**Contract No:**

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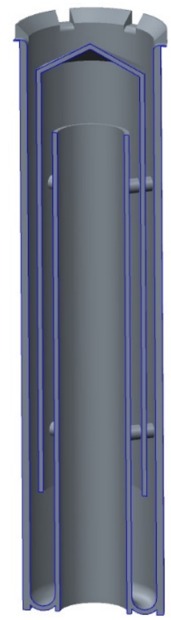
# Extraction of Mercury Utilizing 3D Printed Media - Mercury Extraction Coalescer (MEC)

The presence of mercury in environmental or industrial settings presents a number of issues from bio-accumulation to production of toxic by-products. The primary objective of this project was the development of a 3D printed component designed to act as a coalescing filter for the removal or segregation of elemental mercury from aqueous streams. The use of 3D printing allows for the design and integration of surface microstructures and internal geometries that could be difficult if not impossible to achieve through traditional manufacturing techniques. The initial phase of testing focused on the integration of 3D printed components into both environmental remediation testing (university subcontracted testing) and simulations of high-level nuclear waste processing (SRNL). Structures ranged from simple torturous paths that provided regions where the elemental mercury could settle out of the recirculation process to micro-structured frits that have increased surface area for aid in droplet coalescence and surface adsorption.



## Intellectual Property Review

This report has been reviewed by SRNL Legal Counsel for intellectual property considerations and is approved to be publicly published in its current form.

## SRNL Legal Signature

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**Signature** **Date**

# Extraction of Mercury Utilizing 3D Printed Media - Mercury Extraction Coalescer (MEC)

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Subcontractor: C. Huffman (Western Carolina University)

Thrust Area: ES

Project Start Date: October 1, 2018
Project End Date: September 30, 2019

*Mercury is a persistent environmental hazard that is strictly regulated. The design of a 3D printed coalescer was proposed to facilitate segregation and/or adsorption of elemental mercury from aqueous solutions. 3D printing techniques were employed to generate designed surfaces and internal geometries that would otherwise be very difficult to near impossible through traditional manufacturing processes.*

*The proposed coalescer was designed to take advantage of advancements in 3D printing to incorporate surface sub-structures and material compositions targeted specifically at mercury adsorption. The initial phase of research targeted the design of physical structures that could assit with adsorption or segregation of mercury from acidic condensate, rendering it isolated and preventing recirculation back into the chemical process, as well as implementation into standard environmental remediation techniques for contaminated aqueous solutions. Future work was to focus on formulating reactive coalescers to improve chemisorption along with physisorption.*

## FY2019 Objectives

- Design 3D printable components with microstructures targeted at mercury segregation
- Print 3D components from various compositions (plastic, ceramic, metal)
- Integrate designs into current technology so as to minimize disruption of current processes
- Evaluate various designs at nominal testing conditions to determine operability and compare efficiency

## Introduction

Mercury is a known neurotoxin and its release to the environment is strongly regulated by the EPA.[1] Removal of mercury from aqueous systems is of high importance to environmental management and remediation entities. This proposal sought to improve the current technology by increasing the segregation of elemental mercury from acidic condensate. Surface structures, sub-structures, and chemistries have been shown to produce tunable interactions with liquids. Properties such as phobicity/philicity can be controlled to repel and attract various species based on the physical interactions

[1] A. F. Gruss, R. Rodriguez, D. W. Mazyck,"Mercury Oxidation by UV Irradiation: Effect of Contact Time, UV Wavelength, and Moisture Content", *Ind. Eng. Chem. Res.*, 56, 6131-6135, (**2017**).

with surface features. One of the best-known natural examples of this is the lotus leaf (Figure 1).[2] Unique surface protrusions, as observed under various magnifications, take advantage of the surface tension of water to prevent wetting. The experimental approach of this project was to utilize 3D printing techniques to generate internal geometries, surface microstructures, and component chemistries sufficient to provide segregation of mercury from acidic aqueous media.

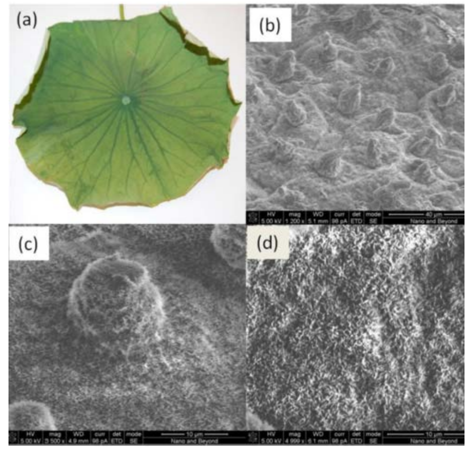


**Figure 1.** Lotus leaf surface sub-structures under varying magnifications.

The initial phase of this project utilized a UV-curable resin printer to produce intricate 3D printed components that advanced from simple isolation to more advanced micro-structured segregation. Preliminary designs were developed to provide a torturous path for the progression of the aqueous solution resulting in the settling-out of the elemental mercury. This initial design has been integrated into the current equipment utilized for simulated high-level waste chemical processing experiments performed at the Savannah River National Laboratory. Other 3D designs have been produced that contain internal geometries targeting increased solid-liquid contact or are composed of a resin-ceramic composite that has been heat-treated to generate a ceramic-only component.

The current state of the project has shown the initial success of integration of 3D printed components into the current process technology without disruption of processing and enhancement of the segregation of elemental mercury from the acidic condensate recycle stream. The stage has also been set for the incorporation of reactive 3D printed components which will improve on the enhancement provided by the addition of the coalescer.

## Approach

There were two stages to the first phase of this research: stage one was the design and printing of coalescers, stage two was the integration of printed components into equipment and testing.

To accomplish the design and printing of practical devices, literature concerning surface structures and sub-structures that aid in liquid-liquid separations was reviewed and utilized to influence the design of micro-features. The printer equipment selection was based on the ability of the FormLabs Form2 printer to produce fine details into the micron scale and the ability to utilize different printing material compositions. This gave the flexibility to approach the direct manufacture of surface substructures specifically designed to perform liquid-liquid separations. The ability to use multiple materials or even modify existing materials makes the FormLabs platforms ideal for R&D activities. We could quickly transition from polymethacrylate to ceramic printing materials with no down-time between modifications. In addition, the company supports DIY modification of resins to generate custom materials; an important feature for the second phase of testing presented below in the Future Works.

[2] Y. Yoon, D. Kim, J-B Lee,"Hierarchical micro/nano structures for super-hydrophobic surfaces and super-lyophobic surfaces against liquid metal", *Micro and Nano Systems Letters*, 2, (**2014**).

**Figure 2.** Left) 3D design of Multi-Turn insert coalescer and right) an adapter design for integration of coalescer between condenser connector (top) and Mercury Water Wash Tank (MWWT, bottom).

The integration of the printed components into current testing equipment (Figure 2) was a necessary proof-of-concept for the broader application goal due to the fact that larger facilities that would require this addition are typically difficult to modify. For example, to make any changes in the Defense Waste Processing Facility (DWPF) at the Savannah River Site (SRS), a majority of interactions with equipment must be performed remotely with a crane making any modification difficult at best. By designing to integrate into current testing equipment, flexibility of the component and manufacture process may be highlighted. The use of 3D printing allowed rapid, cost-effective modification to component designs to evaluate various integration schemes. Once integrated, the coalescer testing was combined with other simulated waste reprocessing testing due to the scale of required preparation and oversight. To ensure the efficiency of the steam stripping process, the mercury must be suspended in solution as relatively small droplets and distributed near the surface. This suspension/distribution process is aided by the inclusion of insoluble solids such as sludge solids. To accommodate these necessary additions to the process, testing was combined with simulated Sludge Receipt and Adjustment Tank (SRAT) and Slurry Mix Evaporator (SME) tank chemical processing being performed concurrently to examine alternative antifoams. Initial tests were performed with a high-level waste sludge simulant that was designed to foam significantly during reprocessing so as to represent a worst-case-scenario for the antifoam. This testing has little impact on the mercury steam stripping process and the extraction of mercury from the process has little impact on the evaluation of the antifoam, so the combined tests were ideally suited to run concurrently. A coalescer designed with a simple torturous path was placed in-line with the acidic condensate and condensing mercury. To accommodate the coalescer, an adapter was designed to fit between the condenser and the traditional Mercury Water Wash Tank (MWWT). Once testing is completed, the used coalescer and any trapped liquid or material was removed from the setup and analyzed for mercury by ICP-AES.

For environmental remediation scenario testing, coalescers were provided to the Dr. Carmen Huffman research group at Western Carolina University to integrate into their setup. The preliminary examination was performed with a single 1in. diameter coalescer sectioned into approx. 1in. sections and placed in solutions of varying concentrations of aqueous contaminants. The metal concentration was allowed to come to equilibrium between the aqueous phase and the coalescer and an adsorption capacity will be calculated.

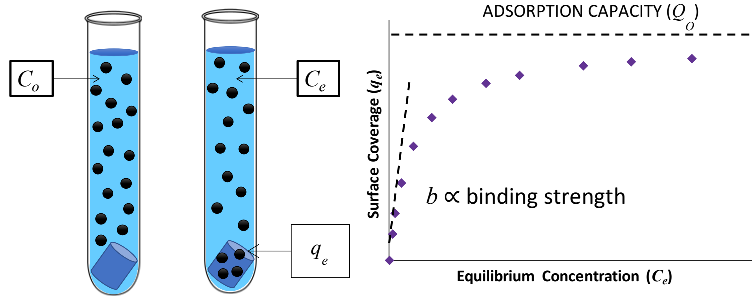


**Figure 3.** Adsorption capacity ($Q_o$) can be calculated using the equilibrium concentration ($C_e$), the surface coverage ($q_e$), and the binding strength ($b$) by fitting the data to the Langmuir equation:

$$q_e = \frac{bQ_oC_e}{1 + bC_e}$$

## Results/Discussion

After some initial complications associated with the learning curves on the printing process and the 3D design software, a variety of coalescer designs were produced and printed in both polymethacrylate plastic and silica ceramic (Figure 4).

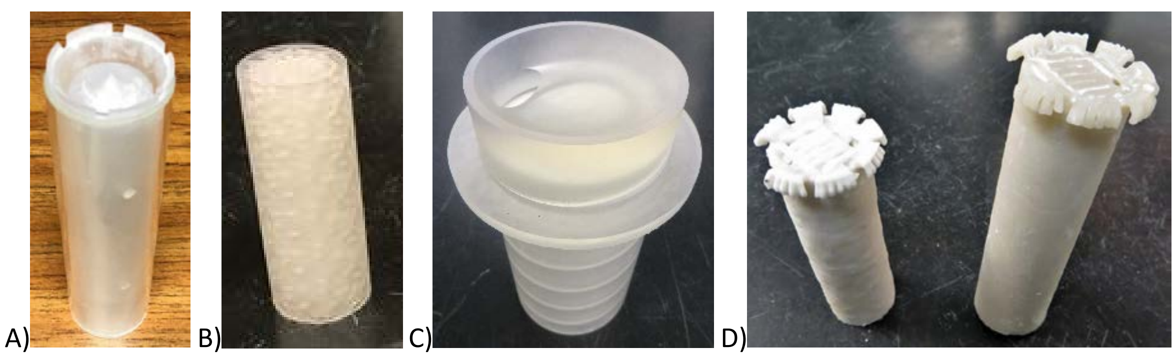


**Figure 4.** From left to right, a collection of coalescer inserts as follows: (A) polymethacrylate 1in multi-turn insert, (B) polymethacrylate 1in frit-like column, (C) polymethacrylate 3in centrifugal column [printed by J. Bobbitt], and (D) ceramic SRNL frit-like column after (left) and before (right) sintering.

The first designs were printed in plastic and at a diameter of 3in. to examine feasibility of printing the concepts as well as to fit the initial integration scheme involving a 3in. Teflon bushing to be placed between two components of the typical SRAT/SME offgas stream. Successive plastic designs were scaled down to a 1in. diameter and set up to fit into a modified adapter between the condenser and MWWT involving two separate Teflon fittings and a glass tube. The move to utilize a glass tube was closer to what could be anticipated as the available space in a chemical processing facility, such as DWPF: a process pipe responsible for transporting material. We were able to show that, first, the 3D printing method gives us the capability to modify designs quickly with little to no impact to the component manufacturing process (unlike traditional injection molding processes) and, second, that components could be designed and manufactured to fit within the available confines of typical processing environments with minimal impacts to process equipment. Whereas the simulated equipment required some minor modifications, full-scale process pipes would require minimal updates to accommodate such an addition.

Following the initial simple designs, more complexity was bred into the designs as the 3D design and printing process was further explored. After overcoming small learning curves associated with 3D design software and the necessary intricacies associated with transitioning from design to physical print, smaller and small microstructures were explored. The two initial designs were simple torturous paths; second generation designs were more akin to frits or filters; third generation designs began pushing the limits of what is achievable with the Form2 in terms of surface microstructures. Figure 5 shows the latest design attempting to produce a lotus leaf-like surface sub-structure. As can be seen in the image of the actual print under a microscope, some surface detail is lost at that scale with the utilized parameters, but there is a potential to optimize the design and printing process to improve definition.

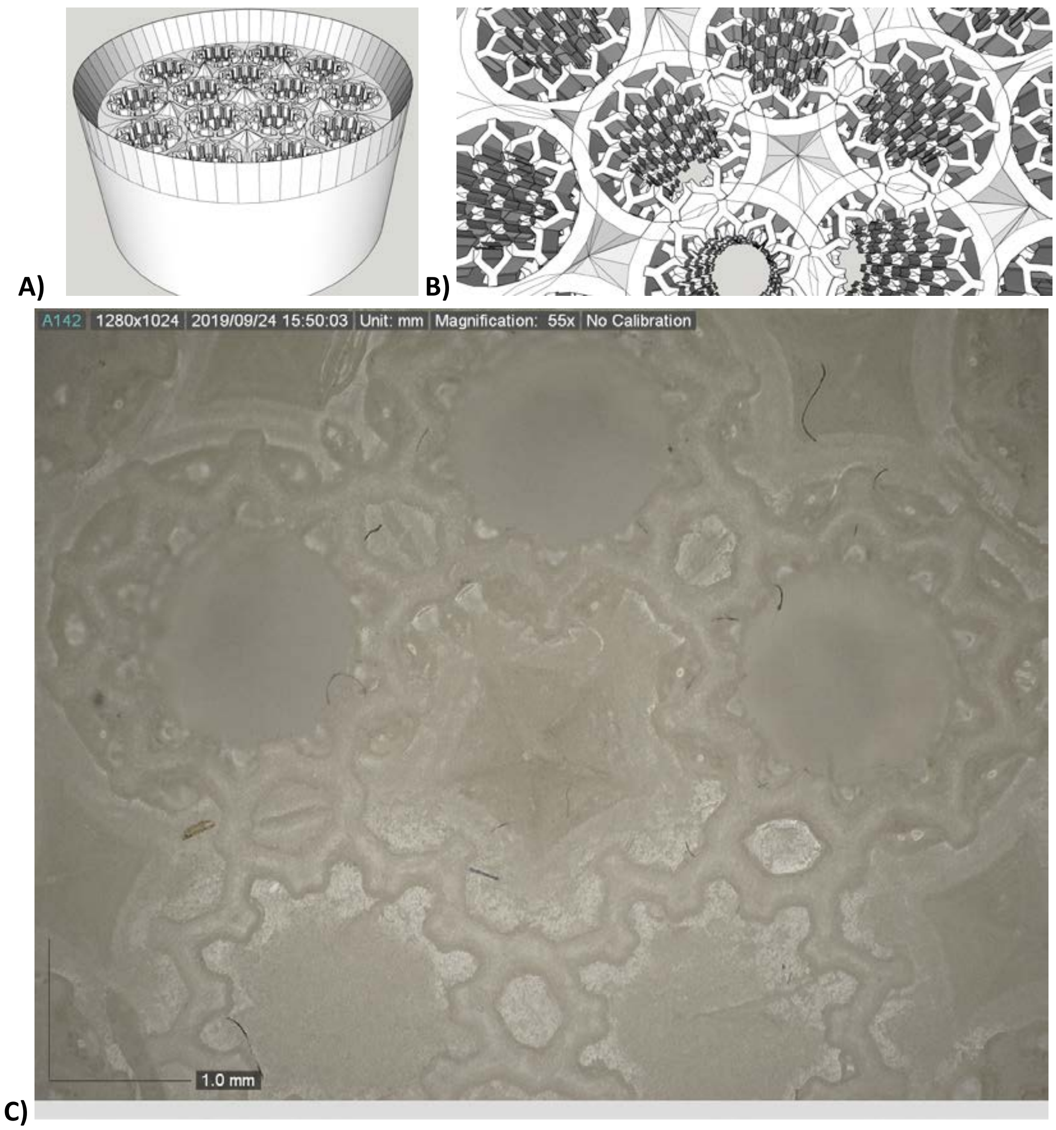


**Figure 5.** The 3D design from the software showing the A) overall structure and B) detail of the channels. C) the physical print achieved as viewed under a magnification.

To expand on functionality, attempts to print in ceramic were made and also proved to be successful after another small learning curve to understand the printing process changes required to accommodate the differences in material. A column with a frit-like internal structure (Figure 4, image D) was successfully printed and sintered, first, to remove the supporting polymer containing the ceramic particles and, second, to fuse the ceramic particles together into a porous glassy piece. Due to the internal complexity of the component, there was some structural distortion as the polymer did not all bake out at the same rate from all sides. This also resulted in a slightly more porous structure than anticipated, evidenced by the rough surface and some spots of black residue (likely trapped carbon). Additional modification of the bake-out and sintering heating profile is required to produce a fully glassy product with minimal distortion. However, for this application, a porous structure is actually preferable as it provides additional surface area for solid-liquid interactions.

With successfully printed components, testing was conducted to examine, one, the impacts to other processing parameters from the incorporation of the torturous path and, two, the enhancement of mercury removal, if any. The simplest design (Figure 2 and Figure 4, image A) at a diameter of 1in. and utilizing the two Teflon bushings connected by a glass tube was inserted into SRAT/SME testing for a new antifoam with our new equipment from Mettler Toledo: the RC1 (Figure 6). Day-shift only testing was performed and steam-stripping steps were shortened due to testing constraints, but the concept was efficiently examined. An addition of 7.0336 grams of mercury (II) oxide was made to the simulant sludge with a theoretical product of 6.514 grams of elemental mercury. Of this theoretical amount, approximately 1.55 grams of mercury was recovered in the coalescer. This was determined based on soaking the coalescer in an aqua regia solution, diluting to a set volume, and analyzing the mercury concentration within the solution via Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP-AES). Even with the abbreviated testing and the simplest design, the coalescer segregated nearly 25% of the mercury from the process.

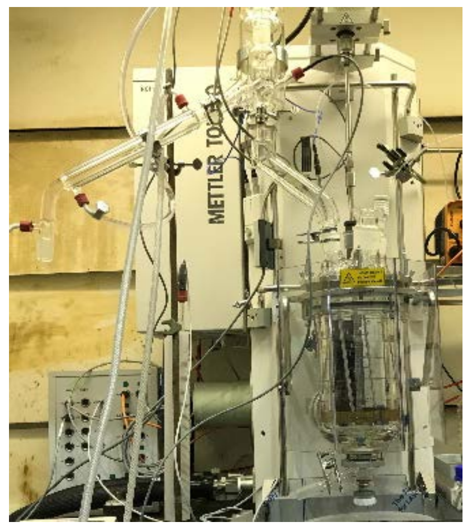

**Figure 6.** Reaction calorimeter, RC1, from Mettler Toledo.

Testing in the environmental remediation protocols utilized by Dr. Carmen Huffman at Western Carolina University is on-going.

## FY2019 Accomplishments

- 3D printed increasingly complex coalescer components in decreasing sizes and increasing surface sub-structure complexity.
- Printed components in multiple materials, examining manufacturing parameter changes and inherent finished material limitations.
- Integrated 3D printed component into prototypical SRAT/SME testing with minimal impact to currently engineered components and operating parameters/procedures.
- Integrated 3D printed component into environmental remediation testing through university subcontract (Dr. Carmen Huffman, Western Carolina University).

## Future Directions

- Increase complexity of surface sub-structures and internal geometries to improve physisorption and chemisorption.
- Examine additives to resin prior to printing to generate reactive 3D printed components and increase chemisorption alongside physisorption.
- Examine additional printing materials and compare for efficiency of printing sub-structures as well as efficiency of mercury physisorption and chemisorption.
- Potential to patent material combinations, printed components, and / or improved methodology.

## References

1. A. F. Gruss, R. Rodriguez, D. W. Mazyck,"Mercury Oxidation by UV Irradiation: Effect of Contact Time, UV Wavelength, and Moisture Content", *Ind. Eng. Chem. Res.*, 56, 6131-6135, (**2017**).
2. Y. Yoon, D. Kim, J-B Lee,"Hierarchical micro/nano structures for super-hydrophobic surfaces and super-lyophobic surfaces against liquid metal", *Micro and Nano Systems Letters*, 2, (**2014**).

## Acronyms

| | | |
|---|---|---|
| DWPF | - | Defense Waste Processing Facility |
| ICP-AES | - | Inductively Coupled Plasma – Atomic Emission Spectroscopy |
| MEC | - | Mercury Extraction Coalescer |
| MWWT | - | Mercury Water Wash Tank |
| NDA | - | Non-Disclosure Agreement |
| SME | - | Slurry Mix Evaporator |
| SRAT | - | Sludge Receipt and Adjustment Tank |
| SRNL | - | Savannah River National Laboratory |
| SRS | - | Savannah River Site |
| WCU | - | Western Carolina University |

## Intellectual Property

A non-disclosure agreement (NDA) was entered between Dr. Huffman (WCU) and SRNL to protect the potential patentability of the device concept, designs, modifications, and uses.

## Total Number of Student Researchers

One student researcher was a part of Dr. Huffman’s researcher group at WCU; all of their work was performed off-site at the university. Two undergraduate summer interns performed work on-site and provided hands-on manipulation of the 3D printed components and some design consultation.