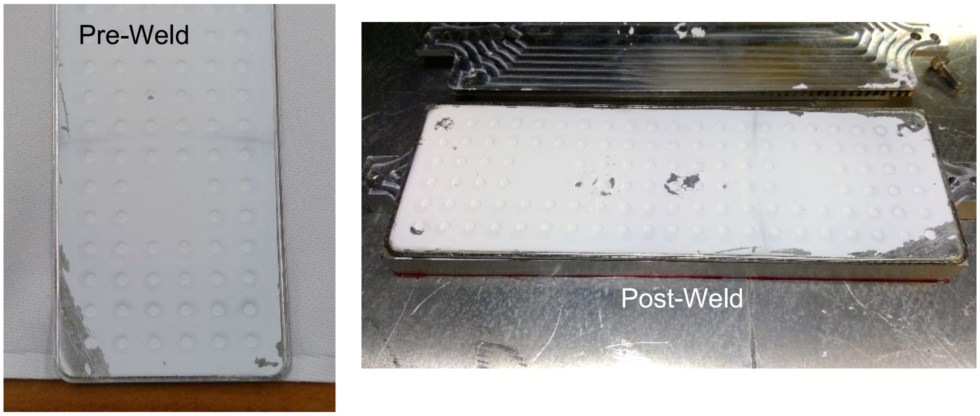


Figure 13. Views of Sample Pre-Weld (left) and Post-Weld (right)

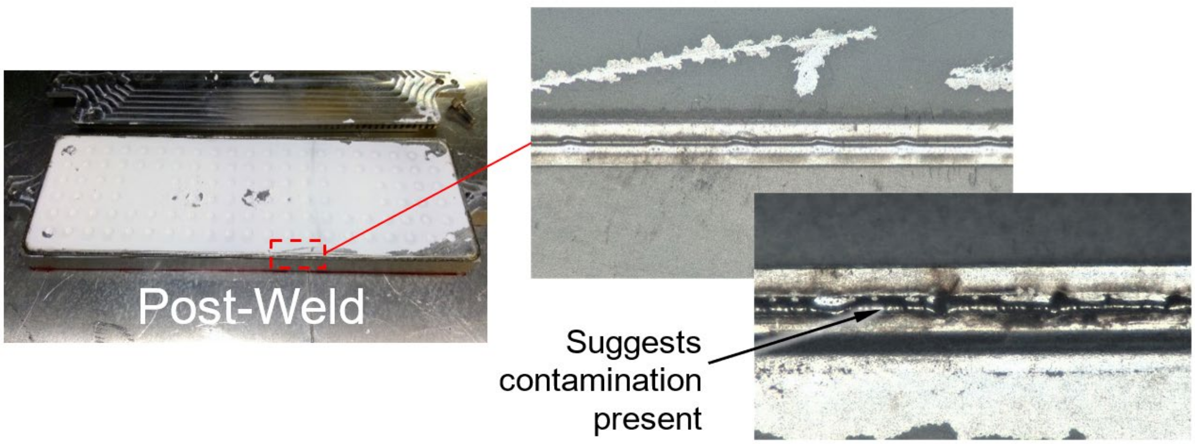


Figure 14. Close-Up of Initial Weld Results

Our second attempt utilized the thermo-cure polymer binder samples provided by RTI. Figure 15 shows the results of the weld trial. In this trial, we swabbed the perimeter flange with alcohol prior to welding to remove any potential contaminants. The weld process produced excellent results. The process produced a uniform weld free of obvious separations or other imperfections. In addition, we did not observe any visible damage to the MOF coating in the proximity of the weld and as such do not anticipate any damage to the MOF resulting from the weld process. As these plates do not include penetrations and sealing features that would allow for hermeticity testing, we were not able to assess the weld at this level. However, the visually inspected quality of the weld suggests that we will have no difficulty achieving the fabrication objectives of this program.

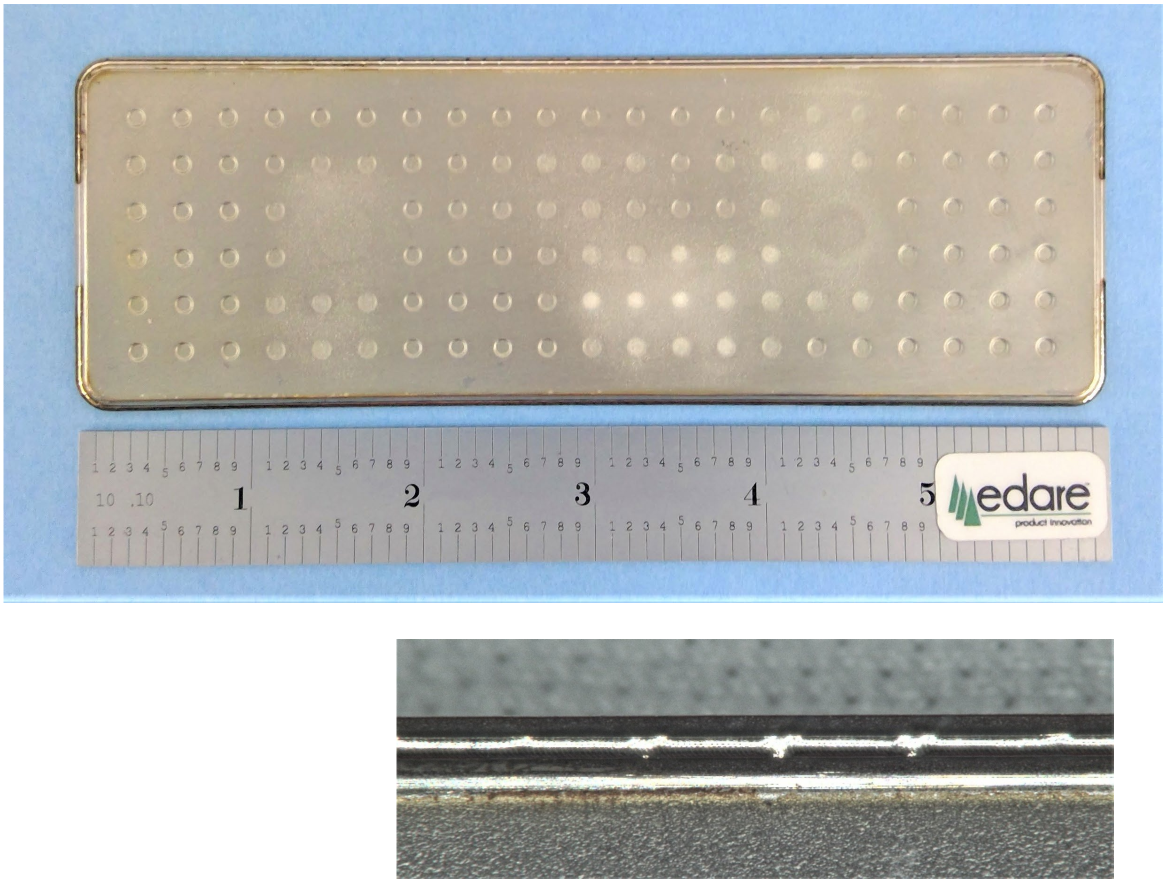


Figure 15. Weld Results of a Thermo-Cured Polymer Binder Coating Sample

3.3 Test Rig

We designed and built an experimental facility to measure the adsorption and desorption behavior of the MOF coating material. Figure 16 shows a schematic of the test facility, and Figure 17 shows it assembled with key components identified. We use dry air from our laboratory compressor as the working fluid. For adsorption testing, we route the airflow through a membrane mass exchanger to add water vapor. During desorption testing, the airflow bypasses the mass exchanger. We adjust temperature and relative humidity at the test section inlet using a heater positioned just upstream of the test section.

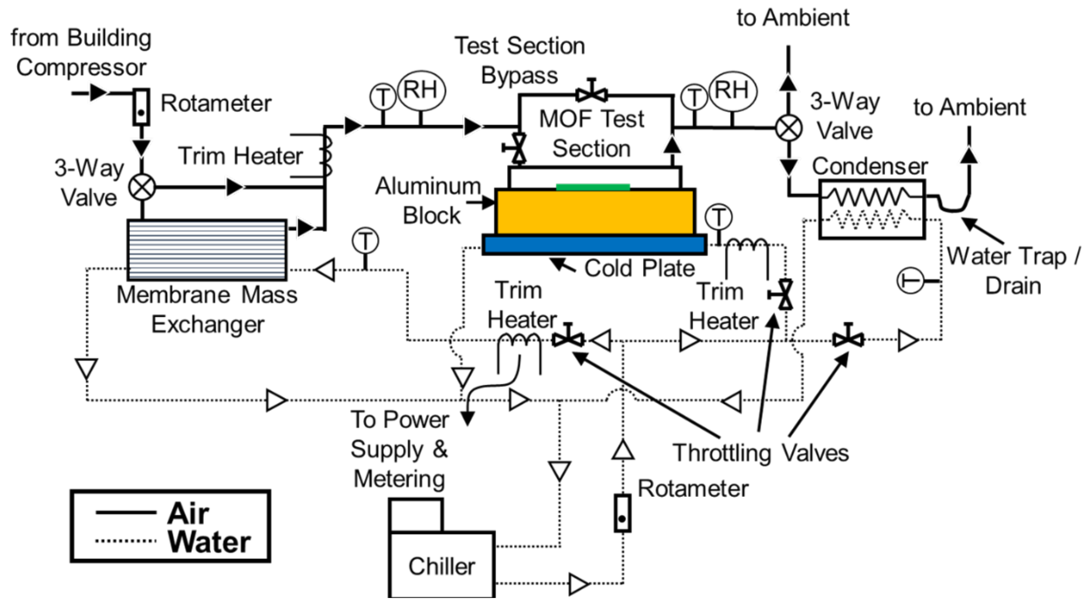


Figure 16. Schematic of the Atmospheric Water Harvesting Test Facility Used to Measure Performance of MOF-Coated Samples.

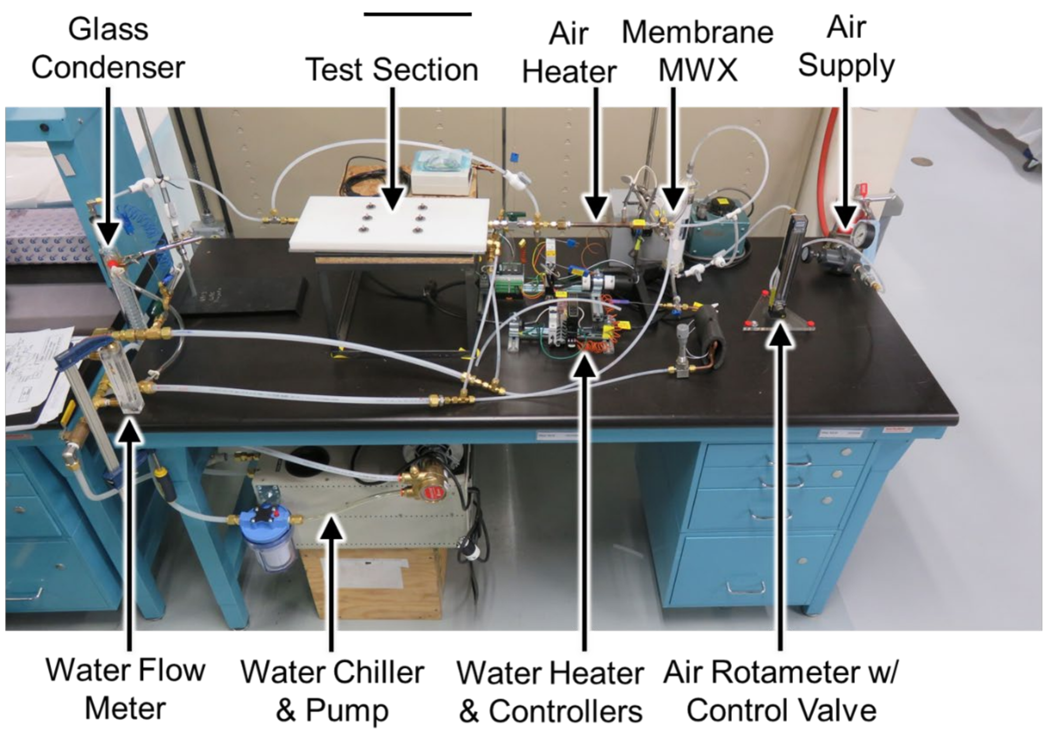


Figure 17. Photo of the Atmospheric Water Harvesting Test Facility

Figure 18 shows a schematic (top) and photos (bottom) of our test section. Key features in the plastic top plate include (1) tapped inlet and exit ports, (2) inlet/exit plena, (3) O-ring groove, and (4) adjustable flat plate to set gap height above our MOF-coated sample. Closed-cell, compressible foam seals the back side of this adjustable plate to prevent flow from bypassing our

MOF-coated sample plate. The MOF sample plate sits in a pocket machined into the aluminum baseplate. We control temperature of the MOF sample using a cold plate mounted to the back of the aluminum baseplate.

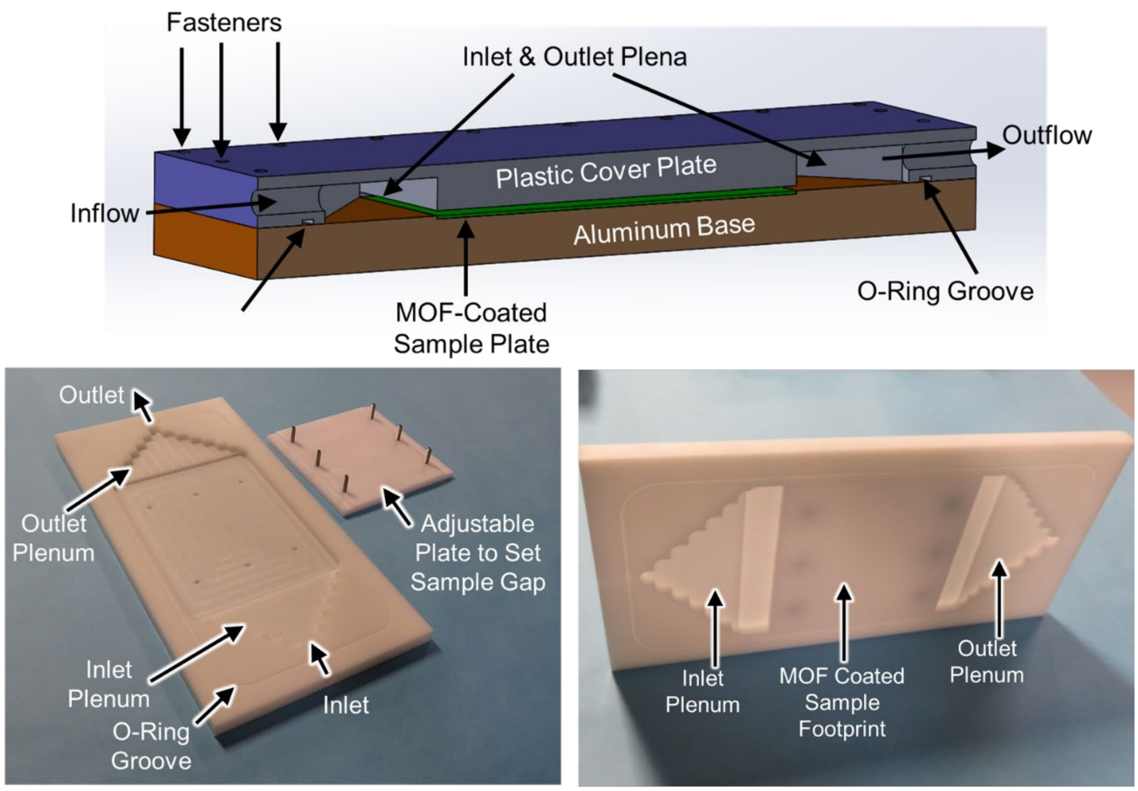


Figure 18. Schematic (top) and Photos (bottom) of Our MOF-Coated Sample Test Fixture. The thin aluminum baseplate is not pictured.

Airflow through the test section either transfers water to or collects water from the MOF-coated sample plate. The flow of water into or out of the MOF coating depends on whether the system is operating in adsorption or desorption mode. We measure the temperature and humidity of airflow exiting the test section, after which airflow either exhausts to ambient or passes through a secondary condenser where we collect harvested water.

Key measurements in our MOF test facility are:

1. Temperature and relative humidity entering the test section.
2. Temperature and relative humidity exiting the test section.
3. Test section body temperature.

We use these measurements to determine mass of water adsorbed/desorbed in the MOF as a function of time, average adsorption/desorption temperature for the MOF, and verify the fraction of water removed from air in our condenser.

To monitor humidity upstream and downstream of the MOF test coupon, we installed sensors based on the Sensirion SHT35 humidity and temperature sensor. The SHT35 is a CMOS-based sensor able to operate between 0% and 100% RH. The humidity sensor has a vendor specified accuracy of +/- 1.5 %RH with a 0.1 %RH repeatability and a response time of eight seconds. The temperature sensor has a vendor specified accuracy +/- 0.2°C with a repeatability of 0.06°C and a response time of two seconds. The wide range of operability, rapid response time, and high accuracy make these sensors attractive compared to other COTS options available. We utilized a Grove breakout version of this sensor and developed custom microcomputer-driven hardware and software to monitor and report sensor values during the test. Figure 19 shows the sensor hardware. During operation, the microcomputer continuously (~30 ms/sample) monitors the I2C interface of the SHT35 sensor Grove breakout boards and reports the results to a LabVIEW via a USB connection. Our LabVIEW VI integrates this data with the rest of the instrumentation monitored during test. In post processing the data, we utilize both the relative humidity and the temperature from the sensor to determine the dew point at each sensor.

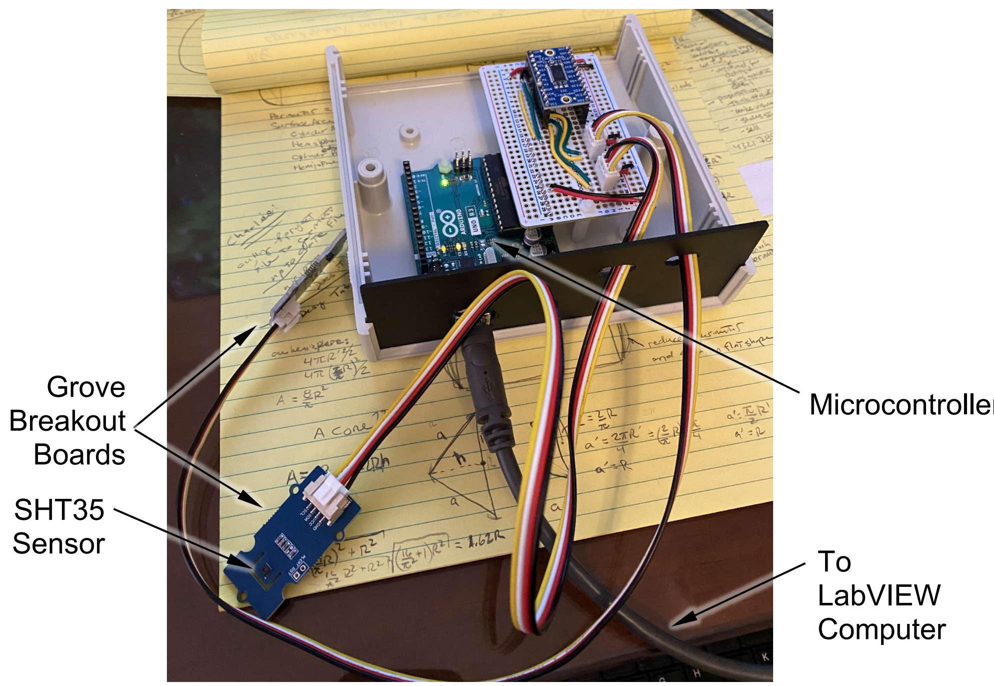


Figure 19. Custom Relative Humidity Sensor Hardware Based on the Sensirion SHT35 Sensor Chips. Cover is removed for illustration.

3.4 TEST RESULTS

We have successfully measured water adsorption and desorption from the MOF coatings using one of our coated 6 × 6 in. sample plates. Figure 20 shows measured humidity (top) and temperatures (bottom) for our system during an adsorption half cycle. Prior to beginning the test, we control inlet air conditions (temperature and humidity) by controlling the water temperature through the MWX, controlling the water temperature through the cold plate connected to the base of the test section, and using the inlet air trim heater to adjust air temperature. We send flow through a bypass leg (indicated in Figure 16) during this period to prevent water adsorption prior to the start of the controlled test period. At t = 30s in Figure 20, we close the bypass and begin forcing humid air through the test section. This is observed in the sharp increase in inlet humidity and decrease in outlet humidity, showing that the air flowing through the test section is losing water to the MOF.

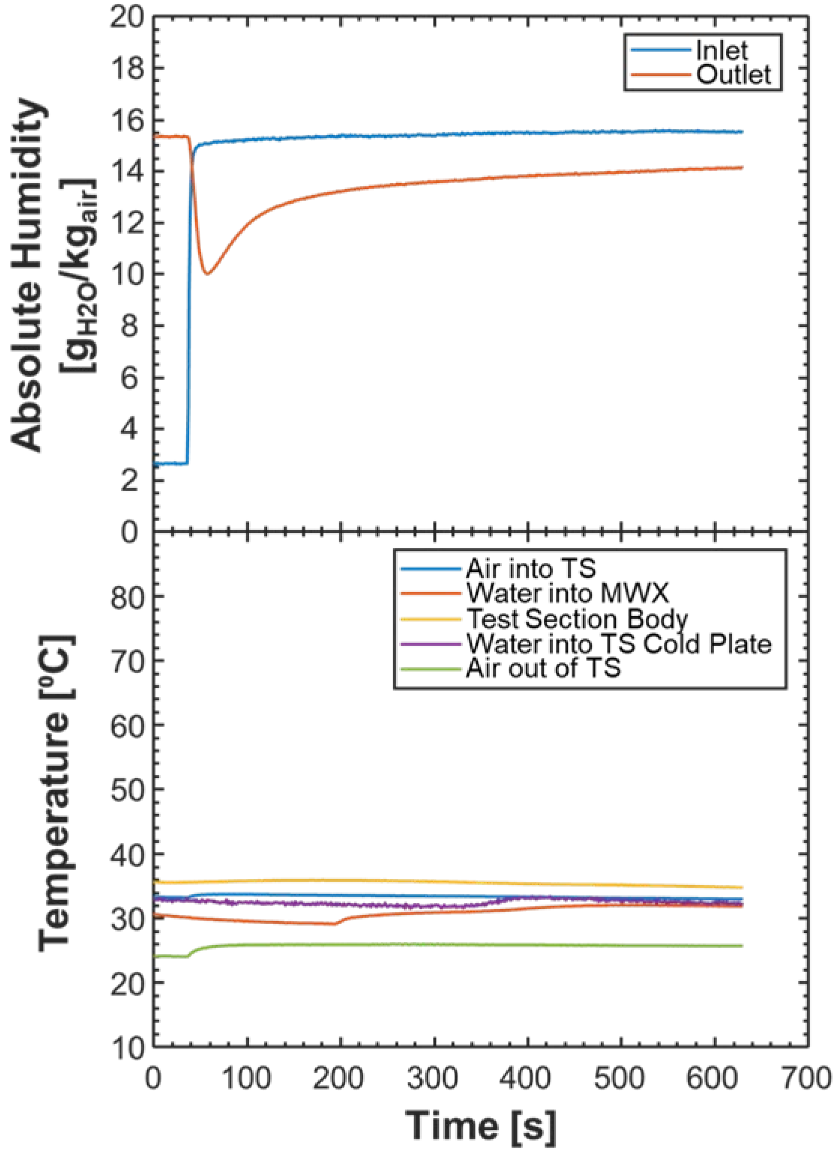


Figure 20. Measured Absolute Humidity Entering and Exiting the Test Section (top) and Temperatures Throughout the System (bottom) at the Start of an Adsorption Half Cycle.

Figure 21 provides similar results for desorption. We observed a large change in water content at the outlet of the test section just after beginning the desorption test. We also noted corresponding water production within our condenser during this period as shown in Figure 22. With these test results, we verified our ability to (1) control conditions of the MOF sample plate and passing airflow to drive adsorption and desorption of water, (2) measure water content changes within the air, and (3) produce water within our condenser.

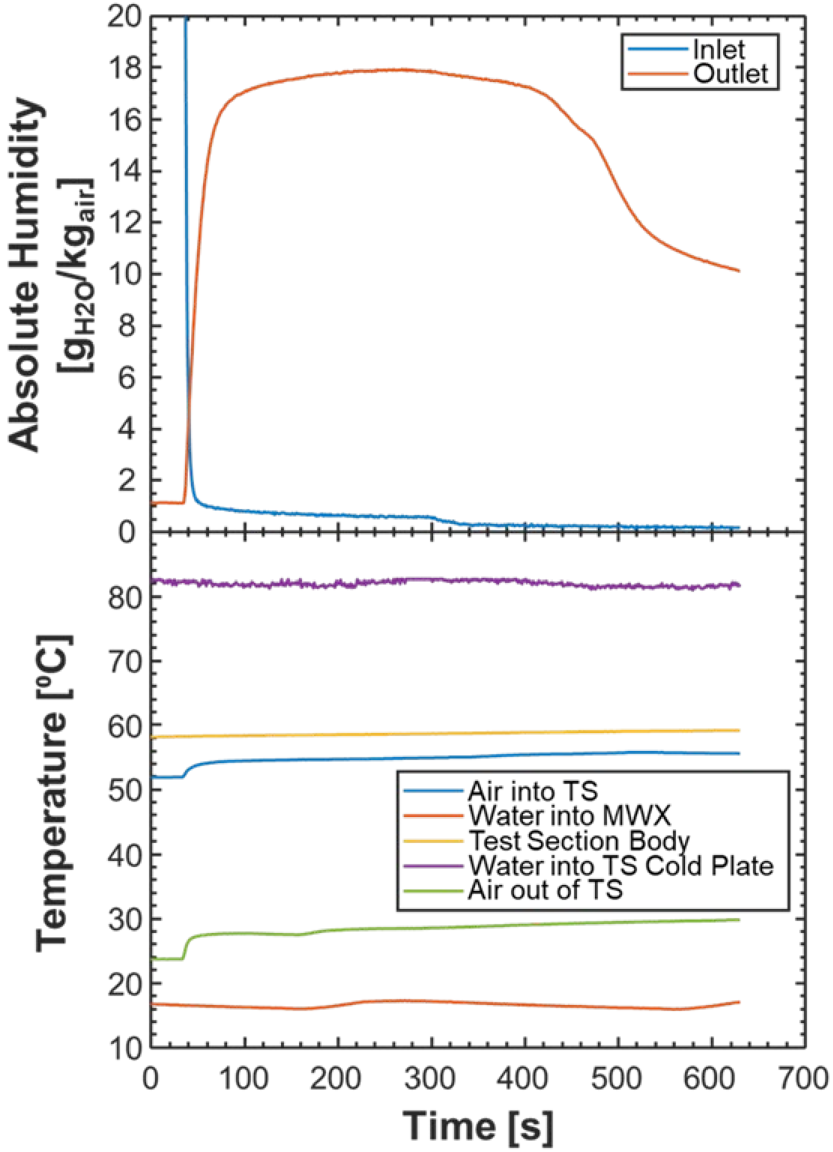


Figure 21. Measured Absolute Humidity Entering and Exiting the Test Section (top) and Temperatures Throughout the System (bottom) at the Start of a Desorption Half Cycle.

Figure 22. Initial Water Production in Our Condenser During a Desorption Half Cycle

We ran similar test conditions with three different airflow rates to determine how sorption rates depend on airflow. Figure 23 provides plots of inlet and exit absolute humidity for adsorption and desorption tests conducted at 1, 3, and 6 std. L/min airflow. 1 std. L/min results correspond to data shown in Figure 20 and Figure 21. The general shape of adsorption and desorption curves are the same for each flow rate, but we observed much sharper peaks with higher separation between inlet and outlet water content at higher airflow rates. This indicates sorption rates are higher at higher air flowrates (over the range tested here), but the period over which sorption is efficient becomes much shorter. We discuss these trends in greater detail in the next section.

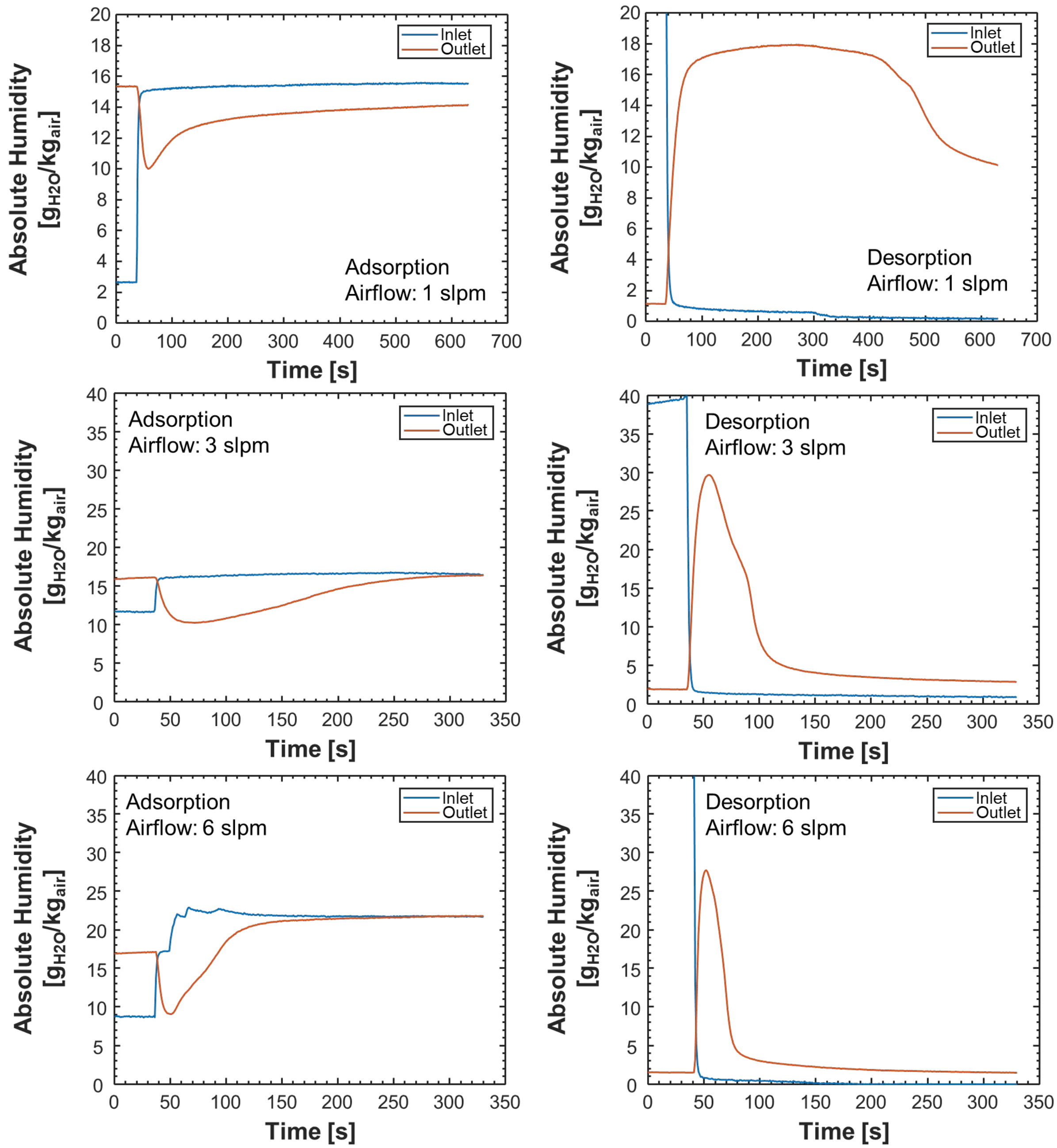


Figure 23. Adsorption and Desorption Test Results for Three Different Airflow Rates Showing the Importance of Airflow on Sorption Rate.

3.5 Assessment of Test Results

Table 4 summarizes the sorption test results shown in Figure 23. Sorption rates are calculated by taking the difference between curves in Figure 23 and multiplying by airflow rate. We observed higher airflow rates produced higher peak sorption rates with shorter optimal half cycles. Averaging water ad/de-sorbed over half cycle times for each flow rate provided a number for average sorption rate in mg/s for each set of test conditions. This number is a key outcome of our Phase I testing, as it provides a baseline with which we can scale our Phase II system design.

Table 4. Summary of Sorption Testing During Phase I

Airflow Rate	1 std L/min		3 std L/min		6 std L/min	
Test Configuration	Adsorption	Desorption	Adsorption	Desorption	Adsorption	Desorption
Plate Temperature [ºC]	35.9	58.4	55.9	89.8	54.5	91.7
Air Inlet Temperature [ºC]	33.7	54.5	39.6	47.1	31.6	50.2
Air Inlet Relative Humidity [%]	46.6	1.8	35.2	5.2	68.6	10.8
Peak Sorption Rate [mg/s]	0.25	0.75	0.36	2.3	1.4	6.0
Optimal Half Period (Est.) [s]	300	300	120	120	75	75
Average Sorption Rate Over Half Period [mg/s]	0.07	0.33	0.30	0.84	0.92	2.0
Water Production per 10 Minutes [g]	0.04	0.20	0.18	0.51	0.55	1.22

Based on data shown in Table 4 and experience gained during testing, we draw the following conclusions from Phase I testing:

1. Over the range of conditions tested, higher airflow rates lead to higher sorption rates over the window of time during which sorption is most efficient. This window shrinks as airflow rate increases.
2. Desorption is very sensitive to temperature. We found increasing MOF temperature to lead to appreciably higher desorption rates at all airflow rates.
3. There are competing effects of temperature on adsorption. Material characteristics (vapor pressure versus temperature) show MOF liquid uptake is higher at lower temperatures, but diffusion of water through the MOF coating is slower. Figure 23 showed higher adsorption rates at higher airflow rates (cases where we elevated MOF temperature to ~55°C), but only over short windows after which water uptake stopped.
4. Information gathered during Phase I testing has helped refine our overall system design concept described in Section 3.6.

3.6 SYSTEM DESIGN

Our Phase I test results showed that we can achieve most efficient water production by moving to shorter half cycles than originally planned in our proposal concept. We used the peak sorption rate of 2.0 mg/s observed in the 6 std L/min case to design our Phase II concept outlined in Table 5. Our peak demonstrated adsorption rate was only half of this number, but we believe we can further increase adsorption rate after further exploring the parametric performance of our MOF coating in Phase II.

Our Phase II design concept is scaled on two key numbers from our Phase I experiments: sorption rate per unit surface area and residence time of air over the MOF. We believe that by using residence time as a design constraint, we will achieve the sorption rate demonstrated during Phase I experiments and can scale our MWX surface area based on that number. Airflow rate is calculated to provide the necessary amount of water for adsorption at 30°C and 40% RH, and pressure drop is based on local air velocity and plate geometry.

Compared to our proposal concept, our Phase II design has roughly 20% more mass and approximately double the system volume. It is based on demonstrated sorption rates, however, which we expect to exceed after further coating optimization in Phase II. It also satisfies the initial design constraints outlined in the solicitation as shown in Table 6.

Table 5. Summary of Phase II Preliminary Design Alongside Proposal Concept and System Requirements

Parameter	Phase II Design Concept	Proposal Concept
Water Production per Day [L]	14	14
Average Sorption Rate [mg/s-m^2]	86	186
Half Cycle Time [s]	75	600
Cycles per Day [-]	576	72
MOF Surface Area [m^2]	1.88	0.86
Plate Design (LxWxt) [in]	3 x 4 x 0.02	6 x 2 x 0.02
Airflow [CFM]	25.4	52.1
Airflow ΔP [in H_2O]	0.3	2.2
Number of Plates [-]	244	109
MWX Module Dimensions (LxWxH) [in]	3 x 4 x 5.61	6 x 2 x 2.51
Sorbent Coating Thickness [μm]	100	150
MWX System Mass [kg]	5.4	4.5

Table 6. Requirements for Water Harvester and Phase II Concept Design Specifications			
Parameter		**Solicitation Value**	**Phase II Design**
Water production rate	L/day	14	14
Ambient relative humidity		40%	40%
Max fuel consumption	kg/day	0.5	0.7
System weight	lb_m	< 20	11.9
Operating temperature range	°F	25 to 125	25 to 125
Production cost	$	< 100	< 100 (target)

By using our Phase I test results as the basis of our Phase II conceptual MWX design, we have increased confidence in our ability to develop a system that meets the requirements outlined in the initial solicitation. We believe further coating optimization work and a better understanding of parametric influences on sorption rates will lead to a lightweight, efficient system for atmospheric water harvesting for individual soldiers.

4 CONCLUSIONS AND RECOMMENDATIONS

4.1 CONCLUSIONS

Conclusions from Phase I are as follows:

- The RTI team developed an excellent procedure for coating high loadings of MOF (up to 80 wt.%) into surfaces, exhibiting excellent mechanical properties without compromising the water adsorption performance of the MOF. This is the first time that loadings of MOFs this high have been achieved in a surface coating on stainless steel metal.
- Thin layers of MOF can be applied to MWX plates with excellent adhesion.
- The assembly process for the MWX sorbent beds is compatible with the MOF coatings.
- The Phase I test rig is able to measure water harvesting performance of sample MOF coatings.
- We have measured water sorption and desorption rates in the Phase I test rig and used these results to update our system conceptual design.

4.2 RECOMMENDATIONS

Recommendation for the remainder of Phase I are as follows:

- Test the potability of water produced by the MOF sorbent (Option phase).
- Produce a detailed concept design for the water harvesting devise (Option phase).

We believe that the results of the Phase I Base justify continuing work through the Option phase and Phase II. The Phase II project would include design and assembly of a complete, self-contained MWX system and measurement of its performance under realistic operating conditions.

Additionally, we recommend considering additional funding for R&D focused on optimizing the MOF coating considering equilibrium water sorption characteristics, coating mechanical properties, and kinetics of water transport in the coating. This activity would consider a broader range of coating formulations than could be addressed in the Phase II project.

5 PHASE II PLANS

Key activities in Phase II are as follows:

1. Optimize the MOF coating. The goal will be to assess critical tradeoffs and produce a coating that will meet Army requirements for the water harvesting device. This activity will entail extensive coating trials, cyclic sorption testing, and assessments of tradeoffs related to operating conditions, equilibrium properties, and kinetics of the coating. RTI will optimize the formulation of the different components of the MOF coating to maximize the water uptake and kinetics for MOF-coated plates. Creare will measure performance and assess system impacts.
2. Optimize the sorbent beds. We will design the microchannel sorbent beds to maximize water production using the optimized MOF coating. The beds will be designed to meet the fabrication constraints of the HAM process. We will build sub-scale sorbent beds and measure their performance in a separate-effects test rig. Data from these tests will be used to optimize the overall system design.
3. Finalize the system design. Based on the results of the coating and sorbent bed optimization tasks, we will specify the critical design parameters of the prototype MWX. We will then select balance of plant components, including air fans, water pumps, combustor, and controls. We will produce a mechanical design for the key components and an overall layout design for the integrated MWX system.
4. Build a test facility for demonstrating operation of the MWX. We will design and build an environmental chamber that will enable us to demonstrate operation of the MWX under well-controlled conditions that simulate the specified range of operating environments.
5. Build land test a prototype MWX. We will build a prototype MWX to measure performance under conditions that simulate operation in the field. The prototype will be as close to a final product as possible, except that the level of integration may be compromised to enable detailed measurement of process parameters that would not be needed in a final product.