**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 (SO42-) 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 (S2-), 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.