Environment and Natural Resources Trust Fund
2016 Request for Proposals (RFP)

Project Title: **ENRTF ID: 063-B**

On-Site Removal of Metal-Sulfide Particles from Mining Waters

Category: B. Water Resources

Total Project Budget: $ 497,758

Proposed Project Time Period for the Funding Requested: 3 years, July 2016 to June 2019

Summary:

This project will develop a clean real-time sensing and on-site chemical treatment technology for the removal of metal sulfide contaminates from Minnesota waters impacted by copper-nickel-sulfide mining.

Name: Cari Dutcher

Sponsoring Organization: U of MN

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Location

Region: NE

County Name: Aitkin, Carlton, Cass, Cook, Itasca, Lake, St. Louis

City / Township:

Alternate Text for Visual:

(A) Minnesota regions to be impacted by mineral sulfide mining (Image- Minnesota map); (B) On-site mining water contamination pathways (Photo-Evaporation ponds); (C) Proposed on-site sensing and chemical treatment process (Images-Flocculation treatment)

_____ Funding Priorities	_____ Multiple Benefits	_____ Outcomes	_____ Knowledge Base
_____ Extent of Impact	_____ Innovation	_____ Scientific/Tech Basis	_____ Urgency
_____ Capacity Readiness	_____ Leverage	_____ TOTAL	_____%

PROJECT TITLE: On-Site Removal of Metal-Sulfide Particles from Mining Waters

I. PROJECT STATEMENT

Minnesota's hotly debated copper-nickel sulfide mining activities can produce discharge waters with high concentrations of toxic sulfides and heavy metals, ***which can impair Minnesota's water quality*** in key regions including the St. Louis River basin watershed, Lake Superior, Boundary Waters, and Mississippi River. ***New, easily implemented technologies are urgently needed*** to remove metal-sulfide contaminants at mining facilities and prevent the formation of sulfate from sulfides. **To address these challenges, our project will develop and implement real-time chemical sensing and on-site treatment technologies for the flocculation and enhanced removal of metal sulfide contaminants, cleaning Minnesota's copper-nickel mining impacted waters.**

Unlike organic contaminants, heavy metals discharged from Copper-Nickel (Cu-Ni) sulfide mining activities are not biodegradable and accumulate in the environment and in living organisms, making their removal from wastewater an important issue to sustain environmental and human health. Cu-Ni sulfide mining can cause long-lasting contamination not only around the mines but also in areas well downstream. Some of the currently proposed mining operations in northern Minnesota would be located in the St. Louis River basin, a watershed that contains many wetlands, floodplains and lakes that are also natural habitats of wild rice and ultimately drain into Lake Superior. To protect these regions, the Minnesota Pollution Control Agency (MPCA) proposed new sulfate concentration guidelines. Facilities such as mining operations that discharge sulfide, sulfate and heavy metal-rich waters will be *facing the challenge to implement new technologies* in order to keep sulfate concentrations below the critical concentrations calculated for their impact area.

Of particular concern are colloidal contaminants, which consist of particles that are too small to be removed by conventional filtering. An attractive technology for the removal of heavy metals and sulfide particles from wastewater is coagulation and flocculation followed by sedimentation and filtration. Coagulation/flocculation uses water-soluble polymers with ionizable groups (polyelectrolytes) to form larger aggregates of heavy metals and colloidal metal sulfide particles, which can then be removed from the wastewater with conventional means. Until now, there are only a few methods suitable to systematically determine the optimal dosing parameters for efficient heavy metal removal from complex systems that contain natural organic matter and suspended mineral sulfide particles. New real-time sensing technologies are needed that are oriented to the removal of simultaneously occurring pollutants (e.g., particles, organic matter, and metals) in mining-impacted waters. The proposed study will result in fully optimized coagulating agent dosing to *remove heavy metals and metal sulfide precipitates* from Minnesota's mining impacted waters.

II. PROJECT ACTIVITIES AND OUTCOMES

Activity 1: Develop Real-Time Chemical Sensors for Contaminant Detection **Budget: $ 177,531**

This activity will develop chemical sensors that selectively detect freely dissolved polyelectrolytes, metals, mineral oxides, and copper-nickel sulfide concentrations. The sensors will be employed in aqueous systems that represent the chemical make-up of natural and mining-impacted aquatic environments of Northern Minnesota.

Outcome	Completion Date
1. Development of a chemical water sensor that selectively detects freely dissolved polyelectrolyte, for use in determining real-time, on-site flocculent dosing requirements.	Dec 31, 2016
2. Development of a chemical water sensor that selectively detects both freely dissolved copper and nickel *ions*, and copper and nickel sulfide *particle* concentrations as a function of key water treatment conditions such as acidity and natural organic matter concentrations.	June 30, 2017
3. ***Deploy the sensors*** at a Northern Minnesota mining facility along Duluth Complex Rocks.	June 30, 2018

Activity 2: Define Polyelectrolyte Dosing Criteria for Large-Scale Metal-Sulfide Removal Budget: $ 144,446

This activity will optimize dosing of polymeric coagulating agents for the removal of heavy metals from mining-impacted waters. Model test systems will consist of aqueous salt-containing suspensions of mineral particles, natural organic matter, and heavy metals, to isolate the role of competing chemical interactions during flocculation. Once optimized, water samples collected at field test-sites and mineral mining facilities will be used, and the coagulating agent dosing criteria for large-scale implementation will be determined.

Outcome	Completion Date
1. Optimization of flocculation (metal removal) in aqueous model solutions.	Dec 31, 2017
2. Optimization of flocculation (metal removal) in water from mining facilities.	June 30, 2018
3. ***Define critical chemical dosing parameters*** for larger scale technology implementation.	June 30, 2019

Activity 3: Enhance On-Site Metal-Sulfide Removal and Precious Metal Recovery Budget: $ 175,781

This activity will enhance the efficiency of metal removal and the solid phase flocculent stability in mining pits and evaporation ponds. The flocculents' ability to resist breakage in water flows will be measured using a state-of-the-art flow cell, and the molecular structure and chemical bonds will be quantified using cryogenic electron microscopy and fluorescence dyes specific for metals. The activity will result in quantification of the optimized flocculent strength and stability, *to minimize resuspension of the coagulated metal-sulfide contaminants into the water during removal, as well as an enhanced recovery of the precious metal-containing flocculent.*

Outcome	Completion Date
1. Quantification of metal content and bonding in flocculents using analytical microscopy.	Dec 31, 2017
2. Quantification of the hydrodynamic stability of flocculent using engineered flow fields.	June 30, 2018
3. ***Define user guidelines for on-site*** removal and recycling of the precipitated flocculent.	June 30, 2019

III. PROJECT STRATEGY

A. Project Team/Partners

The team consists of Principal Investigator (PI) Cari Dutcher and co-PIs Phil Buhlmann and Sebastian Behrens from the University of Minnesota. *Activity 1 will be directed by Co-PI Buhlmann* (Professor, Dept. of Chemistry) who is an expert in chemical sensing. *Activity 2 will be directed by PI-Dutcher* (Assistant Professor, Department of Mechanical Engineering) who is an expert in the dynamics of polymer and particle solutions. *Activity 3 will be directed by Co-PI Behrens* (Associate Professor, Dept. of Civil, Environmental and Geo-Engineering; BioTechnology Institute) who is an expert in environmental microbiology and microbial ecology.

B. Project Impact and Long-Term Strategy

This research will develop an efficient and easy to implement water treatment technology that decreases the concentration of heavy metals and colloidal metal sulfide particles in waters discharged from mining operations, reducing the environmental risk of mining in Minnesota and preserving Minnesota's water quality. Through collaboration with the Minnesota Department of Natural Resources (MNDNR), representative water samples from active and proposed Minnesota mine sites will be selected and obtained. Results of this research will be shared with the MNDNR and Minnesota Pollution Control Agency (MPCA) to promote the development of new technologies at on-site locations to remove sulfate, heavy metals, and colloidal metal sulfide precipitates from waters impacted by mining operations. ***The long-term project impact will be the protection of Minnesota's precious aquatic ecosystems, including Lake Superior, the Boundary Waters, and the Mississippi River.***

C. Timeline Requirements

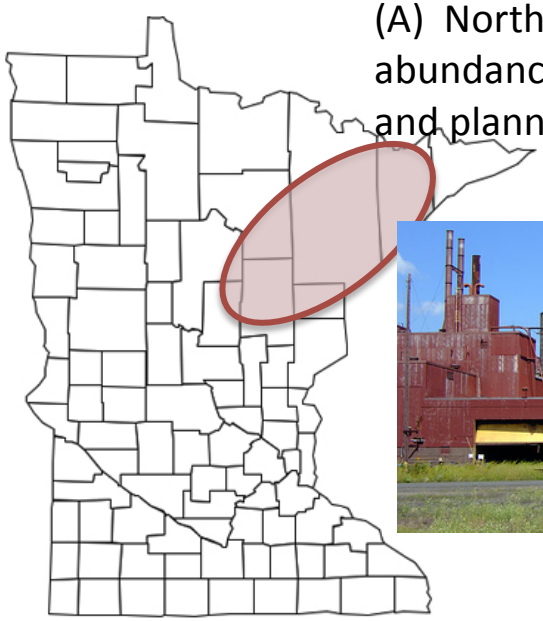
The project will be completed in three years.

IV. TOTAL ENRTF REQUEST BUDGET 3 years

BUDGET ITEM	AMOUNT
Personnel:	$ -
Prof. Cari Dutcher, Project Manager, director of Activity 2: Flocculation studies on Mining Water, 3 weeks/ year of salary and benefits, 10% of total salary, 75% salary, 25% benefits	$ 30,903
Prof. Sebastian Behrens, co-Investigator, director of Activity 3: Stability and Metal Sulfide Removal Efficiency of formed flocs, 3 weeks/ year of salary and benefits, 10% of total salary, 75% salary, 25% benefits	$ 31,335
Prof. Philippe Buhlmann, co-Investigator, director of Activity 1: Develop a Chemical Sensor for Detection of Freely Dissolved Polymer, Mineral Oxides, and Copper-Nickel Sulfide Concentrations, 3 weeks/ year of salary and benefits, 10% of total salary, 75% salary, 25% benefits	$ 33,085
Year 1 and 2: Three Full-time Graduate Research Assistant, Data collection and analysis, 24 months of salary and benefits (including tuition), 50% FTE, 54% salary, 46% benefits	$ 276,138
Year 3: Two Full-time Graduate Research Assistant, Data collection and analysis, 12 months of salary and benefits (including tuition), 50% FTE, 54% salary, 46% benefits	$ 81,297
Professional/Technical/Service Contracts: User fees Univeristy Imaging Centers; equipment reservation cost charged by the hour ~$50 including digital cameras and image processing software for confocal laser scanning micrcosope and scanning electron microscopy with energy dispersive X-ray spectroscopy; University of Minnesota Genomics Center (UMGC) - DNA sequencing, quantitative PCR -> identification and enumeration of sulfate reducing bacteria (210 samples per run; $1250 per run).	$ 9,000
Equipment/Tools/Supplies: Disposable chemicals (polyacrylamide; Fe and Co-Ni; Bentonite, Fe-oxide, Co-Ni sulfides; humic and fulvic acids; hydrophobic polmer and plasticizer for measuring electrode, frits and silver/silver chloride for reference elements, receptor compounds for chemical selectivity of sensing membrane, and spectroscopy solvents), Consumable supplies (Bottles, Pipettes, Flasks, Vials, Weighing dishes, towels, water bottles, tubing, gloves, needles, nanopore filters)	$ 33,000
Acquisition (Fee Title or Permanent Easements):	N/A
Travel: In-state travel to collect water and sediment samples from aquatic ecosystems in NE Minnesota impacted by copper-nickel sulfide mining along the St. Louis River Basin; on-site testing of chemical sensor.	$ 3,000
Additional Budget Items:	N/A
TOTAL ENVIRONMENT AND NATURAL RESOURCES TRUST FUND $ REQUEST =	$ 497,758

V. OTHER FUNDS

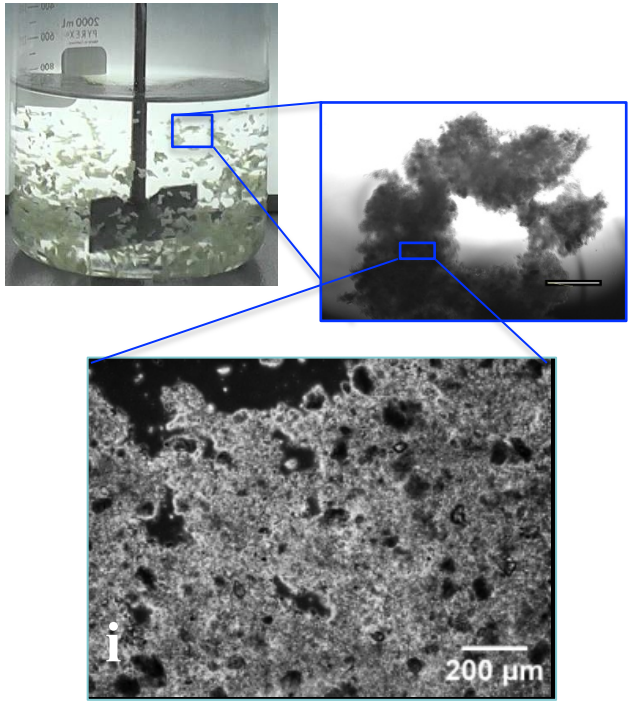
SOURCE OF FUNDS	AMOUNT	Status
Other Non-State $ To Be Applied To Project During Project Period:	N/A	N/A
Other State $ To Be Applied To Project During Project Period:	N/A	N/A
In-kind Services To Be Applied To Project During Project Period: The University of Minnesota does not charge the State of Minnesota its typical overhead rate of 52% of the total modified direct costs (graduate tuition and academic fringe are excluded).	$ 186,757	secured
Funding History (team): 3M Nontenured Faculty Award (Dutcher, 45k); University of Minnesota College of Science and Engineering and Department of MEchanical Engineering Start-up Funds (Dutcher, 800k); Boston Scientific "Chemical Sensor" (Buhlmann, 41k); IREE Institute on the Environment, University of Minnesota "High Energy Density, Nanostructured Supercapacitors for Electrical Energy Storage" (Buhlmann, 695k); German Science Foundation 2012-2015 "Iron cycling in freshwater sediments under oxic and anoxic conditions" (Behrens, 185k*); German Science Foundation 2011-2014 "Microbial processes and iron-mineral formation in household sand filters used to remove arsenic from drinking water in Vietnam" (Behrens, 308k*); German Science Foundation 2012-2015 "Abundance, activity, and interrelation of phototrophic and chemotrophic microbial iron oxidation in freshwater sediments " (Behrens, 301k*); LGFG Fellowship, State of Baden-Württemberg Germany 2013-2014 "Biochar effects on microbial nitrous oxide formation in soils - composition and activity of the nitrous oxide-forming microbial community" (Behrens, 114k*); German Science Foundation 2011-2014 Research Unit: "Natural halogenation processes in the environment - Direct and indirect formation of organohalogens by microorganisms" (Behrens, 381k*) (*using 1:1 Euro to US Dollar conversion)	$ 2,868,898	N/A
Remaining $ From Current ENRTF Appropriation:	N/A	N/A



(A) Northern Minnesota has an abundance of ***mineral sulfide deposits*** and planned mining locations (map, left).

(B) Mining activity results in mineral-sulfide contaminants in tailings runoff, groundwater, mine pits and basins, surface runoff, and ***evaporation ponds*** (photo, below).

Mining evaporation pond
(http://www.ertech.com.au)



(C) To ensure clean Minnesota waters, we will develop ***real-time sensing*** and ***on-site chemical treatment*** (flocculation, above) technologies to remove metal sulfides from mine waters and enhance metal recovery.

Project Title: *On-Site Removal of Metal-Sulfide Particles from Mining Waters*

Project Manager Qualifications

CARI S. DUTCHER, Assistant Professor, Mechanical Engineering

Professional Preparation

Illinois Institute of Technology	Chemical Engineering	B.S., 2004
University of California, Berkeley	Chemical Engineering	Ph.D., 2009
University of California, Davis	Air Quality Research Center	2009-2013

Current Appointments

- Benjamin Mayhugh Assistant Professor, Mechanical Engineering, UMN, 2013-present
- Graduate Faculty in Chemical Engineering and Materials Science, UMN, 2013-present

Publications (past three years)

- Ohm, P., Asato, C., Wexler, A.S., Dutcher, C.S. An Isotherm-Based Thermodynamic Model for Electrolyte and Non-Electrolyte Solutions, incorporating Long- and Short-Range Electrostatic Interactions. J. Phys. Chem. A. (*accepted*, 2015)
- Woehl, T.J., Chen, B. J., Heatley, K., Talken, N.H., Dutcher, C.S., Ristenpart, W.D. Bifurcation in the equilibrium height of colloidal particles near an electrode in oscillatory electric fields. Physical Review X. (*accepted, 2015*)
- Cai, C., Stewart, D. J., Reid, J.P., Zhang, Y., Ohm, P., Dutcher, C.S., and Clegg, S.L. Organic Component Vapor Pressures and Hygroscopicities of Aqueous Aerosol Measured by Optical Tweezers. J. Phys. Chem. A, 119 (4), pp 704-718 (2015).
- Woehl, T.J., Heatley, K., Talken, N.H., Dutcher, C.S., Ristenpart, W.D. Electrolyte Dependent Aggregation of Colloidal Particles near Electrodes in Oscillatory Electric Fields. *Langmuir*, 30 (17), 4887-4894 (2014).
- Dutcher, C.S., Woehl, T.J., Talken, N.H. & Ristenpart, W.D. Hexatic-to-disorder transition in colloidal crystals near electrodes: Rapid annealing of polycrystalline domains. *Physical Review Letters*, 111, 128101 (2013).
- Wexler, A.S. & Dutcher, C.S. Statistical Mechanics of Multilayer Sorption: Surface Tension, *Journal of Physical Chemistry Letters*, 4 (10), 1723-1726 (2013).
- Dutcher, C.S. & Muller, S.J. Effects of moderate elasticity on the stability of co- and counter-rotating Taylor-Couette flows. *Journal of Rheology*, 57 (3), 791 - 812 (2013).
- Dutcher, C.S., Ge, X., Wexler, A. S. & Clegg, S. L. An isotherm-based thermodynamic model of aqueous solutions, applicable over the entire concentration range. *Journal of Physical Chemistry A*, 117 (15), 3198-3213 (2013).

Selected Honors and Awards

3M Nontenured Faculty Award 2015–2017 • National Science Foundation – Atmospheric and Geospace Sciences Postdoctoral Research Fellowship, 2011–2013 • American Association of University Women Selected Professions Dissertation Year Fellowship, 2008–2009 • National Science Foundation Graduate Research Fellowship, 2005–2008

Organization Description

The University of Minnesota-Twin Cities Campus is the oldest and largest campus of the University of Minnesota system, and with over 50,000 students. The University's mission is to change lives—through research, education, and outreach, and to apply expertise to meet the needs of Minnesota.