



Effect of two dolomitic industrial by-products on pH control, leachate chemistry and plant response in acidic-metalliferous mine waste  
by Laureen Susan Kelly

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:**

Flux Bar Residue and DiCalcium Silicate are dolomitic industrial by-products produced by Northwest Alloys in mining magnesium from dolomite. These by-products were tested on acidic-metalliferous mine wastes to evaluate their effectiveness as alternative liming amendments. A series of pressure cell tests and a greenhouse study were conducted using the by-products to amend Lehigh Coal Waste and/or Opportunity Tailings. Pressure cell leachates were analyzed to determine reduction in soluble metals, arsenic and salts in amended mine wastes compared to unamended wastes. Release of chloride and nitrogen in leachates from the by-products was monitored. Greenhouse trials evaluated plant growth in tailings amended with the by-products compared to controls.

Flux Bar Residue and DiCalcium Silicate were effective in reducing soluble metals and arsenic in acidic-metalliferous mine wastes. DiCalcium Silicate reduced soluble salts, but Flux Bar Residue did not. Flux Bar Residue released significant chloride into leachates in excess of water quality standards. Downward migration of chloride released by Flux Bar Residue can be minimized by using Flux Bar Residue in combination with another amendment or by amending the upper portion of a waste with Flux Bar Residue and the lower portion with another amendment. Neither Flux Bar Residue nor DiCalcium Silicate contributed significant soluble nitrogen species into leachates. No germination occurred in Flux Bar Residue amended tailings due to its chloride content. Germination and growth did occur in DiCalcium Silicate amended tailings, but growth was very poor compared to tailings amended with traditional lime products. Flux Bar Residue and DiCalcium Silicate are recommended for use in repositories or other non-vegetative scenarios to treat acidic-metalliferous mine wastes.

**Key words:** Liming, By-products, Chloride, Mine waste, Tailings.

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**APPROVAL**

of a thesis submitted by

Laureen Susan Kelly

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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## ABSTRACT

Flux Bar Residue and DiCalcium Silicate are dolomitic industrial by-products produced by Northwest Alloys in mining magnesium from dolomite. These by-products were tested on acidic-metalliferous mine wastes to evaluate their effectiveness as alternative liming amendments. A series of pressure cell tests and a greenhouse study were conducted using the by-products to amend Lehigh Coal Waste and/or Opportunity Tailings. Pressure cell leachates were analyzed to determine reduction in soluble metals, arsenic and salts in amended mine wastes compared to unamended wastes. Release of chloride and nitrogen in leachates from the by-products was monitored. Greenhouse trials evaluated plant growth in tailings amended with the by-products compared to controls.

Flux Bar Residue and DiCalcium Silicate were effective in reducing soluble metals and arsenic in acidic-metalliferous mine wastes. DiCalcium Silicate reduced soluble salts, but Flux Bar Residue did not. Flux Bar Residue released significant chloride into leachates in excess of water quality standards. Downward migration of chloride released by Flux Bar Residue can be minimized by using Flux Bar Residue in combination with another amendment or by amending the upper portion of a waste with Flux Bar Residue and the lower portion with another amendment. Neither Flux Bar Residue nor DiCalcium Silicate contributed significant soluble nitrogen species into leachates. No germination occurred in Flux Bar Residue amended tailings due to its chloride content. Germination and growth did occur in DiCalcium Silicate amended tailings, but growth was very poor compared to tailings amended with traditional lime products. Flux Bar Residue and DiCalcium Silicate are recommended for use in repositories or other non-vegetative scenarios to treat acidic-metalliferous mine wastes.

Key words: Liming, By-products, Chloride, Mine waste, Tailings.

## CHAPTER 1

### INTRODUCTION

#### Background

Soil acidity is a common occurrence in both natural and drastically disturbed environments. In either case, neutralization of the acidity is often a requirement if plant establishment and growth are desired. In the case of drastically disturbed lands, such as lands disturbed by mining, neutralization of the acidity may also be necessary to prevent ground and surface water contamination by metals and other compounds such as salts.

In the state of Montana, where this research was conducted, there are thousands of abandoned and active mine sites where acid materials and the acid drainage from them are problematic. Similar sites exist throughout the United States and the world in general, with mined areas high in precipitation and pyritic materials posing the most severe problems. Some abandoned mine sites pose such threats to the environment that they have been classified as Superfund sites under the authority of the Comprehensive Environmental Response, Compensation and Liability Act and are administered by the U.S. Environmental Protection Agency. Sites such as these may require tremendous amounts of lime to neutralize and reclaim their soils and waste lands. In this investigation, "lime" refers to any calcium or magnesium amendment which ameliorates soil acidity, not just calcium oxide (CaO). Large

amounts of lime will be required for the Silver Bow Creek/Butte Area Superfund site, the largest U.S. Superfund site, which has 2,500,000 cubic yards of tailings and contaminated or impacted soils along Silver Bow Creek's flood plain alone that must be reclaimed (MDEQ and EPA 1996). This could require up to a million tons of lime, which is more than is available at this time in Montana.

Superfund sites, abandoned mine lands administered by individual state Abandoned Mine Reclamation Bureaus, and active sites would significantly benefit from availability of alternative, unconventional lime sources that were both available when needed and affordable. Northwest Alloys in Addy, Washington produces magnesium from dolomite. The refining process results in numerous by-products, two which are of particular interest for their potential as liming materials. These two by-products are Flux Bar Residue and DiCalcium Silicate.

Prior to weathering, Flux Bar Residue is primarily composed of magnesium oxide, magnesium chloride, potassium chloride, calcium chloride, magnesium nitride and magnesium fluoride, in order of decreasing composition percentage. Prior to weathering, DiCalcium Silicate is primarily composed of calcium silicate, calcium aluminate, iron oxide, magnesium oxide and calcium oxide, in order of decreasing composition percentage. The majority of these constituents affords a neutralizing ability. It can be assumed that hydroxides and carbonates are present in these by-products due to hydrolysis and carbonation reactions that occur during weathering. DiCalcium Silicate is stockpiled in the Northwest Alloys slag pit, and was the sample source used in this project. The Flux Bar Residue sampled for this research came from a stockpile resulting from processing of Northwest

Alloys' Flux Bars by L-Bar Products, Inc. near Chewelah, Washington prior to the year 1991 before the L-Bar plant shut down. An amount of 50,000 tons of this Flux Bar Residue was stockpiled as by-product by L-Bar between 1977 and 1983 (L-Bar Draft Phase 1 RI Report).

### Objectives and Hypothesis

The purpose of this thesis project was to evaluate the effectiveness of Flux Bar Residue (FBR) and DiCalcium Silicate (DiCal) as liming amendments for acidic-metalliferous mine wastes. The by-products were tested on two acidic-metalliferous mine wastes - Lehigh Coal Waste and Opportunity Tailings. The objectives of this project were as follows:

- Determine select physical and chemical characteristics of FBR and DiCal.
- Evaluate the effectiveness of FBR and DiCal in raising pH and reducing soluble metals in acidic-metalliferous mine waste (Lehigh Coal Waste and Opportunity Tailings).
- Quantify by-product chloride and nitrogen species attenuation and mobilization characteristics when used to amend acidic-metalliferous mine waste (Opportunity Tailings).
- Evaluate plant growth on tailings amended with FBR and DiCal.

The hypothesis of this project was that the alkaline by-products Flux Bar Residue and DiCalcium Silicate would be effective in raising the pH of acidic mine waste, thereby reducing soluble metals and facilitating plant growth.

## CHAPTER 2

### LITERATURE REVIEW

#### Formation of Acidity from Pyritic Materials

Pyrite ( $\text{FeS}_2$ ), which occurs in association with hardrock mineral assemblages and in highly reduced, depositional sedimentary environments (Jennings and Dollhopf 1993, Pulford 1991), is the most common sulfide mineral found in these formations. Pyrite, upon exposure to water and oxygen, weathers and produces acidity which results in sulfuric acid drainage. Other potentially acid producing sulfide minerals are pyrrhotite ( $\text{Fe}_{1-x}\text{S}$ ), chalcopyrite ( $\text{CuFeS}_2$ ), sphalerite ( $\text{ZnS}$ ) and arsenopyrite ( $\text{FeAsS}$ ). Pyrite is not only the dominant sulfide mineral given it is thermodynamically favored, but also the most reactive (Elberling et al. 1994).

Pyrite is commonly brought into contact with the atmosphere by coal and hardrock mining. Coal refuse may contain waste coal, rock pyrites, slate, shale, mill tailings and clay (Pietz et al. 1989), and as such is a potential acid producer. Tailings, which are finely ground wastes that remain after recovering metals from ores by milling and smelting are also potential acid producers. Pyrite may be found in waste rock dumps and other mine spoils.

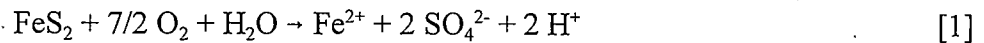
The rate of oxidation of pyrite depends on several parameters. The first of these is particle morphology. There are three general classes of pyrite particle morphology: euhedral,

massive, and framboidal. Euhedral morphology is where the crystals of the pyrite are of regular atomic arrangement. Euhedral morphology is common in hardrock environments. Massive morphology is characterized as noncrystalline masses that lack regular atomic arrangement. Framboidal morphology is spherical aggregates of crystalline pyrite. Massive pyrite is more reactive than euhedral pyrite due to the irregular electron distribution within the atomic structure of the crystal (Jennings and Dollhopf, 1993). These irregularities or defects, which are common in massive pyrite, serve as reactive weathering sites. Both massive and euhedral pyrite will generate the same amount of acid; the difference is in the rate of acid production. The total surface area of pyrite will also enhance weathering rates, but the total reactive surface area is dominant over the effect of particle size.

A second parameter that effects the rate of oxidation of pyrite is the diffusion of oxygen. According to Elberling et al. (1994), the oxidation of tailings during the first few years is controlled by particle size, kinetic rates and the oxygen diffusion coefficient, with kinetic controls dominating after initial deposition when oxidation rates are the highest. However, later rates of pyrite oxidation are controlled by oxygen diffusion. Kinetic rates of the reaction are faster than the oxygen diffusion rates at these later times. The highest rates of later pyrite oxidation therefore occur in unsaturated, coarse particle size environments where the diffusion of oxygen is the highest. According to Evangelou and Zhang (1995), the diffusion coefficient of oxygen from air to water is 1/10,000 of that through the waste atmosphere; clearly, low saturation environments will enable oxygen diffusion best. The transition from kinetic control at early times to oxygen diffusion control at late times is given the following explanation. As oxidation progresses, the pyrite particle becomes smaller and

there is a decrease in oxygen consumption with time; the oxidation front is therefore able to move downward in the profile. Because of the greater diffusion distance and length of time for diffusion, the concentration of oxygen becomes lower at greater depths. The end result is a control of late oxidation by oxygen diffusion rates for tailings and other fine and moderate textured wastes. According to Nakamura et al. (1994), oxidation of large pyrite particles is controlled by rate of the surface chemical reaction. This would support Elberling's finding that when oxygen diffusion is not limiting, kinetics control the rate of oxidation.

Pyrite oxidation (Evangelou and Zhang 1995) in an environment with a pH > 3.5 begins with the initial oxidation of pyrite:



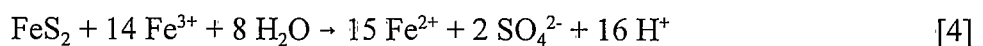
$\text{Fe}^{2+}$  (ferrous iron) is further oxidized by  $\text{O}_2$  into  $\text{Fe}^{3+}$ :



$\text{Fe}^{3+}$  (ferric iron) hydrolyzes into iron hydroxide:



During the initial stages of pyrite oxidation, most of the iron released ends up as iron hydroxide due to relatively high pH on the pyrite surfaces. However, as acidity is produced, the pH begins to drop. When it drops below pH 3.5, the activity of free ferric iron increases and it begins to oxidize the pyrite much faster than oxygen:



This reaction in low pH environments produces 16 moles of acidity for each mole of pyrite. *Thiobacillus ferrooxidans*, an acidophilic chemolithotrophic bacteria commonly present in

acidic sulphur environments along with other such bacteria, are able to catalyze the oxidation of ferrous iron to ferric iron (Equation [2]) by a factor greater than  $10^6$ . This results in high rates and amounts of acid production and the resultant sulfuric acid ( $\text{SO}_4^{2-} + 2 \text{H}^+ \rightarrow \text{H}_2\text{SO}_4$ ).

### Metal and Chloride Toxicity in Plants

#### Metal Toxicity in Acidic Environments

The solubilities of elements vary with changes in pH. The solubility of the plant nutrients nitrogen, potassium, phosphorus, magnesium, sulfur and boron are highest around pH 6.5 in mineral soils and 5.5 in organic soils (Miller and Donahue 1995). At pH levels above and below 6.5, these nutrients will become less soluble, and therefore less available to the plant. MacLean and Dekker (1976) reported decreased extraction of potassium with 0.1 N acetic acid with increasing acidity of tailings. Nitrogen and potassium may form ammoniojarosite and jarosite respectively, at low pH (Ivarson 1973). Phosphorus may readily combine with iron in acid sulfate materials, forming an insoluble precipitate (Murakami 1968). Processes such as these result in a low soil nutrient status in acidic environments.

It is not uncommon for the pH of many pyritic mine wastes to be 2.0 or lower. An even greater problem than low nutrient availability in acidic environments is high soluble metal contents. Mine wastes are enriched in metals. At low pH levels, these metals solubilize and quickly reach phytotoxic levels. Jahiruddin et al. (1986) reported an increase in DTPA extractable zinc and iron at low pH. Also, copper and manganese concentration in  $\text{NH}_4\text{OAc}$  extracts increased with increasing acidity. Reis et al. (1983) found that wheat uptake of



copper and iron was significantly higher at pH levels below 6.5 than at pH 7.5 and above, indicating greater solubilities of these metals at low pH. MacLean and Dekker (1976) recorded the release of large amounts of soluble manganese, iron, and aluminum from acid tailings when not adequately limed. Lewis (1986) lists the following as the pH at which particular metals begin to precipitate: ferric iron - 2.0; aluminum - 4.1; chromium and copper - 5.3; ferrous iron - 5.5; lead - 6.0; nickel and cadmium - 6.7; cobalt - 6.9; zinc - 7.0; mercury - 7.3 and manganese - 8.5.

Reddy (1993) found that an increase in the concentration of sulfate due to pyrite oxidation can increase the solubilities of aluminum and iron. In pH environments of 5.1 to 6.6, gibbsite ( $\text{Al}(\text{OH})_3$ ) is the common aluminum precipitate formed in saturated  $\text{Al}^{3+}$  solutions, and controls the activity of  $\text{Al}^{3+}$ , keeping it at a low level. In acid sulfate mine waters with pH levels below 5.1, jurbanite ( $\text{Al}(\text{OH})(\text{SO}_4) \cdot 5\text{H}_2\text{O}$ ) is the common aluminum precipitate formed and controls the  $\text{Al}^{3+}$  activity. However the activity of  $\text{Al}^{3+}$  is greater in this low pH range, as a result of the greater solubility product of jurbanite compared to gibbsite. Similarly, amorphous iron ( $\text{Fe}(\text{OH})_3$ ) controls the  $\text{Fe}^{3+}$  activity at higher pH's, while it appears that melanite ( $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ ) controls the solubility of  $\text{Fe}^{3+}$  at low pH. Melanite has a greater solubility product than amorphous iron, resulting in higher levels of soluble iron at low pH.

Low pH clearly results in increased solubility of many metals, which can bring about toxicity characteristics in plants growing in the acidic waste, or may prevent plant growth entirely. Plants vary as to their particular response to a toxic concentration of a metal. Maple responds to copper at concentrations of 4 mg/L with interveinal chlorosis and reddening of

leaves and stunting of lateral roots, and to 20 mg/L with interveinal chlorosis and no new growth. Birch responds to copper with chlorosis at 4 mg/L and with no visible axillary development and stunted lateral roots at 20 mg/L (Heale and Ormrod 1983). Exceptions may be noted with plants showing higher tolerances for the metal of interest and could be useful for revegetation of contaminated areas.

Total arsenic concentrations in unpolluted soils typically range from 1.2 to 97 ppm (Shacklette et al. 1974), total copper concentrations from 3 to 50 ppm and total lead less than 100 ppm (Connor and Shacklette 1975). Manganese concentrations of 400 to 500 ppm are generally toxic to plants (Gough et al. 1979). Levels of 250 to 600 ppm total zinc concentrations are usually phytotoxic (EPA 1987). Total soil iron as well as total aluminum may be as high as 10% (Connor and Shacklette 1975) and total sulfur up to 500 ppm in normal soils (Beaton et al 1968). Total cadmium is less than 3 ppm in unpolluted soils (Wixson 1977). Potassium chloride extractable nitrogen levels, which are also of interest to this thesis, are commonly less than 14 ppm (Munshower 1994a).

### Chloride Toxicity

Chloride may affect plant growth as the chloride ion or as chloride salts. Chloride is present in high concentrations in Flux Bar Residue as magnesium chloride, potassium chloride and calcium chloride, and is the impetus for this review of chloride toxicosis. Chloride is a necessary nutrient to plants in small amounts (Broyer et al. 1954, Johnson et al. 1957). Chloride is required for some photosynthetic reactions, in particular chloroplasts, and may be necessary for the translocation of carbohydrates in plants (Eaton 1966). Tobacco

plants were able to take up 50% of the chloride in the top 12 in of soil. This enabled a plant tissue concentration of 3.73% in soil with 37 ppm chlorine (Myhre 1956). These higher chloride levels may be toxic to plants.

Corn growth decreased at 23 to 45 ppm soil chloride when applied as potassium chloride fertilizer (Younts and Musgrave 1958). Lower rates than this resulted in delayed maturity. In a pot experiment, chloride did not delay germination but effects on plants were detectable within 16 days of planting. Parker et al (1983) reported injury to soybean plants at 150 ppm soil chloride (chloride present due to KCl fertilizer) and death at 300 ppm chloride. Chloride toxicity was observed as early as 1 month after planting. Parker et al. describe the following symptoms of soybean chloride toxicity. During vegetative growth and flowering, the lower leaves may absciss while the upper leaves appear fine. Symptoms worsen and more vegetation is affected as the season progresses. Margins of older leaves turn yellow, and then blade edges begin to curl followed by necrosis. Symptoms move from the base upward until all foliage is affected. New leaves may develop at an abscissed leaf site, but leaf scorch will begin to affect these. The most notable symptom in progressed stages of the disease is scorching of the leaf blade. Drought will exacerbate the symptoms. The existence of more tolerant cultivars was noted. Eaton (1966) lists common symptoms of excess chloride that agree with Parker's description: burning of leaf tips or margins, bronzing, premature yellowing and abscission of leaves, and chlorosis. Reduced leaf size and slower growth rates are also typical of chloride toxicosis.

Chloride accumulates in plant tissues with age, but does not move from old to new tissues (Eaton 1966). A few milliequivalents of chloride per liter are optimal for the

substrate. Above this level growth is depressed. Chloride accumulation decreases when nitrate and sulfate concentrations are high (Hayward and Long 1943) while chloride accumulation increases when calcium is the dominant cation in the root (Elgabaly 1962). Elgabaly also showed that plants with lower negative potentials in the roots exhibit decreased chloride uptake. Such characteristics dispose certain plants to higher chloride tolerances. Cotton, flax, corn and barley are all plants with high tolerances for chloride from 50 to 100 meq/L (producing 80% growth) (Eaton 1942).

Toxicity with chloride may be due to increased cation accumulation and to cation imbalances in addition to its effects as a toxic anion. Chloride additions increase the osmotic pressure of the substrates which results in an increase in the osmotic pressure of the tissue fluids. Toxicity effects are linear - the relation between substrate chloride and plant tissue chloride concentrations and the relation between growth depression and substrate chloride concentrations are both linear except at the extremes (Eaton 1966).

### Salt Toxicity

Soluble salts are inorganic salts more soluble than gypsum. Salts may be composed of the cations  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$  and  $\text{NH}_4^+$  and the anions  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{HCO}_3^-$ ,  $\text{NO}_3^-$  and  $\text{CO}_3^{2-}$  (Miller and Donahue 1995). Few plants grow well when a saturated paste extract electrical conductivity (EC) reading is greater than 16 dS/m. Many plants become affected at EC's between 4 and 8 dS/m.

Salt content has several affects on plants. Large amounts of soluble salts make it osmotically difficult for plants to absorb water. This osmotic effect is designated for

instances when plants show similar degrees of growth depression when grown on substrates containing different types of salts but of osmotically equal concentrations (Eaton 1996). This serves to differentiate general salt effects as opposed to specific ion effects of particular types of salts which have specific effects on enzymes which are responsible for the utilization and production of organic compounds and therefore plant growth. Specific ion effects are responsible for foliar symptoms which are dependent on the particular plant and the ion of interest. A specific ion effect could also be an ion's effect on the soil, such as sodium which in high concentrations can cause soil dispersal and crusting.

Salts not only make water absorption more difficult, but saline soils may also pull water from the plant during drought (exosmosis). Plants must expend energy absorbing water and excluding excess ions from metabolically active sites. Salt may result in decreased calcium uptake by roots which leads to decreased hydrogen ion extrusion from roots and resultant root acidification (Burgos et al. 1993). Characteristic effects of salt toxicity are slowing or inhibition of seed germination, particularly if salt is added after the critical level of seed hydration is reached (Thomson 1986), slower growth, decreased root growth and smaller leaf size (Terry et al. 1996). Most damage occurs when salts are present during early stages of growth (Eaton 1996) while plant salt tolerance increases with maturity. Nitrogen use efficiency also decreases with salinity (Rolston et al. 1996).

Salt tolerance differs among plants. Perennial ligneous species tend to be more salt tolerant than annual herbaceous plants (Burgos et al. 1993). Plants with high membrane permeabilities to salt are able to maintain turgor (Packer et al. 1986). Species able to exclude salt ions by the root cells or excrete salts by use of salt glands are characteristically salt

tolerant (Gorham et al. 1985). *Agropyron intermedium*, chosen for use in this thesis, exhibits good salt tolerance with a 12% growth reduction at electrical conductivities of 7 dS/m (Munshower 1994).

### Phytostabilization and Intermediate Wheatgrass

#### Phytostabilization

Plant-based remediation of contaminated soils may be accomplished either by decontamination of the soil or by stabilization of the pollutants within it (Cunningham et al. 1995). Decontamination of the soil may be accomplished by either phytoextraction, where plants accumulate the soil toxins and are then harvested, or by phytodegradation, where plants convert the contaminants into non-toxic substances. Stabilization of the pollutant by plants, or phytostabilization, may include an alteration of a soil's chemistry via amendments or by action of the plant and its microflora. These alterations together with other stability changes brought to a site by plant growth reduce or eliminate a pollutants risk to the environment. A phytostabilization plan which involves treatment of contaminated soil (acidic-metalliferous mine waste) with lime and subsequent planting of the soil to increase its stability is the scheme of this research project. Phytostabilization will therefore be discussed here rather than phytoextraction or phytodegradation.

There are several amendments besides lime which may be added to an acidic metalliferous soil to sequester the contaminants. These include fly ash, sludges and phosphates. Taylor and Schuman (1988) demonstrated that both fly ash and lime substantially increased the pH of acidic spoil and resulted in similar plant biomass. However,

possible contaminants in fly ash, such as boron, may be a concern. Joost et al. (1983) achieved successful revegetation of coal refuse using either sewage sludge or limestone. However, the nitrogen content of sludges may pose a threat to water sources or may result in grass nitrate contents in excess of acceptable feed levels. Also, because a sludge's sequestering power comes from its adsorption capacities, sludges may not neutralize acidity. Phosphates precipitate metals out of solution, but do not neutralize acidity. Lime sequesters contaminant metals by raising soil pH which then reduces metal solubility.

The chosen amendment is incorporated into the site, resulting in sequestration of the contaminant. Plant growth is then possible on the site. Additions of mulches and fertilizers are usually also necessary. Plants for a site are chosen based on the site's characteristics. If the pH of the soil is less than 3.7 to 4.0, acid neutralizing amendments will need to be added as this is the lower limit to most selected acid-tolerant species (Vogel 1984). Selected native species have been shown to have multiple element tolerances (Hutchinson and Kuja 1978). If possible, seed selected from plants volunteering on a contaminated site should be used for the remediation, as they are demonstrating a tolerance to the contaminant.

Plant growth on a site helps reduce wind and water erosion. A high seedling establishment will result in the development of many separate roots. This more compact root community results in better erosion control (Day and Ludeke 1982). It should be noted that wind erosion must be controlled during establishment by mulches or petroleum binding agents to prevent sandblasting of seedlings (Nielson et al. 1972). Plants may also reduce the risk of contaminant migration into ground and surface waters due to increased water consumption (Cunningham et al. 1995). Root respiration could also serve to decrease the

amount of oxygen available for sulfide oxidation. However, according to Veldhuizen et al. (1987), vegetation gave negligible to no reduction in acid generation and acid water on reactive tailings. Farmer and Richardson (1981) found that heavy stands of grass did not cause a detectable reduction in sulfide oxidation. If leaching is reduced, it is possible to expose more tailings to oxidation by a lowering of the water table due to increased water consumption. Plants do give aesthetic appeal to a site (Johnson and Bradshaw 1977, Johnston et al. 1975) and improve the physical and chemical characteristics of waste. Roots can also serve to take up any remaining non-sequestered contaminants, and sequester these in the roots (Cunningham et al. 1995). For this reason it is important to choose plants that are poor contaminant translocators in order to prevent consumption of toxins by wildlife, since these plants are not harvested as in phytoextraction. Some plant species are capable of further sequestering contaminants by redox reaction or by precipitation of a contaminant into an insoluble form.

#### Intermediate Wheatgrass

*Agropyron intermedium*, commonly known as Intermediate wheatgrass, was the species chosen for this thesis project. It is of the family Poaceae, subfamily Pooideae, and tribe Triticeae. A simple description of *Agropyron intermedium* is that it has a two sided terminal spike with the spikelets laterally pressed along the main rachis. It is rhizomatous with stout culms up to a meter in height. Blades are 5-12 mm wide, there are 3-8 fertile florets per spikelet, glumes are thick, and the margins on lower leaf sheaths are usually ciliate (Lavin and Rumely 1995). The most recent classifications place *Agropyron intermedium*



into the *Thynopyrum* genus. This change in classification results from the genetic composition of Intermediate wheatgrass, or how readily it pairs with chromosomes of other species during metaphase 1 of meiosis, rather than a classification based on morphology of the grass. This paper will refer to Intermediate wheatgrass as *Agropyron intermedium* (or *A. intermedium*).

*A. intermedium* is known to exist in Montana in the Beaverhead, Big Horn, Gallatin, Sanders, Teton, and Yellowstone Counties (Lavin and Rumely 1995). It is an introduced grass of the Northern Great Plains and the Intermountain Region. The first introduction of *A. intermedium* came from a population growing in Trans Ural Siberia (Barnes et al. 1995). It grows widely from southern Europe to western Pakistan, but rarely exists further north than 30°N. *A. intermedium* prefers well-drained areas with annual precipitation around 35 cm (15-20 in) and soils of a sandy loam to clay loam texture. It does well if the soil pH is between 5.5 and 8.0 (Munshower 1994b). *A. Intermedium* is commonly found at elevations ranging from 1524 m to 2225 m (5,000 - 7,300 ft).

*A. Intermedium* has grown well on many reclaimed areas. This is due to a number of characteristics that predispose this species for success. It is fairly drought tolerant, partly due to its ability to grow roots up to 2.7 m (9 ft) deep; it also is quite salt tolerant. It experiences no growth reduction in soils with electrical conductivities as high as 5 dS/m (5 mmhos/cm). In addition to its being drought tolerant, it can also withstand flooding and high water tables with a decent amount of resiliency (Munshower 1994). It establishes quickly, with vigorous early growth, making it an excellent soil stabilizer for fragile sites. However, because it establishes quickly, it can be difficult for plants such as native grasses, forbs, shrubs and

trees to compete with it. Its rhizomatous root system further enhances its competitiveness, yet also adds to its stabilizing abilities. Considerations of the reclamation site, such as need for immediate erosion control and site stability, will need to be weighed before planting *A. intermedium*. Other characteristics of *A. intermedium*, such as its winter hardiness and tolerance of high temperatures, also make it a strong reclamation species.

Intermediate wheatgrass, a cross-pollinating species, has been used extensively in the west as a forage crop and in combination with alfalfa as a forage crop, because it prevents alfalfa from lodging. *A. intermedium* greens up nicely in the fall if moisture is available (Munshower 1994) and can suppress growth of undesirable shrubs. It also retains its forage quality quite well after fall frosts. *A. intermedium* can be a very productive forage and is widely adapted, making it a good choice for a hay crop. However, its use has met with resistance because of its lack of longevity beyond 4 or 5 years when under intense management (Barnes et al. 1995). Intense grazing and close defoliation reduce its longevity, especially during early development.

The number of seeds per pound of *A. Intermedium* average around 85,000. *A. intermedium* should be drill seeded to a depth of approximately 2.5 cm (1 in.) at a rate of 2 to 7 pounds of pure live seed per acre depending on the desired outcome. Low rates are for mixed stands as would be desired on a reclaimed coal mine in order to meet diversity requirements, while the highest rates would result in pure stands as might be desired for a hay crop. This grass should be seeded between late fall and mid-spring (Munshower 1994).

There are definite advantages to the use of *Agropyron intermedium* for reclamation, phytostabilization or other use. Its best attribute is its ability to tolerate a range of conditions

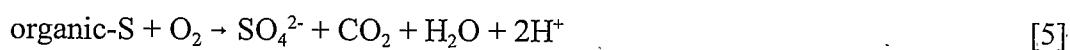
which is so essential on many drastically disturbed sites where a prime habitat cannot often be provided. However, given it is an introduced, cool season grass, consideration must be given to whether the positive traits of *A. intermedium* outweigh the fact that its presence will make it difficult for less competitive species to develop, or to what types of seeding regimes might reduce its competitiveness. In this manner, the best use of *Agropyron intermedium* can be made.

### Liming Science

The pH of a soil solution is equal to the negative log of the hydrogen ion concentration. The hydrogen ions or acidity may result from several sources in natural soils. These sources include humus, aluminosilicate clays, hydrous oxides of iron and aluminum, soluble salts and carbon dioxide. Carboxyl, phenolic and amino reactive groups of humus are capable of binding hydrogen ions. These hydrogen ion saturated groups can behave as weak acids by dissociating in water. Aluminosilicate clay minerals, such as kaolinite and montmorillonite, have both a permanent and a pH dependent charge. Hydrogen may associate/dissociate from hydroxyl groups or bound water of the crystal lattice. Hydrous oxides of iron and aluminum exist as coatings on soil minerals or are interlayers within them. When the pH of the soil decreases, these hydrous oxides hydrolyze to release hydrogen. The cations of soluble salts will exchange with adsorbed aluminum and hydrogen, resulting in an increased acidity of the soil solution. Increasing partial pressures of carbon dioxide in the soil due to root and microbial respiration result in the formation of carbonic acid, which is able to lower soil pH. High concentrations of aluminum are associated with acid soils. In

acid soils,  $H^+$  and  $Al^{3+}$  are in equilibrium. (Nelson and Tisdale 1966, Sparks 1995).

As discussed earlier in this chapter under "Pyrite Oxidation", acid spoils/drainage are a common problem for coal and hardrock mines due to the oxidation of reduced sulfur forms in the overburden (Harvey and Dollhopf 1986). The reactions involved in the production of acidity in mine spoils are the pyrite oxidation reactions [Equation 1, 2, 3 and 4] and the hydrogen released from organic sulfur:



If organic-S is linked to an amine group, an additional mole of acidity will be formed. Pyrite oxidation is the greatest contributor to acid production in spoils, but organic-S is also an important contributor.

If the acidity of a soil/spoil is too great, metals become very soluble, and vegetative growth is reduced or prevented. This poses threats to vegetation and the environment. The production of active acidity from potential acidity can be described thus:



The potential acidity HA in the presence of water can dissociate into active acidity  $H^+$  and the accompanying anion (Nelson and Tisdale 1966). Potential acidity can exist as any of the undissociated forms of hydrogen occurring in natural soil as discussed above for humus, aluminosilicate clays, etc. In sulfide rich mine wastes, it exists as unoxidized pyrite and organic-S. The active acidity is the dissociated hydrogen in either soils or mine wastes. The  $Al^{3+}$  ion is also considered active acidity in natural soils. Neutralization is accomplished by reacting and acid (HA) with a base (BOH) to form water and a salt:



In natural soils,  $H^+$  will be neutralized first, then aluminum which hydrolyzes and then precipitates as  $Al(OH)_3$  (Thomas and Hargrove 1984). In mine wastes, the active acidity is neutralized. As more sulfur is oxidized and more  $H^+$  is produced, the potential acidity becomes slowly neutralized over time. The most common amendment used in both agriculture and mine reclamation to neutralize acidity is lime. The remaining discussion of liming science will focus on mine reclamation liming science, though much of the following discussion will hold true for agricultural liming.

Although there are other methods than liming to deal with acid spoils and acid mine drainage, such as barrier methods which isolate pyrite from oxygen and water, anti-bacterial methods to inhibit the activity of *Thiobacillus ferrooxidans*, and alternative land uses such as constructed wetlands (Pulford 1991), the most common method of dealing with acid problems are chemical methods, especially the use of lime chemicals. Lime is generally defined as any calcium or magnesium amendment which ameliorates soil acidity and releases calcium or magnesium ions into the soil (Munshower 1994, Nelson and Tisdale 1966).

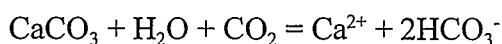
There are many types of lime amendments. A listing of lime amendments follows along with their chemical formulas and calcium carbonate equivalences (CCE) for the pure material:

<u>Name</u>	<u>Chemical Formula</u>	<u>CCE</u>
quicklime, lime	CaO	179%
slaked lime, hydrated lime	Ca(OH) <sub>2</sub>	136%
calcite, calcitic limestone	CaCO <sub>3</sub>	100%
dolomite	CaMg(CO <sub>3</sub> ) <sub>2</sub>	109%

dolomitic limestones	$\text{Ca}_{1-x}\text{Mg}_x\text{CO}_3$	varies
magnesite	$\text{MgCO}_3$	119%
slags	primarily $\text{CaSiO}_3$	65-90%

The calcium carbonate equivalence or CCE of an amendment is its capacity to neutralize acidity compared to an equal mass of pure crystalline calcite. The molecular composition of an amendment determines its neutralizing value. For example, given that one molecule of  $\text{CaCO}_3$  (molecular weight = 100) will neutralize two molecules of hydrogen, and one molecule of  $\text{MgCO}_3$  (molecular weight = 84) will neutralize 2 molecules of hydrogen, and the equation  $84/100 = 100/x$ , and  $x = 119$ , then the CCE of  $\text{MgCO}_3$  is 119% (Lewis 1986, Nelson and Tisdale 1966). Other bases are available for neutralizing acidity, such as NaOH (caustic soda), KOH,  $\text{Na}_2\text{CO}_3$  (soda ash) and  $\text{NH}_3$  (anhydrous or gaseous ammonia), but these compounds may increase suspended solids by acting as clay dispersants and may put water resources, plant/aquatic life and soil structure in jeopardy (Evangelou and Warner 1983) and are not recommended.

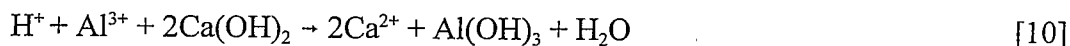
$\text{CaCO}_3$  neutralizes acidity according to the equations below (Stumm and Morgan 1996). Upon the release of a calcium ion and bicarbonate ions from  $\text{CaCO}_3$ , the  $\text{Ca}^{2+}$  ions displace  $\text{H}^+$  ions off cation exchange sites. The  $\text{HCO}_3^-$  ion then combines with the  $\text{H}^+$  ions to eventually form water and carbon dioxide gas.



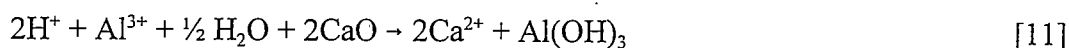
An alternative reaction which shows concurrent metal precipitation (presented here using aluminum) with acid neutralization is:



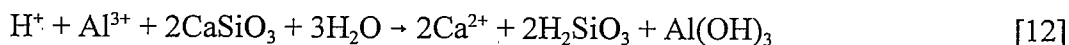
Other carbonate containing lime amendments neutralize acidity in a similar manner. Hydroxide containing compounds, such as hydrated lime, are able to directly contribute hydroxyls to neutralize acidity:



Oxides of calcium and magnesium react with water to release calcium ions and precipitate metals as hydroxides:



(Nelson and Tisdale 1966, Thomas and Hargrove 1984, Sparks 1995). Silicates complex or precipitate metals. Metasilicic acid is produced but is weak relative to  $\text{H}^+$ :



$\text{CaSO}_4$  (gypsum) has been used with success in liming weathered, aluminum dominated agricultural soils (Farina and Channon 1988) but cannot be used in pyritic environments because of the production of sulfuric acid upon incorporation and subsequent lowering of spoil pH (Pietz et al. 1989):



Neutralization of acidity raises the pH of the acid soil or waste. As the pH rises, surface functional groups of many soil organic compounds and phyllosilicate clay minerals deprotonate. The CEC of the soil or waste is thereby increased, resulting in greater sorption of metals (Sparks 1995). Reduction in soluble metals by neutralization of acidity with lime is therefore a result of both metal precipitation reactions and sorption of metals.

The following reactions demonstrate the mellowing of lime to  $\text{CaCO}_3$  over time

which may take 6 to 12 months in the field:

	<u>Minesoil pH</u>
$\text{CaO} + \text{H}_2\text{O} = \text{Ca}(\text{OH})_2$	9-12
$\text{Ca}(\text{OH})_2 = \text{Ca}^{2+} + 2\text{OH}^-$	9-12
$\text{OH}^- + \text{CO}_2 = \text{HCO}_3^-$	-----
$\text{HCO}_3^- + \text{OH}^- = \text{CO}_3^{2-} + \text{H}_2\text{O}$	-----
$\text{CO}_3^{2-} + \text{Ca}^{2+} = \text{CaCO}_3$	< 8.5

This weathering can be accelerated by bubbling  $\text{CO}_2(\text{g})$  through an amended sample (Dollhopf and McDaniel 1997). It is requisite to plant growth that a soil not be seeded until mellowing has been accomplished.

Liming has proven successful in ameliorating acidity, thereby reducing soluble metals via precipitation or sorption and facilitating plant growth. It is a viable alternative to coversoil (Olsen and Chong 1991). Wallace (1989) found that liming reduced trace element toxicity to plants. He also found that liming reduced some trace element interactions. Liming not only neutralizes acidity but serves to decrease sulfide oxidation rates because of oxide accumulation on pyrite surfaces (Nicholson et al 1990). It hydrolyzes most heavy metals which precipitate as metal hydroxides (Evangelou and Zhang 1995). Liming increases phosphorus availability, and aids flocculation of fine textured soils. Riggs et al. (1995) achieved successful use with calcitic limestone, though dolomitic limestone proved better because of magnesium additions to the soil which improved grass nutritive value. Muse and Mitchell (1995) were able to increase the pH of soil significantly higher with lime by-products from pulp and paper mills than with agricultural lime; the pH remained higher than



when dolomitic limestone was used, and soil and plant tissue concentration of metals and nutrients were acceptable. This evidence indicates potential use for industrial by-products as alternative lime sources. These examples demonstrate the advantages of the use of lime products; however, there are some disadvantages to the use of lime products. In high sulfate soils, calcium containing lime products could cause the precipitation of gypsum and an increase in the suspended solids of acid mine drainage (Evangleou and Warner 1983). There is also evidence that crystallization of iron oxides on calcite surfaces can occur (Clarke et al. 1985), which could reduce calcite solubility. Overliming can result in decreased availability of micronutrients. Lastly, additions of calcitic limestone may significantly decrease exchangeable magnesium (Riggs et al. 1995); however, the increase in exchangeable calcium can be beneficial for plants.

The fineness of lime will determine its reactivity and therefore its effectiveness. To enable sufficient solubility of lime, particles should pass a 60 mesh sieve (0.25 mm) (Meyer and Volk 1952). Particles of this size or smaller will have enough surface area per unit mass to react at a useful rate with a minimal amount of material (sufficient mass per volume). Particles that pass a 60 mesh sieve but also have a spongy surface texture will have even greater reaction rates, as will softer particles (Nelson and Tisdale 1966). Certain compounds are innately more soluble than others. Calcitic limestone is more soluble than dolomitic limestone (Riggs et al 1995). A final and major factor in determining the effectiveness of a lime product is its neutralizing capacity or calcium carbonate equivalence as discussed earlier. It is also best to use a mixture of a fast reacting lime agent such as  $\text{CaO}$  or  $\text{Ca(OH)}_2$  and a slow reacting lime agent like  $\text{CaCO}_3$  in order to provide immediate neutralization and

long term neutralization of acid produced over time (Harvey and Dollhopf 1986, Neuman et al. 1993).

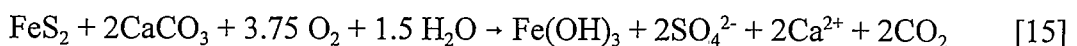
To determine the lime requirement for agricultural soils, an SMP Buffer test is used which determines exchangeable or soluble acidity, or the active acidity (McLean 1982). This test has also been used to successfully determine the active acidity of mine wastes (Schafer 1985). The potential acidity of mine wastes must be determined in addition to the active acidity in order to incorporate sufficient lime to neutralize all acidity that will form from sulfide oxidation over time. There are two ways to determine potential acidity: acid-base accounting (ABA) and weathering cells.

The Sobek method (1978) of ABA uses a series of extractions to separate acid producing sulfur forms from non-acid producing sulfur forms. The first two extractions of the mine waste sample, a hot water extraction and a hydrochloric acid extraction (3:2, HCl:H<sub>2</sub>O), remove the sulfates. The third extraction, an HNO<sub>3</sub> extraction (1:7, HNO<sub>3</sub>:H<sub>2</sub>O), and the residual sulfur remaining after the third extraction contain the acid producing sulfides and acid producing organic-S (Harvey and Dollhopf 1986).

After determining the neutralization potential (NP), which is a measure of the carbonates and other neutralizing agents that may exist in a sample, the following equation gives the ABA for a sample:

$$\text{ABA} = \text{NP} - \{(\% \text{HNO}_3 \text{ extractable S} + \% \text{Residual S})31.25\} \quad [14]$$

The 31.25 term by which the percentages of acid producing sulfur forms are multiplied by is based on the following equation:



From this equation (2 moles of  $\text{CaCO}_3$  neutralize one mole of  $\text{FeS}_2$ ), the molecular weights of iron (55.847 g), sulfide (65.12 g) and  $2\text{CaCO}_3$  (200.18 g), and given that the Sobek ABA is based on sulfur, it is determined that 1 gram of S is neutralized by 3.125 grams of  $\text{CaCO}_3$  ( $65.12 \text{ g}/200.18 \text{ g} = 3.125$ ). The amount of lime required to neutralize a six inch acre slice of 1% sulfur as pyrite is 31.25 t/1000 t (Jennings 1996). Hence the term 31.25 in Equation [14]. Cravotta et al. (1990) holds that this term should equal 62.5 or an amount between 31.25 and 62.5 given that the  $\text{CO}_2$  in Equation [15] may not all exsolve, but rather that some of the  $\text{CO}_2$  will dissolve.

The lime requirement given by the acid base account may overestimate the amount of acid producing sulfur. Reduced sulfur forms that are not acid producing may carry over into the third and fourth extractions. Similarly, current knowledge may overestimate acid production from organic-S [Equation 5]. In addition, there are differences in reactivity of pyrite derived from different sites (Jennings 1996). Sources of error such as these may lead to overliming and wasteful use of funds. There is some potential for underestimation of ABA by overestimation of NP. This occurs when compounds such as siderite ( $\text{FeCO}_3$ ) contribute to NP as determined by a lab, but do not actually provide neutralization.

Giving consideration to these many sources of error, the following equation has been developed to calculate the total  $\text{CaCO}_3$  required for a mine waste in tons of  $\text{CaCO}_3$  per 1000 tons of waste (Dollhopf et al. 1996):

$$\begin{aligned} \text{Total CaCO}_3 \text{ Required, t/1000 t} = & [(\% \text{HNO}_3 \text{ ext. S} + \% \text{ Residual S})31.25 \\ & + 23.44(\% \text{HCl ext. S}) + \text{t/1000 t Active Acidity}]1.25 \end{aligned} \quad [16]$$

Using this equation and the CCE of the lime product in question, the amount of < 60 mesh

material needed for complete acid neutralization for the rest of time can be determined.

An alternative form to ABA in determining potential acidity is the use of simulated natural chemical weathering via humidity cells. These cells control the temperature, air, moisture, and catalytic microbes of the test sample's environment. CARWA, or computerized automated rapid weathering apparatus (Harvey and Dollhopf 1986) is able to produce results within 24 hours, whereas manual laboratory weathering studies take 6 to 12 weeks. CARWA simulates 3 weathering cycles which is equivalent to one year of weathering in the field.

## CHAPTER 3

### METHODS

#### Site Descriptions

The two mine wastes sampled for this project are located in Montana. Their locations and descriptions are described here.

#### Lehigh Coal Waste

The Lehigh Maintenance Project (Figure 1) is located in Judith Basin County in central Montana. Coal waste for this project was collected from a stockpile at the site which resulted from underground coal mining during the period 1914 to 1921 (Dollhopf and McDaniel 1997). This coal waste is very acidic due to the weathering of its pyritic materials. It is high in soluble aluminum and sulfate, as well as being enriched with other potentially toxic metals. Salinity levels of this waste are also strongly elevated.

#### Opportunity Tailings

The Opportunity Tailings Ponds (Figure 2) are located in southwest Montana just outside the town of Opportunity. These tailings resulted from the smelting of copper ore, primarily ore mined in Butte, Montana over a seventy year period, which were sluiced from the Anaconda Smelter to the Opportunity Ponds. These ponds covering approximately 5,000

















































































































































































































































































































































































