Environment and Natural Resources Trust Fund
2010 Request for Proposals (RFP)

LCCMR ID: 230-G

Project Title:

Mercury Removal via STC for Compliance with Great

LCCMR 2010 Funding Priority:

G. Creative Ideas

Total Project Budget: $ $683,669

Proposed Project Time Period for the Funding Requested: 2 years, 2010 - 2012

Other Non-State Funds: $ $0

Summary:

A pilot unit employing a novel catalyst will be installed for mercury removal from coal-fired power scrubber water at an Xcel Energy host facility in Minnesota after bench scale testing.

Name: David Mazyck

Sponsoring Organization: University of Florida

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Location:

Region: Metro

County Name: Washington

City / Township:

_____ Knowledge Base _____ Broad App. _____ Innovation

_____ Leverage _____ Outcomes

_____ Partnerships _____ Urgency _____ TOTAL

PROJECT TITLE: Mercury Removal via STC for Compliance with Great Lakes Initiative

I. PROJECT STATEMENT

Mercury (Hg) is a toxic pollutant that bioaccumulates in the aquatic food chain and can lead to adverse neurological effects, particularly in the developing fetus and during early childhood. Additionally, some scientists have recently linked Hg to a cause of autism and ADHD in children (Bernard et al., 2001; Cheuk and Wong, 2006). The Minnesota Pollution Control Agency (MPCA) estimates that 58% of Hg emissions from Minnesota sources come from power plants, and thus reduction of Hg emissions in this sector has been a priority. This proposal addresses the need to tackle mercury as related to energy production, as identified in the Legislative-Citizen Commission on Minnesota Resources (LCCMR) Six-Year Strategic Plan.

The Minnesota Mercury Emissions Reduction Act of 2006 will result in a 90% reduction of Hg emissions from six generating units at three of Minnesota's largest coal-fired power plants. This reduction will be achieved in part by modification of dry or wet scrubber systems in these plants (MPCA, 2006). Flue gas desulfurization (FGD) systems (e.g., wet scrubbers) have the co-benefit of capturing oxidized Hg while reducing gaseous sulfur dioxide (SO_2) emissions. In wet FGD, an aqueous lime or limestone solution is sprayed into flue gas to react with SO_2, converting it to "scrubber sludge", a wet by-product (Fig. 1). Although FGD processes lead to a reduction in Hg emissions at the stack, this results in the presence of Hg in scrubber sludge. Upon dewatering of scrubber sludge, Hg may partition into the solid or liquid (i.e., water) fraction, depending on the operational differences of FGD systems and type of coal used (EPRI, 2005). As FGD systems are optimized to obtain greater Hg removal, the levels of Hg in scrubber water and/or solids will increase. In addition, it was recently discovered that oxidized Hg can be reduced to elemental Hg (a highly volatile form) within the FGD system, causing the reemission of elemental Hg to the gas phase (i.e., Hg is reintroduced to the stack). Thus technologies that can collect and stabilize Hg, preventing reemission and maximizing removal, are being sought.

Little emphasis has been placed on aqueous-phase Hg removal technologies. With strict emerging standards, such as the Great Lakes Initiative (regulating aqueous Hg discharges to below 1.3 ppt) it is imperative that technologies for trace level Hg removal from water be investigated. Traditional technologies for Hg removal from water, such as activated carbon, have not been proven capable of removing Hg from water to sufficiently low ppt levels.

It is herein proposed to investigate the effectiveness of a novel adsorbent material developed at the University of Florida (UF), Silica-Titania Composites (STC), for the removal of Hg from coal-fired power plant scrubber water to trace ppt levels. In limited preliminary bench-scale studies (Fig. 2) with ash pond water from Minnesota Power's Laskin Energy Center, the STC have achieved Hg concentrations as low as 1.5 ppt as verified by a third party. This facility must comply with the Great Lakes Initiative by 2010. The purpose of the proposed study is to improve upon the preliminary data in order to consistently achieve Hg concentrations below 1.3 ppt.

II. DESCRIPTION OF PROJECT RESULTS

The investigation of the effectiveness of the STC will be carried out in two phases. The first phase will consist of bench-scale optimization using water samples from Xcel Energy's Allen S King Plant in MN and the second phase will consist of a pilot-scale study at the same facility.

Result 1: Bench-scale optimization **Budget:** $ 294,249.24

Batch adsorption experiments will be conducted with scrubber water in custom-designed glass reactors. The reactor contents will be continuously stirred via magnetic stirrer. At the end of the designated residence time, the reactor contents will be filtered via sterile 0.45-micron syringe filters to remove the STC from solution. All influent and effluent Hg concentrations will

be analyzed via EPA Method 1631. The effect of STC formulation, particle size, dose, and residence time on Hg removal efficiency will be evaluated to determine the most effective and economical system design.

Deliverable	**Completion Date**
1. Data from bench-scale studies (influent and effluent Hg concentrations obtained with different STC and contact times)	*4/1/2011*

Result 2: Pilot-scale verification **Budget:** $ 389,420.17

Results of bench-scale studies will be used to determine the design of a pilot-scale system to remove Hg from scrubber water on-site at Xcel Energy's Allen S King Plant. The pilot system will be fabricated and installed. Influent and effluent Hg concentrations will be monitored and reported. Figure 1 shows two potential example locations for the pilot system within the FGD process, which would also be the locations for full-scale systems.

Deliverable	**Completion Date**
1. Pilot-scale system design (drawings)	*4/1/2011*
2. Pilot-scale system fabrication, delivery, and installation	*7/1/ 2011*
3. Data from pilot-scale study (influent and effluent Hg concentrations obtained during continuous operation)	*1/1/2012*

III. PROJECT STRATEGY

A. Project Team/Partners

The key investigators on this project will be Dr. David Mazyck, Associate Professor at UF's Department of Environmental Engineering Sciences and Chief Technology Officer at Sol-gel Solutions, LLC (Sol-gel), and Dr. Anna Casasús, Research and Development Director at Sol-gel. UF is a leader in environmental engineering research and Dr. Mazyck has a strong research program in pollution control technology. Sol-gel was started in 2004 to facilitate commercialization of the STC technology developed at UF. Sol-gel exclusively licensed the technology from UF and has been working on its further development for a variety of applications, including those in the chlor-alkali and coal-fired power industries. The mission of Sol-gel is to help industries meet objectives related to product quality and environmental regulations through the proper selection of commercially-available technology or research and development of novel solutions. One such company, Xcel Energy Corporation, is motivated to find a solution for Hg removal and has agreed to provide water samples, a host facility for the proposed pilot unit, assistance with pilot study integration, and expertise related to the plant operations. A letter of support to this aspect is included.

B. Timeline Requirements

The time required to achieve project results is 18 months as indicated by the completion dates above.

C. Long-Term Strategy

This project would not directly require further investment for demonstration at the proposed scales. Thus, the next step toward commercialization would be the fabrication and installation of a near full-scale prototype or full scale systems. The research team would seek an agreement with Excel Energy for collaboration in putting forth funding for the next phase.

Project Budget

IV. TOTAL PROJECT REQUEST BUDGET (*1.5* years)

BUDGET ITEM	AMOUNT
Personnel:	$ -
PI: Dr. Mazyck, FTE: 0.16, %sal: 77, %benefits: 23, duration: 18 months	$ 37,025
Co-PI: Dr. Boyer, FTE: 0.08, %sal: 77, %benefits: 23, duration: 18 months	16,650
Project Manager: Riley, FTE: 0.16, %sal: 77, %benefits: 23, duration: 18 months	32,375
Administrative Coordinator: Strekalova, FTE: 0.22, %sal: 77, %benefits: 23, duration: 12 months	15,166
Post Doc: TBD, FTE: 1.0, %sal: 81, %benefits: 19, duration: 18 months	117,543
Graduate Students: TBD, FTE: 2.0, %sal: 93, %benefits: 7, duration: 18 months	81,408
Contracts:	$ -
Sol-Gel Solutions LLC. Pilot system design, fabrication, installation, and monitoring.	$ 250,000
Equipment/Tools/Supplies:	$ -
Teledyne Leeman Labs Hydra AF Gold Plus Mercury Analyzer and Accessories	$ 35,000
Materials required for manufacturing and sieving Silica-Titania Composites, bench-scale studies for optimization of the STC for mercury removal from water, costs for sample analyses during bench and pilot-scale studies. Materials include the following: Ethanol, TEOS, Hydrofluoric acid, Nitric acid, TiO2, Deionized water, Teflon containers, Pellet molds, Stir bars, Pipettes, Disposable pipette tips, Weighing dishes, Disposable gloves, Custom glass reactors, Mortar and pestle, Stainless steel sieves, Ball mill, Chemicals for mercury analyses, Erlenmeyer flasks and graduated cylinders, Glass vials and sample bottles, shipping costs, third party verification of random mercury sample analyses, TOC analyses, Metals analyses, Inorganic analyses	$ 50,000
Travel:	$ -
Out-of-State: Travel between the University of Florida in Gainesville to Minneapolis, MN pilot study sites at XCEL Energy facilities.	20,000
Additional Budget Items:	
Tuition - calculated on established monthly rates by the university as follows: Jul-Aug 2010: $675.72/month, Sep 2010 - Aug 2011: $777.07/month, Sep - Dec 2011: 893.64/month	$ 28,502
TOTAL PROJECT BUDGET REQUEST TO LCCMR	$ 683,669

V. OTHER FUNDS

SOURCE OF FUNDS	AMOUNT	Status
In-kind Services During Project Period: *Indicate any in-kind services to be provided during the funding period. List type of service(s) and estimated value. In-kind services listed must be specific to the project.*	$ -	
Funding History: *Indicate funding secured prior to July 1, 2010 for activities directly relevant to this specific funding request. State specific*	$ -	

IV. REFERENCES

Bernard, S., Enayati, A., Redwood, L., Roger, H. and Binstock, T. (2001) Autism: A Novel Form of Mercury Poisoning. *Medical Hypotheses* **56**(4): 462 – 471.

Cheuk, D.K.L. and Wong, V. (2006) Attention-Deficit Hyperactivity Disorder and Blood Mercury Level: A Case-Control Study in Chinese Children. *Neuropediatrics* **37**: 234 – 240.

Electric Power Research Institute (2005) The Fate of Mercury Absorbed in Flue Gas Desulfurization (FGD) Systems. Accessed May 2008: <http://www.epriweb.com/public/000000000001009955.pdf>

Minnesota Pollution Control Agency (2006) Reducing mercury emissions from power plants in Minnesota. Planning/Pollution Prevention-Sustainability fact sheet #4.08.

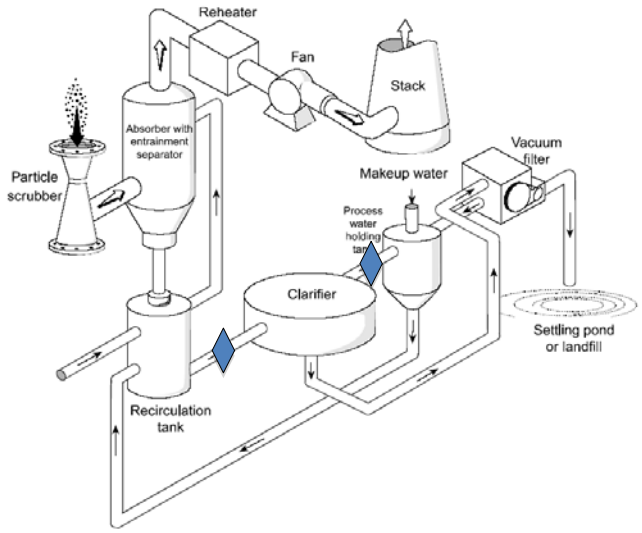

Fig.1: Two potential installation locations for STC system (indicated by blue diamonds).

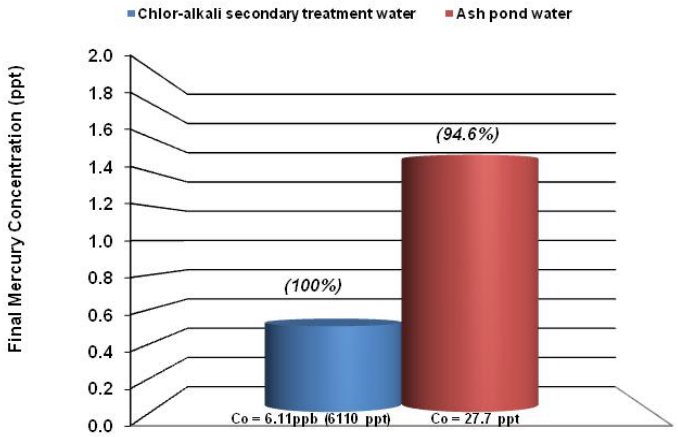

Fig.2: Lowest Hg concentrations achieved in bench-scale results. 'Co' indicates the initial (untreated water) Hg concentration. For chlor-alkali water, the treated Hg concentration was below detection (below 0.51 ppt). Percent removal is indicated in black bold italics between parentheses.

DAVID W. MAZYCK, PH.D.

(a) Professional Preparation

- The Pennsylvania State University
  Civil Engineering B.S. (1995)
- The Pennsylvania State University Environmental Engineering M.S. (1996)
- The Pennsylvania State University Environmental Engineering Ph.D. (2000)
- US Army, Army Corps of Engineers Technical Drafting Specialist 1989-1991

(b) Appointments

Associate Chair for Research and Graduate Coordinator (January 2007-Present)
Associate Professor (August 2006-Present)
Assistant Professor (July 2000-August 2006)
University of Florida, Department of Environmental Engineering, Gainesville, Florida

- Leads a nationally and internationally recognized research program dedicated to advancing the current understanding of adsorption phenomena, photocatalysis, and air/water purification through novel engineered systems. Develops courses to educate engineers in the field of environment engineering, specifically water treatment design and adsorption phenomena.
- Technical Lead for Water Recovery (NASA Environmental Systems Commercial Space Technology Center) (2001-Present)

(c) Publications most closely related to project

- Stokke, J.M. and **Mazyck**, D.W. Development of a regenerable system employing silica-titania composites for the recovery of mercury from end-box exhaust at a chlor-alkali facility. *Journal of the Air & Waste Management Association* 58(4):530-537, 2008
- Stokke, J.M. and **Mazyck**, D.W. Photocatalytic degradation of methanol using silica-titania pellets: Effect of pore size on mass transfer and reaction kinetics. ES&T 42(10):3803-3813, 2008
- Pitoniak E, Wu CY, **Mazyck** DW, Powers KW, Sigmund W. Adsorption Enhancement Mechanisms of Silica-Titania Nanocomposites for Elemental Mercury Vapor Removal. *Environ. Sci. Technol.* 2005; 39(5): 1269-1274.
- Pitoniak E, Wu CY, Londeree D, **Mazyck** D, Bonzongo JD, Powers K, Sigmund W. Nanostructured Silica-Gel Doped with TiO2 for Hg Vapor Control**,** *Journal of Nanoparticle Research* 2003; 5: 282-292.

(d) Research Facilities

The University of Florida maintains one of the nation's leading sorbent research facilities under the direction of Dr. David W. Mazyck. Dr. Mazyck's research focuses on the purification of air and water via adsorption, photocatalysis, and/or a combination of the two for maintaining public health. Fundamentals of adsorption are used to tailor adsorbents through the optimization of physical (e.g., pore size distribution) and chemical (e.g., electron density) properties. More specifically, the surface chemistry of carbonaceous (e.g., activated carbon) and silica adsorbents are studied to better understand the adsorbent-adsorbate interface. The robustness of these adsorbents is enhanced through the incorporation of photocatalysts (e.g., TiO_2) to either improve remediation efficiency/capture or to accomplish in-situ regeneration. In seven years, Dr. Mazyck has secured more than $4.0 M is extramural grants and contracts including funding from DOE, NSF, EPA, NSF, and NASA. Since joining the University of Florida in 2000, Dr. Mazyck has published over 34 journal articles, has been presenter or co-author in over 46 oral presentations and 16 posters in national and international conferences, has one patent issued and five pending, and has graduated or is advising 9 Ph.D. candidates, 20 M.S. students, and more than 40 undergraduates.

(e) Responsibilities

Dr. Mazyck will oversee all research activities to ensure that tasks are completed by the proposed deadlines with the proper quality control. All acquired data will be compiled, analyzed, and condensed by the team at UF and Sol-gel into a series of charts and graphs that summarize the various test procedures, results and conclusions for integration into various required reports.