USGS

WATER RESOURCES RESEARCH GRANT PROPOSAL

Title: Development of microbial biobarriers for the control of acid rock drainage from mine tailings.

Focus Categories: ACD, G&G, HYDGEO

Keywords: Acid Mine Drainage, Biobarriers, Biostimulation, Water Chemistry

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Non-Federal Matching Funds Pledged: $19,912

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Congressional District: Montana at large.

Statement of Critical Regional or State Water Problems

Acid rock drainage (ARD) from abandoned hard rock mine lands is a major environmental problem that impacts both ground- and surface water throughout the Western United States and is a major contributor to loss of habitat for fisheries. Abandoned mine lands (AML) often contain unmined mineral deposits, waste rock, and mine tailings which contain high concentrations of metals in the form of metal sulfides. When oxygen-containing rainwater, streamwater, and/or groundwater comes into contact with these materials, chemical oxidation reactions occur which liberate the bound metals into solution and may radically lower the pH of the receiving water. Many AMLs are located on public land (State, US Forest Service, or US Bureau of Land Management) or on patented parcels enclosed by public lands. It is therefore in the interest of these agencies, and the US Geological Survey (USGS) to foster innovative, cost-effective solutions to ARD.

The USGS has recognized the importance of ARD and, in 1997, began the AML Initiative, which focuses on two watersheds heavily impacted by historic mining activities (Montana’s Boulder River Drainage and Colorado’s Animas River basin). The research effort proposed herein will compliment the stated goals of this Initiative in the design and implementation of AML cleanup methods by providing proof of principle for the use of microbial stimulation to reduce ARD.

Statement of Results or Benefits

The purpose of this research is to further develop an inexpensive and potentially widely applicable treatment technology to utilize indigenous microorganisms within mine tailings to abate ARD at its source. The proposed research will provide critical application information necessary to implement this technology at the field scale. Specifically, the results of this research will provide the necessary data to determine water and nutrient application rates and schedules that result in lowered ARD from tailings from an abandoned mine in Montana. Nutrient and water application data will be correlated with populations and activity of indigenous microorganisms such that acid reduction processes can be optimized. This information will allow an economic as well as a scientific assessment of this technology for potential application to other AML sites.

In keeping with the missions of the CBE and the Montana University System Water Center, this proposal includes a plan for the transfer of research results to industrial field practitioners to assure rapid adoption and use of technological advances. This will assist Montana businesses in attaining a leadership position in developing biological treatment methods for use at abandoned mine sites. The work proposed herein is a first step in the application of biobarrier technology to mine waste remediation. It is anticipated that the results from this work will spawn further efforts to fully develop this technology for broad application.

Nature, Scope, and Objectives of Research

Technological Background

ARD arises from waste rock and mine tailings containing sulfide minerals and lacking acid-consuming carbonate minerals. Sulfide minerals, such as pyrite (FeS_2) are oxidized to form sulfate when water-containing oxygen infiltrates tailings. This process is described by the following reaction:

$$4FeS_2 + 15O_2 + 2H_2O \rightarrow 4Fe^{3+} + 8SO_4^{2-} + 4H^+ \qquad (1)$$

The activity of bacteria, such as *Thiobacillus ferrooxidans*, which are capable of oxidizing inorganic sulfur compounds, greatly accelerates this reaction (Brierley, 1978). The ferric iron (Fe^{3+}) produced in the above reaction also contributes to pyrite oxidation:

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \qquad (2)$$

T. ferrooxidans is also capable of oxidizing ferrous iron (Fe^{2+}) produced in the above reaction:

$$4Fe^{2+} + O_2 + 4H^+ \rightarrow 4Fe^{3+} + 2H_2O \qquad (3)$$

Thus, the ferric iron is regenerated and is capable of oxidizing more pyrite. The key to breaking this cycle is the prevention of the initial oxidation of pyrite. Bound with iron, the sulfur in pyrite is unable to participate in the microbially catalyzed reactions that cause acid generation. Prevention of oxygen infiltration into tailings is necessary to prevent oxidation of pyrite and subsequent acid generation and mobilization to ground and surface waters. An innovative method to prevent oxygen transport into tailings is the construction and maintenance of a biologically active barrier within the near-surface zone of the tailings. This barrier is made up of naturally occurring aerobic and facultative bacteria which utilize dissolved oxygen in the infiltrating water and therefore maintain the reducing conditions which are necessary for pyrite to remain bound in mineral form.

The application of reactive barriers to chemically alter groundwater is a nascent but rapidly growing field. Recent reports in the literature document the use of compost and other organic substrates to support microbial populations capable of altering the pH and oxidation-reduction potential (ORP) of influent waters, thus promoting the removal of dissolved metals from solution (Benner, *et al*., 1997). Researchers at the Center for Biofilm Engineering (CBE) together with MSE Technology Applications of Butte, MT have investigated the microbial processes involved with the establishment and maintenance of subsurface and near surface microbial barriers for hydraulic control and microbially catalyzed reactions (Cunningham *et al*., 1997). These experimental systems have shown that biobarriers constructed of aerobic or facultative organisms can successfully remove oxygen from infiltrating water to trace levels. Application of the biobarrier concept to acid producing mine tailings in a controlled laboratory setting is the logical next step in the development of this technology.

The premise of this technology is that the application of a nutrient-containing solution to the surface of acid-producing tailings will stimulate the growth of naturally occurring aerobic and facultative bacteria within the tailings. These indigenous bacteria will then consume all available dissolved oxygen from the infiltrating water as they metabolize the added organic carbon. The need to add other essential nutrients, such as nitrogen and phosphorus, depends on the availability of these compounds in the tailings. The consumption of more energetic electron acceptors (e.g., oxygen and any available nitrate) will likely create conditions favorable for the growth of fermentative and sulfate reducing bacteria (SRB). Sulfate is typically present in high concentrations in mine wastes. The activity of SRB is desirable in that it consumes acid and stabilizes metals by H_2S-mediated metal sulfide precipitation. Laboratory-scale experiments have demonstrated that biobarriers are capable of generating conditions suitable for SRB growth (James *et al*., 1995).

The stimulation of bacteria in the tailings may also result in decreased infiltration capacity due to the production of bacterial slime (extracellular polysaccharides), thereby resulting in less overall water movement into the tailings. This is not a necessary condition for the successful application of the technology, however, it may assist in reducing overall acid production from the tailings. Chemical alteration of the infiltrating water is expected to be the primary mechanism of action while physical alteration of the tailings pore space may be a beneficial secondary effect.

Research Scope and Objectives

The proposed research will encompass the acquisition of mine tailings from a suitable site in Montana (Mammoth Mine, South Boulder River drainage), laboratory experimentation with these tailings in column experiments, and the transfer of technological advances through commercialization links. Specific research objectives are:

> 1) Confirm the ability of nutrient dosing to stimulate indigenous aerobic and facultative bacteria in mine tailings from the abandoned Mammoth Mine (South Boulder River, MT).
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> 2) Determine the extent to which the permeability of mine tailings is reduced by bacterial growth.
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> 3) Determine the extent to which effluent metals are reduced from pre-nutrient addition conditions.
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> 4) Determine the longevity of effect of a single dosing of nutrient to mine tailings in a column reactor.
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> 5) Optimize nutrient dosing protocols based on the results of objectives 1-4.
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> 6) Perform initial work necessary to incorporate experimental results into a mathematical model to predict biological and geochemical reactions within mine tailings.
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> 7) Transfer relevant research findings to industry through the publication of results and the development of workshops for information dissemination.

Though the work proposed herein will be conducted solely in a laboratory setting, it will be done with the intention of applying this technology to field sites. A common concern expressed by regulatory and site managers is whether a treatment based on biologically mediated reactions can be expected to continue operating in winter months. This concern is well founded in light of the marginal performance of wetlands-based treatments for acidic mine-adit drainage. The application proposed herein differs from a constant flow condition (such as mine adit drainage, which does not stop despite sub-freezing winter temperatures) in that the conditions which would cause the tailings bacteria to cease activity (i.e., sub-freezing conditions in the tailings pile) would also tend to stop water movement into the tailings. Acidic drainage through tailings during winter months is limited by freezing conditions. Another concern is ability of bacteria in tailings to survive freezing conditions over the winter, and to resume activity as the spring thaw increases snow-melt infiltration into the tailings. It is expected that freezing conditions will result in very little bacterial mortality, since freezing to –70C is the preferred method of bacterial culture preservation. Whether the bacteria can resume activity to the extent necessary to prevent acidic drainage from the tailings as cold snow-melt infiltration begins is not so easily answered. At field sites, the springtime performance of the technology will depend on accumulated snow, tailings depth, slope, aspect, and ambient temperature conditions. The experimental work proposed herein will not attempt to address bacterial response to freezing, but subsequent work will involve freezing small scale columns and thawing them under the influence of infiltrating water. It is recognized that this is an important consideration for field application.

Methods, Procedures, and Facilities

This proposal encompasses two sets of column experiments using mine tailings collected from the abandoned Mammoth Mine site, located 15 miles south of Cardwell, Montana. Prior work at the CBE has identified this as a potential site for the application of biological ARD remediation due to high metals content and the presence of acidic drainage from tailings piles. The two sets of experiments include large diameter (12”) and small diameter (2”) columns, as described below:

Large Column Experiments

The large column experiments will address objectives 1) through 4) above, and will provide data for the modeling and commercialization efforts outlined in objectives 6) and 7). For the large column experiments, tailings will be packed into 3 PVC columns (12” diameter, 40” length). After they are initially filled with tailings, columns will be flooded from below to expel all air from pore spaces, then drained to promote settling. After settling, columns will receive additional tailings until the 40” depth is achieved. Following this, the columns will be flooded from below a second time and again allowed to slowly drain. Prior laboratory work with soil columns has shown that this method works well to prevent channeling in fine-grained, unconsolidated materials, such as tailings. Tailings will be analyzed for mineralogical and microbiological content prior to packing. Tailings will be assayed for Aluminum, Arsenic, Cadmium, Cobalt, Copper, Iron, Lead, Magnesium, Manganese, and Zinc. Microbial analyses will include total heterotrophic bacteria, sulfur oxidizing bacteria, sulfate reducing bacteria, and total direct counts.

Because most field sites receive periodic moisture and are not submerged, columns will be operated in an unsaturated condition and will receive intermittent influent water. After packing, all 3 tailings columns will receive influent water at a rate of 15 ml/min for 30 minutes each day. Influent water will be de-chlorinated tap water. This represents both a more realistic and more challenging condition than would saturated columns. Column effluent water will be monitored daily for pH and oxidation-reduction potential (ORP). After stabilization of pH and ORP (approximately 2 weeks is expected), column effluent will be analyzed for metals, anions, and bacteria to establish baseline conditions. After establishment of baseline effluent conditions, 2 columns will receive a single dose treatment of carbon (molasses) and nutrients (if prior testing indicates low levels of N or P) dissolved in water. The third column will receive an equal amount of unamended water as a control. The nutrient dose will be approximately 3 liters and will contain 10 g/l molasses and N in the form of fertilizer grade urea (if necessary) and P in the form of dibasic Potassium Phosphate (K_2HPO_4), if necessary. The molasses flux to the surface of the columns is therefore 30g/0.073 m^2 (411g/m^2). Column effluent pH and ORP will continue to be monitored on a daily basis following nutrient amendment. Dissolved metals, anions, and microorganisms will be monitored in column effluent on a bi-weekly basis following initial nutrient amendment. The effects of a single dosage of molasses and nutrients will be measured for as long as the treated columns exhibit significantly different effluent pH, ORP, and dissolved metals as compared to the control column. The permeability of tailings columns will be tested both before and after molasses treatment through the performance of infiltration tests. These tests will involve application of a set quantity of standing water to the surface of the columns and subsequent measurement of the time necessary for full infiltration.

Small Column Experiments

A bank of 12 small diameter (2") columns will be assembled to perform testing relevant to objective 5), optimization of nutrient dosing. These columns will be packed according to the protocol outlined above, and will be operated at a water application rate of 24 ml/day. This application rate provides a water flux of 12 mm/day (0.48 inches/day) which is twice that used in the large column experiments. Nutrient doses used in the small column experiments will be set at three levels, 200 g/m^2, 400 g/m^2 and 800 g/m^2. Each dosage level will be applied to three columns, and three control columns will receive only water influent. Column effluent will be monitored for pH, ORP, dissolved metals, and microbial colonization in a similar manner as the large columns. The effectiveness of each nutrient dose rate will be determined based on the longevity of effect and the extent to which pH is increased and dissolved metals are reduced. The results of these experiments will be compared to the results of the large column experiments for consistency. Results from both large and small column experiments will provide information needed to model the bacterial and chemical reactions occurring in the mine waste. These results will also provide valuable information for optimizing treatment protocols for field use.

Modeling

Computer modeling efforts to be performed within the contract period of this proposal are limited to the identification and initial application of the experimental (column) data to a one-dimensional flow model which accounts for bacterial growth and utilization of organic carbon, mineral oxidation, pH, dissolved oxygen, and dissolved metals. This model must take into account both the non-equilibrium conditions of the columns with respect to bacterial growth following the addition of nutrients, and the growth of populations of anaerobic bacteria (such as sulfate reducing bacteria) as they impact metals solubility and pH.

Timeline

Large and small column experiments will be initiated immediately following notification of funding. These experiments will be operated for a period of at least two weeks prior to the first addition of nutrients. Following nutrient addition, column effluents will be monitored as described above for a period of 4-20 weeks, until effluent parameters have stabilized. At this time, large columns will receive and additional dosing of nutrient (if necessary to preserve anaerobic conditions). Small columns will be destructively sampled to determine bacterial colonization within the columns, and to determine any mineralogical changes via surface characterization techniques. Data collection is expected to be complete by week 30. Modeling efforts will begin at approximately week 6 and will continue until week 40. Development of technology transfer materials (publications, workshop materials) will occupy weeks 40-50. Submittal of research findings for publication and presentation of workshops will occur within 18 months of the start of funding.

Related Research

The role of iron and sulfur-oxidizing bacteria (such as *Thiobacillus ferrooxidans*) in accelerating ARD from mine tailings has been recognized for decades (Silverman and Lundgren, 1959), and current research to expand our understanding of acid rock drainage from both a chemical and biological perspective is broad in scope and extensive in depth. The majority of the work dealing with utilizing microbial processes to mitigate ARD focuses on using constructed wetlands to treat mine discharge waters. Wetlands have been noted to have the ability to assist the precipitation and retention of very high concentrations of metals such as copper, iron, manganese, and uranium (Shinners, 1996; Howard *et al*., 1989). The work proposed herein differs from the traditional constructed wetlands approach in that the intention with this work is to prevent the initial acidification of runoff water from mine tailings, rather than treating it once it has acidified.

From an application standpoint, the proposed work has more in common with research which seeks to remediate contaminated groundwater through the use of reactive biobarriers. In this work, indigenous or introduced microorganisms are stimulated *in situ* through the addition of organic carbon and nutrients (James *et al*., 1995). The objective of constructing barriers of this type is either to utilize the microorganisms to assist the detoxification of a contaminant as it flows past the barrier, or to inhibit the flow of groundwater past the barrier by plugging the pore spaces of the aquifer with bacterially produced extracellular polymers. The proposed work is similar to the former condition, where water flow is not necessarily restricted by the microorganisms, but they mediate beneficial reactions within the subsurface. The body of knowledge created in biobarrier work (Cunningham *et al*., 1997) contributes significantly to the understanding of bacterial movement and response to introduced nutrient sources, both of which are necessary prerequisites to successful application of the proposed technology.

Information Transfer Plan

Data collected from experimental and modeling efforts will be condensed into a cohesive explanation of the response of mine tailings columns to the addition of various concentration of carbon and nutrients. This information will be used to answer the following questions regarding application of this technology at field sites:

1. What is the response time for aerobic and facultative microorganisms to begin activity following nutrient addition?

2. How long does the effect of a single nutrient treatment last in columns?

3. What effect does raising effluent pH and lowering effluent ORP have on metals in column effluent?

4. How do populations of sulfate reducing bacteria, sulfur oxidizing bacteria, and general heterotrophic bacteria change within the columns as a function of time, nutrient amendment, pH and ORP?

5. Can a 1 Dimensional computer model be used to help predict the pH and metals content of column effluent?

6. What scale-up issues must be considered in applying this technology to field sites (snowmelt, freeze-thaw cycles, preferential flow channeling, etc.)?

These questions will be answered (to the extent the data allows) in publications in scientific journals and in a workshop format. The CBE in general and the principal investigator in particular have extensive experience in the development and delivery of workshops for the transfer of technologies useful to industrial researchers and field practitioners. The information gathered in this study will be complied in a workshop format and delivered to interested parties (regulators, engineers, etc.) in a one day session in Bozeman, Montana. The principal investigator will cooperate with MSE scientists and Montana Department of Environmental Quality regulatory personnel to identify the potential audience base. This base is expected to include consulting engineers, regulators, academicians, and parties liable for site remediation. Special effort will be made to include Native American tribal representatives.

References

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