Environment and Natural Resources Trust Fund
2020 Request for Proposals (RFP)

Project Title: **ENRTF ID: 095-B**

Storing Sulfide Produced from Sulfate-Containing Wastewater Safely

Category: B. Water Resources

Sub-Category:

Total Project Budget: $ 280,790

Proposed Project Time Period for the Funding Requested: June 30, 2023 (3 yrs)

Summary:

Sulfate in wastewater is a major concern in Minnesota. We propose to process biproducts of sulfate remediation to produce bricks to safely store sulfur.

Name: Lee Penn

Sponsoring Organization: U of MN

Job Title: Professor

Department: Chemistry

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Minneapolis MN 55455

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Web Address:

Location:

Region: Statewide

County Name: Statewide

City / Township:

Alternate Text for Visual:

Dissolved sulfate can get into water ways and cause harm. We propose to lock sulfate into stable bricks, which is safer.

_____ Funding Priorities _____ Multiple Benefits _____ Outcomes _____ Knowledge Base

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

_____ Capacity Readiness _____ Leverage _______ TOTAL _____%

PROJECT TITLE: Storing Sulfide Produced from Sulfate-Containing Wastewater Safely

I. PROJECT STATEMENT

Anthropogenic sulfate can alter sulfur cycling in natural freshwater aquatic systems, and this can cause environmental impacts including methylmercury production, eutrophication, and adverse impacts on aquatic organisms. In particular, excess sulfate in Minnesota surface waters is a concern due its harmful impacts on wild rice ecosystems. ***We propose to immobilize and remove excess sulfate using naturally occurring microbes and iron mining waste materials to make bricks of sulfide-minerals that are easy to store and economically useful.***

Sulfate (SO_4^{2-}) dissolves in water, which means sulfate can move through ground and surface water. Sulfate is a major component of industrial (e.g. mining, paper mills) processes and municipal wastewater, and can degrade water quality and cause extensive ecosystem damage. In natural and engineered systems, sulfate is converted by microbes into other dissolved sulfur species, most importantly, sulfide (S^{2-}), which is toxic. Conversions from sulfate to sulfide (both dissolved forms) are achievable, but storing sulfur in a stable solid form is challenging. Our research team has developed a promising cost-effective biological removal of sulfate coupled with sulfide sequestration using locally available iron minerals as solids containing iron and sulfur. The solid product is manageable but its stability upon exposure to water and air has not been examined. Such stability is important for determining management and disposal/storage strategies to prevent release of sulfate back to the watershed.

We propose to use locally available iron mine waste materials to effectively capture sulfur into a solid material, which would prevent sulfate from spreading into surrounding waters. The resulting material could be used in future processing. We will test sulfur-containing minerals to identify those with the highest stability and develop a process to produce those targets using waste mining materials and the sulfide produced by sulfate wastewater treatment. Our expected outcome is a process for converting the sulfide into a solid brick. The brick will enable stable and safe sulfur storage over realistic time frames (several years). The resulting sulfur-storage bricks could be used as a resource for a variety of manufacturing applications (i.e., casting plants, foundries).

Major Results Expected:

1. **Process to generate bricks that store sulfur safely over realistic time frames (several years).**
2. **Characterize the bricks before and after exposure to air and/or water.**
3. **Prototype system to produce the sulfur-storing bricks.**

Deliverables: Open scientific presentations and papers addressing the above objectives; patents for methods to produce a sulfur-storing material using our new method; prototype system.

II. PROJECT ACTIVITIES AND OUTCOMES

Activity 1: ***Determine which minerals best retain sulfur.***

We will prepare and evaluate materials for use in the safe, short-term (ca. several years) storage of sulfur contaminants from waste streams. First, we will test pure iron-bearing minerals. We will expose the reference minerals to high-strength sulfide wastewater (e.g. mine water) under Minnesota weather conditions (freeze-thaw cycles) and characterize the products and their stability upon exposure to air and/or water.

Second, we will develop the process for producing the most stable sulfur-bearing minerals. Here, we leverage ongoing work of a sulfate reduction process that produces a solid containing iron and sulfur. We will combine that solid with various minerals found in mining waste in order to produce a sulfur-storage material and test the resulting materials for stability upon exposure to water and air (sulfur-leaching tests). Processes that lead to the more stable products will be further refined while processing that leads to the less stable products will be rejected. We will characterize all materials involved in this work using four primary methods: X-ray diffraction, Raman Spectroscopy, Scanning Transmission Electron Microscopy with Electron Energy Loss Spectroscopy and Energy Dispersive Spectroscopy , and mineral magnetic measurements.

ENRTF BUDGET: $ 146,395

Outcome	Completion Date
1. Sulfur-leaching results from experiments using natural and synthetic reference minerals and simulated mining waste water, groundwater, and surface water	*Summer 2020*
2. Treatment protocol to fabricate the stable sulfur-storage bricks	*Spring 2021*

Activity 2: *Enhance the stability of solids that store sulfur in a manageable form, refine process*

We propose a method using mining waste materials, such as waste rock or tailings, to store sulfur safety, even with exposure to water and air and freeze/thaw cycles. Here, we focus on mixing the solids produced by the sulfate reduction process with mining waste materials that contain target reference minerals identified during activity I. The resulting mixtures will be pressed into bricks and heat-treated. Resulting bricks will be characterized using the four primary methods mentioned above. We have access to a suite of well-characterized waste rock and tailings materials through our collaboration with researchers at the NRRI (Natural Resources Research Institute). Our preliminary results demonstrate that iron carbonate (siderite) may be a promising candidate, which could mean that mining waste material rich in iron carbonate could be effective in preparing the sulfur-storage bricks. Finally, the sulfur-storage bricks will be subjected to leaching experiments to address two important questions:

1) Is the material sufficiently stable, such that it can serve as a manageable form of sulfur storage?
2) Which processing protocols enhance stability?

Expected outcome: Tested process for producing sulfur-storage bricks that will be stable over time periods of years. We will identify the conditions in which the material is stable and could become less stable. This will facilitate sulfate remediation from mining wastewater, and the sulfur-storage bricks could be used as a resource for future processing (i.e., a new source of iron).

ENRTF BUDGET: $ 134,395

Outcomes	Completion Date
1. Quantitative leaching results and stability results	*Fall 2021*
2. Refined treatment procedure to minimize sulfur loss under environmental conditions	*Summer 2022*

III. PROJECT PARTNERS: Partners receiving ENRTF funding

Name	Title	Affiliation	Role
Dr. R Lee Penn	Professor	U of Minnesota-TC, Chemistry	Project Director
Dr. Joshua Feinberg	Professor	U of Minnesota-TC, Earth Science	Investigator
Dr. Chan Lan Chun	Professor	U of Minnesota-Duluth, NRRI, Civ Engineer.	Collaborator
Dr. Nathan Johnson	Professor	U of Minnesota-Duluth, Civ. Engineer.	Collaborator

IV. LONG-TERM- IMPLEMENTATION AND FUNDING:

Holding sulfur in a solid and manageable form will close the loop between sulfate remediation from wastewater and preventing release of sulfur species into nearby fresh water sources (e.g., lakes, rivers, groundwater). We will develop economical method for producing a solid material that can effectively and safely store sulfur. We will use waste materials produced by iron mining activities. We will rigorously quantify the stability of the product material in order to predict the realistic storage time of the product material and identify conditions that compromise the stability of the bricks. Success will lead to the broader application of removal of sulfate from mining wastewater by way of biological sulfate reducing processes.

V. TIME LINE REQUIREMENTS:

The project will take 36 months to complete. Progress on all activities will begin as soon as the project starts.

Attachment A: Project Budget Spreadsheet
Environment and Natural Resources Trust Fund
M.L. 2020 Budget Spreadsheet
Legal Citation:
Project Manager: Prof. R. Lee Penn
Project Title: Storing Sulfide Produced from Sulfate-Containing Wastewater Safely
Organization: University of Minnesota - Twin Cities and Duluth
Project Budget: 280,790
Project Length and Completion Date: 36 months, 2023
Today's Date: 9 April 2019

ENVIRONMENT AND NATURAL RESOURCES TRUST FUND BUDGET	Budget	Amount Spent	Balance
BUDGET ITEM			
Personnel (Wages and Benefits)	$ 188,790	$ -	$ 188,790
*Supervising principal investigators (4 collaborators) - **Total of $69,328***			
R. Lee Penn (project manager, UMN-TC; 0.5 month summer salary per year + fringe = 29287); supervise graduate student; perform electron micrscopy on samples; evaluate data and design experiments.			
Joshua Feinberg (co-principal investigator, UMN-TC; 0.5 month summer salary per year + fringe = 19013); supervise graduate student; perform rock magnetic measurements; evaluate data and design experiments.			
ChanLan Chun (co-principal investigator, UMD; 0.25 month summer salary per year + fringe = $9643); supervise graduate student; provide the pre-treatment materials (iron sulfides); quantify sulfide species in solution from leaching experiments; evaluate data and design experiments.			
Nathan Johnson (co-principal investigator, UMD; 0.25 month summer salary per year + fringe = 11385); supervise graduate student; evaluate data and design experiments.			
Graduate student (to be determined; 3 years funding plus fringe); co-advised and working in close collaboration with members of each PI's research group; Design and execute experiments for developing methods for preparation of the solid that holds sulfur in a manageable state. Perform experiments testing the stability of the new materials. Characterize materials. Total of $119461			
Technical Services:			
User fees for instrumentation (electron microscopes, X-ray scattering equipment, spectroscopic methods) at the University of Minnestoa - College of Science and Engineering's Characterization Facility ($10k/yr)	$ 30,000	$ -	$ 30,000
Repairs and maintenance	$ 10,000	$ -	$ 10,000
Equipment/Tools/Supplies			
Chemicals (metal salts, sulfur, standards, buffers, water purification supplies, high temperature vessels, and supplies for materials characterization ($10k/yr)	$ 30,000	$ -	$ 30,000
Capital Expenditures Over $5,000			
Research-grade and programmable laboratory kiln optimized for reproducible processing of materials. This equipment is substantially more specialized than a conventional kiln. The system enables control of the atmosphere as well as monitoring temperature during processing. This equipment will be used for its full useful life and made available to other researchers at no charge.	$ 12,000	$ -	$ 12,000
Travel expenses in Minnesota			
Quarterly travel between UMN-Twin Cities, UMN NRRI, and UMN-Duluth for all researchers involved over all three years of the project.	$ 10,000	$ -	$ 10,000
COLUMN TOTAL	$ 280,790	$ -	$ 280,790

SOURCE AND USE OF OTHER FUNDS CONTRIBUTED TO THE PROJECT	Status (secured or pending)	Budget	Spent	Balance
Non-State:		$ -	$ -	$ -
State:		$ -	$ -	$ -
In kind:		$ -	$ -	$ -
The investigators will also devote 1% time per year in kind ($1,507). Because the project is overhead free, laboratory space, electricty, and other facilities/adminstrative costs (54% of direct costs excluding permanent equipment and graduate student academic year fringe benefits) are provided in-kind	secured	$ 259,280		

Other ENRTF APPROPRIATIONS AWARDED IN THE LAST SIX YEARS	Amount legally obligated but not yet spent	Budget	Spent	Balance
Past and Current ENRTF Appropriation: Solar Cell Materials from Sulfur and Common Metals (M.L. 2014) Past appropriate was $474,000 and focused on solar cell thin film materials composed of earth abundant metals combined with sulfur. There is no overlap with the work proposed here.	$ -	$ 494,000	$ 494,000	$ -

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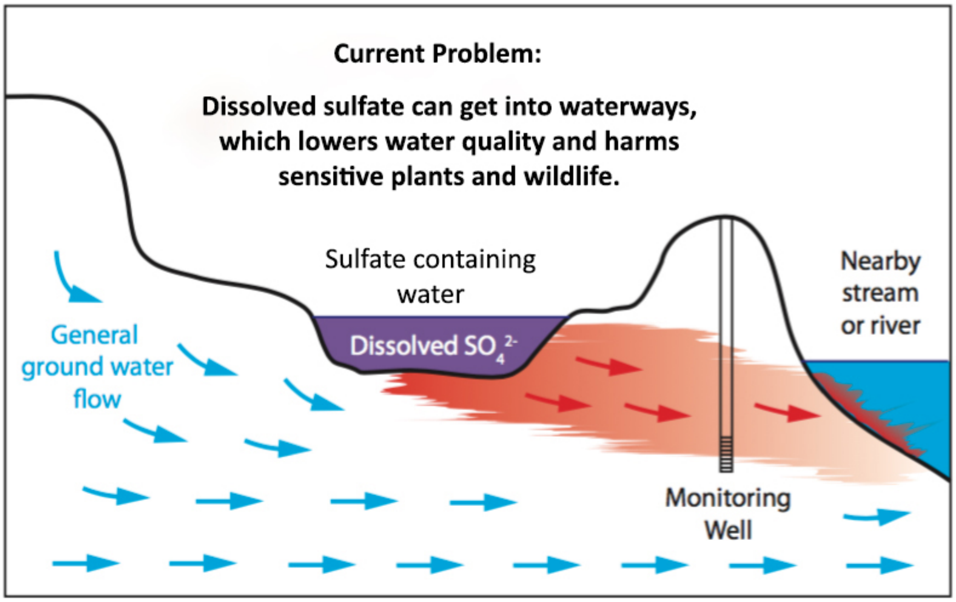
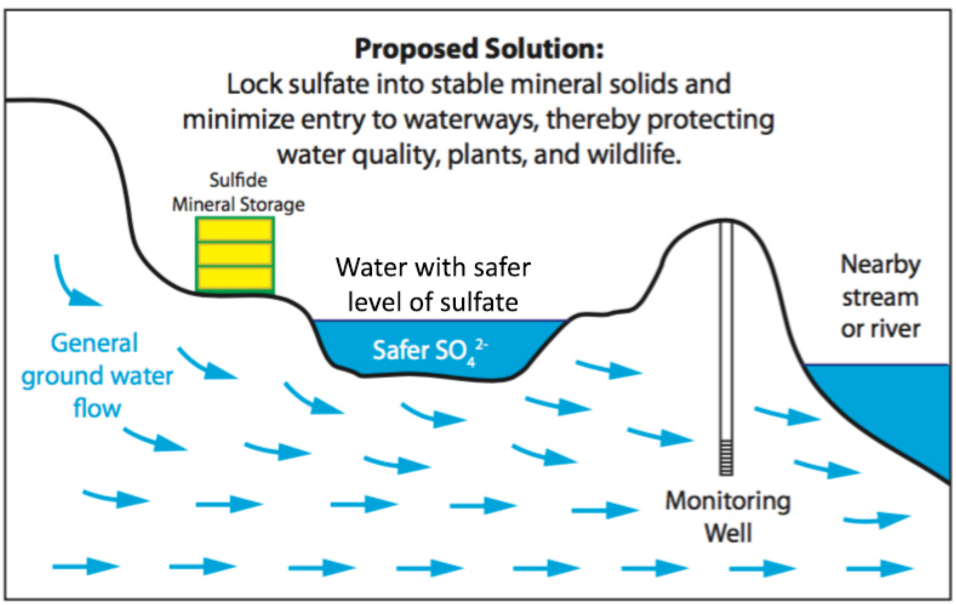
B. Visual Component or Map





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Project Management and Qualifications: Dr. Lee Penn will lead the project and work closely with Drs. Joshua Feinberg, Chan Lan Chun, and Nathan Johnson in coordinating experiments geared towards developing a process for storing sulfide safely at MN mining sites. They will co-advise one graduate student.

Prof. Lee Penn is the project manager and has extensive experience in materials synthesis of a broad diversity of technologically important materials, including metal oxides and hydroxides, metal sulfides, metals, and metal organic framework materials. In addition, the Penn research group uses a broad range of techniques to characterize the structure, properties, and reactivity/activity of both natural and engineered materials. In addition, the Penn research group uses a broad range of environmental chemistry methods in order to examine how minerals change in reactive conditions. Penn will be responsible for synthesis and characterization of reference minerals and characterizing the sulfate reduction biproducts (obtained from the Duluth investigators) and products of leaching experiments and heat treatments. Current Position: Professor, Department of Chemistry, University of Minnesota – Twin Cities. Education: Beloit College, Chemistry B.S., 1988-1992; University of WI, M.S. and Ph.D. in Materials Science, 1992-1998; and Postgraduate Training at Johns Hopkins University, Sept. 1998 - April 2001.

Prof. Joshua Feinberg is a mineralogist with over 19 years of experience working as a geoscience professional for state and federal natural resource agencies, for private environmental consulting corporations, and as a university professor overseeing federally funded scientific research. Feinberg uses a combination of geophysical and materials science approaches to characterize minerals. Feinberg will perform the rock magnetic measurements, which encompass a suite of techniques that can quantify trace amounts of Fe-oxide, Fe-sulfide, Fe-carbonate, and Fe-phosphate minerals at ppm concentrations, determine whether materials are crystallineor amorphous a s well as quantify their average particle size. Current Position: Associate Professor, Department of Earth Sciences, University of Minnesota – Twin Cities. Education: Carleton College, Geology Major, 1993-1997; Univ. of California, Berkeley, Ph.D. in Earth and Planetary Sci, 2000-2005; and Postgraduate Training at the University of Cambridge, July 2005-October 2007.

Profs. Chan Lan Chun and Nathan Johnson are environmental engineers in the Department of Civil Engineering at the University of Minnesota – Duluth campus. Their research focuses on the fate and transport of chemical contaminants in natural and engineered systems. **Chun and Johnson** are collaborators and will co-lead activities related to characterizing solutions from leaching experiments. Through the work funded by Chun's Minnesota Mining Innovation Grant (Development of iron liberation methods to sustainable biological sulfate removal from mine water), the UMD team can provide the product of sulfate reduction to our team. In addition, Chun and Johnson have a large array of mining waste materials, including tailings, waste rock, and even waste ore and have access to providing additional materials as needed.

Organization Description: The University of Minnesota offers world-class facilities for the completion of this project. Materials characterization will be performed in the UMN Characterization Facility, which includes a variety of electron microscopes and X-ray diffractometers for inspection, and the Institute for Rock Magnetism, which includes a variety of magnetometers and Mössbauer spectrometers. Chun is a member of the NRRI (Natural Resources Research Institute), an applied research organization whose mission is to deliver research solutions to balance Minnesota's economy, resources and environment for resilient communities.