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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

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 assist 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. 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.

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. Initial designs have been integrated into the current equipment utilized for simulated high-level waste chemical

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).

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processing experiments performed at the Savannah River National Laboratory. Other 3D designs have been produced that more advanced internal geometries or are composed of alternate materials.

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.

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. The ability to use multiple materials or even modify existing materials makes the FormLabs platforms ideal for R&D activities. We could quickly transition between printing media with no down-time between modifications



Figure 1. (Left) 1 in. adapter and (right) 3 in. adapter designs for the integration of coalescers between the SRAT/SME condenser connector (top) and Mercury Water Wash Tank (MWWT, bottom).

The integration of the printed components into current testing equipment (Figure 1) 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,

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so the combined tests were ideally suited to run concurrently. A coalescer 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 coalescer sectioned into approx. 1 in. 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 2).

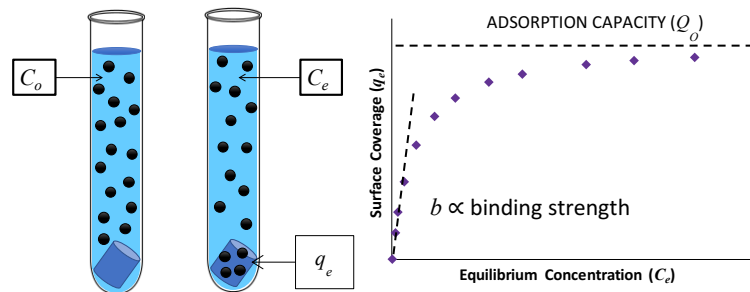


Figure 2. Adsorption capacity (Q_o) can be calculated using the equilibrium concentration (C_e), the surface coverage (q_e), and the binding strength (b) by fitting the data to the Langmuir equation:

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

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 various materials.

The first designs were printed in plastic and at a diameter of 3 in. to examine feasibility of printing the concepts as well as to fit the initial integration scheme involving a 3 in. Teflon bushing to be placed between two components of the typical SRAT/SME offgas stream. Successive plastic designs were scaled down to a 1 in. 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 coalescers as the 3D design and printing process was further explored. After overcoming small learning curves associated with the design software and the necessary intricacies associated with transitioning from digital design to physical print, smaller and more complex microstructures were explored.

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To expand on functionality, attempts to print in additional material compositions 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.

With successfully printed components, testing was conducted to examine, one, the impacts to other processing parameters from the incorporation of the restricted path and, two, the enhancement of mercury removal, if any. The simplest design at a diameter of 1 in. 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 3). 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.

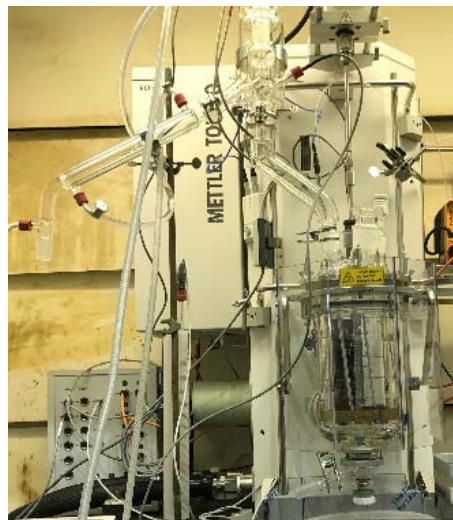


Figure 3. Reaction calorimeter, RC1, from Mettler Toledo.

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 additional printing media to increase chemisorption alongside physisorption.
- 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.