



Clean tailing reclamation : revegetation of mill tailings following removal of pyrite and heavy metals  
by Jane Marie Krueger

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Land Rehabilitation

Montana State University

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**Abstract:**

Mine tailings responsible for widespread water and soil degradation are prevalent throughout the western United States. Tailings are an environmental problem due to the presence of metal sulfides, primarily pyrite, and elevated heavy metal concentrations. In addition, tailings are often incapable of supporting plants because of acidity, salt toxicities, poor texture, and nutrient deficiencies.

Because pyrite was not of economic value it was not recovered in the mining process. Upon exposure to the atmosphere, residual pyrite in tailings oxidizes and generates acid. Once acid is generated, heavy metals present in the tailings are mobilized and released into the environment. Cleaning or reprocessing of tailings to remove residual pyrite and heavy metals was evaluated as a reclamation technology.

Tailing materials from three sites (an active copper mine, a Superfund site, and an abandoned tailings pond) were collected and reprocessed. Successful mineral separation resulted in a small amount of metal sulfide concentrate and a large volume of reprocessed tailings that had a low metal sulfide content. Total metal concentrations were reduced in the cleaned material and elevated in the metal sulfide concentrate when compared to the original, uncleaned tailings.

A laboratory leaching experiment was conducted to investigate the water soluble chemistry of the cleaned tailings, uncleaned tailings, lime amended tailings, and a topsoil/sand mixture. Quantities of elements in the leachate were generally highest in the uncleaned tailings. In a greenhouse trial, vegetative performance (height, weight, vigor, root development, tissue metal content) of plants grown in cleaned tailings and lime amended tailings was compared to that of plants grown in unamended tailings and topsoil/sand. While plants grown in topsoil performed best, plants grown in cleaned tailings and lime amended tailings exhibited better growth than those grown in unamended tailings.

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FOLLOWING REMOVAL OF PYRITE AND HEAVY METALS

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This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

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Date December 3, 1997

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## ABSTRACT

Mine tailings responsible for widespread water and soil degradation are prevalent throughout the western United States. Tailings are an environmental problem due to the presence of metal sulfides, primarily pyrite, and elevated heavy metal concentrations. In addition, tailings are often incapable of supporting plants because of acidity, salt toxicities, poor texture, and nutrient deficiencies.

Because pyrite was not of economic value it was not recovered in the mining process. Upon exposure to the atmosphere, residual pyrite in tailings oxidizes and generates acid. Once acid is generated, heavy metals present in the tailings are mobilized and released into the environment. Cleaning or reprocessing of tailings to remove residual pyrite and heavy metals was evaluated as a reclamation technology.

Tailing materials from three sites (an active copper mine, a Superfund site, and an abandoned tailings pond) were collected and reprocessed. Successful mineral separation resulted in a small amount of metal sulfide concentrate and a large volume of reprocessed tailings that had a low metal sulfide content. Total metal concentrations were reduced in the cleaned material and elevated in the metal sulfide concentrate when compared to the original, uncleaned tailings.

A laboratory leaching experiment was conducted to investigate the water soluble chemistry of the cleaned tailings, uncleaned tailings, lime amended tailings, and a topsoil/sand mixture. Quantities of elements in the leachate were generally highest in the uncleaned tailings. In a greenhouse trial, vegetative performance (height, weight, vigor, root development, tissue metal content) of plants grown in cleaned tailings and lime amended tailings was compared to that of plants grown in unamended tailings and topsoil/sand. While plants grown in topsoil performed best, plants grown in cleaned tailings and lime amended tailings exhibited better growth than those grown in unamended tailings.

## INTRODUCTION

Mine tailings pose an environmental threat due to the presence of metal sulfides, particularly pyrite ( $\text{FeS}_2$ ). Pyrite, which is commonly associated with metal ore deposits, is not recovered by milling activities and remains in tailings. Upon exposure to the atmosphere, pyrite oxidizes, releasing acidity, which in turn leads to increased solubility of heavy metals often present in tailings. Mobilized heavy metals pose a threat to all organisms via a variety of pathways resulting in bioaccumulation in plant and animal tissues. Current reclamation technologies for all tailings deposits are of three types: capping, in-place stabilization through use of chemical amendments (phytostabilization), and subaqueous disposal.

A cost-effective, permanent tailing reclamation alternative was investigated. This technique used mineral processing and land reclamation techniques. Clean Tailing Reclamation (CTR) employs mineral separation technologies to remove metal sulfides from tailing material through gravimetric and flotation separation. After reprocessing tailings to remove metal sulfides, CTR employs vegetative stabilization utilizing chemical (lime) amendments. The lime application rate for neutralization of acid generated in tailings is decreased by removal of pyrite and other acid-forming metal sulfides, resulting in more cost effective reclamation. Further cost reductions can be achieved by recovery of desirable metals such as gold, silver, copper, and zinc. Funds generated by the recovery of economically profitable metals can be used to offset reclamation costs.

Clean Tailing Reclamation offers the benefits of a cost effective methodology that remediates tailings on a permanent basis by elimination of acid generation potential and removal of heavy metal contaminants, thus reducing human health and environmental risks. In addition, economic profit may be gained through recovery of desirable metals.

## OBJECTIVES OF CLEAN TAILING RECLAMATION

The objectives of CTR include: 1) development of an alternative, cost effective, permanent method for tailing reclamation, 2) reprocessing to reduce the acid generation potential, toxicity, mobility, and bioavailability of heavy metal contaminants in tailing materials, 3) establishment of vegetation on tailing materials that otherwise could not support vegetation and 4) recovery and recycling of economically valuable mineral resources present in tailings as waste minerals and environmental contaminants.

## LITERATURE REVIEW

Extent of Minewaste Impacts

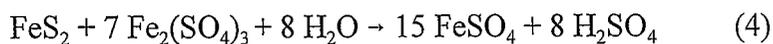
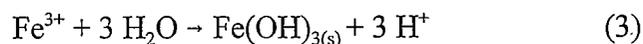
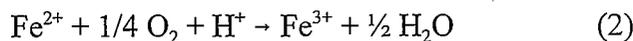
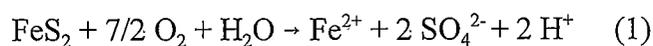
A history of poor tailings disposal practices across the U.S. has resulted in large scale ecological disruptions caused by acid mine drainage (AMD), surface and ground water contamination, nutrient-poor soil with little or no vegetation, and subsequent erosion. In Montana there are over 20,000 inactive or abandoned mine sites that cover 153,800 acres and contribute to 1,118 miles of damaged streams. An equally astounding 80,000 inactive or abandoned mine sites that cover 136,653 acres and impact 200 miles of streams have been reported in Arizona (Friel et al. 1991). The U.S. Bureau of Mines estimates that mine waste adversely affects over 12,000 miles of streams and rivers and over 18,000 acres of lakes and reservoirs in the U.S. (Evangelou and Zhang 1995).

Although some attempts have been made to clean up such sites, the current technologies are expensive. Based on past remediation activities, Montana estimates its total remediation costs at \$912,280,000 (including Superfund sites) (Friel et al. 1991). Arizona has projected remediation costs of \$654,200,000 (Friel et al. 1991). The Mineral Policy Center in Washington, D.C., estimates there are 557,650 abandoned hardrock mine sites nationwide and that the cost of clean up will range from \$32.7 to \$71.5 billion (Lyon et al. 1993). Because such large-scale remediation efforts are necessary, and because the currently applied methods are so costly, it has become an environmental and economic priority to find new and effective means of dealing with the problem of tailings disposal.

Tailings threaten soil and water quality via production of acidity and mobilization of heavy metals. Acidity generated by pyrite oxidation can lead to low pH conditions in soil and surface water resulting in mortality of terrestrial and aquatic organisms. Heavy metals, which often occur at elevated levels in mine tailings, become mobilized in acidic conditions. Some heavy metals are essential to plants and animals in limited quantities. Nonessential heavy metals or essential metals at toxic levels pose a threat to all organisms via a variety of pathways resulting in bioaccumulation in plant and animal tissues.

#### Pyrite Oxidation

Tailings pose an environmental and human health hazard due to sulfide oxidation and the subsequent production of acidity and mobilization of heavy metals. Pyrite ( $\text{FeS}_2$ ) is commonly associated with metal ore deposits. Pyrite is not a mineral recovered by processing activities even though it is brought to the surface of the earth during mining operations. The oxidation of pyrite upon weathering by water and oxygen is represented by the following chemical equations:



(Evangelou and Zhang 1995). As the equations show, acidity is generated, resulting in degradation of water quality in areas where mining occurs or has occurred in the past.

Although pyrite oxidation is not fully understood and many factors may contribute to acid production, several variables have been shown to influence the rate of pyrite oxidation. The presence of microorganisms can accelerate the rate of oxidation. Bacterial oxidation of pyrite is carried on primarily by *Thiobacillus ferrooxidans*, a strain of aerobic, chemolithotropic, acidophilic bacteria, which accelerates oxidation by breaking down the pyrite lattice structure. These bacteria thrive in conditions of low pH and high concentrations of sulfur, iron, and other metals (Taxiarchou et al. 1994). Pyrite oxidation is consequently mediated by microbial activity. Other common sulfide-oxidizing bacteria include *Thiobacillus thiooxidans*, *Leptospirillum ferrooxidans*, and *Sulfolobus* (Taxiarchou et al. 1994).

Pyrite oxidation rate may also be related to the mineralogy and physical characteristics of tailings. Fine textured tailing materials characterized by small particle size are readily oxidizable due primarily to the abundance of reactive surfaces. As particle size decreases, the ratio of surface area to particle mass increases, resulting in increased surface area for oxidation of smaller grain sizes. Mineralogical defect has also been demonstrated to exert an important control on sulfide reactivity (Jennings 1993). Impure pyrite has been found to oxidize faster than pure pyrite (Quipsel et al. 1952). Different sulfide minerals exhibit different rates of oxidation due to variation in crystalline lattice structure. Pyrrhotite (FeS) oxidizes faster than pyrite, as does marcasite (Deer et al. 1972). Oxidation rates also vary among pyritic compounds with different origins. For example, sedimentary pyrites oxidize more readily than either igneous or metamorphic pyrites (Tiwari et al. 1984).

Nicholson et al. (1990) reported that the rate of pyrite oxidation decreased over time and with increasing particle size. Oxidation rates decreased dramatically over the first 2500 hours, with smaller decreases over the following 7500 hours. This decrease in oxidation rate is believed to have resulted from formation of an oxide coating on the surface of pyrite particles. The coating created an oxygen concentration gradient across the oxide layer that resulted in a resistance to reaction.

The duration and condition of tailing storage can also affect the rate at which pyrite oxidation occurs. In an accelerated-weathering test procedure, it was reported that the oxide coating found on pyrite particles may alter during weathering. Cracks and fissures may develop exposing fresh pyrite surfaces to oxidizing conditions. It was also reported that the characteristics of the coating differed between pyrite stored under dry and wet conditions. "Dry" oxidation (stored in argon) resulted in oxidation products of Fe and S at the surface, forming a coating. In contrast, pyrite stored under "wet" conditions (stored in air) resulted in the possible dissolution and reprecipitation of Fe and S products with no oxide coating formation, allowing the rate of oxidation to remain high. These factors would affect the rate of oxidation of pyrite and, subsequently, the extent of acid production (Chander et al. 1994).

### Tailings Reclamation

Current tailing reclamation practices are of three main types: capping, in-place stabilization (phytostabilization), and subaqueous disposal. Three types of capping

methodologies exist: impervious seals (compacted clay covers and membrane liners), capillary barriers (breaks in the continuity between topsoil and contaminated materials), and chemical barriers (material to neutralize acid and precipitate metal at waste/amendment interface) (Reclamation Research Unit 1993).

Capping addresses five potential risks of exposure of biological receptors to tailings: direct contact, ingestion, inhalation of airborne particulates, runoff of contaminated water to surface or ground water, and percolation of contaminated water to ground water (Lewis-Russ and duPont 1994). A study at the Golden Sunlight Mine in Montana investigated the effectiveness of three capping techniques in preventing tailings recharge from precipitation. The treatments were 71 cm of coversoil overlying 139 cm of waste rock; 69 cm of coversoil overlying a 70 cm clay cap overlying 82 cm of waste rock; and 94 cm of coversoil overlying 128 cm of borrow material. All techniques were effective in preventing tailings water recharge. The cover soil/clay cap/waste rock did undergo some water changes during a ten year storm event while the coversoil/waste rock and coversoil/borrow material continued to dry throughout the year. In all three cases, however, the tailings showed no water recharge. After one year, no significant difference in plant cover was recorded among the three treatments (Strong 1994).

An impervious clay seal was constructed at the Rum Jungle Mine in Northern Territory, Australia. The wastes were covered with a 3-layer cap consisting of a basal compacted clay layer as a moisture barrier, a sandy clay loam as a moisture retention zone to support vegetation and prevent the clay layer from drying out, and a layer of gravelly sand on top to prevent erosion and moisture loss in the dry season (crushed rock was used

as final layer on one site). A reduction in ingress of water, oxidation rate, and oxygen transport have all been observed with successful vegetation growth (Bennett et al. 1988).

Limited information is available on use of capillary barriers. However, they have been suggested as a way to interrupt movement of salts into cover soils (Spiers and Coortin 1974, Munshower 1993, Strong 1994).

Chemical barriers have been used in revegetation programs in Butte, Montana. Lime barriers 4 to 6 cm thick were placed below 50 cm thick coversoils. This technique has been successful, but a limited number of plant species has established in the cover soil (Keammerer et al. 1992). In some cases, a geochemical barrier may naturally exist underneath tailing material. The geochemical barrier may contain buffering materials, i.e., calcium carbonate. In Arizona a tailings impoundment has been found to have over 150 feet of buffering material underlying it (with a neutralization capacity of 190 to 530 tons  $\text{CaCO}_3$  per ton soil) able to neutralize acidity within 28 feet below the bottom of the tailings. Under circumstances of predominantly upward movement of water in tailings due to evaporation exceeding precipitation rates, fine-grained tailings provide a physical barrier to percolation of water (Lewis-Russ and duPont 1994).

In-place stabilization of tailing material through the use of plants (phytostabilization) is another tailing reclamation alternative. This approach can involve the use of amendments (usually lime) to raise the pH of acid tailings to a level tolerable to plant species. Several different soil amendments are being researched as possibilities. In one study, the long term (10 year) performance of plants grown in phytotoxic abandoned mine spoil (pH=3.4) amended with digested municipal sewage sludge, power plant

flyash, papermill sludge, or limed topsoil was analyzed. The amendments were incorporated 10 cm into the spoil with a rototiller. The sewage sludge, papermill sludge, and topsoil amendments proved superior to flyash in maintaining plant cover with little differences occurring among the sludges and the limed topsoil (Pichtel et al. 1994).

At a Superfund site in Anaconda, Montana, lime amendments were incorporated into the top 24 inches of an abandoned tailings impoundment. Determination of lime requirement was performed by acid-base account (ABA) analytical methods (Sobek et al. 1978). After extensive site characterization, lime, compost, and fertilizer were applied and incorporated into waste materials to provide a suitable growth media for plant establishment (Reclamation Research Unit 1996).

Researchers at the Blackbird Mine in the Salmon National Forest in Idaho reclaimed an abandoned mine tailings area by incorporating 900 lb/acre of lime to a depth of about 8 inches. The area was then amended with organic material and seeded. Within two years, the area began to reacidify (Richardson and Farmer 1981).

Remediation of tailings by subaqueous disposal rather than surficial disposal is another option currently employed. Where appropriate, tailings are mixed with either freshwater or seawater to create a diluted tailings slurry. In seawater the slurry is piped through an outfall pipeline terminating at depths of 30-112 meters (Poling and Ellis 1995, Jones and Ellis 1995). Submarine tailings disposal (STD) is thought to limit the exposure of tailings to weathering by submergence in sea water. Careful site reconnaissance and planning must be carried out to guard against tailings resuspension and upwelling, smothering of benthos, and trace metal contamination from acid rock drainage (Ellis et al.

1995). Both successes (Jones and Ellis 1995, Ellis et al. 1995) and failures (Poling and Ellis 1995) of the technology have been reported.

### Limitations of Current Reclamation Techniques

Current reclamation techniques are subject to some limitations. Inadequate reclamation results in the continued threat of environmental hazards.

Capping and amending tailings can be very expensive. Several reclamation alternatives were evaluated for cost at a Superfund site in Anaconda, Montana. The expense of capping 2508 acres of tailings with topsoil was estimated at \$87,254,000. The cost of amending the tailings with lime was estimated at \$62,787,000 (CDM 1997).

Frequently, adequate amounts of cover material are difficult to locate. If coversoil must be transported to the site from another source, the costs may outweigh the benefits (Williamson et al. 1982). A major concern of the capping technique is that the tailings are still present on the site with the same potential to create AMD and heavy metal contamination. Erosion of the cap would re-expose the tailings to weathering processes. Clay barriers can crack and plastic liners can be damaged or deteriorate, both of which render the capping technique useless (Pulford 1991).

Amending with lime (or other chemical amendments) poses the threat of reacidification once the neutralizing capacity of the amendment has been exhausted. Soils that had been amended with sixty-four tons of lime per acre reacidified within seven and one-half months of planting at a site in Utah, causing plant mortality (Nielson and

Peterson 1972). However, efforts have been made to improve accuracy in determining lime requirements (Sobek et al. 1978).

Subaqueous disposal puts tailings in continuous contact with water. Continual contact with water leaves room for speculation regarding mobilization of metals and further production of AMD (Evangelou and Zhang 1995)..

### Innovative Tailings Reclamation Methodologies

Reprocessing tailings in an effort to remove heavy metals and pyrite has recently come to the forefront as an innovative technique to smelter waste. By removing pyrite, and consequently the potential for acid generation, tailings may be able to support plant populations with little or no lime amendment and reduce the cost of current reclamation practices. Tailing cleaning also has the benefit of permanently removing metallic constituents deleterious to ecological receptors. No further possibility for tailings to produce acid by pyrite oxidation would be present. Capping, amending, or disposing of tailings subaqueously do not offer such an advantage.

At INCO Ltd. Clarabelle Mill in Canada, sulfide minerals were removed from tailings material using froth flotation with additional flotation residence time with a sulfuric acid addition. The following conclusions were reached: 1) up to 94% of INCO's main tailings can be converted to low sulfur tailings, 2) low sulfur tailings showed a net neutralizing potential, while non-reprocessed tailings remained potentially acid generating, 3) low sulfur tailings produced neutral seepage with low nickel, iron, and

sulfate concentrations even after 1400 mm of cumulative rainfall and three peak oxidation periods, and 4) low oxygen consumption in low sulfur tailings, (Stuparyk et al. 1995).

In another study, four samples of tailings from three operating mines were characterized for acid generating potential and reprocessed to remove sulfide minerals (Humber 1995). The samples contained 2.34% S, 4.15% S, 3.5% S, and greater than 20% S. All four samples showed an acid producing potential exceeding the neutralization potential. Using flotation, researchers were able to reduce the sulfur content to a range of 0.15-0.35% S, corresponding to recovery rates of 93%-98%. This indicated a good possibility of producing materials with low acid producing potential.

In some instances reprocessing may yield quantities of desirable metals high enough to pay for the cost of recovery. Bench tests performed on copper-bearing open-pit strip waste showed considerable recovery of copper following crushing, sizing, flotation, and leaching techniques. Eight to fifteen percent recovery of other precious metals (gold and silver) was demonstrated (McKinney et al. 1973). According to Cristovici (1986), historic gold recovery by amalgamation and gravity concentration processing facilities was low. Such tailings may still hold significant amounts of recoverable gold.

Researchers discovered the optimum grinding size for gold flotation was 60% to 70% less than  $74\mu\text{m}$ . At this particle size a gold recovery of about 92% would be attained for a concentrate of greater than 20 grams gold/ton. A forty-eight hour cyanidation gave the best results, regardless of grain size. Cristovici and others concluded that the profitable recovery of gold from tailings ponds was feasible with a relatively simple process.

Currently, reprocessing of tailings is being implemented at the Cleveland Mill Superfund site in New Mexico. Froth flotation has been evaluated as the best way to reduce metal concentrations in tailings materials at an abandoned metal mine (predominantly lead and zinc) (Ecology and Environment, Inc. 1993). Eighteen acres along Little Walnut Creek and one of its tributaries comprise the site. Two main tailings piles, a cobbed ore pile, hillside waste piles, dust piles, and roadbed soils make up the bulk of the waste. Excavation and transportation of material to a processing plant has been deemed the most economical and environmentally sound alternative for treatment of the waste material (U.S. Environmental Protection Agency 1993).

## METHODS

Collection and Preparation of Tailings

Three tailings sites were chosen for the study: 1) an active copper mine (CM), 2) a Superfund site (SS), and 3) an abandoned tailings impoundment (AT). Materials were field collected by hand excavation at each site from the 0-60 cm depth. Six composite samples were collected from the AT site across a 72 m transect along the face of the tailings dam. Five composite samples were collected from the SS tailing ponds after removal of a surficial (2.5-5 cm) lime layer placed to prevent blowing of the unvegetated tailings. Five composite samples were collected from the CM tailing pond near the discharge point.

Tailing materials were collected in the fall of 1995, transported to Montana State University (MSU) Bozeman, Montana, and dried in a soil drying oven at 40°C. Samples were mixed and composited in a tractor mounted-PTO driven mixer with forty alumina spheres (five centimeter diameter) to break up aggregates resulting from drying. Milling was not necessary with CM tailings. Following disaggregation each material was passed through a 2.0 mm sieve. Rock greater than or equal to 2.0 mm in diameter was removed and stored separately from fine tailings. Materials less than 2.0 mm in diameter were placed in plastic containers, covered, and stored at the plant growth center at MSU. A portion of the material less than 2.0 mm in size was placed in separate 19 liter containers and shipped to a commercial laboratory for reprocessing.

### Reprocessing of Tailings

Bench scale separation of each material by both flotation separation and gravimetric separation was performed in advance of processing the larger samples. Greater than 100 kg dry weight of each material was reprocessed following bench scale determination of the most effective technique.

Gravimetric separation was evaluated by passing a 2 kg sample from each site across a Wilfley table to collect concentrate, middlings, and tailing fractions. The table concentrate was further upgraded on a Mozley Mineral Separator (Lakefield Research 1996).

Flotation separation tests were performed on 1 kg samples of the tailing materials. Necessary pH adjustments were made with  $\text{Ca}(\text{OH})_2$ . Reagents employed included potassium amyl xanthate and frother methyl iso-butyl carbinol. Because of unsatisfactory results with the AT sample, the flotation separation test was repeated employing grinding of the sample for ten minutes per kg in a ball mill. Sulfidization was also investigated as a method of increasing sulfide removal in the AT sample (Lakefield Research 1996).

Upon completion of bench scale gravimetric and flotation separation tests, the bulk materials were processed. The SS and AT tailings were separated by flotation and the CM tailings by gravity segregation. These reprocessed materials were then dried and shipped back to MSU for use in laboratory and greenhouse testing.

## Chemical and Physical Characterization of Tailings

### Acid-Base Account

Bulk tailings and reprocessed (clean) tailings were sent to a commercial laboratory for acid-base account analysis. Sulfur fractions and neutralization potential were determined using USEPA methods (1974, 1978). Exchangeable acidity (Mehlich 1953) and SMP single-buffer lime requirement (Shoemaker et al. 1962) were analyzed.

Upon receipt of the laboratory results of acid-base account analysis, calcium carbonate ( $\text{CaCO}_3$ ) and calcium hydroxide ( $\text{Ca}(\text{OH})_2$ ) were added in a 60%:40% ratio to both reprocessed and non-reprocessed tailings (Tables 1 and 2). The additions of each material,  $\text{CaCO}_3$  or  $\text{Ca}(\text{OH})_2$ , were adjusted reflecting measurement of calcium carbonate equivalence in the wastes (USEPA 1987).

### Particle Size Analysis

Bulk density of the three tailings was determined by weighing a known volume of oven-dried soil. The weight of dry soil was divided by the volume of soil to calculate bulk density. Soil particle size analysis was also performed on each of the three tailings materials (non-reprocessed) using the Gee and Bauder method (1979).

### Scanning Electron Microscope Evaluation of Tailings Samples

Tailing materials from each site and each treatment (bulk, clean and high-grade) were prepared for scanning electron microscope (SEM) and energy dispersive spectroscopy (EDS) evaluation. A polished aluminum stub was coated with conductive colloidal graphite paint followed by representative fractions of each tailing material. Prior to imaging, the samples were coated with carbon to provide a conductive surface for imaging.

### Total Metal Analysis

Subsamples were collected from each sample and submitted to a contracted laboratory for total metal analysis by x-ray fluorescence spectroscopy (Ashe Analytics 1995). These same samples were also resubmitted to an additional laboratory for analysis by acid digestion followed by inductively coupled plasma spectroscopy (ICP) analysis for elements requiring lower detection limit resolution (USEPA 1987).

### Tempe Cell Study

A method for evaluating mine wastes soluble metal concentrations using Tempe pressure cells (modified Soil Moisture Equipment model 1400) was employed. Modification to the Tempe cell apparatus included the use of 8.4 cm lengths of 7.6 cm I.D. Schedule 40 clear PVC pipe. Tempe cells were cleaned with a sequential rinse of

150 ml 1:10 HCl, 50 ml .01 M CaCl<sub>2</sub>, 50 ml .025 M Ca(OH)<sub>2</sub>, and finally by 750 ml of deionized water.

Experimental design consisted of four treatments: 1) a control of unamended tailings (U), 2) lime amended tailings (L), 3) cleaned tailings (C), and 4) lime amended clean tailings (CL). In addition, a 50% topsoil/50% sand mixture (TS) was evaluated. Four treatments of tailings from the three sites (CM, SS, AT) and the TS treatment underwent five replications.

Deionized water was added to 200 grams of each treatment to achieve saturation. Saturated materials were allowed to sit for 24 hours before being placed in an 8.75 cm O.D. (7.6 cm I.D.) Tempe cell fitted with a 1 bar standard flow porous ceramic plate. One-half bar pressure was applied until leachate collection slowed to two to three drops per minute (approximately 30 minutes).

The first leach cycle was collected in a 100 ml graduated cylinder. Upon completion of the first cycle, the leachate was tested for pH, electrical conductivity (EC) and then acidified to a pH of less than two with concentrated nitric acid (HNO<sub>3</sub>). A quantity of deionized water equivalent to the amount of leachate collected was reintroduced into the Tempe cell, stirred into the material, and allowed to stand for one half hour. One half bar pressure was then exerted on the chamber for one hour or until dripping slowed to approximately three drops per minute from the bottom of the chamber. Leachate was again measured for pH, EC, and subsequently preserved for metal determinations. This procedure was repeated until three pore volumes were collected (4-10 leach cycles, depending on material).

Leachates were preserved with concentrated nitric acid and refrigerated to prevent precipitate formation prior to laboratory metal analysis (approximately two weeks).

Inductively coupled plasma spectroscopy was used to measure metal concentrations in each pore volume. Elements analyzed include boron, calcium, copper, iron, potassium, magnesium, manganese, sodium, phosphorus, sulfur, zinc, chromium, cadmium, arsenic, and aluminum.

For water soluble metal analysis, leachates collected from each run (4-10 leach cycles) were composited into three samples indicative of each of the three pore volumes collected. This compositing within runs was required to account for variability in the water holding capacity of each sample and to reduce analytical costs. Five replications of each of the four treatments (U, L, C, CL) at each of the three sites were performed. The TS mixture was also evaluated as a reference to the mine tailing samples evaluated.

#### Greenhouse Study of Plant Performance

The experimental design of the greenhouse study consisted of four treatments (U, TS, L, CL) from each of the three sites (CM, SS, AT). Two plant species were evaluated for growth response, *Elymus cinereus* (Basin wildrye) and *Poa pratensis* (Kentucky bluegrass). Five replications were performed, resulting in a total of 120 growth tubes.

The unamended controls were comprised of tailings that had undergone no reprocessing or lime amendment. The topsoil cap treatments consisted of the 50% topsoil/50% sand mixture placed over unamended tailings to mimic a field implemented

capping technique. The lime treatments were tailings that had undergone no reprocessing but had been amended with lime to remediate acidic conditions. Cleaned treatments consisted of reprocessed tailings amended with necessary amounts of lime to remediate acidity. Liming requirements for both the L and CL treatments were dictated by the acid-base account. It is emphasized that though lime was added to both the L and CL treatments, the rates were markedly less in the CL treatment (Table 1).

The U treatment sample was prepared by mixing dried and sieved tailings in a tractor-mounted PTO-driven mixer for five to seven minutes with appropriate amounts of EKO compost and fertilizer (N, P, K, B) to bring the control treatment to equal organic matter and nutrient status as that of the topsoil/sand mixture. Quantities of tailings, amendments, and fertilizer are shown in Tables 1 and 2.

Treatments requiring lime amendment (L and CL) were mixed with sufficient amounts of  $\text{CaCO}_3$  (60%) and  $\text{Ca(OH)}_2$  (40%) to achieve the laboratory measured deficit in neutralization potential. A tractor-mounted PTO-driven cement mixer was employed for five to seven minutes to mix the tailings with the lime amendments. Amended tailings were placed in labeled containers each equipped with approximately 5 m of Tygon tubing (0.6 cm I.D.) with slits cut along the length. Tailings were wetted and mixed with water and allowed to sit for 48 hours, after which, the saturated soil pH of each material was measured. Because pH levels were above 8.5 in the CM and SS tailings, a pressurized tank of  $\text{CO}_2$  was attached to the Tygon tubing. Carbon dioxide was allowed to circulate through tailings until the saturated paste pH measured between 7.0

Table 1. Quantities of tailings, topsoil/sand, Ca(OH)<sub>2</sub>, CaCO<sub>3</sub>, EKO compost, and fertilizer used in greenhouse experiment.

Treatment*/ Site**	Sample mass (kg)	Ca(OH) <sub>2</sub> (g)	CaCO <sub>3</sub> (g)	EKO compost (kg dry weight)	N-P-K-B (g)
CL/CM	72.48	224.7	442.1	4.26	0.41-3.05- 11.05-.03
CL/SS	71.15	234.8	469.6	4.18	0.41-3.0- 10.85-.03
CL/AT	77.88	54.5	101.2	4.58	0.46-3.3- 11.87-.03
L/CM	73.42	547.0	1086.6	4.32	0.41-3.1- 11.19-.03
L/SS	80.43	3800.3	7540.3	4.73	0.46-3.4- 12.26-.03
L/AT	80.13	136.2	268.4	4.71	0.46-3.4- 12.21-.03
U/CM	71.82	0	0	4.22	0.41-3.04- 10.95-.03
U/SS	70.45	0	0	4.14	0.41-2.98- 10.74-.03
U/AT	77.73	0	0	4.57	0.45-3.29- 11.85-.03
TS	147.6	0	0	0	0

\*Treatment Codes

CL=lime amended clean

L=lime amended

U=unamended control

TS=topsoil/sand mixture

\*\*Site Codes

CM=active copper mine

SS=Superfund site

AT=abandoned tailings impoundment

Table 2. Rates of lime amendment, organic matter, and fertilizer additions to tailings used in greenhouse experiment.

Treatment*/ Site**	mg Ca(OH) <sub>2</sub> / kg tailings	mg CaCO <sub>3</sub> / kg tailings	mg EKO compost/ kg tailings	mg N-P-K- B/ kg tailings
CL/CM	3100	6100	58,800	5.7-42.1- 158.6-0.4
CL/SS	3300	6600	58,700	5.8-42.2- 152.5-0.4
CL/AT	700	1300	58,800	5.9-42.4- 152.1-0.4
L/CM	7450	14800	58,800	5.6-42.2- 152.4-0.4
L/SS	47250	93750	58,800	5.7-42.3- 152.4-0.4
L/AT	1700	3350	58,800	5.7-42.4- 152.3-0.4
U/CM	0	0	58,800	5.7-42.3- 152.5-0.4
U/SS	0	0	58,800	5.8-42.2- 152.4-0.4
U/AT	0	0	58,800	5.8-42.3- 152.5-0.4

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and 8.2. No CO<sub>2</sub> was circulated through the AT tailings because measured pH was 7.15 after addition of water and a 48 hour incubation period. Once near neutral pH conditions were established in all three sites, the samples were again placed in a tractor-mounted PTO-driven mixer for seven minutes with EKO compost and fertilizer (N, P, K, B). Quantities were sufficient to elevate the organic matter and nutrient levels in the treatment to levels observed in the TS treatment (Tables 1 and 2).

Preparation of the TS treatment was performed by mixing topsoil and sand in a one to one ratio by volume. A total of 140.4 kg soil and 100.3 kg sand were mixed for five to ten minutes. The material was then placed into three labeled sample containers. Topsoil nutrient levels were obtained from Plant Growth Center personnel (Table 3).

Upon completion of sample preparation, growth tubes were prepared for plant response studies. Ten centimeter I.D., 70 cm long PVC tubes were used as growth tubes. Each tube was split lengthwise on a bandsaw and held together with a hose clamp to allow for root observation at the termination of plant growth. Caps with a drainage hole were placed on the bottom of the tubes. The bottoms of the tubes were covered with 10 cm of untreated tailing material (no lime, EKO compost, or fertilizer). A thin marker horizon of perlite was sprinkled on top of the untreated tailings to aid in distinguishing the interface between untreated and treated materials. Tubes were then filled to within 2 cm of the top of the tube with the appropriate treatments (U, L, CL, and TS). The TS treatment was prepared by placing 45 cm of topsoil over 5 cm crushed limestone (6-9 mm size fraction) which formed a capillary barrier between the topsoil and underlying

Table 3. Chemistry of topsoil/sand mixture used in Tempe cell and greenhouse experiments.

	Organic Matter (%)	NO <sub>3</sub> -N (mg/kg)	P-Olsen (mg/kg)	K (mg/kg)	pH	EC (dS/m)
Rep 1	11.6	75	21.2	170	6.9	1.84
Rep 2	14.2	86	19.8	130	7	1.9
mean	12.9	80	20	150	7	1.87
50/50 mix*	6.5	40	10	75	---	---

\*50/50 mixture of topsoil and sand assumes that the sand contributes no organic matter or nutrients; the values are half the soil values (statements not applicable to pH or EC).

untreated tailings. Two layers of burlap were placed between the topsoil and lime horizons to prevent sediment transport from the topsoil into the lime barrier. The lime layer served the dual purpose of capillary and geochemical barrier separating the topsoil and unamended tailings. Filled growth tubes were then wetted and filled to the top with additional material as needed to correct for settling. Tubes were seeded with either of two species, *Elymus cineris* (Basin wildrye, Magnar cultivar) or *Poa pratensis* (Kentucky bluegrass, Park cultivar) with 10 seeds per tube.

Tubes were maintained in a climate controlled plant growth facility. Seeds were initially misted with water twice daily. Because some of tubes were showing no germination due to drying of the soil surface, tubes were watered with 100 ml in the morning and 20 ml in the afternoon. After two weeks, tubes were watered with 100 ml per day. Upon completion of germination, plants were culled to three plants per tube. After 30 days, tubes were watered with 75 ml in the morning only. After 45 days,

watering was conducted every other day, and after 95 days watering was reduced to 75 ml every two days.

After approximately 120 days, above ground biomass was collected. Upon harvesting, Munsell plant color, number of plants, height of each plant, and vigor were recorded. Plants were then clipped approximately 1 cm above the surface of soil (to avoid the collection of material contaminated with soil that had splashed onto plants during watering) and placed in labeled paper sacks.

Tubes were carefully disassembled to allow description of root development, Munsell soil color, depth of treatment, and general comments about soil. Particular attention was paid to the maximum depth of rooting and rooting characteristics at the unamended/treatment boundary.

Vegetation was dried at 65-70°C for 48 hours, after which biomass weights were recorded to the nearest milligram. Biomass from the AT material was clipped into equal to or less than 0.6 cm pieces and composited according to treatment (U, L, CL and TS). Materials were placed in plastic Whirl-pak bags, labeled, and sent to a contracted laboratory for metal analysis. Because of the small quantity of biomass produced in the CM and SS materials, no samples were available for metal determinations.

### Greenhouse Study of Sunflower Plant Performance

A second greenhouse study evaluated growth response of *Helianthus annuus* (sunflower, Sundak cultivar). Twelve 40 cm long, 10 cm I.D. PVC growth tubes were used. Tubes were filled with L or CL tailings utilizing the same amendment rates as described above. Each tube was planted with four seeds approximately 2.5 cm deep. Twelve tubes were planted (three sites, two treatments, one species, two replications).

Tubes were watered with 100 ml daily for two weeks. After two weeks, watering was reduced to 100 ml every other day until date of harvest. Upon establishment, plants were culled to one plant per tube. Plants were allowed to grow for 77 days. Plant height was recorded in addition to a brief general description of plant appearance and health. Stems, leaves, and flowers were harvested separately, placed in labeled paper bags, and dried in a plant drying oven at 65-70°C for 48 hours.

Plant biomass was ground, placed in labeled plastic Whirl-pak bags, and sent to a laboratory for tissue metal analysis. *Helianthus annuus* stem and leaf tissue were composited for each site and treatment to provide sufficient tissue for the metal analysis. Flowers were analyzed independently by site and treatment.

## RESULTS AND DISCUSSION

Reprocessing Effectiveness for Removal of Sulfides from Tailings

Successful reprocessing of all three materials was achieved, resulting in two products: a high grade sulfide concentrate comprised of approximately 10% of the original mass, and a cleaned silicate material comprised of approximately 90% of the original mass. Through reprocessing, metal sulfides were recovered, resulting in a decrease in metal sulfide content in the cleaned tailings while the high grade concentrate became enriched relative to the field collected tailings. This resulted in elevated mean total metal levels in the high grade concentrate while the lowest mean total metal levels were found in the cleaned tailings. Iron and copper data exemplify this point clearly. The high grade iron and copper concentrations were an order of magnitude higher than those in the cleaned tailings (Figures 1 and 2) for the CM site.

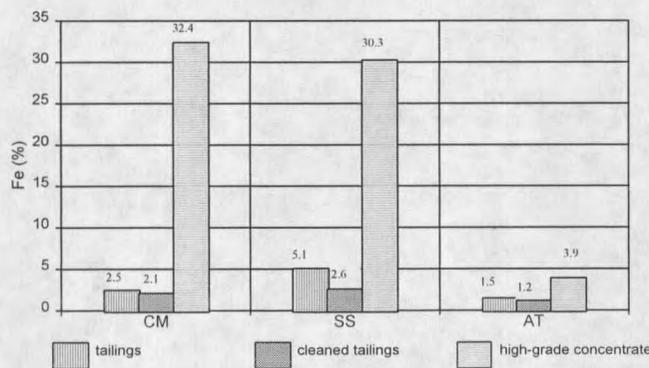


Figure 1. Mean total iron concentration of tailings, cleaned tailings, and concentrate.













































































































