Environment and Natural Resources Trust Fund
2017 Request for Proposals (RFP)

Project Title: **ENRTF ID:** **058-B**

Sulfate and Metal Removal from Northeast MinnesotaWaters

Category: B. Water Resources

Total Project Budget: $ 298,325

Proposed Project Time Period for the Funding Requested: 2 years, July 2017 – June 2019

Summary:

A sustainable, cost-efficient, and commercially competitive water treatment technology will be developed to remove sulfate and heavy metals from mining-impacted waters in Northeast Minnesota, using real-time sensing and on-site treatment.

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Sponsoring Organization: U of MN

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Location

Region: Northeast

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

City / Township:

Alternate Text for Visual:

In reactor #1, sulfate is reduced by bacteria to sulfide, which helps precipitate heavy metal contaminants. The sulfide-metal particles are removed efficiently in reactor #2 using an organic polymer surfactant, permitting metal recycling. Use of on-line chemical sensors minimizes waste and assures the quality of the cleaned water.

_____ Funding Priorities _____ Multiple Benefits _____ Outcomes _____ Knowledge Base

_____ Extent of Impact _____ Innovation _____ Scientific/Tech Basis _____ Urgency

_____ Capacity Readiness _____ Leverage _______ TOTAL ______%

PROJECT TITLE: Sulfate and metal removal from Northeast Minnesota waters

I. PROJECT STATEMENT

We propose to develop a sustainable, cost-efficient, and commercially competitive water treatment technology to remove sulfate and heavy metals from waters in Northeast Minnesota. This proposal provides an efficient and eco-friendly water treatment solution for removing harmful sulfate and toxic metals from watersheds impacted by ongoing and intended mining activities. The two-year project combines biological water treatment for sulfate and metal removal with online sensing and eco-friendly sedimentation of metal sulfide particles using organic flocculation agents. This new and efficient combination of water treatment technologies will significantly reduce the costs of water clean-up compared to current technologies and facilitate profitable precious metal recovery.

Ongoing and planned mining operations in Minnesota produce effluents with high sulfate concentrations, which reduce the water quality in aquatic ecosystems and pose a significant technical and economic challenge. Water treatment technologies that use bioreactors for biological sulfate reduction are recognized as an efficient and cost-effective means to remove sulfate and improve water quality. In these systems, sulfate-reducing bacteria catalyze the reduction of sulfate to sulfide, which is then removed by precipitation with iron chloride. However, this process generates effluents of low pH and elevated chloride concentrations, requiring further costly water purification, e.g., by neutralization, centrifugation, and membrane-based filtration.

The improved technology proposed here will facilitate the removal of suspended metal sulfides by using organic coagulating agents. Large water-soluble organic polymers with charged functional groups (polyelectrolytes) are particularly valuable as coagulating agents because they bind efficiently to particulate metal sulfides and are environmentally friendly. This aids in metal sulfide removal from water by sedimentation without the negative impacts caused by current water treatment strategies. **The project consists of three activities that will bring together the synergistic strength and advantages of <u>biological water treatment</u> with <u>"online" chemical sensing</u> and <u>novel coagulation technology</u>.** By advancing applied research in these interdisciplinary research areas, it will be possible to (i) optimize process parameters, (ii) keep cost low, and (iii) guarantee a high effluent water quality. The market maturity of our treatment technology will be demonstrated with respect to efficiency and sustainability via comparative cost analysis, considering that the concentrated metal cations (e.g., Cu, Ni, Zn) in the collected sulfide solids have significant recycle value. By including students in the proposed research activities, the project will educate the next-generation scientists and engineers.

II. PROJECT ACTIVITIES AND OUTCOMES

Activity 1: ***Biological sulfate reduction in lab-scale bioreactors*** **Budget: $ 112,541**

We will set up bench-scale bioreactors (chemostats, continueous mixed cultures) with sulfate and metal-rich water collected from field sites in the Northeast region of Minnesota. We will optimize chemostat performance by controlling flow rate, nutrient feed and biomass production as well as the chemistry of the feed and effluent water. Modern molecular biology techniques will be used to characterize the composition and activity of the sulfate reducing microbial community in order to optimize process resilience and functional stability.

Outcome	Completion Date
1. *Bench-scale sulfate-reducing bioreactors setup with mining waters from NE Minnesota*	June 30, 2018
2. *Quantification of reactor performance parameters by tuning flow and feed conditions*	June 30, 2019
3. *Microbial community characterization to optimize process resilence and stability*	June 30, 2019

Activity 2: ***"Online" chemical sensing of sulfate, sulfide, and metals*** **Budget: $ 93,325**

Electrochemical sensors will be developed to monitor continuously ("on-line") the concentrations of sulfate, sulfide, heavy metals ions, and excess coagulating agents in (a) the bioreactor that converts the sulfate to sulfide, (b) the reactor used to precipitate the metal sulfides, and (c) the clean water effluent leaving the water treatment system. These sensors will (i) guarantee the quality of the clean water effluent by optimizing the bioreactor and coagulation/precipitation process parameters, and (ii) keep the cost of water purification low by preventing the use of excess amounts of coagulating agents.

Outcome	Completion Date
1. Development of sensors for metal, sulfide, and sulfate quantification	June 30, 2018
2. Development of sensors for the detection of excess coagulation/flocculation agents	June 30, 2018
3. Sensor integraton into bioreactor monitoring and control of metal sulfide precipitation	June 30, 2019

Activity 3: *Metal sulfide flocculation with organic coagulating agents* **Budget: $ 92,459**

This activity will optimize dosing of polymeric coagulating agents for the removal of heavy metals. Test systems will consist of salt-containing suspensions of mineral particles, natural organic matter, and heavy metals, to elucidate 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 coagulating agent dosing criteria for large-scale implementation will be determined. This activity will enhance the efficiency of metal removal and the solid phase flocculent stability. 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 microscopy and fluorescence dyes. This 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. Quantify metal sulfide removal efficiency and optimal flocculant concentration	June 30, 2018
2. Characterize stability of sedimented organic polymer metal sulfide flocs	Dec 31, 2018
3. Produce field application guide and market maturity analysis	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 Behrens* (Associate Professor, Dept. of Civil, Environmental and Geo- Engineering; BioTechnology Institute) who is an expert in environmental microbiology and microbial ecology. *Activity 2 will be directed by Co-PI Buhlmann* (Professor, Dept. of Chemistry) who is an expert in chemical sensing. *Activity 3 will be directed by PI-Dutcher* (Assistant Professor, Dept. of Mechanical Engineering) who is an expert in the dynamics of polymer and particle solutions. The PI of each activity will use the requested funds to cover research expenses and the support a graduate student.

B. Project Impact and Long-Term Strategy

This research will lead to an efficient and economic water treatment technology that removes sulfate and from waters in Northeast Minnesota, reducing the environmental impact of mining and preserving Minnesota's water quality. Results from this research will be presented to environmental engineers, engineering consultants and scientists in academia, industry, and at state agencies such as the Minnesota Department of Natural Resources (MNDNR) and the Minnesota Pollution Control Agency (MPCA). Research will be presented at regional and national conferences, and shared with the MNDNR, MPCA, and professionsals in the area of mine water treatment to promote the implementation of the new technologies to clean waters impacted by mining operations. Results will also be disseminated through scholarly publications and will be leveraged for federal and state grant applications. ***The long-term project impact is the eco-friendly sustainable advancement of Minnesota's economy while protecting Minnesota's water resources and pristine aquatic ecosystems.***

C. Timeline Requirements

The project will be completed in two years.

2017 Detailed Project Budget

Project Title: Sulfate and metal removal from Northeast Minnesota waters

IV. TOTAL ENRTF REQUEST BUDGET 2 years

BUDGET ITEM	AMOUNT
Personnel:	$ -
Prof. Cari Dutcher, Project Manager, director of Activity 3: Metal sulfide flocculation, 2 weeks/ year of salary and benefits, 5% of total salary, 75% salary, 25% benefits	$ 13,899
Prof. Sebastian Behrens, co-Investigator, director of Activity 1: Biological sulfate reduction in lab-scale bioreactors, 2 weeks/ year of salary and benefits, 5% of total salary, 75% salary, 25% benefits	$ 13,981
Prof. Philippe Buhlmann, co-Investigator, director of Activity 2:“Online” chemical sensing of sulfate, sulfide, and metals, 2 weeks/ year of salary and benefits, 5% of total salary, 75% salary, 25% benefits	$ 14,765
Three 75% Graduate Research Assistants (1 per activity), Data collection and analysis, 37.5% FTE, 54% salary, 46% benefits (including tuition)	$ 211,080
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	$ 4,000
Equipment/Tools/Supplies: 4 reactor vessels and a peristaltic pump, 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)	$ 40,000
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	$ 600
Additional Budget Items	N/A
TOTAL ENVIRONMENT AND NATURAL RESOURCES TRUST FUND $ REQUEST =	$ 298,325

V. OTHER FUNDS

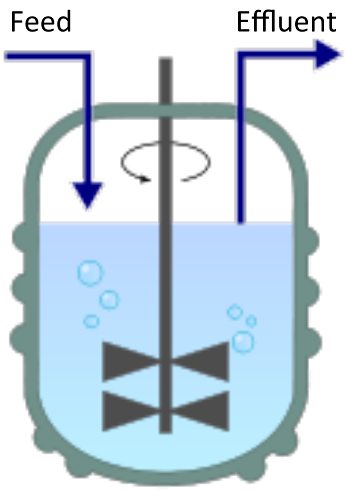
SOURCE OF FUNDS	AMOUNT	Status
Other Non-State $ To Be Applied To Project During Project Period	N/A	N/A
Other State $ To Be Applied To Project During Project Period	N/A	N/A
In-kind Services To Be Applied To Project During Project Period: The University of Minnesota does not charge the State of Minnesota its typical overhead rate of 53% (FY2017) and 54% (FY2018) of the total modified direct costs (graduate tuition and academic fringe are excluded).	$ 116,277	secured
Funding History: NSF CAREER Award (Dutcher, 477k), 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); NSF "In-Situ Cyanide Monitoring in Gold Mine Effluents" (Buhlmann, 150k); Carestream "Development of a Nitrate Selective Electrode" (Buhlmann, 31k); University of Minnesota - Office of the Vice President for Research (2015-2016) Research Infrastructure Investment Program Award “High-Throughput Single Cell Isolation by Fluorescence-Activated Cell Sorting” (Behrens, $500k), MnDrive Seed Grant (2015-2016) “Engineered biochars for sulfate removal from mine water” (Behrens, $65k), German Science Foundation (2015-2018) “Deciphering stable isotope fractionation (δ13C; δ37Cl) during reductive dehalogenation of chlorinated ethenes: Effects of bacterial growth physiology and expression of key enzymes” (Behrens, $376*), 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)	$ 4,467,898	N/A
Remaining $ From Current ENRTF Appropriation:	N/A	N/A

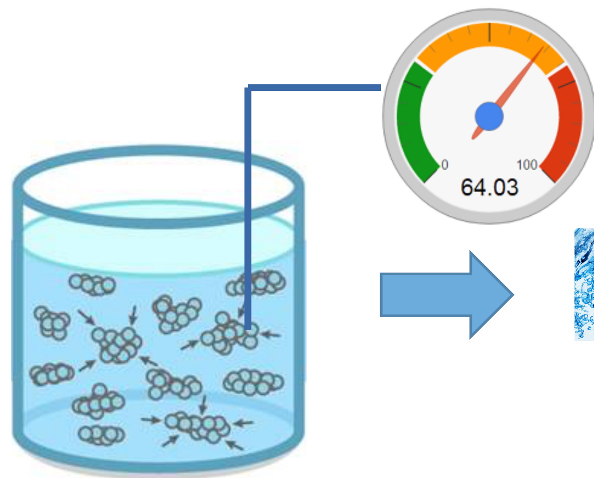
Biological Sulfate-to-Sulfide Conversion (Reactor 1)

Metal Sulfide Removal by Flocculation (Reactor 2)

Chemical Sensors for Reaction Optimization and Quality Assurance

Mining process water, containing sulfate and metals (such as copper, nickel, and zinc)





Clean water

In reactor #1, sulfate is reduced by bacteria to sulfide, which helps precipitate heavy metal contaminants. The sulfide-metal particles are removed efficiently in reactor #2 using an organic polymer surfactant, permitting metal recycling. Use of on-line chemical sensors minimizes waste and assures the quality of the cleaned water.

Project Manager Qualifications and Organization Description

Cari S. Dutcher is a Benjamin Mayhugh Assistant Professor of Mechanical Engineering at the University of Minnesota, Twin Cities, with a graduate faculty appointment in the Department of Chemical Engineering and Materials Science. Her research interests are in complex fluids and multiphase flows, with applications in environmental remediation. She currently serves as the vice chair for American Association for Aerosol Research (AAAR) Aerosol Physics Working Group. Dutcher recently received the 3M Non-Tenured Faculty and NSF CAREER awards. Prior to joining the University of Minnesota, Dutcher was an NSF-AGS Postdoctoral Research Fellow in the Air Quality Research Center at the University of California, Davis. Dutcher received her B.S from Illinois Institute of Technology (2004) and her Ph.D. from the University of California, Berkeley (2009), both in Chemical Engineering. While at UC Berkeley, Dutcher was supported by an NSF Graduate Research Fellowship and an American Association of University Women Fellowship.

Sebastian F. Behrens is an Associate Professor Civil, Environmental, and Geo- Engineering at the University of Minnesota. Dr. Behrens' research focuses on linking environmental processes to the spatial-temporal distribution and metabolic activity of key functional groups of microorganisms. He follows an interdisciplinary approach that combines the disciplines biogeochemistry, microbiology, and molecular biology to understand the basic microbial ecology principles driving the biogeochemical cycling of metals and metalloids, the biodegradation of organic contaminants, and the emission of greenhouse gases from the molecular to the ecosystem scale. The gained knowledge on microbial transformation processes in natural and engineered ecosystems is then implemented in order to optimize microbial remediation approaches, resource recovery, and the biological treatment of water (drinking water, surface water, groundwater, or waste water), thereby spanning the gap between basic and applied research aspects of bioremediation. Behrens received his B.S. in Biology (1997) and Diploma in Microbiology (2000) from the University of Bremen in Germany, and Ph.D. in Microbial Ecology (2003) from Max Planck Institute for Marine Microbiology.

Philippe Buhlmann is Professor and director of graduate studies in the Department of Chemistry at the University of Minnesota. He obtained an MS degree (1989) and a PhD (1993) from the Department of Natural Sciences, Swiss Federal Institute of Technology (ETH), Zürich. He was a postdoctoral fellow of the Japan Society for the Promotion of Science (1993–1994) and a research associate (1994–2000) at the Department of Chemistry, School of Science, The University of Tokyo. He joined the University of Minnesota in 2000. The common theme of research in the Buhlmann group is the application of molecular recognition and, in particular, the use of synthetic receptors for electrochemical sensing in complex real-life environments. One goal is the development of new strategies that permit the use of robust chemical sensors that excel not only in the laboratory but withstand the harsh conditions of long term monitoring, e.g., in the environment, in industrial process control, or upon implantation into the human body. Research achievements include the development of sensors with detection limits in the parts-per-trillion range and selectivities exceeding 1:10E13. His particular expertise lies in the field of potentiometric ion sensors (as proposed here for heavy metal ion detection) and ion transfer voltammetry (as it will used for polyelectrolyte sensing). Buhlmann has published 1 book, 4 patents, and over 120 publications, which have been cited over 9000 times with an H index of 40.

Organization Description. The University of Minnesota is one of the largest, most comprehensive, and most prestigious public universities in the United States (http://www1.umn.edu/twincities/about). The laboratories and offices of the PI and co-PIs contain all the necessary fixed and moveable equipment and facilities needed for the proposed studies.