COOPERATIVE ECOSYSTEMS STUDIES UNITS

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MECHANISMS OF BIOREACTOR-BASED MINE WATER TREATMENT

REPORT: TASK 3

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Ronald L. Crawford, PhD
Director
University of Idaho
Environmental Biotechnology Institute

Problem Statement and Significance

Acid mine drainage (AMD) causes billions of dollars of damage to natural vegetation, silvaculture, rivers, watersheds, natural habitats, and aquatic life (Tabak et al., 2003). Subsurface drainage and surface runoff from mining sites have negatively impacted water quality in streams and lakes in the Coeur d'Alene Basin in Northern Idaho (Figure 1), including in Lake Coeur d'Alene itself (McNary et al., 1995). One of the nation's largest Superfund sites now exists in the area as a legacy of past mining of metals such as lead, silver, and zinc (Wong, 2004). For the past 25 years, litigation has been on the rise over impacts from metal pollution, and consequently funding to mitigate environmental impacts of AMD has also increased. Commercial systems for treating AMD have focused on recovering metals from high-volume AMD that contains high metal concentrations such as the Berkeley Pit in Butte, Montana. Tabak et al. (2003) cite several such approaches. Another example of such an approach is an electrochemical process developed by Electrochemical Design Associates that is applicable to high-volume, high-metal-concentration AMD but not to low-volume abandoned mine drainage. Our low-cost technology will be applicable to the bulk of abandoned mine drainage sites where a passive approach is preferred. To date no comprehensive design solution exists for these abandoned mine sites.

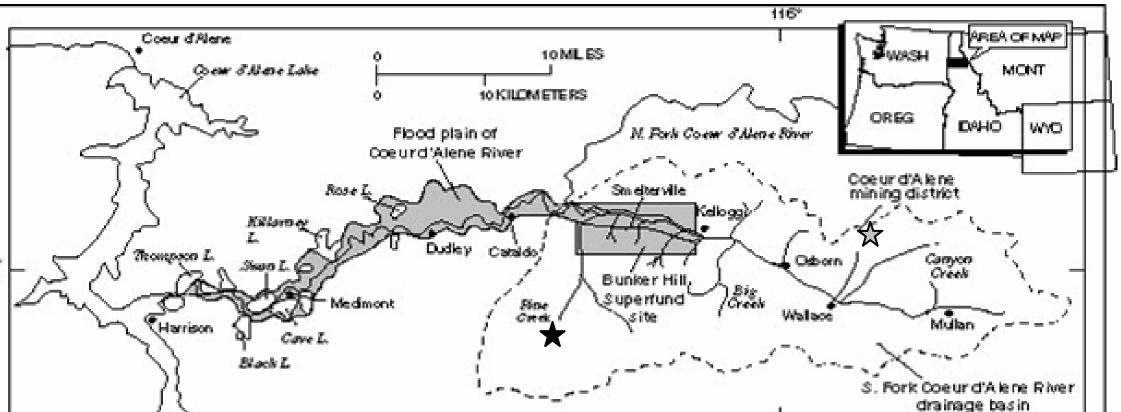

Figure 1. Coeur d'Alene River Basin watershed with Bunker Hill Superfund Site shown in boxed area. The black star indicates the location of the Upper Constitution mine and the grey star Mother Lode mine (Map source: BLM).

Description of the Research Program

Under the cooperative agreement that is the subject of this final report, the University of Idaho undertook a study of the mechanisms whereby compost-based bioreactors installed by the US

BLM in several AMD sites in the Coeur d'Alene Basin of Northern Idaho (Figure 1) remove metals for AMD discharges. The objective was to determine if removal mechanisms were based on abiotic, biological or combination of these two processes. Results indicated that a combination of biotic and biological processes was responsible for the effectiveness of this technology.

Environmental Benefits

Positive benefits of this research will include the following. 1) It will provide evidence for the future development of scalable, passive treatment systems for removal of metals from mine drainages leaching from abandoned hard-rock mines such as those found in EPA Region 10 but also for other similarly impacted areas nationwide. Though simple in design, future systems can be engineered for optimal metal removal efficiency, thereby keeping both installation and long-term maintenance costs lower than other available technologies. 2) The bioreactors will be capable of treating waters with complex mixtures of toxic metals. 3) The bioreactors will remove targeted metals to concentrations that meet or exceed US EPA surface water protection standards. 4) Removal of metals from mine discharge waters will protect the ecological health of receiving streams within presently affected watersheds (e.g., the Coeur d'Alene Basin) and protect their uses for fishing and other forms of recreation that are important to the economies of the region. 5) Removal of metals from mine drainage waters prior to their entry into the primary streams of the region will protect the health of citizens in downstream communities who use these resources for drinking water (e.g., Lake Coeur d'Alene and the Spokane River).

Challenging aspects identified during this project include the following. 1) Though inexpensive as compared to other technologies (e.g., water impoundment and lime precipitation of metals; ion-exchange or complexation of metals in synthetic matrixes), the installation and long-term maintenance of installed bioreactors will still require investments by local communities and/or federal, state and local governments. 2) Occasional monitoring of bioreactor performance will be required (e.g., quarterly performance measurements). 3) Compost-based matrixes employed in the bioreactors will eventually become saturated with metals and need replacement. Contaminated materials will require disposal. Disposal costs can be minimized by using existing disposal areas in the region where large quantities of materials such as mine tailings presently are being collected. 4) Removal of metals from mine seepages does not eliminate all the sources of toxic metals entering these watersheds of hard-rock mining areas. Vast piles of mine tailings are also found in these areas and contribute additional sources of leachate that must be treated as well. However, the combined contributions of the many smaller abandoned mine seepages are very significant and their treatment will measurably improve the overall water quality of the region's watersheds.

The above challenges also exist for alternative treatment strategies. The simplicity and low cost of our operationally optimized compost-based bioreactors should ensure that the overall benefits of the technology will outweigh the costs of its implementation.

Results of Characterization of Metal Removal Mechanisms from Field Samples Obtained from Compost Bioreactors

UI researchers examined matrix materials form several bioreactors being used to remove metal contamination from mine effluent before it enters the primary watershed of the Coeur d'Alene Basin. The prototype bioreactors being employed are permeable, largely anaerobic barriers composed of organic compost and straw mixed with gravel that sequester toxic metals from mine waters directed through the reactor matrix material. The anaerobic compost bioreactor is an innovative mine water treatment method that has been applied with initial success at numerous abandoned mine sites (Gammons and Frandsen, 2001) and is similar in concept to constructed wetlands, anaerobic bioreactors, and permeable reactive barriers. The materials commonly used for the compost in the system are a mixture of cobbles, composted organic matter, and fibrous materials which are of low cost and readily available near the sites where they are to be used. Laboratory studies have shown that AMD can be effectively treated in compost reactors (Willow and Cohen, 2003; Waybrant et al., 2002).

Permeable compost barriers were installed by the US BLM at several mine sites as a pilot-scale remedial application to examine heavy metal removal efficiency from several mine seepages (Figure 2). Field and laboratory studies were conducted by UI researchers at the Upper Constitution and Mother Lode mines to determine the metal removal mechanisms. These barrier systems were found to offer several metal removal mechanisms including reduction, surface adsorption, ion exchange, and precipitation. Metals were removed as sulfides, hydroxides, carbonates, and through chelation by organic matter. This makes the systems complex but robust. Compost barriers were most effective under anaerobic conditions that promoted the growth of sulfate-reducing bacteria. Optimum conditions were pH of 5-8, redox potential <-100 mV, and toxic metal concentrations <20 mg L^{-1}. These conditions appear to have been achieved in the sites examined at the two abandoned mines studied in northern Idaho (Wong, 2004). Over an eight-month period, a permeable compost barrier was shown to be an effective treatment for AMD. Results from the field studies suggested that flow rate and retention time greatly affected the removal efficiency of the heavy metals as well as the distribution of the metals in the compost materials. AMD average flows of 300 and 50 L min^{-1} for the two AMDs each with 126 m^3 barriers reduced most heavy metal concentrations to below EPA water quality criteria for freshwater aquatic life (Table 1). However, high effluent concentrations occurred during spring run-off when flow rates as high as 500 L min^{-1} were recorded (Wong, 2004). These high flow rates corresponded to a retention time of approximately two hours in the compost barrier. At these low retention times, heavy metal concentrations in the effluent, especially Pb, were above the EPA water quality criteria.

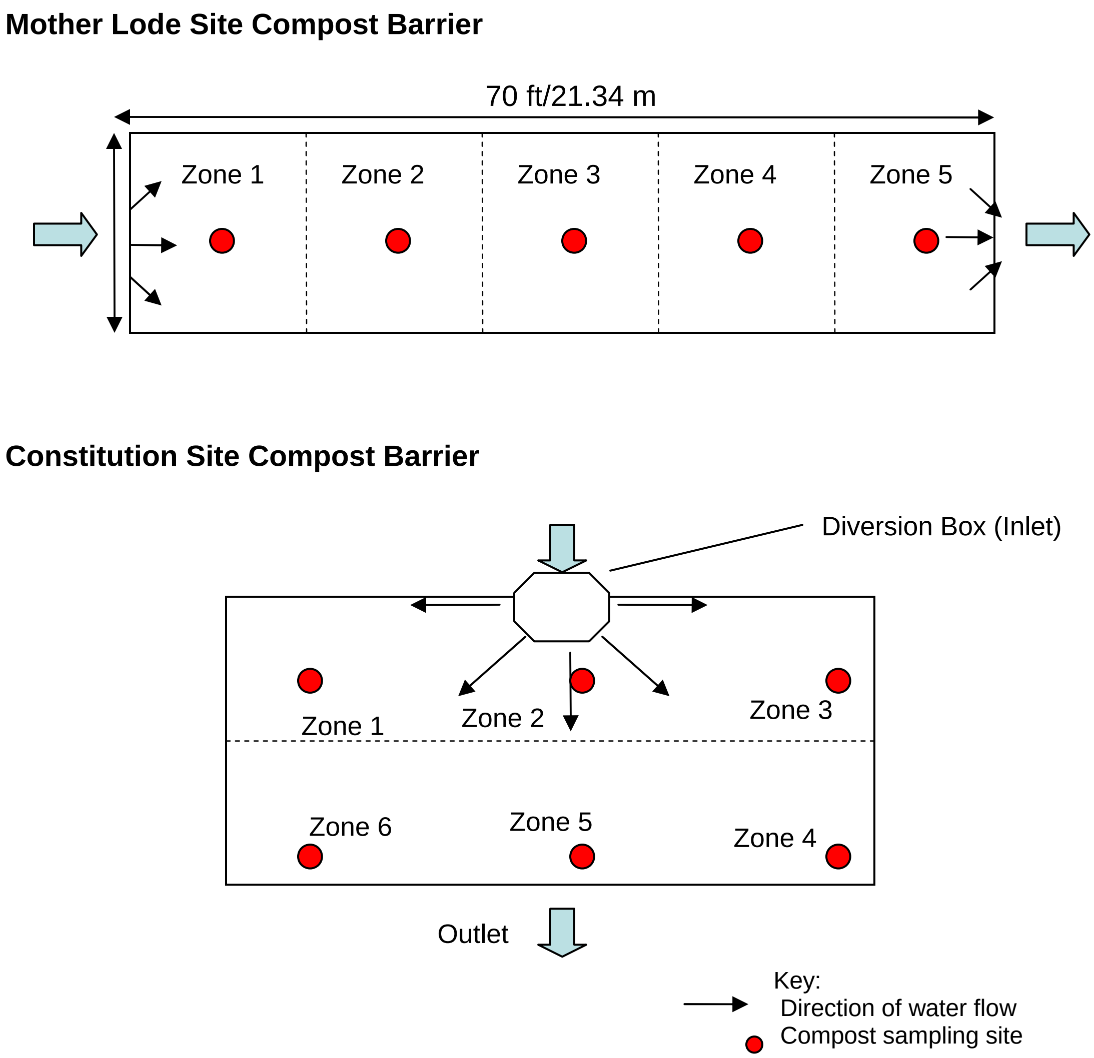

Figure 2. Schematic (top view) of compost barrier in Constitution and Mother Lode sites (Wong, 2004).

Table 1. Water quality data, anions, and concentration of metals prior to and after treatment by compost barriers installed at Upper Constitution and Mother Lode sites along with the EPA criteria for metals in ambient fresh waters (Wong, 2004).

	Constitution		**Mother Lode**		
	Influent	Effluent	Influent	Effluent	EPA Water Quality Criteria for Freshwater Aquatic Life
Temperature (°C)	8.6	10.2	6.6	9.5	
Conductivity	35	107	239	297	
	$\mu g\ L^{-1}$				$\mu g\ L^{-1}$
Al	113	88	211	16	50-200
As	87	43	154	4	150
Cd	49	5	13	bdl	0.25
Cr	3	1	16	bdl	100
Cu	34	12	280	4	9
Fe	14	13	210	34	1000
Mn	5	3	197	224	50b
Ni	33	1	4	bdl	52
Pb	43	14	593	4	2.5
Tl	34	4	bdl	bdl	1.7b
W	47	30	49	12	*NA*
Zn	1044	5	1559	64	120
	$mg\ L^{-1}$				
SO_4	4.6	4.0	95.0	49.2	
$CaCO_3$	10.3	17.3	140.5	168.4	

Note*: bdl (Below detection limit), NA (No data available). Source: United States Environmental Protection Agency, 2002.

Results of AMD Laboratory Treatment Research

A laboratory column experiment was also conducted to treat various mine runoffs from different sites to assess the performance of compost-based mixtures under controlled conditions. Results from the column study showed that removal of sulfate and generation of sulfide and carbonic acid occurred. The column successfully removed all heavy metals (Al, As, Cd, Cr, Cd, Ni, Pb, Tl, and Zn) with the exception of Fe and Mn. A sequential extraction (Rudd et al., 1988; Korolewicz et al., 2001) of compost sample showed that As, Cd, Cu, Ni, Tl, and Zn were mostly found in the sulfide fraction, Pb in the carbonate fraction, and Cr in the residual fraction. Findings from the column study suggest that the retention time in the field applications should be within 30 to 60 hours and that the flow rate should be regulated. However, these engineering parameters need further evaluation through the development of bioreactor kinetic models.

We also examined compost barrier samples using microbial phospholipid fatty acid (PLFA) analyses to determine the types of microorganisms present and to establish correlations between biological and chemical reactions. PLFA are essential components of the membranes of all cells, except Archaea, thus their profiles allow for examination of most, if not all, of the important members of most microbial communities. Since phospholipids breakdown rapidly upon cell death, PLFA analysis is also an accurate method for quantifying the amount of viable microbial biomass in an environment. Table 2 shows that anaerobic sulfate-reducing bacteria (SRB) were present in the biobarrier matrix (approximately 3.3% of the total population), suggesting that sulfate-reducing processes were occurring in the barrier. The presence of anaerobic metal reducers (Table

2) indicates the likelihood of microbial reduction of Mn^{4+}, As^{5+}, Cr^{6+}, and Fe^{3+} within the barrier, with a total of 1.6 and 1.1 pmol PLFA/g dry weight of compost barrier material in Upper Constitution and Mother Lode biobarriers, respectively.

Table 2. Phospholipid fatty acid (PLFA) analysis of compost barriers installed at Upper Constitution and Mother Lode mine sites (Wong, 2004).

Site:	Upper Constitution	Mother Lode
Biomass		
pmol PLFA/g dry weight		7299
Cells/g dry weight	9.70E+08	1.46E+08
Community Structure		
Anaerobic Gram-negatives and Firmicutes (terminally-branched saturated PLFA)	20.4	17.5
Proteobacteria (Monoenoic PFLA)	40.3	42
Actinomycetes and SRBs (mid-chain branched saturated PFLA)	2.8	3.3
Anaerobic Metal Reducers (branched monoenoic PLFA)	1.6	1.1

On-going AMD Treatment Research at UI

Presently UI researchers are examining the microbial communities of the bioreactors in detail under continuing support from the US BLM using modern molecular biology tools to confirm the underlying mechanisms of biologically-catalyzed metal sequestration. These analyses will also allow monitoring of functioning bioreactors to confirm that the proper microorganisms are present for optimized metal sequestration. Overall, this combined knowledge of chemistry and biology will allow better reactor design and management in future implementation of mine water remediation projects in the South Fork of the Coeur d'Alene Basin and in other mining areas as well.

These methods and techniques include: (a) isolation of total community DNA from samples of bioreactor matrixes collected from cores of metal sequestration zones; (b) amplification of phylogenetic marker genes from the purified DNA by use of the polymerase chain reaction (PCR) and universal 16S rDNA for eubacterial and archaeal members of the microbial community; (c) grouping of these markers by use of restriction fragment length polymorphism (RFLP) patterns; (d) sequencing of representatives of each unique RFLP group; and (e) construction of phylogenetic trees showing the composition of the microbial communities observed.

Conceptual Model of Metal Removal Processes of Compost-Based Bioreactors

These simple barrier systems were found to provide both abiotic and biotic metal removal mechanisms, including metal reduction, surface adsorption, ion exchange, and precipitation. All heavy metals of concern were removed (Al, As, Cd, Cr, Cd, Ni, Pb, Tl, and Zn). Metals were removed as sulfides, hydroxides, carbonates, and through chelation by organic matter. Compost barriers should be most effective through rigorous maintenance of anaerobic conditions that promote the growth of sulfate-reducing bacteria. Optimum conditions are pH of 5-8, a redox potential <-100 mV, and individual toxic metal concentrations <20 mg L^{-1}.

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