Environment and Natural Resources Trust Fund
2019 Request for Proposals (RFP)

Project Title: **ENRTF ID: 074-B**

Storing Sulfide Safely at MN Mining Sites

Category: B. Water Resources

Sub-Category:

Total Project Budget: $ 536,161

Proposed Project Time Period for the Funding Requested: June 30, 2022 (3 yrs)

Summary:

Sulfate in mining wastewater is a major concern in Minnesota. We propose to process biproducts of sulfate remediation to produce bricks for safe storage of sulfur at MN mining sites.

Name: Lee Penn

Sponsoring Organization: U of MN

Title: Professor

Department: Department of Chemistry, Twin Cities campus

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Minneapolis MN 55406

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Web Address

Location

Region: Statewide

County Name: Statewide

City / Township:

Alternate Text for Visual:

Current Problem: Dissolved sulfate in tailings ponds threatens water quality. Proposed Solution: Produce sulfur storing solid to inhibit sulfate transport into waterways.

_____ Funding Priorities _____ Multiple Benefits _____ Outcomes _____ Knowledge Base

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

_____ Capacity Readiness _____ Leverage _______ TOTAL ______%

____ If under $200,000, waive presentation?

PROJECT TITLE: Storing Sulfide Safely at MN Mining Sites

I. PROJECT STATEMENT

Safe management of mining wastewater is an urgent need in the state of Minnesota and in the United States. Sulfate is a problematic pollutant generated during mining. Sulfate reduction produces sulfide, which needs to be managed safely. ***We propose to combine products of sulfate reduction with mining waste materials to store sulfide in a stable brick. This would enable safe storage of sulfur at MN mining sites.***

Sulfate (SO_4^{2-}) dissolves in water, which means sulfate can move through ground and surface water. Sulfate is a major component of acid mine drainage, which can degrade water quality and cause extensive ecosystem damage. Sulfate is converted by microbes into other dissolved S-based species, most importantly, sulfide (S^{2-}), which is toxic. The negative impacts of these species are extensive and include toxicity towards aquatic organisms, increased mercury methylation (a toxic compound), and eutrophication of lakes. In addition, there is a major and negative impact on wild rice, which is economically, culturally, and ecologically important. Conversions between sulfate and sulfide (both dissolved forms) are relatively easy, but storing sulfur in a stable solid form is challenging.

We propose to take the sulfide produced by sulfate reduction and combine it with available mining waste material to produce a solid material that can safely store sulfur at MN mining sites. The resulting material would then be available for future processing. Our project will test sulfur-containing minerals to identify those with the highest stability and develop a process to produce those targets from the sulfide biproducts produced by sulfate wastewater treatment. Our expected outcome is a process for converting the sulfide into a solid brick. The brick will enable stable sulfur storage over realistic time frames (several years). The goal is to hold the sulfur in a safe and manageable form, ready for future processing.

Major Results Expected:

1. **Green method to convert sulfide into a solid to hold sulfur in a manageable state.**
2. **Quantitative evaluation of the stability of the solids upon exposure to air and/or water.**
3. **Prototype treatment system to produce the sulfur storing solid.**

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

II. PROJECT ACTIVITIES AND OUTCOMES

Activity 1: ***Determine which minerals best retain sulfur under conditions common at MN mining sites.***

We will prepare and evaluate materials for potential to safely store sulfide for short-term (ca. several years) storage at mining sites. First, we will test reference minerals for stability. We will expose the reference minerals to mining waste-water and freeze-thaw cycles.

Second, we will develop the process for producing the most stable S-bearing minerals. Here, we leverage ongoing work by Investigators Chun and Johnson. They have developed a sulfate reduction process that produces a solid containing iron and sulfur. These solids are not stable upon exposure to water and air. We will use that material in experiments aimed at developing a process to produces the most stable storage material. Processes that produce more of the stable minerals will be further refined while processing that produces less stable minerals will be rejected. We will characterize all materials involved in this work using four primary methods: X-ray diffraction (XRD), Raman Spectroscopy, Scanning Transmission Electron Microscopy (STEM) with Electron Energy Loss Spectroscopy (EELS) and Energy Dispersive Spectroscopy (EDS), and rock magnetic measurements.

Outcome	Completion Date
1. Quantitative leaching experiments using natural and synthetic reference minerals and simulated mining waste water, groundwater, and surface water	*Summer 2020*
2. Treatment protocol to convert biproducts to a stable S-storage brick	*Spring 2021*

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

We propose that combining the solids produced by sulfate reduction with other mining waste materials, such as waste rock or tailings, could produce a sulfur storage material that is stable against exposure to water and air as well as freeze/thaw cycles. Here, we focus on mixing the products from activity 1 with mining waste materials, pressing that material into bricks, and heat-treating. 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 researcgers at the NRRI (Natural Resources Research Institute). Our preliminary results demonstrate that iron carbonate (siderite) reacts with dissolved sulfide, which could mean that iron carbonate is a good additive for generating stable S-storage bricks.

Finally, the S-storage bricks will be subjected to leaching experiments to address two important questions:

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

Expected outcome: Tested process for producing S-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 S-storage bricks could potentially provide a resource for future processing (i.e., a new source of iron).

Outcomes	**Completion Date**
1. Quantitative leaching 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

The Natural Resources Research Institute (NRRI) is a University of Minnesota Duluth applied research organization. NRRI's mission is to deliver research solutions to balance Minnesota's economy, resources and environment for resilient communities.

IV. LONG-TERM- IMPLEMENTATION AND FUNDING:

Holding sulfur in a solid and manageable form will close the loop between sulfate remediation from mining waste water and preventing release of sulfur species into nearby fresh water sources (e.g., lakes, rivers, groundwater). We will develop and economical method for producing a solid material that is stable over the time frame of a few years, and we will use waste materials produced by mining activities. We will rigorously quantify the stability of the product material in order to predict the realistic storage time of the product material. Success will lead to the broader application of removal of sulfate from mining waste water by way of 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.

2019 Proposal Budget Spreadsheet

Project Title: Storing Sulfide Safely at MN Mining Sites

IV. TOTAL ENRTF REQUEST BUDGET *3* years

BUDGET ITEM (See "Guidance on Allowable Expenses")	**AMOUNT**	
PERSONNEL -- TOTAL		$ 432,161
Supervising principal investigators (4 collaborators) - R. Lee Penn (project manager, UMN-TC; 1 month summer salary per year + fringe = 452,772); supervise post-doc and graduate student; perform electron micrscopy on samples; evaluate data and design experiments. **Joshua Feinberg** (co-principal investigator, UMN-TC; 1 month summer salary per year + fringe = $45,572); supervise post-doc and graduate student; perform rock magnetic measurements; evaluate data and design experiments. **ChanLan Chun** (co-principal investigator, UMD; 0.5 month summer salary per year + fringe = $17,531); supervise post-doc and 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; 0.5 month summer salary per year + fringe = 20,328); supervise post-doc and graduate student; evaluate data and design experiments.	$ 136,203	
Personnel: <u>Post-doctoral researcher</u> (to be determined; 3 years funding plus fringe); co-advised; 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.	$ 181,699	
Personnel: <u>Graduate student</u> (to be determined; 3 years funding plus fringe); co-advised and working in close collaboration with the post-doctoral researcher; 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.	$ 114,259	
Equipment/Tools/Supplies: 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 ($12k/yr)	$	36,000
Equipment/Tools/Supplies: 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
Equipment/Tools/Supplies: chemicals (metal salts, sulfur, standards, buffers, water purification supplies, high temperature vessels, and supplies for materials characterization ($12k/yr)	$	36,000
Equipment/Tools/Supplies: repairs and maintenance	$	10,000
Travel: Quarterly travel between UMN-Twin Cities, UMN NRRI, and UMN-Duluth for all researchers involved over all three years of the project.	$	10,000
TOTAL ENVIRONMENT AND NATURAL RESOURCES TRUST FUND $ REQUEST =	$	536,161

V. OTHER FUNDS *(This entire section must be filled out. Do not delete rows. Indicate "N/A" if row is not applicable.)*

<u>SOURCE OF FUNDS</u>	**<u>AMOUNT</u>**	**<u>Status</u>**
Other Non-State $ To Be Applied To Project During Project Period: None	NA	
Other State $ To Be Applied To Project During Project Period:	NA	
In-kind Services To Be Applied To Project During Project Period: 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 ($257,773)	$ 259,280	
Past and Current ENRTF Appropriation: 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.	NA	
Other Funding History: Minnesota Mining Innovation Grant, "Development of iron liberation methods to sustainable biological sulfate removal from mine water". University of Minnesota Duluth (October 1, 2016 - June 30, 2018).	$ 267,700	

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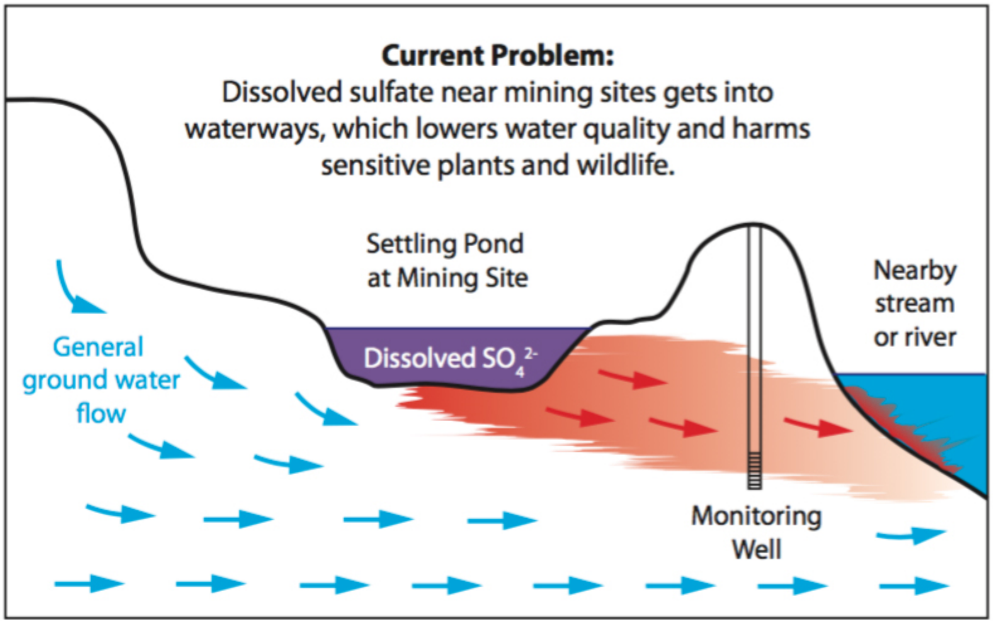
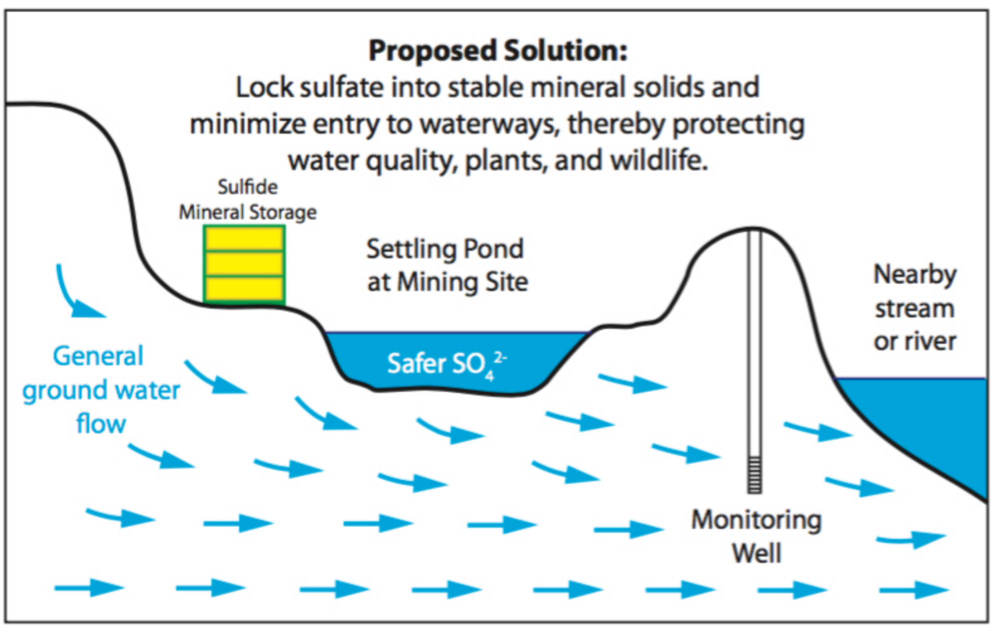
B. Visual Component or Map





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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 and one post-doctoral researcher. The post-doctoral research will serve as a mentor towards the 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 crystalline or amorphous as 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.