

## Part 1. Cover Page

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Research Topic Theme:	Theme 2: Freshwater Oil Spill Response
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## Part 2. Background and Context:

Oil discharges into the environment are unintentional and stochastic by definition. Oil transport by barge and pipeline often occurs through remote regions. Response effectiveness can be hampered by the logistic complications that come with responding in locations with little to no infrastructure. One of the alternative response measures (ARMs) used in marine environments has been burning oil slicks *in situ*. The ramifications of *in situ* burning (ISB) are less studied in freshwater contexts than in marine environments. ISB as a response option in freshwater environments carries with it several concerns spanning the purely ecological (e.g., long term residue impacts, pyrogenic chemical products, wildfire ignition source when near shorelines) to the purely anthropocentric (e.g., drinking water contamination and burning smoke and ash). Despite these concerns, controlled ISB experiments and ISB utilization during marine oil spill response (e.g., the *Deepwater Horizon* spill in the Gulf of Mexico in 2010) have demonstrated the potential to eliminate more than half of spilled oil.

Specific to the Great Lakes region, there are complications and concerns that have limited the use of ISB in response and pre-approval of ISB as part of contingency planning. There are concerns with the smoke and volatile gases produced potentially impacting populated areas. There are concerns with ISB residues that may sink creating a more persistent situation that may be more expensive to remediate than if more classic methods of oil removal had been used. However, classic oil spill removal and recovery techniques do produce large volumes of contaminated water in addition to the recovered oil itself. Often, the volume of contaminated water is manyfold greater than the volume of recovered oil. Removed oil and collected contaminated water cannot be discharged back into any portion of the Great Lakes under the bi-national CANUSLAK agreement between Canada and the United States of America. When response is required in remote regions with little to no infrastructure, the retention of large volumes of oil and water rapidly become the limiting factor in the scope and effectiveness of response.

#### *State of the Science*

The effectiveness of ISB is related to the oil type, weathering state, and slick thickness. This can limit the circumstances when oil can be burned effectively. Oils with smaller aliphatic and aromatic fractions are less conducive to efficient ISB. Most ISB field experience and laboratory research has used natural and conventional crude oils. Less is known about the range of effectiveness and about burn byproducts from nonconventional and synthetic crude oils. Dilbit and other heavy synthetic crude oils may become highly recalcitrant to classic ISB very soon after the initial spill event as their diluents evaporate and the slick spreads to thicknesses less than two millimeters. This often limits response options to mechanical recovery methods, which in turn, produce large volumes of retained waste as described above.

Burn products from classic ISB include smoke particulates, gases such as carbon monoxide, sulfur dioxides, nitrogen oxides, and hydrocarbon volatiles (e.g., BTEX), which are all produced depending on oil composition and combustion chemistry [API Technical Report 2016]. All of the above can present an acute health hazard for responders, wildlife, and any residents near the spill. Furthermore, classic ISB can produce solid and semi-solid residues that can sink in freshwater. There is an operational gap between classic ISB, burning of oil slicks on water, and the disposal of mechanically recovered oil and contaminated water.

Prometheus Pyrology Solutions (PPS) has conducted extensive ISB research, including new approaches to ISB. One such approach is the “Oleum Oubliette”, a low-emission spray combustor for emulsified crude oil [Torrey et al. 2019]. The 2019 report details the design and testing of a device that disposes of recovered crude oil that has become emulsified with water. Their proposed approach allows for the *in-situ* disposal of collected oil in a way that attempts to bypass many of the concerns with classic ISB of slicks on the water. In brief, the device by

Torrey et al. delivers on its promises of combusting recovered oil with emissions greatly reduced compared to classic ISB with daily burn rates on the order of several hundred barrels of oil per day. This may be sufficient to dispose of the assumed collection capacity of a vessel of opportunity skimming system.

The above combustion system, and the one designed by Prestige Environmental Remediation Associates [Lee et al. 2012], can be improved upon. Both systems reduce but do not eliminate incomplete combustion products, and neither system is designed to eliminate waste that consists primarily of water.

### *Relevance of the Research*

This proposed work directly relates to Theme 2, by the development of new technology that will expand the ability of a remote response to safely dispose of collected waste in a way that eliminates the operational resource drain of storage and transportation of wastes. This would free up critical resources to be allocated to oil spill recovery and containment.

The Public lab seeks to produce a system that considers the infrastructure limitations of waste storage, transport, and disposal in remote regions, as well as to drastically improve the emission profile of the combustion exhaust. The system proposed by Public and collaborators will have the potential to be a one-system-one-response option for the management of oil spill removal waste streams. This would remove the need for large volume on-site waste storage, the logistics of transporting waste for disposal, and free up more ship time for response operations.

The Public lab proposes to design and test a self-confining air-plasma toroidal (SCAPT) combustor. This system will operate in a similar fashion to the “Oleum Oubliette” in that a jet of dropletized waste will be introduced into a combustion chamber. Whereas the burner system used a plasma arc to initially ignite the flame and thereafter relied on physical confinement, the SCAPT combustor will be a series of toroid (donut shapes) of steam and air plasmas that are held in place by relatively weak electromagnets and their own induced interacting magnetic fields and plasma vortex rotation [Ombrello et al. 2010; Yusupaliev et al. 2007; Ramasamay et al. 1996; Beispiel et al. 2019]. Much like the previously mentioned combustors, this system will use the extreme temperatures achieved within the chamber to reduce the contaminants to their component elements. The older combustors operate at several hundred degrees, but this new system will operate with several toroids ranging in temperature from several thousand degrees Celsius to tens of thousands degrees Celsius, thus assuring that the exhaust will not contain any measurable amounts of intact petroleum compounds.

The staged gradient and the extremes of temperature in the proposed system allow for a greater flow rate than the other combustors. Instead of barrels per hour, the maximum throughput possible with the SCAPT would be more than two orders of magnitude greater for oil/emulsions and share a similar waste disposal rate with contaminated waters (expected to be around 5 to 10

L/min). The SCAPT would be able to operate in a continuous flow from crude to water, so that waste could be disposed of as it is generated during response, simplifying logistics of operation.

#### *Operational Relevance*

The SCAPT would allow for scalable hydrocarbon waste disposal in situ for spill response in areas with limited or no infrastructure to store or transport waste.

#### *Other funding*

Dr. Public's lab is currently conducting work funded by Michigan Sea Grant, the Lorem Freshwater Heritage Foundation, EPA STAR, and a partnership with the Green EGU initiative. The projects supported by Michigan Sea Grant and the Lorem Freshwater Heritage Foundation are focused on beach clean up and do not relate to the proposed GLCOE work. Projects supported by the Green EGU initiative are similar to the proposed work but have been focused on using similar technology in saltwater environments. The EPA STAR grant fund is being leveraged for this project, as it supports the stipend for the graduate student who will work on this project. Dr. Public expects to apply for the next round of funding with the Lorem Freshwater Heritage Foundation, hoping to build on the findings of the proposed GLCOE project proposed here.

Dr. Beispiel has secured a grant partnership with Snider Syngas to investigate self-containing air-plasma technology towards hydrogen gas production from municipal wastes. This work does not directly relate to the proposed GLCOE work, but equipment procured and constructed to for that work is being leveraged to reduce costs to conduct the proposed work which does align with GLCOE interests. Dr. Beispiel has two open applications for funding, one with the Department of Science and Technology and one with National Science Foundation: Plasma Physics. Dr. Beispiel will be re-applying with the next National Science Foundation: Plasma Physics funding opportunity. If the Beispiel lab is awarded one or both of these grants, those funds would not directly contribute to the proposed word but would be leveraged to further reduce costs of future work to develop the proposed system to the next technology readiness level.

#### **Part 3. Problem(s) statement:**

Oil spill response in remote areas can produce large volumes of waste without proper infrastructure to store, transport, and dispose of those wastes.

#### *Project Goals*

The goals of this project are to (1) construct a laboratory scale self-confining concentric air-plasma toroids combustor as proof-of-concept. (2) Validate the stability of the self-confinement

through a range of simulated waste stream flow rates. (3) Validate the stability of the self-confinement through a range of simulated crosswinds and adverse weather conditions. (4) Assess performance at lab scale using four representative oils at three different weathering states.

#### Part 4. Technical Approach/Research Design

##### *Personnel*

Jane Q. Public, PhD                      Project Lead                      20% time

Dr. Public will serve as the project lead, subject matter expert on oil chemistry, and direct supervisor for Ms. Du Bois, and Ms. Paracelsus.

Elke Beispiel, PhD                      Technical Lead                      10% time

Dr. Beispiel will serve as the subject matter expert on plasma physics and engineering, and direct supervisor for Ms. Kiesler, and Dr. Hamilton.

Hedwig E. Kiesler                      Senior Technician                      30% time

Ms. Kiesler will serve as the lead technician and software engineer.

Alice Du Bois                      Research Assistant                      50% time

(Note, this is the limit of EGU student participation)

Ms. Du Bois is a student of Dr. Public and will be contributing labor to the project as part of her master's thesis. Ms. Du Bois will be expected to produce a peer reviewed publication based on her contributions.

Margaret Hamilton, PhD                      Researcher                      75% time

Dr. Hamilton is a post-doctoral scholar with Dr. Beispiel's lab and will be contributing labor to the project as part of her career development. Dr. Hamilton will be expected to coauthor the software that controls the SCAPT, as well as no fewer than two peer-reviewed publications.

Theola Paracelsus                      Junior Technician                      35% time

Ms. Paracelsus is a technician in Dr. Public's lab and will contribute labor to the project under the supervision of Ms. Kiesler.

##### *Metrics*

The measures of progress and success will be defined by the individual stages of the project.

Project goal 1: The proof-of-concept SCAPT will be declared a success when it:

- a) Reliably ignites, defined as achieving self-confined plasma in nine out of ten consecutive attempts.
- b) Is stable, defined as maintaining temperature and density for ten minutes.

Project goal 2: Will be assessed in finding the limits of internal operation for the lab scale SCAPT. Success will be defined as the establishment of

- a) The steam inflow rate that destabilizes the plasma by quenching.
- b) The hydrocarbon concentration that exceeds the capacity of the SCAPT to decompose to single carbon compounds.

Project goal 3: Will be assessed in finding the limits of operation for the lab scale SCAPT to simulated weather conditions possible during a response. Success will be defined as the establishment of

- a) The ambient high temperature that overwhelms the cooling mechanisms of the SCAPT, and the ambient low temperature that prevents SCAPT starting.
- b) The strength of a crosswind that would significantly interfere with the operations of the SCAPT.

Project goal 4: SCAPT performance for each oil and weathering state will be measured by the resulting ions in the exhaust as total percentage relative to the ideal (CO and CO<sub>2</sub> only).

Overall progress of the project will be measured by having met or failed to meet the above definitions for each goal by the timeline given in Part 5, below.

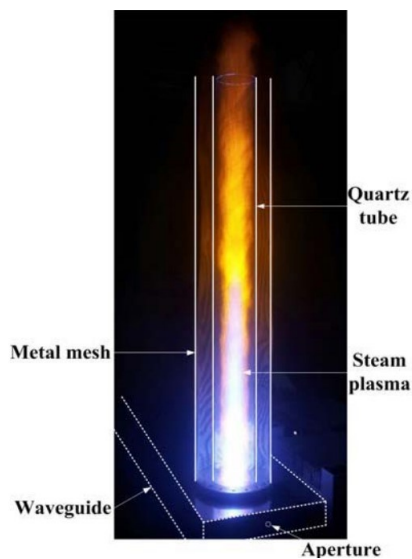
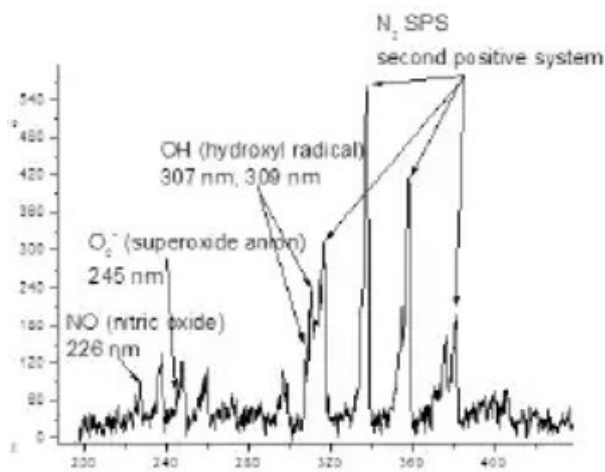


Figure 1. Example steam plasma from Hong et al. 2015.

## *Approach*

### Principal of Operation

The fundamental operating principals behind the SCAPT are that chemical bonds break at high enough temperatures, and that momentum and mass are different enough among elements to allow for continuous separation. In brief, water (contaminated or not) is heated in a microwave chamber until it remains liquid only due to the confinement of the chamber walls. This water automatically undergoes the phase change to steam upon entering the steam-plasma microwave chamber at the base of the SCAPT system. High-powered microwaves force the phase change from steam to water plasma, and water into a mixture of hydrogen plasma, oxygen plasma, and hydroxyl radicals. An example of a steam plasma tested by Hong et al. (2015) is shown in Figure 1. The initial plasma mix is then shaped by the flow of air-plasma from a central axis plasma torch into the initial plasma toroid. Spray nozzles introduce the waste into the first plasma torus.



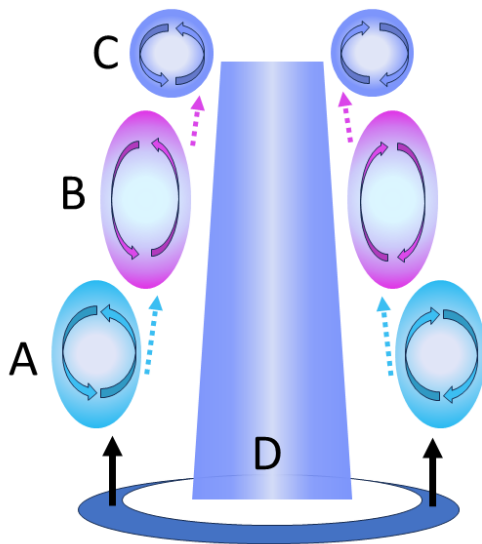
*Figure 2. Radical ion emission spectra in the ultraviolet range. Figure adapted from Hong et al. 2012.*

### **Radiolysis of water into radicals**

A combination of high temperatures, abundant free oxygen in diatomic and plasma phases, and high temperature radical species begin the breakdown of large hydrocarbon contaminants. UV light emission from hydroxyl, nitrogen oxide, and superoxide ions ranges from peaks in the “vacuum UV”, UV-C, to near visible UV-A (Figure 2). This ionizing radiation requires shielding for the SCAPT operators, but also accelerates the hydrocarbon decomposition.

### Radical reflux by toroid rotation

Hydroxyl radical concentration is monitored by emission spectra to allow for dynamic adjustment of the steam plasma toroid by adjusting microwave input. The interface between the initial steam plasma toroid and the following plasma toroid is controlled by a combination of the electromagnetic cage, the input flow rates, and the central axis air-plasma flow. This “smoke ring” style flow forces the heaviest molecules to the edges of the toroid surface. The outer surfaces of the toroid are both self-confined and additionally confined by electromagnetic fields. This “flings” the heavier masses out at predictable angles based on their mass. The heaviest masses leave the toroid only to be swept back into it by the plasma stream inflow. The lightest multiatomic masses (i.e., the hydroxyl and nitrogen oxide radicals) are ejected at the boundary layer of the steam-plasma and central axis air-plasma flows and are churned back into the toroid until they are thermally decomposed to hydrogen and oxygen.



*Figure 3. Simplified cutaway diagram of the three toroids and central air-plasma axis. A) the primary steam-plasma toroid that directly receives the waste. B) the secondary plasma toroid that receives the breakdown ions from the primary and reduces them to single-atom ions. C) the tertiary toroid that controls the final release of the ions and allows for some controlled compound creation. D) the central air-plasma axis.*

### Thermal decomposition of carbon, nitrogen, sulfur, and metals

Secondary and tertiary self-confined plasma toroids are supported and shaped by the central air-plasma axis while microwaves control the temperature of the plasma toroids. The secondary toroid temperature is maintained within the range to thermally decompose remaining multiatomic ions into single atom ions only. The individual mass differences (with variance due to isotopes) predict the angle of exit for each element from the secondary toroid. These



predictions allow for the control of their residence times in the final, tertiary toroid.

### **Countercurrent thermal conservation and controlled exhaust phase change**

The primary purpose of the tertiary toroid is to recapture some of the plasma and heat of the system. The secondary purpose is to stage the cooling of the plasma so that more desirable compounds are thermodynamically favored (e.g.,  $N_2$  and  $O_2$  rather than  $NO_x$ ).

#### Experimental Design

Project Goal 1: Ignition reliability will be tested by ignition attempts in rounds of ten. Each ignition must result in all three plasma toroids formed after one second and clearly distinguishable by microwave interferometry.

Stability will be tested by ten runs, each lasting ten minutes. A run is a success if the density and temperature of each toroid remains within bounds that have been empirically determined to completely thermally decompose hydrocarbons.

Project Goal 2: The SCAPT will be subjected to ten replicate runs that start with the normal steam flow rate established from Goal 1, increasing the flow rate until self-containment failure by quenching is achieved. Quadratic approximation linear modeling of the likelihood of failure will determine the safe operating range of steam inflow under ideal conditions.

Then, constraining the steam flow to the median rate between too little to maintain toroid self-confinement and the rate established as the beginning of risking quenching, a mixture of petrodiesel and water will be introduced. The fraction of hydrocarbon to water will be increased until breakthrough is established, where multiple-carbon molecules are observed in the exhaust.

Project Goal 3: The SCAPT will be operated at the median values for steam inflow and hydrocarbon content. A combination of heat lamps and forced air heaters will simulate operations under ambient temperatures up to 45 degrees Celsius (record high in Michigan is  $44^\circ\text{C}$ ). Lower temperatures will be simulated by inflow from a liquid air dewar into the exhaust of laminar flow fan. Freezing temperatures will be simulated down to  $-55^\circ\text{C}$  (record low in Michigan is  $-52^\circ\text{C}$ ).

An adjustable speed fan will be used to augment the fume hood's air intake to achieve simulated sustained winds of 35 km/h (just below the lower bound of small craft advisory). The SCAPT will be run with median values for steam inflow and hydrocarbon content, and at room temperatures in ten replicate runs. Each replicate run will begin with the base crosswind simulation of the fume hood's operation, each minute the inflow will be augmented by the fan

until the SCAPT loses stability or the simulated crosswind reaches the maximum wind for one minute without SCAPT failure.

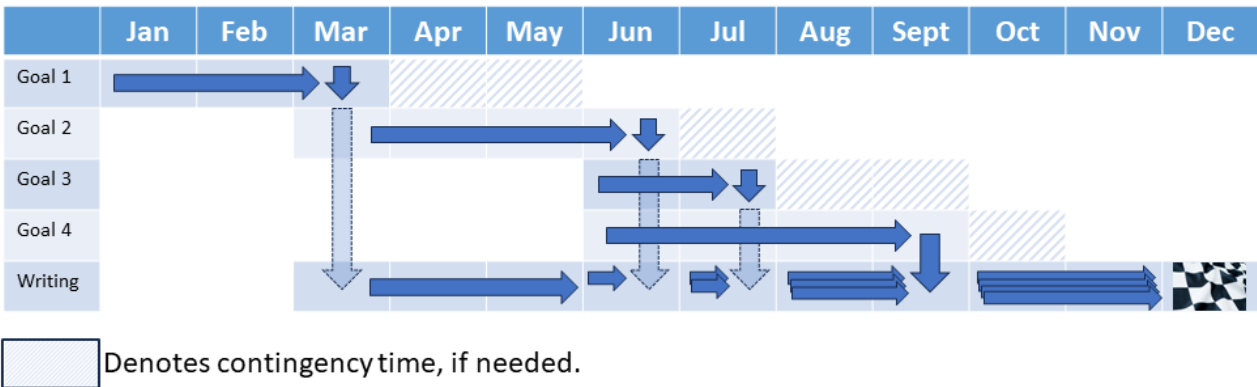
Project Goal 4: Four oils will be used; No. 6 fuel oil, a light natural crude oil, a heavy natural crude oil, and a synthetic crude oil. Each will be used neat (unweathered), moderately weathered, and heavily weathered. Artificial weathering will consist of heating to 45°C in a large crystallization dish, under a constant stream of air for 24 h (moderately weathered) to 168 h (heavily weathered), with a rocker to provide agitation.

SCAPT will be operated at the medians of the parameters explored in the previous three goals. Oil will be fed into the SCAPT at a constant rate, for five minutes while the exhaust is monitored for breakthrough as per goal 2. Each oil will be run in triplicate, per weathering state.

### Facilities

The Beispiel lab is well equipped from previous self-confined plasma work. The Public lab provides the facilities for the safe storage, handling, and weathering of oil.

### Part 5. Research Schedule



### Part 6. Deliverables

#### Deliverable 1

Blueprint for proof-of-concept SCAPT system. The blueprint document will detail the design (schematics) and capabilities of the SCAPT system as proven by the project. Where the SCAPT components and implementation depart from prior art, the Public and Beispiel labs will apply for

patents. The next step being to move the SCAPT system into a higher technology readiness level (TRL).

#### Deliverable 2

Peer-reviewed publication 1, to be submitted to *Journal of Fictitious Plasma Physics*. This planned manuscript would focus on the advancements in self-confining toroids and of their use in the novel context of freshwater environmental response. This will disseminate the fundamental scientific advancements as well as raise awareness of this realm of application to a scientific community (plasma physicists) that may not have considered the potential applications of their own research to the many aspects of oil spill response, and preparedness.

#### Deliverable 3

Peer-reviewed publication 2, to be submitted to *Hazardous Waste and Hazardous Materials*. This planned manuscript would focus on plasma thermal decomposition of hydrocarbon waste and the possibilities of use with wastes that may be associated with oil spills, such as polyfluorinated compounds from marine firefighting foams.

#### Deliverable 4

Peer-reviewed publication 3, to be submitted to *Marine Pollution Bulletin*. This planned manuscript would focus on the operational role of oil spill waste management and in situ disposal by SCAPT as an avenue of “minimum regret” oil spill response operation philosophy and overall environmental risk reduction during response.

#### Deliverable 5

Final Project Report, to be submitted to the GLCOE. The writeup will follow the project summary template provided by the GLCOE. It will outline the steps taken to complete the project, the outcomes, and detail what did and did not work about this approach. It will be made available so that the GLCOE can use this as an example to communicate about the work with the public until the peer-reviewed publications are published.

#### Deliverable 6

Conference abstract submitted to Fictitious Physics Annual Conference. Dr. Hamilton will submit an abstract outlining this proposed work to the upcoming Fictitious Physics Annual Conference. Each year, this conference convenes 3,000 researchers across the field of Physics. This year, there is a session on the real-world application of plasma-based tools that Dr. Hamilton hopes to present in, exposing others in the field to the applications of plasma physics to oil spill research and hopefully creating new avenues for collaboration.

#### Deliverable 7

Quarterly Progress Reports as described in section IIIe(iii) of the BAA.

#### Deliverable 8

Monthly Meeting Minutes as described in section IIIe(iii) of the BAA.

## Part 7. Detailed Cost Proposal

Cost Category	Detail/Description	Qty/Rate	Cost
Direct Costs/Salaries and wages	Jane Q. Public, PhD; Project Lead	0.2*	\$16,000.00
Direct Costs/Salaries and wages	Elke Beispiel, PhD; Technical Lead	0.1*	\$7,500.00
Direct Costs/Salaries and wages	Hedwig E. Kiesler; Senior Technician	0.3*	\$15,000.00
Direct Costs/Salaries and wages	Margaret Hamilton, PhD; Researcher	0.75*	\$45,000.00
Direct Costs/Salaries and wages	Theola Paracelsus; Junior Technician	0.35*	\$12,250.00
Fringe Benefits	Jane Q. Public, PhD; Project Lead	0.265*	\$4,240.00
Fringe Benefits	Elke Beispiel, PhD; Technical Lead	0.265*	\$1,987.50
Fringe Benefits	Hedwig E. Kiesler; Senior Technician	0.154*	\$2,310.00
Fringe Benefits	Margaret Hamilton, PhD; Researcher	0.356*	\$16,020.00
Fringe Benefits	Theola Paracelsus; Junior Technician	0.154*	\$1,886.50
Equipment	Control Computer System	1	\$6,000.00
Materials and supplies	Purchase of additional supplies to build proof-of-concept.	1	\$5,000.00
Materials and supplies	Open Access Journal Fees (3 publications)	3	\$10,500.00
External test facility	Not applicable	0	\$0.00
Domestic travel	Travel to the Fictitious Physics Annual Conference	2	\$5,000.00
Domestic travel	Ann Arbor, MI GLCOE Annual Collaborative	1	\$2,500.00
Subawards	Not applicable	0	\$0.00
Other direct costs	Not applicable	0	\$0.00
Indirect Cost	Negotiated indirect cost rate	0.25	\$37,798.50
Contracting Agreement Fee		0.05	\$9,449.63
Sub-total: Personnel			\$122,194.00
Sub-total: Supplies			\$21,500.00
Sub-total: Facilities			\$0.00

Sub-total: Travel	\$7,500.00
<b>TOTAL COST</b>	<b>\$198,442.13</b>

\* 9-month appointments have been converted to full time equivalent of a 12-month appointment.

*Admin and Fringe* – EGU administrative and fringe benefit rates are standard based on the current rate agreement with the Department of Health and Human Services Facilities and Administrative Rate Agreement dated May 12, 2023. Fringe benefit rates are calculated as a percentage of salary. Direct labor costs/salaries are based on full time equivalents for a 12-month appointment.

*Control computer system* – This is a custom-built computer that will operate every component of the SCAPT system, the electromagnets, valve actuators, the sensor suite (infrared temperature, ion spectrum, microwave interferometry, etc.), and microwave emitters. All input and controls are integrated in a custom software suite to allow for advance algorithmic stability control in the same software as the manual control. The computer system is necessary equipment that is inseparable to the SCAPT.

*Materials and supplies* – Bulk supplier electromagnet wires from a proven high-temperature alloy as per Beispiel et al. (2019). Consumables and items needed for SCAPT construction, e.g., feedstock metal powders for 3D printing, plate and ingot metal for CNC milling, sensor wiring, connectors, and adaptors. Laboratory chemical supplies (organic solvents for cleaning). Laboratory PPEs necessary for work with hydrocarbons, cryonic liquids, UV light emitters, and high heat.

*Domestic Travel* – two travelers to Fictitious Physics Annual Conference, one traveler to GLCOE Annual Collaborative

Leveraged funds:

- Alice Du Bois, Research Assistant, salary and fringe benefits are covered by the EPA STAR grant.
- The Public Lab has three oil types on hand and will not require funds to acquire and ship oils for this project.
- Most materials are provided in-kind by Snider Syngas resulting in a small \$10,000 materials budget for this project.

## Part 8. References

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