Technique development for determining total lime requirement for acid mine sites
by Luther John Russell

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

Abstract:
Surface coal mining and hard rock mining operations often expose iron sulfide minerals (e.g. pyritic sulfur) and organic sulfur containing substances to a new oxidizing environment. Acid generation from the oxidation of these materials often inhibits the revegetation of mine spoils. A total lime requirement must be determined to mitigate existing acidity and prevent re-acidification from the continued oxidation of sulfide and organic sulfur containing materials. Traditional agricultural lime rate determination methods are not appropriate for mined land situations where the majority of acid production is from the weathering of relatively insoluble minerals such as pyrite. Because of this limitation, acid-base accounting has become the standard in the reclamation industry for the estimation of lime requirements for acid mine spoils. This method, however, has technical limitations and frequently leads to erroneous results.

Thus, there is a need for the development of a reliable methodology to determine the total lime requirement for acid mine wastes. In this study, simulated weathering chambers were designed to examine acid production potential of mine waste materials under weathering conditions similar to the natural mine site. This methodology eliminated errors in interpretation of acid-base account data and provided a more accurate lime rate recommendation for acid mine spoils.

TECHNIQUE DEVELOPMENT FOR DETERMINING TOTAL LIME REQUIREMENT FOR ACID MINE SITES

by

Luther John Russell

A thesis submitted in partial fulfillment
of the requirements for the degree

of

Master of Science

in

Land Rehabilitation

MONTANA STATE UNIVERSITY
Bozeman, Montana

March 1984

APPROVAL

of a thesis submitted by

Luther John Russell

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.

Feb. 29 1984
Date

DJ Dollhopf
Chairperson, Graduate Committee

Approved for the Major Department

2-29-84
Date

Arthur E. Linton
Head, Major Department

Approved for the College of Graduate Studies

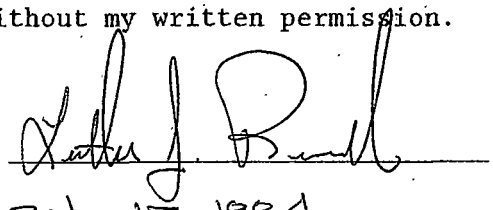
3-2-84
Date

Henry L Parsons
Graduate Dean

STATEMENT OF PERMISSION TO USE

In presenting this thesis in partial fulfillment of the requirements for a master's degree at Montana State University, I agree that the Library shall make it available to borrowers under rules of the Library. Brief quotations from this thesis are allowable without special permission, provided that accurate acknowledgement of source is made.

Permission for extensive quotation from or reproduction of this thesis may be granted by my major professor, or in his absence, by the Director of Libraries when, in the opinion of either, the proposed use of the material is for scholarly purposes. Any copying or use of the material in this thesis for financial gain shall not be allowed without my written permission.

Signature 

Date March 15, 1984

ACKNOWLEDGEMENTS

I wish to express my appreciation to Dr. Douglas J. Dolhopf of the Reclamation Research Unit at Montana State University for his assistance in the development and execution of this study. I would also like to thank Dr. Ralph Olsen for his sagacious advice and sense of humor; Dennis R. Neuman for his analytical expertise and perspective; and Dr. Frank Munshower for his editorial suggestions. I also wish to thank the Anaconda Minerals Company for funding this study.

I further wish to express my heart-filled appreciation to my parents and family who have given me freedom and support in the pursuit of my goals; Mr. John Lawson for his counsel and comraderie; Ms. Meg Fry for her moral support; and finally, to Buck, whose faithfulness could move a mountain.

TABLE OF CONTENTS

TABLE OF CONTENTS--Continued

LIST OF TABLES

LIST OF TABLES--Continued

LIST OF FIGURES

LIST OF EQUATIONS

ABSTRACT

Surface coal mining and hard rock mining operations often expose iron sulfide minerals (e.g. pyritic sulfur) and organic sulfur containing substances to a new oxidizing environment. Acid generation from the oxidation of these materials often inhibits the revegetation of mine spoils. A total lime requirement must be determined to mitigate existing acidity and prevent re-acidification from the continued oxidation of sulfide and organic sulfur containing materials. Traditional agricultural lime rate determination methods are not appropriate for mined land situations where the majority of acid production is from the weathering of relatively insoluble minerals such as pyrite. Because of this limitation, acid-base accounting has become the standard in the reclamation industry for the estimation of lime requirements for acid mine spoils. This method, however, has technical limitations and frequently leads to erroneous results. Thus, there is a need for the development of a reliable methodology to determine the total lime requirement for acid mine wastes. In this study, simulated weathering chambers were designed to examine acid production potential of mine waste materials under weathering conditions similar to the natural mine site. This methodology eliminated errors in interpretation of acid-base account data and provided a more accurate lime rate recommendation for acid mine spoils.

INTRODUCTION

In response to the 1977 Surface Mining Control and Reclamation Act (public law 95-87) and the 1979 Montana Hard Rock Mining Reclamation Legislation, numerous abandoned mining sites throughout Montana have received increased attention as being in dire need of rehabilitation. These laws promulgated that federal funds will be made available for reclamation of abandoned hard-rock mine lands; once all abandoned coal mines have been reclaimed or if it can be shown that reclamation of abandoned hard-rock sites is necessary to protect public health and safety. Within this context, the Montana Department of State Lands has begun to inventory abandoned and inactive mine sites for the purpose of prioritizing these sites for future reclamation projects (Deckler 1982).

The Champion Mine site, an inactive silver mine located approximately 24 kilometers northeast of Butte, Montana (46°14' N, 112° 36" W), owned and controlled by the Anaconda Minerals Company, was investigated in this study (Figure 1). A complete characterization of this site is provided by Deckler (1982).

Hard-rock mining operations usually recover "pyritic" minerals and remove their metal content. Mining processes thereby expose sulfide (pyritic-sulfur) containing minerals to the atmosphere. In past mining operations, only the highest grade ore was economically recoverable. Thus, finely disseminated pyritic materials containing

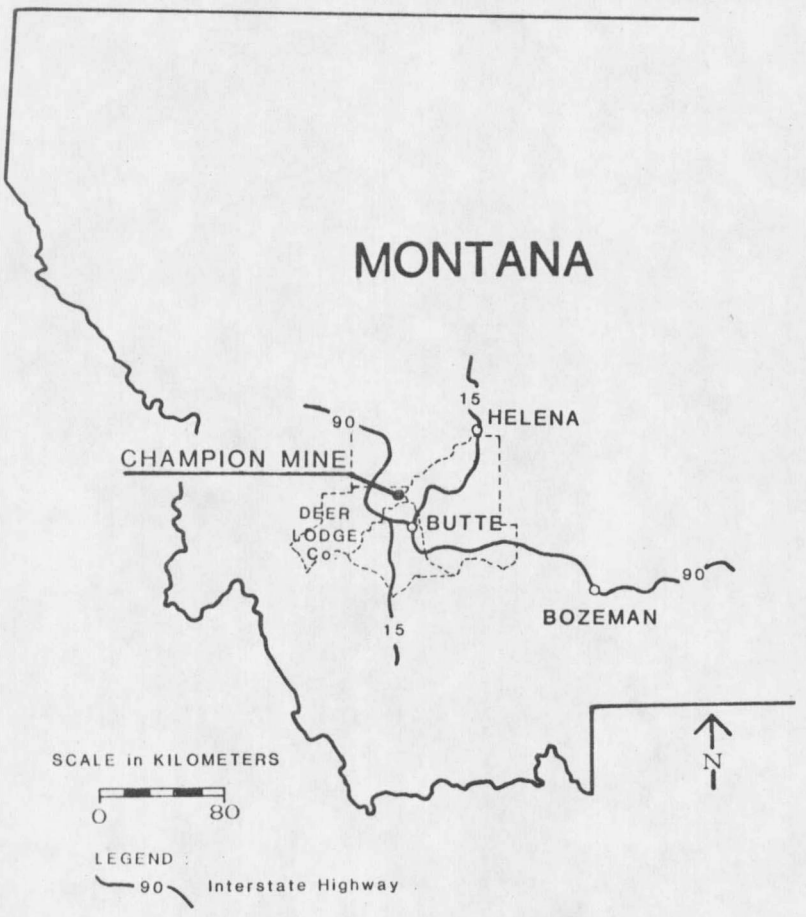


Figure 1. Location of Champion Mine Site.

small quantities of metals were left behind in gangue and mill tailings. Acid production from the oxidation of these materials often inhibits the revegetation of mine spoils. In addition to their objectionable aesthetic qualities, abandoned hard-rock mine sites are also poor wildlife habitat and grazing land, pollutant sources for water, and pose severe erosion and safety hazards. The establishment of a vegetative cover may reduce or eliminate these problems. Obtaining such a cover is difficult due to steep slope and consequent erosion, poor soil structure, reduced water holding capacity (increased runoff), and extreme acidity of some of these materials. Abandoned mine sites frequently have elevated concentrations of iron (Fe), manganese (Mn), copper (Cu), nickel (Ni), magnesium (Mg), aluminum (Al), and sulfate (SO_4) as well as reduced concentrations of calcium (Ca), potassium (K), phosphorus (P), and nitrogen (N). These elements at abnormal levels may be toxic to plants and thus inhibit the establishment of a vegetative cover (Barnhisel and Massey 1969). Although the mechanisms of plant toxicosis are varied and not fully understood, metals are known to affect metabolic sites within plant cells with particular disruption to respiration and some photosynthetic processes.

Revegetation with species or populations which tolerate low pH, high metal concentrations, and salts would be one potential method for stabilizing mine waste materials. Lime application to reduce spoil acidity and neutralize acid produced by the oxidation of sulfide minerals is another technique to improve revegetation success.

Agriculture lime requirement methods, which are based on active acidity (H+ ions) generally underestimate the total (long-term) lime requirement for mine waste containing sulfur bearing materials. A total lime requirement must be determined which accounts for all forms of acid production, especially sulfide oxidation.

The objectives of this study were to 1) characterize the physical and chemical properties of waste rock and mill tailing material present at the Champion mine site, 2) evaluate current methods of lime rate determination for minesoils, and 3) develop a laboratory weathering procedure to determine the total lime requirement for acid mine spoils.

LITERATURE REVIEW

Acid Mine Drainage Production

Pyritic-sulfur (FeS_2) from mine disturbances may be found in several morphological forms (Arora et. al. 1978, and Caruccio et. al. 1977). The frequently occuring forms of pyrite are massive and framboidal. Massive pyrite consists of solid nonporous grains that are more resistant to oxidation than framboidal pyrite. Framboidal pyrite crystals (<.025 mm diameter) are porous and weakly aggregated into spheroids. Because of the large exposed surface area available for oxidation, nearly four to five times that of massive pyrite (Pugh et. al. 1981), framboidal pyrite is much more reactive and unstable than massive pyrite (Arora et. al. 1978, Smith and Shumate 1970, Caruccio 1968).

The chemical kinetics of pyrite oxidation to form acidity have been determined to be influenced by particle size, oxygen concentration, temperature, degree of saturation, microbial activity and the pH of the soil water solution (Pugh et. al. 1981, Smith and Shumate 1970, Caruccio 1968).

The oxidation of FeS_2 materials often forms hydrous iron sulfates which appear as white and yellow salt crusts on weathered rock surfaces. Natural waters which flow over these salts hydrolyze in water to form acidic, iron and sulfate rich drainages (Geidel 1979). The chemical kinetics explaining the oxidation of FeS_2 and the production of acidity (H^+) are given by the following equations:

$$2\ FeS_2(s) + 7\ O_2 + 2\ H_2O = 2\ Fe^{++} + 4\ SO_4^{=} + 4\ H^+ \quad (1)$$

$$Fe^{++} + 1/4\ O_2 + H^+ = Fe^{+++} + 1/2\ H_2O \quad (2)$$

$$Fe^{+++} + 3\ H_2O = Fe(OH)_{3(s)} + 3\ H^+ \quad (3)$$

$$FeS_{2(s)} + 14\ Fe^{+++} + 8\ H_2O = 15\ Fe^{++} + 2\ SO_4^{=} + 16\ H^+ \quad (4)$$

(Barnes and Romberger 1968, Baker 1975)

The stoichiometry of equation (1) indicates that one mole of FeS_2 will produce two moles of acidity. The ferrous iron (Fe^{++}) generated by equation (1) may readily oxidize to ferric iron (Fe^{+++}) (2) and produce three moles of acidity. Ferric hydroxide [$Fe(OH)_{3(s)}$] which precipitates out of solution as "yellow boy" (3) imparts the red or yellow color which is characteristic of acid mine drainages. Pyrite may also be oxidized anaerobically in the presence of excess ferric iron in solution (Smith and Shumate 1970, Singer and Stumm 1968) with water and further hydrolyze to form sixteen moles of acidity (Eq. 4).

Autotrophic bacteria of the genera Thiobacillus and Ferrobacillus have been found to be present in virtually all acid mine drainage water (Caruccio and Geidel 1978). Under natural conditions oxidation of ferrous iron proceeds very slowly, but the presence of these bacteria may accelerate the rate of acid production (Singer and Stumm 1968, LeRoux et. al. 1980) reportedly by a factor of 500,000 times (Lacey and Lawson 1970). Thus, it is this step (Eq. 2) which is rate-determining in the oxidation of pyrite and formation of acid mine drainage (Singer and Stumm 1968).

The amount of acidity generated is also a function of the alkalinity production potential of the system and the frequency of flushing the oxidation products from the system. The alkalinity

produced is dependant upon the pH of infiltrating water, amount of calcareous materials in the strata, the partial pressure of carbon dioxide, solubility of the specific mineral and time of contact (Caruccio 1968, Caruccio et. al. 1976, and Geidel 1979). The amount of acidity released is also dependant on the time interval between flushing (Geidel 1979). Equilibrium alkalinity levels are reached quickly due to rapid reaction rates and low solubility product, while acid production is slower to reach an equilibrium due to continued oxidation of pyritic materials. Thus, more frequent flushing of mined lands may produce alkaline or mildly acidic drainage while increasing the interval between flushing may increase the amount of acidity released.

The quality of water draining from a mining disturbance is determined then, by the geochemistry of the groundwater, morphology of pyrite within the system, occurence of alkaline materials, presence of bacteria, and the manner in which these are allowed to interact by the nature of the land disturbance (Caruccio 1968).

Organic Sulfur - Acid Production

The sulfur in overburden may occur in three forms: sulfide sulfur (discussed previously), sulfate sulfur and organic sulfur. Sulfate sulfur is a weathering product of pyritic sulfur (Equation 1) and organic sulfur compounds and is generally neglected as a source of potential acidity (Caruccio and Geidel 1978).

Organic sulfur is found in soils and overburden materials primarily in two forms. The first is organic sulfur not bonded directly

to carbon (referred to as "ester sulfate") and is represented by phenolic sulfates (Tabatabai and Bremner 1972, Freney 1967). This is the form in which sulfate is stabilized geochemically. The other form is sulfur which is bonded directly to carbon. This latter form is believed to consist largely of sulfur containing amino acids such as methionine and cysteine (Tabatabai and Bremner 1972).

In the eastern mining regions of the United States, due to the high pyrite-sulfur to organic-sulfur ratio, organic-sulfur has traditionally been thought to lead simply to the formation of sulfate ions with no effect on acidity (Barnes and Romberger 1968). However, stoichiometric analysis suggests that organic sulfur amines may produce three moles of H^+ per mole of cysteine. The non-amine methylmercaptan could potentially produce two moles of H^+ per mole of organic sulfur compound (Dollhoff 1982). If these reactions do occur in the natural minesoil environment, these relationships suggest that the oxidation of organic-sulfur may generally produce approximately one-third of the amount of acidity as pyrite oxidation.

As in eastern regions, pyritic-sulfur may be the primary culprit in the formation of acidity in the West. However, on average pyritic-sulfur may comprise only one-third of the total sulfur content of western minesoils (Schnitzer 1983). Therefore, due to substantial climatic and geologic depositional differences between these regions, organic sulfurs may be playing a role in the acid production phenomena in the west (Schnitzer and Fransway 1982).

Pyritic Sulfur Determination in Soils

As acid production is intimately associated with the rate of pyrite oxidation (Pionke et. al. 1980) an analysis of total pyrite sulfur has traditionally been made on overburden and mine wastes to determine the acid production potential of these materials. Dacey and Colbourn (1979) evaluated twelve direct and indirect methods of pyrite determination and reported that three procedures were most useful: 1) a sequential nitric acid oxidation; 2) a carbonate/bicarbonate roast; and 3) a high temperature oxidation (e.g. LECO) method. A hydrogen peroxide oxidation method, rejected by Dacey and Colbourn, was modified by O'Shay (1982) to increase this method's reproducibility. However, when a sample contains organic matter, this method may overestimate a sample's potential to produce acidity. Consequently, the most widely accepted procedure of pyritic sulfur determination in the west is high temperature oxidation. This method is recommended by the State of Wyoming which requires the determination of acid production potential (Schnitzer and Fransway 1982).

Acid Spoil Metal Toxicity

To reduce the pollution hazard to air and water, acid mine wastes must be stabilized; revegetation is the most preferable method of attaining this objective (Dean et. al. 1974). Vegetation establishment is difficult due to low water holding capacity and poor soil structure. However, the chief limiting factor may be the extreme acidity of some of these materials. The inhibitory effects of low pH

are generally created by secondary causes including an excess of soluble aluminum and manganese, and shortages of available calcium and phosphorus. Acid mine wastes also commonly have elevated levels of iron, copper, nickel, and zinc which may be inhibitory to plant establishment (Barnhisel and Massey 1969).

Lime Amendment Effects

To ameliorate the inhibitory concentrations of heavy metals, lime application to increase soil pH seems necessary to provide a suitable growing medium (Johnston et. al. 1975). MacLean and Decker (1976) reported that metal toxicity restricted growth on six acid pyrite-bearing mine waste samples when inadequate lime was added. However, vegetation response to liming may vary between species. Studies by MacLean and Finn (1967) indicated that the restricted growth of buckwheat (Erigonum flavum) was probably associated with excess magnesium (Mg) in the liming material and with an abnormally low ratio of Ca to Mg in the plants. On the other hand, MacLean and Decker (1976) reported that heavy metals presented no problem to Reed Canarygrass (Phalaris arundinacea) where sufficient lime was used to maintain the pH of the tailings at a level approaching the neutral point. This relationship was in accord with the recognized relationship between pH and metal solubility in soils (Mortvedt et. al. 1972).

The main effects of liming are the provision of adequate soil calcium and hydroxyl ions (5).

$$CaCO_3 + H_2O = Ca^{++} + HCO_3^- + OH^- \quad (5)$$

(Bohn et. al. 1979)

The hydroxyl ions produced from the lime serve to neutralize acidity and raise soil pH. The increased quantities of soluble and exchangeable Ca and Mg are only by-products of liming, although their greater amounts in limed soils may be beneficial to Ca-loving plants such as legumes (Bohn 1979).

Lime reactions with acid, pyritic spoils are unlike those with acid agricultural soils (Grove and Evangelou 1982). In spoils, the oxidation of pyrite generates considerable free acid (6).

$$4\ FeS_2 + 15\ O_2 + 14\ H_2O = 4\ Fe(OH)_3 + 8\ H_2SO_4 \quad (6)$$

The acid released reacts with lime ($CaCO_3$),

$$H_2SO_4 + CaCO_3 = CaSO_4 + H_2O + CO_2 \quad (7)$$

and may produce large quanitites of salts, usually sulfate salts. In an acid, well leached agricultural soil, no salt is generated (8). The added calcium is bound to colloid exchange sites.

$$2(\text{clay-Al}) + 2(\text{clay-H}) + 4CaCO_3 + 2H_2O = 4(\text{clay-Ca}) + 2Al(OH)_3 + 4CO_2 \quad (8)$$

(Grove and Evangelou 1982)

If enough soluble salts are present, seed germination, seedling survival and subsequent plant growth and development may be reduced or prohibited. Calcitic lime ($CaCO_3$) has been reported to be the most effective at reducing the release of soluble Mg salts (Grove and Evangelou 1982).

High initial lime applications a common practice in minesoil reclamation, which greatly increases soil pH (>7.5) may also have

detrimental effects on soil fertility. High lime application rates, through the effects of mass action and macro-micro element interactions may induce deficiencies of such essential elements as boron, magnesium, phosphorous, potassium and manganese. Thus, fertilization often must accompany lime applications on mine soils.

The problem of disposing high pH fly ash produced from electric generating stations has recently inspired research on the use of fly ash as a liming agent on acid mine spoils. However, on coal mined spoils with lime requirements of only 2-20 MT/ha, Adams et. al. (1971) reported that more than 1250 MT/ha of fly ash may be required to neutralize this material. Fly ash is also very poor in essential plant nutrient content, and often contains large quantities of B, Mn, and Al which may be toxic to plant growth. Thus, fly ash may not be an economic or logistic alternative to more traditional liming materials.

Lime Requirement Determination

Agricultural lime determination methods which are based on existing and exchangeable acidity (Dunn 1943, Woodruff 1948, Shoemaker et. al. 1961, Peech 1965, McLean et. al. 1966) generally underestimate the lime requirement of mine wastes where the major source of acidity is the oxidation of pyritic materials. This may lead to the subsequent reacidification of mine wastes and the failure of revegetation efforts (Richardson 1980, Sorensen et. al. 1980, Ogram and Fraser 1978).

The traditional method of determining the lime requirement of acid mine wastes was defined by Smith et. al. (1974) as acid-base

account. Smith reported that material containing 0.1% sulfur, all as pyrite, would yield a quantity of sulfuric acid upon complete oxidation, that would require 3.125 tons of $CaCO_3$ to neutralize 1000 tons of material. In this method, total sulfur is determined by LECO induction furnace, while pyrite sulfur (FeS_2) determination is based on the analysis of iron and extrapolation of sulfur content. Sulfate-sulfur is dissolved and removed with weak hydrochloric acid (HCl). Pyritic iron is insoluble in weak HCl but soluble in strong nitric acid (HNO_3). The difference, Fe(HCl) - Fe(HNO_3) is assumed equivalent to the pyritic iron and consequently to pyritic sulfur. The lime requirement is then estimated by subtracting the neutralizing bases ($CaCO_3$ equivalents) present in the material, as determined with acid-base titration, from the total lime required to neutralize the acid production potential from the pyritic-sulfur content of the material. In situations where all the sulfur present is not pyritic (e.g. western mine soils) Sobek et. al. (1978) provided a procedure for sulfur analysis which would eliminate HCl extractable and non-extractable forms of sulfur not considered to be acid formers. In this method, total sulfur is again determined by LECO induction furnace. However, HCl and HNO_3 soluble sulfur is also determined directly by LECO analyses. Pyritic sulfur is then calculated as the difference between HCl and HNO_3 - extractable sulfur levels.

In determining the lime requirement for the Blackbird Mine in Idaho, Sorensen et. al. (1980) utilized simulated laboratory weathering procedures which increased the amount of reactive (potentially acid producing) sized particles. The total lime requirement was then

determined by the sum of the buffer lime requirement (Shoemaker et. al. 1962) plus the sulfide oxidation lime requirement (LECO) of the reactive fraction and the material which may be made available to oxidation through weathering.

Simulated Weathering

As acid production in mine waste material is influenced by the oxidation of different crystalline forms of pyrite, massive versus framboidal, and the oxidation of non-sulfide sulfur (e.g. organic sulfur), total pyrite concentrations may not be a reliable indicator of potential acidity (Colbourn 1980). Therefore, to more accurately predict acid production in mine soils laboratory weathering studies have been developed.

Laboratory leaching studies are an attempt to simulate on a rapid scale the chemical weathering of overburden and mine waste materials. The first apparatus which controlled the rate and volume of the leaching solution was the soxhlet extractor used by Pedro (1961), and later by Henin and Pedro (1965), and Williams and Yaalon (1982). Singleton and Lavkulich (1978) modified the design of the soxhlet but did not overcome the high extraction temperature requirement, which did not represent a realistic simulation of natural weathering. A further modification was proposed by Sobek et. al. (1982) in an attempt to reduce the high temperature requirement to allow the study of the bacterial role (e.g. Thiobacillus) in the weathering process.

To quantify the acid production potential from coal and overburden materials, Hanna and Bryant (1962) developed a basic cell leaching chamber. Caruccio (1968) modified the technique of Hanna and Bryant and proposed the humidity cell, in which samples were placed in humified plastic containers and flushed at regular intervals with deionized water. These cells provided simple control over air, temperature, moisture, and microbes. Since its development, the humidity cell has been used in numerous studies (Caruccio and Geidel 1981, Caruccio 1980, Caruccio et. al. 1980, Geidel 1979, Smith et. al. 1974). However, procedures for utilizing the humidity cell were not well documented until Sobek et. al. (1978) provided detailed laboratory procedures.

Laboratory weathering cells (humidity cells) allow the creation of conditions favorable to the formation of acid by simulating natural conditions of a mine-site. In such, the impacts of all acid producing materials, not just pyritic sulfur concentration, may be monitored.

METHODS AND MATERIALS

Laboratory Analysis of Field Samples

Soil, waste rock and tailings material were evaluated with respect to various chemical and physical characteristics. A summary of the laboratory analyses performed, procedures utilized, and references are presented in Table 1. Water soluble elements were evaluated by comparison with the water quality criterion established by the U.S. Public Health Service (USPHS) for aquatic life, irrigation waters, livestock and public drinking supplies (U.S. Dept. HEW 1962, U.S. EPA 1976, Nat'l Academy of Sciences and Engineering 1972, McKee and Wolf 1968) (Table 7 - Appendix A). Extractable elements were evaluated by comparison with the Montana Department of State Lands criteria for suspect levels within overburden materials (Table 8 - Appendix A).

Cation exchange capacity (CEC) of these samples was determined by summation of exchangeable bases and exchangeable acidity (Black et. al. 1965). The ammonium acetate (NH_4OAc) was buffered to pH 3.6 for all materials with pH < 5.5 (as determined in a saturation paste extract), and at pH 7.0 for materials with pH > 5.5.

Total and pyritic sulfur was determined on air dried samples that had been dry sieved to pass a 60 mesh (<.25 mm) screen. Total sulfur was determined by LECO Sulfur Analyzer (Table 1). Pyritic sulfur was determined by analysis of iron and extrapolation of sulfur

Table 1. Laboratory procedures for analysis of soil, mine wastes, and tailing materials.

PARAMETER	PROCEDURE	REFERENCE
Ca, Mg, Na, Zn, Cu, Mn, Fe, Pb, Cd, Ni	Water Soluble	Black et. al. (1965) A.S.A. Monograph #9 Part 2 p. 1015
Ca, Mg, Na, Zn, Cu, Mn, Fe, Pb, Cd, Ni	Amonium Acetate Extractable	Ibid. p. 894.
Mercury	Acid Soluble Soil Hg	Manual of Methods for Chemical Analysis of Water and Wastes EPA-600/4-79-020
Selenium	Hot Water Extracable	Black et. al. (1965) A.S.A. Monograph #9 Part 2, p. 112
Nitrate-N	Chromotropic Acid	Ibid. pp. 1212-1214
Molybdenum	Acid Amonium Oxalate	Ibid. p. 1056
pH	Water Saturated Paste Extract-Electrode	Ibid. p. 920
Sulfate	Water Saturated Paste Extract-Turbidimetric	Ibid. pp. 1108-1110
Phosphorous	HCl and Sulfuric Acid Extraction	Ibid. p. 1041
Particle Size	Hydrometer	Ibid. p. 549
Sodium Adsorption Ratio (SAR)	Water Soluble Calculated $Na/[(Ca + Mg)/_2]^{\frac{1}{2}}$ meq/l	U.S.D.A. Handbook 60, p. 156
Electrical Conductivity (EC)	Water Saturated Paste Extract	Ibid. p. 8
Cation Exchange Capacity (CEC)	Summation	Black et. al. (1965) A.S.A. Monograph #9 Part 2 p. 900.
Total Sulfur	LECO Sulfur Analyzer	A.S.T.M. D2492-79 p. 332
Pyrite Sulfur	Fe (HNO_3) - Fe (HCl) Leachate	Smith et. al. (1974) EPA-670/2-74-070 p. 72
Pyrite Sulfur	S (HNO_3) - S (HCl) Leachate	Sobek et. al. (1978) EPA-600/2-78-054 p. 60
Organic Sulfur	Difference [(Total S) - (FeS_2 - S) - (SO_4-S)]	A.S.T.M. D2492-79 p. 332
Neutralizing Potential		Smith et. al. (1974) EPA-670 2-74-070 p. 72

content (Smith et. al. 1974) and also by the calculation of the difference between HCl-extractable and HNO_3-extractable sulfur (Sobek et. al. 1978). Organic sulfur was calculated as the difference between total-sulfur minus sulfates and pyritic-sulfur. Neutralization potential was determined by treating the samples with a known excess of HCl, heating to insure complete reaction, and titration with sodium hydroxide (Smith et. al. 1974). These values were used to compute the acid-base account for the various mine waste materials.

For this study, it was assumed that the oxidation of one mole of organic sulfur may contribute up to one-third the acid generated by the oxidation of one mole of pyritic sulfure. Therefore, the acid production potential of mine waste materials in this study was determined from sulfur analyses utilizing the following equation:

$$APP = (\%\ \text{pyrite-S})(31.25) + (\%\ \text{organic-S})(10.0) \quad (9)$$

(Smith 1974, Dollhopf 1982)

Where APP is the acid production potential in terms of tons $CaCO_3$ per 1000 tons of material.

The acid production potential was then compared to the inherent neutralization potential of the mine waste material to calculate the acid-base account and develop a lime requirement recommendation.

The SMP buffer agricultural lime determination method (Shoemaker et. al. 1962) was used as a comparison to the acid-base accounting procedure.

Cement plant flue dust from the Ideal Cement Company, Trident, Montana, (Table 2) was utilized as the lime agent because of its high

neutralization potential (86% $CaCO_3$ equivalents) and ease of availability.

Table 2. Physical and chemical analysis of cement plant flue dust.

Particle Size	Oxide Content	
-.60 mm 100%	CaO = 42-48%*	MgO = 1.2%
-.30 mm 99.5%	SiO_2 = 15.8%	K_2O = 2-4%
-.15 mm 95%	Al_2O_3 = 3.5%	Na_2O = 0.2-0.4%
-.015 mm 75%	Fe_2O_3 = 2.0%	

*Equivalent to 86% $CaCO_3$.

Laboratory Weathering Study

Bulk samples of tailings, native soil, and waste rock material chosen for the weathering study were obtained from the Champion Mine, Deerlodge County, Montana, and were selected by judgment to represent the typical material in this project area. These samples were air dried, sieved and 200 grams of the less than 2 mm fraction were evenly spread throughout replicated weathering chambers (Sobek et. al. 1978).

The weathering chambers were constructed of 4 mm (1/8") thick plexiglass sheets and were approximately the sixe of a shoe box (30 cm x 15 cm x 10 cm). Tygon tubing, (8 mm O.D.), connected to a forced air source, supplied a continual air flow over the samples. Humidified air was obtained by running air through an aerating stone in a 125 ml erylenmeyer flask half filled with distilled water. Figure 2 shows a diagram of the weathering appratus.

The weathering procedure involved a seven day cycle of alternate dry-moist air being passed over each sample (Sobek et. al. 1978). On the seventh day, 200 ml of distilled water were added to each sample,

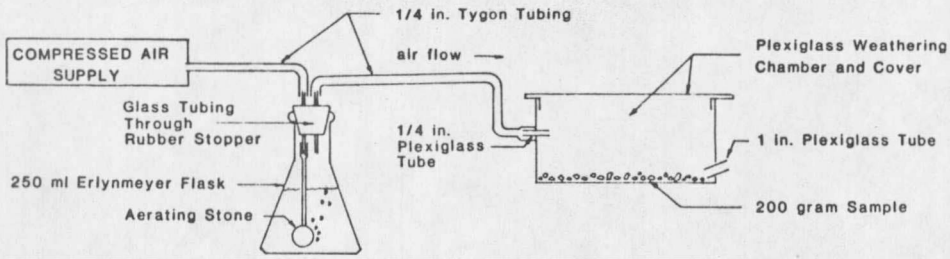


Figure 2. Diagram of weathering chamber apparatus.

agitated with an Eberbach shaker for one hour at 65 strokes per minute, then drained and centrifuged at 1700 RPM for five minutes. The supernatant was monitored for pH, electrical conductivity (EC), and titratable acidity (Table 3).

Table 3. Laboratory procedure for the analysis of mine waste materials following simulated weathering.

PARAMETER	PROCEDURE	REFERENCE
pH	Decanted Extract-Electrode	Rand, M. C. et. al. (1975) pp. 461-465
Electrical Conductivity (EC)	Decanted Extract	U.S.D.A. Handbook 60, p. 8
Titratable Acidity	Titration	Sobek et. al. (1978) EPA-600/2-78-054. p. 184

The soil material was returned to the weathering chamber and the cycle repeated weekly for 28 weeks. The titratable acidity was then converted to calcium carbonate equivalents to calculate the amount of lime needed to neutralize the acid generated from each weathering period (Table 9 - Appendix A).

To create conditions optimum for acid production, each sample was thoroughly moistened and inoculated with 14 ml of an aqueous solution containing Thiobacillus ferrooxidans. Acid water samples were collected from the Sand Coulee Coal Mine, Sand Coulee, Montana, and transported to the Reclamation Research Unit, Bozeman, Montana, in an iced cooler. The bacteria were then cultured following the procedure of Silverman and Lundgren (1959). This solution was then incubated at 30 degrees Celcius for 4 weeks before inoculation of each sample. Following the entire weathering period, a most probable number (MPN) determination was made on these bacteria (Gerhardt 1981).

SITE CHARACTERIZATION

Characterization of the Champion Mine

The Champion Mine is located in the Orofino Creek drainage along the continental divide in southwestern Montana and occupies approximately 2.5 hectares. The area was initially opened to mining during the period 1886-1888. The mine was inactive from 1889 to 1920 at which time the mine reopened, but operations then ceased in June 1923 due to low silver prices. The ore body consisted of a silver bearing quartz vein, 1-8 feet wide, in quartz monzonite country rock. The area receives approximately 56 cm (22 in.) of annual precipitation mostly in the form of Spring, Summer and Fall rains. The undisturbed soil near the Champion Mine may be classified as a Sandy Mixed Typic Cryochrept (Deckler 1982). Vegetation in the area is a mixed coniferous forest with little or no vegetation growing on the waste materials.

The mine disturbance may be divided into an upper waste rock area and lower tailings area. The upper waste rock consists of two types; an extremely acid (pH 2.7) sandy loam textured material, and a near neutral (pH 7.05) sand textured material, which is considered an unsuitable rooting medium because of its high sand content (>80%) and associated low saturation percentage (<20%). The lower tailings material was sampled from three locations and revealed appreciable differences in texture, ranging from loam to silty clay loam (Table 10 - Appendix B). All three of the tailings samples were extremely

acidic (pH 3.0) and so, were treated as a bulk sample for the weathering study. Deckler (1982) classified the mill tailings material from the Champion minesite as Silty to Sandy Mixed Typic Cryofluvents. The electrical conductance of most of the sampled materials was well within the accepted range of salt tolerance of forage species.

Water soluble and ammonium acetate extractable elements are given in Tables 11 and 12-Appendix B). Despite the low pH of the mill tailings and acid waste rock materials, these analyses did not generally reveal inhibitory metal concentrations. Aluminum and manganese concentrations, as expected in low pH soils, appeared elevated. The high manganese levels in both water soluble and ammonium acetate extractable analyses, however, appeared to be offset by much higher calcium levels which would mitigate the inhibitory effect of elevated manganese (Foy et. al. 1969). Other analyzed elements did not appear to be at inhibitory levels.

X-ray difraction analyses did not indicate the presence of pyrite, but because this method is incapable of determining components present in amounts less than five to ten percent, it would have likely overlooked any present. Thin section mineralogical analyses (Table 13 - Appendix B) revealed that quartz dominated the mill tailings and native soil materials and a considerable percentage of it was iron stained and zone weathered. The exact percentage of K-feldspar in these samples was not determined but was likely less than five percent. Thus, the primary acid producing compound within the mill tailings material may be very fine residual pyrite particles. After, 50-90 years of weathering, however, much of the original

pyrite may have been altered to other compounds, mainly hydrated iron oxides such as goethite [FeO(OH)].

RESULTS AND DISCUSSION OF WEATHERING STUDY

Acid-Base Account

Results of the acid-base account for the mine wastes from the Champion Mine site are presented in Table 4. These data indicate that the acid waste rock (pH 2.75) and mill tailing (pH 2.95) materials possessed net acid producing potential. The gray waste rock (pH 7.05) and native soil (pH 6.21) materials included in this study showed a net excess in base equivalents.

Table 4. Acid-Base Account for Champion minesite based on procedure of Smith et. al. 1974.

		Metric Tons $CaCO_3$/ha/15cm			
Material	pH	Lime Req. for total neutralization of material acidity	Lime present in material	Lime needed to neutralize	Excess Lime equiv.
Acid Waste Rock (10YR 5/8)*	2.75	50.10	0.00	50.10	---
Mill Tailings (5YR 8/2)*	2.95	21.45	0.00	21.43	---
Gray Waste Rock (5FY 4/1)*	7.05	33.75	56.75	---	23.00
Native Soil 10YR 2/2*	6.21	8.50	20.43	---	11.93

*Munsel color notations for mine waste and native soil materials.

Lime Requirement Determination

The amount and composition of sulfur within mine waste materials is paramount to the prediction of their acid production potential (equation 9). Results of sulfur fractionation analyses in the Champion mine waste materials are presented in Table 5. These results indicate that the methodologies employed in this study (Smith et. al. 1974 and Sobek et. al. 1978) differ greatly in their estimates of the compositional make-up of sulfur within these materials.

Table 5. Sulfur analyses for Champion minesite based on procedures of Smith et. al. (1974) & Sobek et. al. (1978).

Material	% Total Sulfur Smith	Sobek	% Pyritic Sulfur Smith	Sobek	% Organic Sulfur Smith	Sobek
Waste Rock	1.57	1.40	0.30	0.10	1.27	0.21
Mill Tailings	0.71	0.09	0.11	<0.01	0.60	<0.01
Gray Waste Rock	1.19	0.03	0.14	<0.01	1.05	0.03
Native Soil	0.12	0.01	0.12	<0.01	0.00	<0.01

Based on these sulfur analyses and the neutralization potential of these materials (Table 4) the lime requirement as predicted by the methodologies of Smith et. al. (1974), Sobek et. al. (1978) and Shoemaker et. al. (1961) are presented in Table 6. These data indicate a wide difference in the amount of lime needed to neutralize the acid production on the Champion mine site. For example, in the acid waste rock material Smith's method estimated that 50.1 MT of lime/ha/15 cm was needed to neutralize this material, while Sobek's method

Table 6. Required lime rates as determined by acid-base accounting and agricultural methods.

	Metric Tons $CaCO_3$ to Neutralize 15 cm/Hectare		
Material	Smith (1974)	Sobek (1978)	SMP-Buffer (1962)
Waste Rock	50.10	12.05	30.91
Mill Tailings	21.43	1.1	28.78

suggested that 12.05 MT were required. The SMP method, on the other hand, estimated that 30.91 MT would be required.

To accomodate these differences in rates of lime amendment the acid mine waste materials were limed at a low and high rate with no lime amendment considered a third treatment. The acid waste rock material was limed at the low rate of 13.47 MT/ha (6 tons/acre) and the high rate of 40.86 MT/ha (18 tons/acre). The acid mill tailings material was limed at a low rate of 2.27 MT/ha (1 ton/ acre) and a high rate of 27.24 MT/ha (12 tons/acre).

Laboratory Weathering

Data to show the effects of laboratory weathering on the monitored parameters of electrical conductivity (EC) and hydrogen ion activity (pH) on the mine waste materials and native soil from the Champion minesite are graphically presented in Figures 3-6. Analyses of variance (ANOV) were performed and least significanct differences (LSD) calculated to ascertain whether the relationships illustrated were statistically significant over time and between treatments (Tables 14-27).

Over the first 12 weeks of laboratory weathering, the three treatment levels of no lime, low lime, and high lime were monitored

for all parameters on the two acid materials. Following week 12, the monitoring of the high lime treatment on the acid materials was discontinued as was weathering of the two non-acid materials. Regression analyses were performed after 28 weathering cycles on the titratable acidity liberated from both acid soil materials with the no lime treatment to predict the lime requirements of these materials.

Non-Acid Materials

ANOV analyses were run on the two non-acid materials, gray waste rock and native soil, examined in this weathering study (Tables 14-17). Significant differences at the 95% level were found in both of these materials through time for EC and pH over 12 weeks of weathering.

LSD analyses over time on the gray waste (Table 14) indicated that EC was not significantly different after week 5, and the pH (Figure 3) showed very little statistical stability over 12 weeks time (Table 15). LSD analyses on the undisturbed native soil showed EC stable after week 5 (Table 16), and pH stable after week 8 (Table 17).

Figure 4 shows that for both of the non-acid materials salt concentration is less than the hazardous level (<4 mmhos/cm) and decreases over time. Thus, the weathering of these materials would not be expected to produce inhibitory salt concentrations.

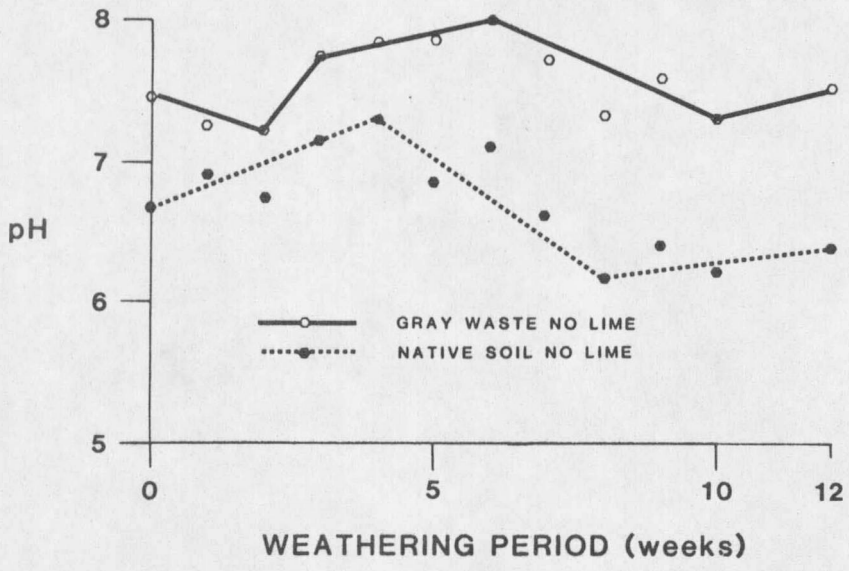


Figure 3. Hydrogen ion activity (pH) of non-acid mine waste and soil materials over time from the Champion minesite.

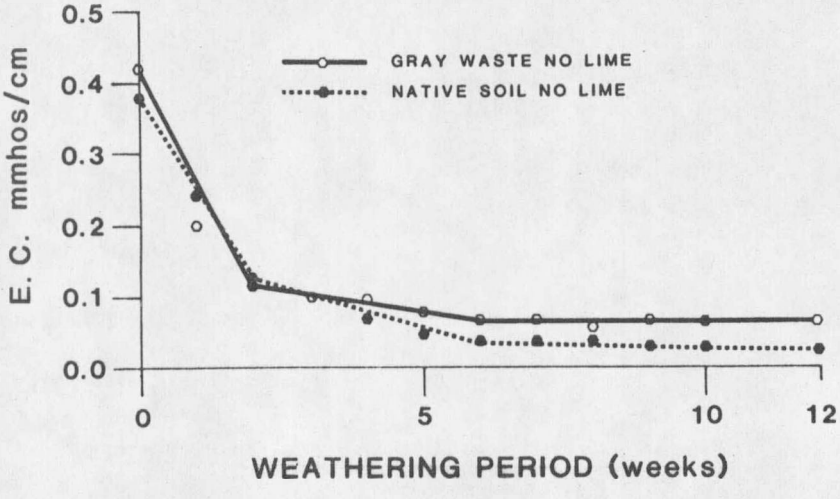


Figure 4. Electrical conductance of non-acid mine waste and soil materials over time from Champion minesite.

No titratable acidity was generated from the gray waste rock material through 12 weeks of laboratory weathering. The native soil with a pH of less than 7.0 may have liberated minute amounts of titratable acidity, but, because this material was not to be amended no titratable acidity measurements were made.

Acid Materials - EC

The oxidation of pyritic sulfur (equations 1-4) and organic sulfur containing compounds produces H+ ions and consequently sulfuric acid (equation 6), which may react with carbonate and silicate minerals and/or a liming agent (e.g. $CaCO_3$) to produce salts, primarily calcium sulfate salts. One hypothesis tested in this study was that lime amendments applied on acid mine waste materials may increase soluble salt concentrations. This hypothesis was evaluated using the parameter of electrical conductance which allowed the monitoring of changes in total soluble salt concentration over time and between lime treatments (Figure 5).

Analyses of EC over 12 weeks of weathering the acid waste rock material indicated a significant (95%) difference over time, treatment and time x treatment interaction (Table 18). LSD analyses showed no significant differences in salt generation between 13.47 MT/ha and 40.86 MT/ha lime amendments, but the EC of the non-limed material was significantly higher than the two limed treatments.

Analyses over 28 weeks of weathering the acid waste rock with no lime and low lime (13.47 MT/ha) treatments also revealed significant differences over time, treatment, and time x treatment interactions

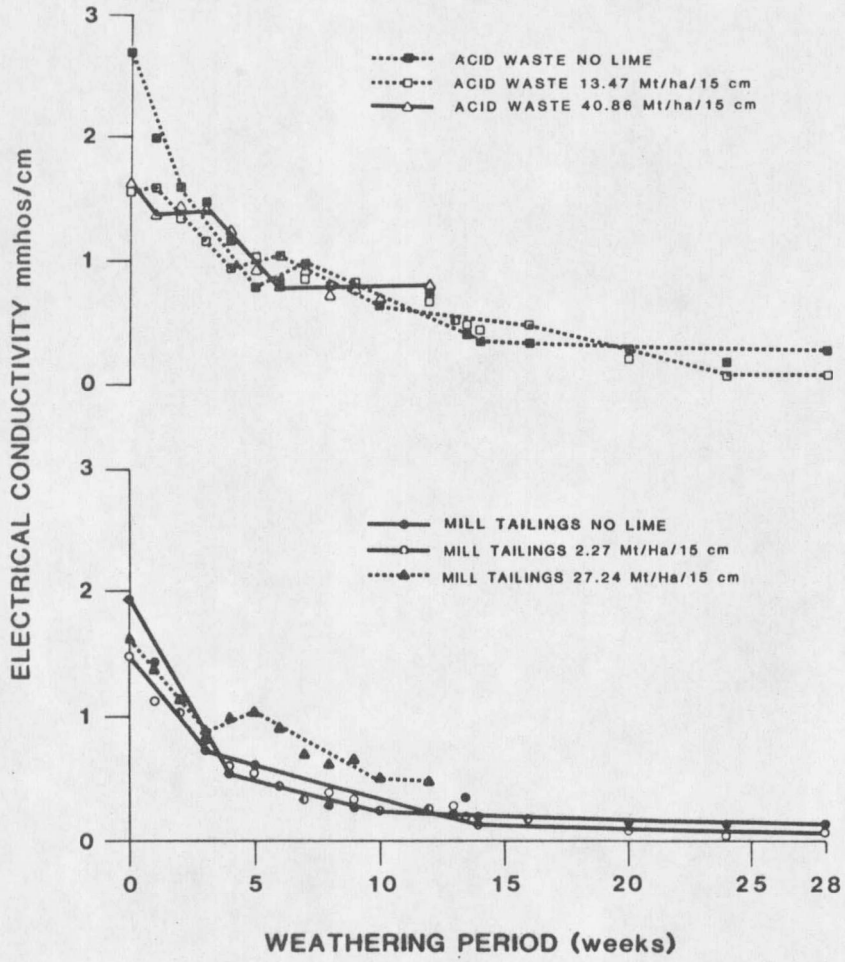


Figure 5. Electrical conductance of acid mine waste materials over time from the Champion minesite. Std. error mean 3 reps. waste rock = .04, tailings .05.

(Table 19). The no lime amendment maintained a significantly higher EC value than the low lime treatment over 28 weeks of weathering at the 95% confidence level.

In the acid mill tailings material analyses of variance on EC (Table 20) revealed a significant difference over time, treatment, and time x treatment interaction over 12 weeks of weathering. LSD

calculated for each treatment indicated that the EC of the high lime treatment (27.24 MT/ha) was significantly higher after 12 weeks than those treatments of no lime and 2.27 MT/ha lime which were statistically similar.

Over 28 weeks of weathering the mill tailings material, time, treatment (no lime and 2.27 MT/ha), and time x treatment interactions were significant at the 95% level (Table 21). LSD analyses showed that the no lime treatment had an EC significantly (95%) higher than the low lime treatment (2.27 MT/ha).

Thus, in both the acid waste rock and mill tailing materials examined in this study EC was not increased by lime amendment. Figure 5 illustrates that EC decreased over time in all three treatments. Even though the high lime treatment in the acid tailings had a statistically significant higher EC, it was never more than 0.3 mmhos/cm greater than the no lime treatment, and was still following a general downward trend over time. In fact, comparison of LSD Analyses (Table 19, 21) on low and no lime treatments over 28 weeks of weathering showed a higher EC value in the no lime treatment in both acid spoil materials. Electrical conductance measures the total amount of ionized constituents (salts) within the minesoil. This result may be due to the weathering of indigenous calcium or magnesium containing compounds in the non-limed wastes which liberated Ca^{++} and Mg^{++} ions into solution. While in the lime treatment these same ions may have been associated with sulfate (a product of sulfur oxidation) as calcium or magnesium sulfate, and thus the measurement of EC would not indicate an increase in total salts.

This refutes the tested hypothesis and suggests that the use of calcium oxide (CaO) in the form of cement plant flue dust will not notably increase total salt generation in these mine waste materials. These results support the work of Grove and Evengelou (1982) who reported that calcitic liming agents were most effective in reducing the generation of soluble salts.

Acid Materials - pH

Hydrogen ion activity (pH) may control the occurence of catalyzing bacteria and affect the preservation or dissolution of pyrite stabilizing carbonates, as well as the solubility of heavy metals. The control of minesoil pH then, may be intimately associated with mitigating the effects of acid mine drainage and ameliorating revegetation difficulties associated with low pH in the rooting zone. Figure 6 illustrates the effect of weathering over time and between lime rate amendment on minesoil pH.

ANOV on pH over 12 weeks of weathering the acid waste rock material (Table 22) showed no significant differences in pH over time, but treatment and time x treatment interactions were significant at the 95% level. LSD analyses indicated that pH levels over the three treatment rates were significantly different. As expected the high lime rate (40.86 MT/ha) had the highest pH and no lime treatment the lowest.

Analyses of pH over weeks 1-28 on the acid waste rock showed that time was not significant (95%) for this material when the no lime and 13.47 MT/ha lime amendments were analyzed together. However, LSD

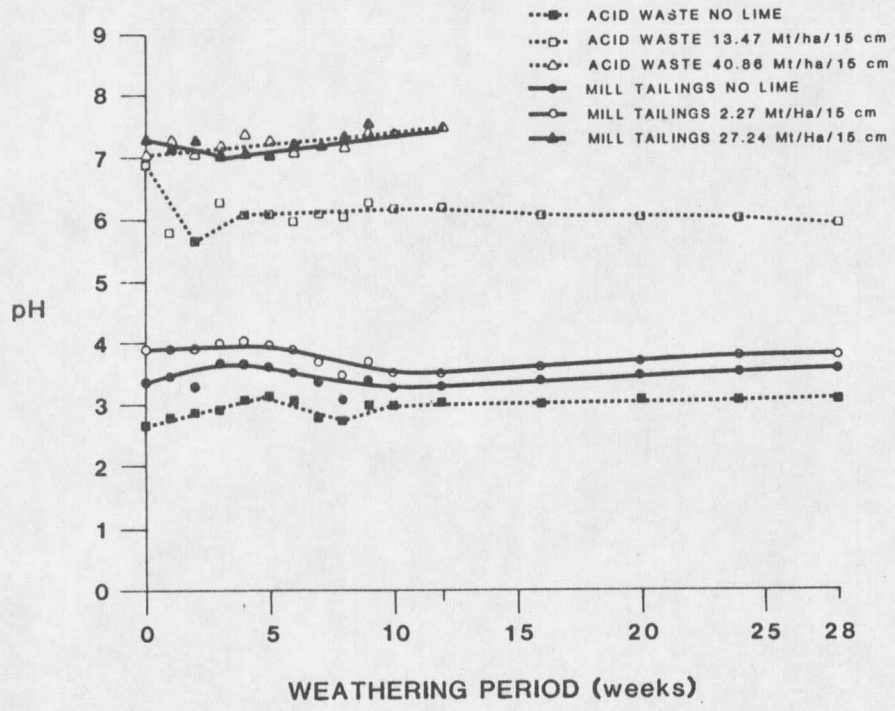


Figure 6. Hydrogen ion activity (pH) of acid mine wastes over time from Champion minesite. (Std. error mean 3 reps. waste rock = .19, tailings .15).

analyses on each treatment separately (Table 23) revealed that there was a significant difference in pH over time. This difference was most meaningful in the low lime treatment and suggests that there was a significant decrease in pH during the first three weeks of weathering following 13.47 MT/ha lime amendment.

In the acid mill tailings material, ANOV on pH over the first 12 weeks of the weathering study showed a significant difference over time, treatment and time x treatment interaction (Table 24). Calculated LSD analyses revealed that the pH of the high lime treatment

was significantly (95%) higher than the pH of the low and no lime treatments which were statistically similar. Over 28 weeks of weathering there was no significant difference in pH between no lime and 2.27 MT/ha treatments (Table 25).

The acid-base account methodlogy of Smith et. al. (1974) estimated that 50.10 MT/ha (22.0 T/A) of lime would be required to neutralize a 15 cm hectare slice of acid waste rock material. Limed at the high rate of 40.4 MT/ha this extremely acid material (pH 2.75) maintained a pH above 7.0 during 12 weeks of laboratory weathering (Figure 6). This suggests that this lime rate provided more than adequate supplies of Ca++ and OH-ions to neutralize the acid generated by sulfur oxidation, and may have been in excess of the true lime requirement needed to neutralize this material. Amended at a rate of 13.47 MT/ha (6.0 T/A), as suggested by the acid base account methodology of Sobek et. al. (1978), the acid waste rock was nearly neutralized (pH 6.9) upon initial lime application. However, after two weeks of weathering the pH of this material dropped significantly to pH 5.8 before stabilizing at a pH of approximately 6.0. This suggests that 13.47 MT/ha of lime nearly neutralized this material, but because the pH was still below 7.0, some acidity was being generated and was apparently not accounted for by this acid base account method. As 13.47 MT/ha of lime nearly neutralized this material it appears that the SMP-buffer recommendation of 30.9 MT/ha may have exceeded the required rate for neutralization.

In the acid tailings material the high lime rate of 27.24 MT/ha as suggested by the SMP-buffer methodology, maintained a pH between

7.0 and 7.5 (Figure 6). As in the acid waste rock, this rate may have exceeded the true lime rate for neutralization of the acid tailings. The methodology of Sobek, which measures sulfur directly, suggested that 1.1 MT/ha of lime would neutralize this material. However, limed at approximately this rate (2.27 MT/ha) the pH of the acid tailings (pH 3.6) was not significantly different from the non-limed treatment (pH 3.4). This indicates that Sobek's methodology greatly underestimated the total lime requirement of the acid tailings material. The acid-base account procedure of Smith et. al. (1974) which extrapolates sulfur content from Fe analysis recommended 21.43 MT lime/ha. This value was between the SMP-buffer (28.78) and Sobek (1.1) lime rate recommendations.

Based on pH analyses, all three of the methodologies examined in this study identified materials which had net acid generating potential. However, none of these methods appeared reliably accurate in predicting the total lime required to neutralize these acid producing materials. These methods either underestimated the total lime requirement, sometimes severely so, or overestimated the total lime requirement.

Microbial Counts Following Weathering

A most probable number determination was attempted following 28 weeks of weathering on the acid tailings material. This is a qualitative procedure with bacterial populations being visually detected through precipitates in serial dilutions. No bacterial population of the genera Thiobaccillus were found viable. Thus, bacteria within

these samples and those introduced at the beginning of this study did not survive the weathering study.

Acid Generation Analysis

The acid generated over 28 weeks of laboratory weathering the acid mine waste materials from the Champion minesite is illustrated in Figure 7. Logarithmic regression analysis on the titratable acidity liberated from 28 weeks of laboratory weathering revealed significant correlations (P=.01) for both the acid tailings (r=.65) and acid waste rock materials (r=.77). Analysis of variance and F value comparisons using 1 and 34 degrees of freedom (Table 26) showed that the Y-intercepts of these two regression lines were not significantly different at the .01 level. This suggests that the initial amount of acidity generated by these two samples was statistically similar. Testing the homogeneity of the slopes (Steel and Torrie 1980) generated by logarithmic regression analysis (Table 26) revealed that the slopes of these two lines were again not significantly different (P=.01). The acid generated from these two mine waste materials, therefore, may be considered similar. An equation was computed to predict the acid production potential of these two materials:

$$\log \text{Acidity (mg } CaCO_3) = 67.91 + (-24.73) \text{ Week} \qquad (10)$$

$$r = .72 \qquad (P=.01)$$

After the first 4 and 6 weeks of laboratory weathering the acid waste rock and acid tailings material respectively, the acid generated weekly remained nearly constant (Tables 27 and 28). This

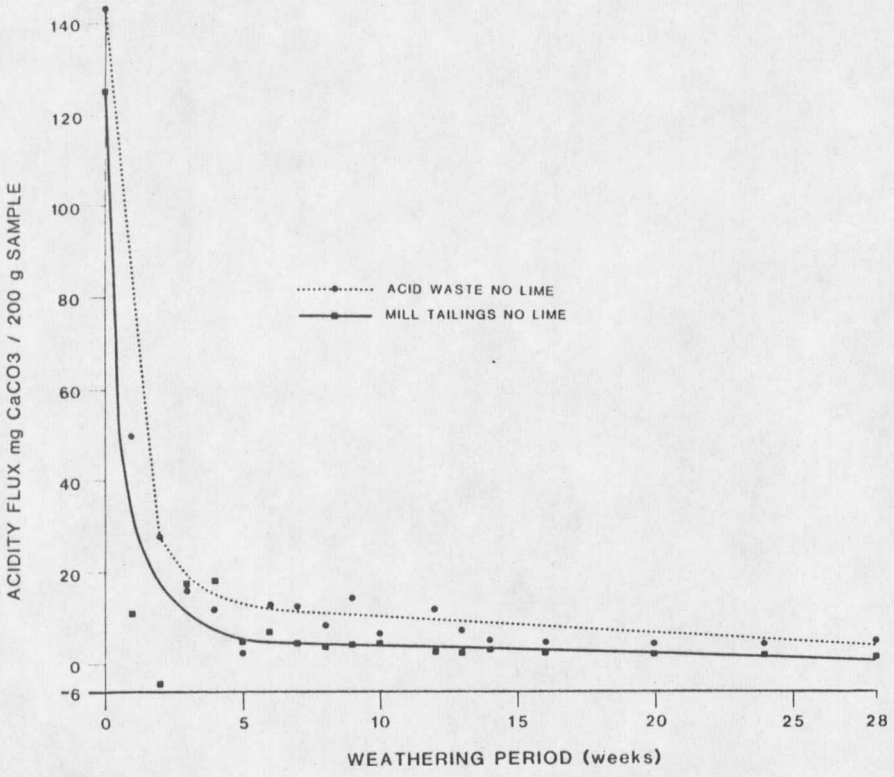


Figure 7. Acid generated over 28 weeks of simulated weathering of acid mine waste materials from the Champion minesite. After week 16 the samples were leached weekly but monitored monthly.

suggests that acid generation peaks during the initial stages (1-6 weeks) of laboratory weathering, then decreases, reaching some low level plateau as the weathering products of sulfur oxidation continue to be leached from the system. The flattening out of these titratable acidity curves (Figure 7) indicates that an indefinite time may be required to completely weather all the acid producing components from these spoil materials. This supports the work of Hanna and Bryant

(1962) who reported that the weathering of sulfur containing materials is a long degradation process, and that acid production may continue from such degradation for an indefinite time. Because of variations in acid and alkaline production kinetics, calculating an acid-base account without the consideration of long term weathering response may lead to erroneous lime rate recommendations. Thus, the laboratory weathering technique utilized in this study may avoid errors in interpreting acid-base account data, and provide a more reliable and accurate lime rate recommendation for acid spoil material.

Not all mine waste materials may be expected to liberate the same amount of acidity. However, associated weathering research by the author on other acid mine spoil materials, has shown that acidic hard-rock mine wastes may be expected to follow similar acid production trends as those presented here. There appears to be an initial high flux of acidity liberated during the first six weeks of laboratory weathering; followed by a characteristic curve after week six which levels out and then slowly decreases over time (Figure 7). Therefore, logarithmic curve fitting analyses may be employed to project a lime rate recommendation.

Lime Rate Recommendation

The main objective of this study was to determine the total lime requirement for these acid mine waste materials. Converting the titratable acidity liberated weekly to metric tons of lime per 15 cm hectare slice of material (Table 9 - Appendix A) allowed a lime rate to be computed. Assuming that there are three wet-dry cycles in the

natural environment of the Champion minesite annually, three weeks of laboratory weathering may represent one year of weathering in the field. Under this assumption a lime requirement projection may be made using a logarithmic curve fitting analysis of the weekly lime rate as determined from titratable acidity. Figure 8 shows the lime requirement over 28 weeks (9.33 years) of laboratory weathering as well as the projected lime requirement for these acid spoil materials. Because there was no significant difference in acid generation between the mill tailings and acid waste rock materials, the curve presented in Figure 8 represents the projected requirement for 100% pure $CaCO_3$ to neutralize both of these acid waste materials.

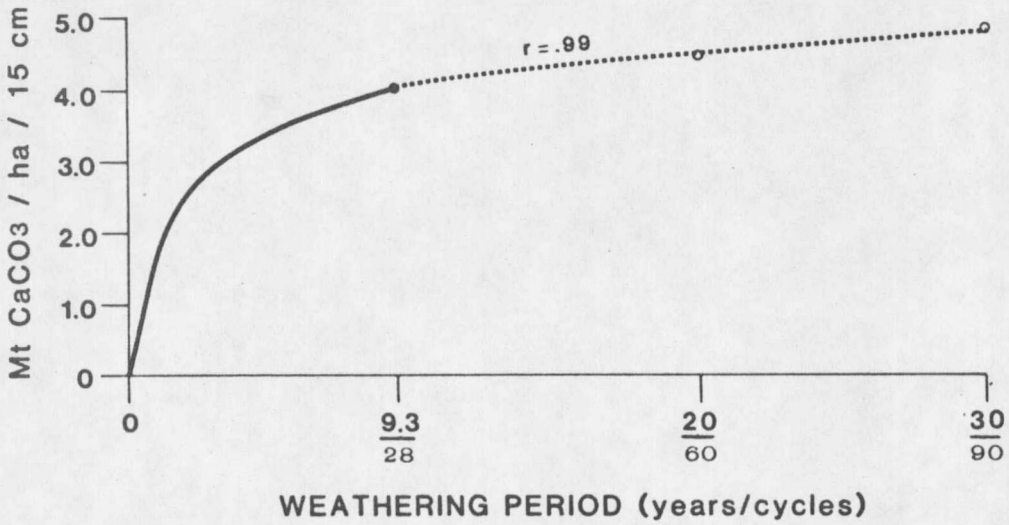


Figure 8. Lime rate requirement through 28 weeks of laboratory weathering and projected lime rate for acid waste materials from the Champion minesite.

Such a curve may be utilized to estimate an appropriate lime rate over a given time period to ameliorate adverse plant growth conditions associated with low minesoil pH. For example, liming these materials for the 20 year time period would require 4.57 MT/ha/15 cm. Such a lime rate in association with a sound fertilization program at time of planting should greatly enhance vegetation re-establishment. Applying lime to meet the estimated acid production for a given time period (e.g. 20 years) may be the most feasible approach to liming minesoils, especially where large amounts of lime are required.

It should be noted that acid-base accounting (Table 4) and the effects of lime amendment on the pH of these materials during the weathering study (Figure 5) suggest that higher lime rates may be required for complete neutralization (pH 7.0) of these materials than projected by this laboratory study. In acid-base accounting the acid production potential was evaluated on the pyritic - S content in the less than 60 M (.25 mm) size fraction. Framboidal pyrite (<.025 mm diameter), however, is the only form of pyrite that is considered acid producing. Therefore, some non-reactive massive pyritic - S may have been considered acid producing in the analyses of these materials. The generally higher acid-base account lime rate recommendations may also have been due to the high level of organic sulfur within these materials. Organic sulfur degradation may be a long-term process. Thus, the lime requirement as determined in this study may account for neutralization of a major proportion of only the acid produced from framboidal pyrite sulfur oxidation. Neutralization of this acid

producing fraction, however, may be paramount in the establishment of a healthy vegetative cover.

Lime application rates are a function of the purity of the lime agent, particle size, reactivity, and depth of incorporation. Not all liming materials are 100% pure, therfore, application rates must be adjusted for the percentage of inert impurities within the liming material. The effectiveness of a liming agent also depends upon the size of the individual particles. If they are coarse, the neutralization reaction will be slight, if they are fine, the reaction will be extensive. Meyer and Volk (1952) reported that the most efficient particle size of a liming material was the 60-80 mesh (.025-.18 mm) sized fraction. Because not all of the applied lime will be chemically available for neutralization, a correction factor of 25% is generally added to a lime application rate to adjust for the lack of quantitative displacement in the liming material. Finally, it is important that the applied lime be thoroughly mixed in the entire region of soil in which root growth is expected. This may be almost impossible when using deep rooted species for revegetation. However, with the equipment available today in the reclamation industry, it is possible to incorporate lime to a depth of approximately 60 cm (2 feet). Therefore, lime rates determined for a 15 cm/ha slice of material (as in this study) must be corrected for the depth of incorporation in the field.

The control and management of minesoil pH has been considered a vital component in successful reclamation of these disturbed areas. Many of the problems encountered in revegetation attempts have

centered on toxic concentrations of soluble heavy metals in the minesoil solution. These problems are only manifested at low pH, therefore, pH management has become a chief concern in the reclamation of hard-rock mine spoils.

Low soil pH, however, is not the direct cause of poor plant growth nor the main factor governing plant distribution or response to liming (Adams and Pearson 1967). Aluminum toxicity is often the major contributor to poor growth in acid mine waste materials. However, conditions necessary for the manifestation of aluminum toxicity have not been universally defined. Arnold and Johnson (1942) reported the best root growth in nutrient solutions between pH 4.0-5.0 when adequate calcium ions were supplied. Adams and Lund (1966) and Howard and Adams (1965) reported that many natural acid soils of the southern United States contain adequate calcium for most crops at pH ranges of 4.0-5.0. Martini et. al. (1977) concluded that liming oxisols of Brazil to a pH between 4.8-5.7 was more valid than raising soil pH to neutrality. Soils of these regions (oxisols and ultisols) are characterized by low soil pH, relatively low CEC, and high saturation with exchangeable aluminum, very similar to hard-rock mine waste materials. If hard-rock mine soils were treated not as temperate agricultural soils but rather as acid ultisols and oxisols, then liming to a pH of less than 7.0 may be a viable management objective. It is theorized that with adequate fertilization and liming to supply calcium ions, vegetation may be successfully reestablished on hard-rock mine spoil material at pH values less than 7.0. Further research should examine plant growth in acid hard-rock mine spoils limed to pH

values less than 7.0 (5.0+) and develop fertilization guidelines for these types of materials.

CONCLUSIONS AND RECOMMENDATIONS

Conclusion

Simulated weathering chambers were developed to verify lime rate predictions made from acid-base account data. The weathering study was designed to examine acid production potential of mine waste materials under weathering conditions similar to the natural minesite environment. These data support the hypothesis that because of variations in kinetics between acid and alkaline production, calculating an acid-base account without consideration of long-term weathering response may lead to erroneous lime rate recommendations. Caruccio et. al. (1980) concluded that the weathering and associated acid production potential of mine waste materials cannot always be accurately predicted by acid-base accounting. For example, the contribution of organic-sulfur oxidation to acid production in western minesoils has received little attention. Dollhopf and Russell (1984) using stoichiometric analyses suggested that organic-sulfur oxidation may potentially contribute 100% as much acid as pyrite-sulfur oxidation. However, it is uncertain as to which organic-sulfur compounds readily decompose and which are more resistant. It should be noted that acid-base account balances utilized in this study were based on the assumption that organic-sulfur compounds contribute one-third the acid production potential as pyrite-sulfur. This relationship has not been quantified and caution should be used in interpreting an

acid-base account when organic-sulfur is present in the material. Thus, the simulated weathering procedure utilized in this study may eliminate such potential errors in interpretation of acid-base account data, and provide a more accurate lime rate recommendation.

It should be emphasized that extrapolation of data from this weathering study to actual field conditions is speculative. Variables in the field cannot be totally controlled in a laboratory situation. These include: 1) microorganisms, 2) CO_2 and O_2 concentrations, and 3) temperature regime. However, analysis of these results and further work by the author, give reason to believe that trends may be predicted from simulated laboratory weathering of mine waste materials. There appears to be an initial acceleration of chemical weathering and acid production, but after 4 to 6 weeks of weathering, samples may adjust toward an equillibrium low level of acid production. Thus, mathematical projections may be made to estimate the total lime requirement of acid mine wastes using simulated laboratory weathering techniques.

Recommendations

The weathering procedure utilized in this study attempted to provide favorable conditions for acid production similar to those found in the natural minesite environment. To better simulate field conditions the author proposes the incorporation of a freeze-thaw cycle to enhance physical breakdown of minesoil samples. Such a cycle would increase the potential oxidation surfaces of mine soil materials and better simulate minesoil weathering processes.

The problem of sucessfully revegetating acid mine spoils goes beyond lime amendments for neutralization of these materials. Naturally occurring acid soils show adequate crop growth at pH values less than 7.0, research in acid hard-rock spoil reclamation should, therefore, address vegetation growth in spoil materials with pH values less than 7.0, and develop fertilization guidelines for these materials. Successful hard-rock spoil reclamation may be better achieved once these materials are treated not as temperate agricultural soils, but rather as naturally occurring acid soils such as the oxisols and ultisols.

Finally, "organic" sulfur is still an uncertain component of the total sulfur content in hard-rock mined land materials. Laboratory sulfur analyses are often in error because of this or other "unknown" sulfur fractions which lead to erroneous acid production estimates. Further research is needed to better identify these sulfur fractions and determine their contribution to the acid production potential in hard-rock mine spoils.

LITERATURE CITED

LITERATURE CITED

Adams, F. and Z. F. Lund, 1966. Effect of chemical activity of soil solution aluminum on cotton root penetration fo acid subsoils. Soil Sci. 101: 193-198.

Adams, F. and R. W. Pearson, 1967. Crop response to Lime in Southern United States and Peurto Rico. IN R.H. Pearson and F. Adams (eds.) Soil Acidity and Liming. Am. Soc. of Agron. Madison, WI, pp. 161-206.

Adams, L. M., J. P. Capp, and E. Eisentrout, 1971. Reclamation of acidic coal-mine spoil with fly ash. Report on Investigations 7504. U.S. Dept. of Interior, Bureau of Mines, Washington, D.C. 29 p.

Arnold, D. I. and C. M. Johnson, 1942. Influence of hydrogen ion concentration on the growth of higher plants under controlled conditions. Plant Physiol. 17: 525-539.

Arora, H. S., J. B. Dixion and L. R. Hossner, 1978. Pyrite morphology in lignitic coal and associated strata in east Texas. Soil Science 125: 151-159.

A.S.T.M., 1979. Standard methods of testing for forms of sulfur in coal. American Society of Testing and Materials. Annual Book of Standards D2492-79, pp. 332-337.

Baker, M., 1975. Inactive and abandoned underground mines - water pollution prevention and control. EPA-440/9-75-007. U.S. Environ. Proct. Agency, Washington, D.C.

Barnes, H. L. and S. B. Romberger, 1968. Chemical aspects of acid mine drainage. J. Water Pollut. Control Fed. 40: 371-384 part 1.

Barnhisel, R. I. and H. F. Massey, 1969. Chemical, mineralogical and physical properties of eastern Kentucky acid-forming spoil materials. Soil Science 5: 367-372.

Black, C. A, 1965. Methods of Soil Analysis. American Society of Agronomy No. 9. Madison, Wisconsin Part 2.

Bohn, H. L., B. L. McNeal, and G. A. O'Connor, 1979. Soil Chemistry. Wiley-Interscience Pub. New York, N.Y.

Caruccio, F. T., 1980. Estimating the acid production potential of coal mine refuse. IN Chadwick and Goodman (eds) The Ecology of Resource Degradation and Renewal. Blackwell Scientific Pub. London, pp 437-443.

Caruccio, F. T., 1968. An evaluation of factors affecting acid mine drainage production and ground water interactions in selected areas of western Pennsylvania. IN Second Symposium on Coal Mine Drainage Research, pp. 107-151, Bituminous Coal Research, Inc.

Caruccio, F. T. and G. Geidel, 1981. Estimateing the minimum acid load that can be expected from a coal strip mine. Symposium on Surface Mining Hydrology, Sedimentaology and Reclamation. Lexington, KY, pp 117-122.

Caruccio, F. T., G. Geidel and A. Pelletier, 1980. The assessment of a stratum's capability to produce acid drainage. Symposium on Surface Mining Hydrology, Sedimentation and Reclamation. Lexington, KY, pp 437-443.

Caruccio, F. T. and G. Geidel, 1978. Geochemical factors affecting coal mine drainage quality. IN Schauer, E. W. and P. Sutton (eds.) Symposium On Reclamation Of Drastically Disturbed Lands. American Society of Agron., Madison, Wis., pp. 129-148.

Caruccio, F. T., J. C. Ferm, J. Horn, E. G. Geidel and B. Baganz, 1977. Paleoenvironment of coal and its relation to drainage quality. EPA 600 / 7-77-067, Springfield, VA.

Caruccio, F. T., G. Geidel and J. M. Sewell, 1976. The character of drainage as a function of the occurence of framboidal pyrite and ground water quality in eastern Kentucky, pp. 1-16 IN Sixth Symposium on Coal Mine Drainage Research. Bituminous Coal Research, Inc.

Colbourn, P., 1980. Estimation of the potential oxidation rate of pyrite in coal mine spoils. Reclamation Review 3: 121-123.

Dacey, P. W. and P. Colbourn, 1979. An assessment of methods for the determination of iron pyrites in coal mine spoil. Reclamation Review. 2: 113-121.

Dean, K. C., R. Havens and M. W. Glantz, 1974. Methods and costs of stabilizing fine sized mineral wastes. Report of investigations 7896. Bureau of Mines, U.S. Dept. of the Interior, 26pp.

Deckler, J. H. 1982. Characterization of four inactive hard rock mines in western Montana. Master of Science Thesis. Montana State University, Bozeman, MT.

Dollhopf, D. J. 1982. Unpublished data. Reclamation Research Soil Scientist. Montana State University, Bozeman, MT.

Dollhopf, D. J. and L. J. Russell, 1984. Assessment of acid producing materials in the northern plains. Symposium on Surface Coal Mining and Reclamation in the Great Plains. Billings, Montana. March 1984.

Dunn, L. E., 1943. Lime requirement determination of soils by means of titration curves. Soil Science 56: 341-351.

Foy, C. D., A. L. Fleming and W. H. Armger, 1969. Differntial tolerance of cotton varieties to excess manganese. Agron J. 61:690-694.

Freney, J. R., 1967. Soil Biochemistry. A. D. McLaren and G. H. Peterson (eds.) Dekker, New York.

Geidel, G., 1979. Alkaline and acid production potentials of overburden material: the rate of release. Reclamation Review, Vol. 2: 101-107.

Gerhardt, P., 1981. Manual of methods for general Bacteriology. American Society for Microbiology. Washington, D.C., p. 188-192.

Grove, J. H. and V. P. Evangelou. 1982. The role of lime in salty spoil genesis. Symp. Surface Mining Hydrology, Sedimentology and Reclamation. Lexington, Kentucky, pp. 1-4.

Hanna, G. P. and R. A. Bryant, 1962. Stratigraphic relations to acid mine water production. Proceedings of the 17th Industrial Waste Conference. Series 112 Engineering Extension Series. Purdue University, pp. 476-492.

Howard, D. D. and F. Adams, 1965. Calcium requirement for penetration of subsoils in primary cotton roots. Soil Sci. Soc. Amer. Proc. 29: 558-561.

Henin, S. and G. Pedro, 1965. The laboratory weathering of rocks. IN Hallsworth and Crawford (eds) Experimental Pedology. Butterworths, London, pp. 15-22.

Johnston, R. S., R. W. Brown and J. Cravens, 1975. Acid mine rehabilitation problems at high elevations. Watershed Management Symposium. Logan, Ut. pp. 66-79.

Lacey, D. T., and F. Lawson. 1970. Kinetics of the liquid-phase oxidation of acid ferrous sulfate by the bacterium Thiobacillus ferrooxidans. Biotech. Bioeng. (1) January, pp. 29-50.

LeRoux, N. W., P. W. Dacey and K. L. Temple, 1980. The microbial role in pyrite oxidation at alkaline pH in coal mine spoil. IN Trudinger, P. A., M. R. Walker and B. J. Ralph (eds.) Biochemistry of ancient and Modern Environments. Australian Academy of Science Canberra, pp. 515-520.

MacLean, A. J. and A. J. Dekker, 1976. Lime requirement and availability of nutrients and toxic metals to plant growth in acid mine tailings. Can. J. Soil Sci. 56: 27-36.

MacLean, A. J. and B. J. Finn, 1967. Amendments for oats in soil contaminated with magnesium lime dust. Can. J. Soil Sci. 47:253-254.

Martini, J. A., R. A. Kochhann, E. P. Gomes, and F. Langer, 1977. Response of Heat Cultivars to Liming in some high Al oxisols of Rio Grande Jo Sul, Brazil, Agron. J. 69: 612-616.

McKee, J. and H. Wolf. 1963. Waster quality criteria. California State Water Resources Control Board Publication 3-A. Sacramento, Ca. 547 pp.

McLean, E. D., S. W. Dunford, and F. Coronel, 1966. A comparison of several methods of determining lime requirements of soils. Soil Sci. Soc. Am. Proc. 30:26-30.

Meyer, T. A. and G. W. Volk, 1952. Effect of particle size of limestone on soil reaction, exchangeable cations, and plant growth. Soil Sci. 73:37-52.

Mortvedt, J. J., P. M. Giordand and W. L. Lindsay (eds.), 1972. Micronutrients in Agriculture. Soil Sci. Soc. Amer. Inc., Madison, WI, 666pp.

National Academy of Sciences and National Academy of Engineering, 1972. Water quality criteria. U. S. Government Printing Office, Washington, D.C., 594pp.

Orgam, D. G. and W. W. Fraser, 1978. Reclamation of high sulfide tailings at Hudson Bay mining and smelting, Flin Flon, Manitoba. Reclamation Review. 1: 19-25.

O'Shay, A. T., 1982. The determination of potential acidity in overburden sediments. Master's Thesis, Texas A&M University, College Station, Texas.

Pedro, G., 1961. An experimental study on the geochemical weathering of crystalline rocks by water. Clay Miner. Bull. 4-266-281.

Peech, M., 1965. Lime requirement. IN Black, C. A. (ed) Methods of Soil Analysis. American Society of Agronomy, Madison, WI.

Pionke, H. B., A. S. Rogowski and R. J. DeAngus, 1980. Controlling the rate of acid loss from strip mine spoil. Environmental Quality 9:694-699.

Pugh, C. E., L. R. Nossner and J. B. Dixion 1981. Pyrite and marcasite surface area as influenced by morphology and pyrite diameter. Soil Sci. Am. J., 45:979-982.

Rand, M. C., 1975. Standard methods for the examination of water and waste water. 14th ed. American Public Health Association. Washington, D.C.

Richardson, B. Z., 1980. Reclamation of acid-producing spoils on a western suface mine IN Jackson, C. L. and M. A. Schuster (eds) High-Altitude Revegetation Workshop No. 4. Colorado State University, Fort Collins, Co. pp. 101-112.

Schnitzer, E. E., 1983. Problems associated with the prediction of sulfur oxidation in sulfur spoils, pp. 17-20 IN Proceedings on Overburden Handling, Casper, WY.

Schnitzer, E. E. and D. F. Fransway, 1982. Strip mine reclamation problems associated with the oxidation of surface spoils in Wyoming. Paper presented to DEQ-LQD Acid-Base Seminar, June 11, Casper, WY.

Shoemaker, H. E., E. O. McLean and P. F. Pratt, 1961. Buffer Methods for determining lime requirement of soils with appreciable amounts of extractable aluminum. Soil Sci. Soc. Am. Proc. 25:274-277.

Silverman, M. P. and D. G. Lundgren, 1959. Studies on the Chemoautotrophic iron bacterium Ferrobacillus Ferrooxidans. I. An improved medium and harvesting procedure for securing high cell yields. Journal of Bacteriology, 77: 642-647.

Singer, P. C. and W. Stumm, 1968. Kinetics of the oxidation of ferrous iron. pp. 12-34, IN Second Symp. on Coal Mine Drainage Research. Bituminous Coal Research, Inc.

Singleton, G. A. and L. M. Lavkulich, 1978. Adaptation of the soxhlet extractor for pedogenic studies. Soil Sci. Soc. Am. J. 42: 984-986.

Smith, E. E. and K. Shumate, 1970. Sulfide to sulfate reaction mechanism. EPA Rept. No. 14010 EPS. Ohio State University, U. S. Gov. Printing Office, Washington, D. C.

Smith, R. M., W. E. Grube Jr., T. Arkele Jr., and A. A. Sobek, 1974. Mine spoil potentials for soil and water quality. West Virginia University EPA-670/2-74-070.

Sobek, A. A., M. A. Bambened, and D. Meyer, 1982. Modified soxhlet extractor for pedogenic studies. Soil Sci. Soc. Am. J. 46: 1340-1342.

Sobek, A. A., W. A. Schuller, J. R. Freeman and R. M. Smith, 1978. Field and laboratory methods applicable to overburdens and mine soils. U.S. Environmental Protection Agency EPA 600/2-78-054.

Sorensen, D. L., W. A. Kneib, D. B. Procella and B. Z. Richardson, 1980. Determining the lime requirement for the Blackbird Mine spoil. J. Environmental Quality 9: 162-166.

Steel, R. G. D. and J. H. Torrie, 1980. Principles and Procedures of Statistics, A Biometric Approach. 2nd Ed. McGraw-Hill, New York.

Tabatabai, M. A. and J. M. Bremner, 1972. Forms of sulfur, and carbon, nitrogen and sulfur relationships in Iowa soils. Soil Sci. 114: 380-386.

U.S. Department of Agriculture, 1969. Agricultural Handbook No. 60, U.S. Government Printing Office. WAshington, D.C.

U.S. Department of Health, Education and Welfare, 1962. Public health service drinking water standards. U.S. Public Health Service Publication 956.

U.S. Environmental Protection Aency, 1976. Quality criteria for water. Office of Water Planning Standards. NTIS-Pb 263 943.

Williams, C. and D. H. Yaalon, 1977. An experimental investigation of reddening in dune sand. Geoderma 19: 181-191.

Woodruff, C. M., 1948. Testing soils for lime requirements by means of a buffered solution and a glass electrode. Soil Science 66: 53-66.

APPENDICES

APPENDIX A

SOIL, OVERBURDEN, WATER QUALITY GUIDELINE AND LIME RATE CALCULATION

Table 7. Water quality criteria.* (mg/l)

CONSTITUTENT	PUBLIC WATER	IRRIGATION	AQUATIC LIFE	LIVESTOCK
Boron	0.01	2.0	---	5.0
Cadmium	0.01	0.01	0.03	0.05
Copper	1.0	0.2	0.02	0.5
Iron	0.3	5.0	1.0	---
Lead	0.05	5.0	0.03	0.1
Manganese	0.05	0.5	1.0	10.0
Nitrate	10.0	---	---	---
pH	6.0-8.5		6.5-9.0	
Selenium	0.01	0.02	---	0.05
Sulfate	250.0	500.0 permissable	---	500.0
Zinc	5.0	2.0	---	25.0

*Criteria from U.S. Dept. of Health, Educ. and Welfare (1962). U.S. EPA (1976) National Acad. of Sci. and Nat'l Acad. of Engr. (1972) and McKee and Wolf (1963).

Table 8. Montana Department of State Lands guidelines (1977) for suspect levels in soils and overburden materials.

Analysis	Suspect Level
Conductance	4-6 mmhos/cm
Sodium Adsorption Ratio	>12
Mechanical Analysis	Clay >40% Sand >70%
Saturation %	None
NO_3-N	>10-20 ppm
NH_4-N	>10-20 ppm
Cd	0.1-1.0 ppm
Pb	pH >6 10-15 ppm pH <6 15-20 ppm
Fe	Unknown
Mn	>60 ppm
Hg	>.04-.5 ppm
Se	>2.0 ppm
Mo	>0.3 ppm
B	>8 ppm
Zn	>30-40 ppm
Ni	>1.0 ppm
Cu	>0.0-1.0 ppm

Table 9. Calculation of lime rate requirement.

$$TA_1 = \frac{B \times N}{C} \times 50{,}000 \times A$$

$$TA_2 = \frac{TA_1}{D} = \frac{X}{100}$$

$$TA_3 = TA_2 - TA_1$$

$$LR_X = (TA_{2X} - TA_{3X-1}) \times 10 \div 2000$$

Where x = weathering time period.

Legend.

A = Volume of Water Extracted (L)

B = Volume of Titrant used (NaOH)

C = Volume of Aliquot (mL)

D = % of Total Water Added to Chamber Extracted

N = Normality of Titrant (NaOH)

TA_1 = Extracted Titratable Acidity (mg $CaCO_3$)

TA_2 = Total Acidity (mg $CACO_3$)

TA_3 = Residual Acidity (mg $CACO_3$)

LR_X = Weekly Lime Requirement (Tons/Acre)

APPENDIX B

MINE SOIL ANALYTICAL DATA

Table 10. Mine waste and soil analyses results of tests performed on combined soil samples collected from Champion Mine, September 1981.

SITE	MATERIAL	DEPTH cm	SAND %	SILT %	CLAY %	TEXTURE* USDA	SAT.	pH	EC mmhos/ cm	CEC meq/ 100g	SAR
CHAMPION	Acid Mine	0-3	60	22	18	SL	27.4	2.7	6.4	43.5	
	Waste	18-22	69	17	14	SL	28.0	2.8	3.4		.0
	Gray Mine	18-22	89	7	4	S	18.2	6.9	0.3	7.6	
	Waste	38-42	88	10	2	S	18.0	7.2	0.3		.3
	Mill	38-42	65	21	14	SL	33.4	3.3	7.8	47.3	
	Tailings	78-82	64	21	15	SL	33.5	2.6	7.7		.0
	Mill	18-22	76	22	2	LS	35.0	3.0	0.7	3.0	
	Tailings	38-42	63	33	4	SL	35.1	3.1	0.7		.1
	Mill	18-22	9	55	36	SiCL	88.8	3.1	3.1	39.5	
	Tailings	38-42	8	56	36	SiCL	85.3	3.2	3.4		.0
	Native	0-3	70	25	5	SL	49.8	6.21	0.6	19.2	
	Forest	18-22	70	25	5	SL	21.3		0.3		.1

* L = Loam, SL = Sandy Loam, SiCL = Silty Clay Loam, SiL = Silty Loam, S = Sand, LS = Loamy Sand

Table 11. Water soluble cations from Champion mine site.

			WATER SOLUBLE CATIONS mg/l									
SITE	MATERIAL	DEPTH cm	Ca	Mg	Na	Zn	Cu	Mn	Fe	Cd	Ni	Al
CHAMPION	Acid Mine Waste	0-3 18-22	263.0	321.2	2.84	8.5	9.6	5.72	300.0	.034	2.16	343.0
	Gray Mine Waste	18-22 38-42	56.0	4.1	8.6	.005	.08	.4	0.1	.005	.04	0.2
	Mill Tailings	38-42 78-82	340.0	563.8	1.4	12.4	12.3	33.2	840.0	.004	2.18	732.0
	Mill Tailings	18-22 38-42	18.4	27.4	1.58	1.8	2.3	2.98	7.92	.01	2.32	14.0
	Mill Tailings	18-22 38-42	418.0	331.5	3.12	3.9	3.4	68.0	2.24	.028	1.96	120.0
	Native Forest	0-3 18-22	103.6	13.2	3.84	.042	.158	.80	0.20	.005	.06	0.2

Table 12. Ammonium acetate extractable ions with extract solution pH approximately equal to that of the sample (μg/g).

SITE	MATERIAL	Ca	Mg	Na	Zn	Cu	Mn	Fe	Pb	Cd	Ni	Al	NO_3-N	P	K	SO_4	EXTRACT pH
CHAMPION	Acid Mine Waste	216.0	294.0	11.4	4.9	3.7	5.1	1236.0	0.9	<0.02	1.0	270.0	1.3	31.3	53.0	---	3.6
	Gray Mine Waste	1448.0	20.4	16.8	0.8	5.0	29.2	1.9	<0.5	0.2	0.8	10.0	1.8	20.5	41.0	0.3	7.0
	Mill Tailings	764.0	400.0	14.3	5.2	6.8	34.0	1640.0	<0.5	<0.02	1.2	460.0	1.0	11.7	50.0	0.1	3.6
	Mill Tailings	80.0	17.8	11.8	1.7	1.6	4.8	272.8	<0.5	<0.02	<0.5	80.0	1.3	29.0	23.2	---	3.6
	Mill Tailings	464.0	436.0	14.1	5.4	5.7	80.2	672.0	<0.5	0.04	2.7	495.0	1.0	65.0	109.0	---	3.6
	Native Forest	2952.0	178.0	21.7	5.6	1.1	23.1	4.3	2.1	0.4	0.7	10.0	1.0	26.5	172.0	3.1	7.0

Table 13. Estimated mineral composition of mill tailings and native forest soil from Champion Minesite using thin section analysis.

	Mill[1] Tailings	Mill[2] Tailings	Native[3] Forest
Quartz	90+	90+	80-85
K-feldspar	?	?	7-9
Biotite	<1	.5	1
Limonite	<1	<1	1
Sericite			3.5
Unidentified Opaques			<.5

[1]Possible weathered pyrite grains
[2]50% quartz is Fe stained, zoned. Pyrite pseudomorph .1 mm
[3]10% quartz stained. Some possible ruby silver ore grains <.25%

APPENDIX C

ANOV AND LSD ANALYSES FOR ACID GENERATION STUDY

Table 14. Analysis of variance and least significant difference of non-acid gray waste rock - EC weeks 1-12 Champion minesite.

A N O V.

Source	D.F.	SS	M.S.	F-Value
Time	11	.3541	.3219E-01	94.96*
Residual	24	.8133E-02	.3389E-03	

LSD Analysis

Factor	Ident.	Mean - EC	
Time	Week 8	.6333E-01	A
	10	.6667E-01	A
	12	.6667E-01	A
	9	.7000E-01	AB
	6	.7000E-01	AB
	7	.7333E-01	ABC
	5	.8333E-01	ABC
	3	.1000	BCD
	4	.1023	CD
	2	.1200	D
	1	.1967	E
	0	.4267	F

Asterisk (*) indicates significance at p = .05. Same letter next to Mean - EC indicates no significant differences between means. Std. error mean over 3 reps. = .01.

Table 15. Analysis of variance and least significant difference of non-acid gray waste rock - pH weeks 1-12 Champion minesite.

A N O V.

Source	D.F.	SS	M.S.	F-Value
Time	11	2.256	.2051	12.36*
Residual	24	.3984	.1660E-01	

Factor	LSD Analysis Ident.	Mean - pH
Time	Week 2	7.213 A
	1	7.267 AB
	10	7.303 AB
	8	7.330 AB
	0	7.473 BC
	12	7.567 D C
	9	7.603 D C
	7	7.720 DE
	3	7.743 DE
	4	7.847 EF
	5	7.853 EF
	6	8.000 F

Asterisk (*) indicates significance at p = .05. Same letter next to Mean - pH indicates no significant differences between means. Std. error mean over 3 reps. = .07.

Table 16. Analysis of variance and least significant difference of non-acid native soil - EC weeks 1-12 Champion minesite.

A N O V.

Source	D.F.	SS	M.S.	F-Value
Time	11	.3685	.3350E-01	108.0*
Residual	24	.7400E-02	.3083E-03	

LSD Analysis

Factor	Ident.	Mean - EC
Time	Week 10	.300E-01 A
	9	.3333E-01 A
	12	.3333E-01 A
	8	.4000E-01 A
	6	.4383E-01 A
	7	.4333E-01 A
	5	.5333E-01 AB
	4	.7333E-01 BC
	3	.9667E-01 C
	2	.1300 D
	1	.2367 E
	0	.3767 F

Asterisk (*) indicates significance at p = .05. Same letter next to Mean - EC indicates no significant differences between means. Std. error mean over 3 reps. = .01.

Table 17. Analysis of variance and least significant difference of non-acid native soil - pH weeks 1-12 Champion minesite.

A N O V.

Source	D.F.	SS	M.S.	F-Value
Time	11	4.424	.4022	7.765*
Residual	24	1.243	.5180E-01	

LSD Analysis

Factor	Ident.	Mean - pH
Time	Week 8	6.163 A
	10	6.233 AB
	12	6.397 ABC
	9	6.410 ABC
	7	6.613 BCD
	0	6.683 CD
	2	6.753 E CD
	5	6.833 EF D
	1	6.913 EFGD
	6	7.097 EFG
	3	7.177 FG
	4	7.280 G

Asterisk (*) indicates significance at p = .05. Same letter next to Mean - pH indicates no significant differences between means. Std. error mean 3 reps. = .13.

Table 18. Analysis of variance and least significant difference of acid waste rock - EC weeks 1-12 Champion minesite.

		ANOV		
Source	D.F.	SS.	M.S.	F-Value
Time	11	16.33	1.484	184.8*
Treatment	2	.6118	.3059	30.08*
Time x Treatment	22	3.256	.1480	18.42*
Residual	72	.5183	.8032E-01	

	LSD Analysis	
Factor	Ident.	Mean-EC
Lime	No Lime	1.229 B
	13.47 MT/ha	1.061 A
	40.86 MT/ha	1.078 A

Asterisk (*) indicates significance at p=.05. Same letter next to mean-EC indicates no significant differences between means.

Table 19. Analysis of variance and least significant difference of acid waste rock - EC weeks 1-28 Champion minesite.

		ANOV		
Source	D.F.	SS.	M.S.	F-Value
Time	17	30.05	1.768	384.3*
Treatment	1	.3804	.3804	82.69*
Time x Treatment	17	2.470	.1453	31.59*
Residual	72	.3312	.4601E-02	

	LSD Analysis	
Factor	Ident.	Mean-EC
Lime	No Lime	.9369 B
	13.47 MT/ha	.8181 A

Asterisk (*) indicates significance at p=.05. Same letter next to mean-EC indicates no significant differences between means.

Table 20. Analysis of variance and least significant difference of acid tailings EC weeks 1-12 Champion minesite.

Source	D.F.	ANOV SS.	M.S.	F-Value
Time	11	17.97	1.634	83.74*
Treatment	2	1.471	.7354	37.69*
Time x Treatment	22	1.025	.4657E-01	2.387*
Residual	72	1.405	.1951E-01	

Factor	LSD Analysis Ident.	Mean-EC
Lime	No Lime	.6894 A
	2.27 MT/ha	.6453 A
	27.24 MT/ha	.9119 B

Asterisk (*) indicates significance at p=.05. Same letter next to mean-EC indicates no significant differences between means.

Table 21. Analysis of variance and least significant difference of acid tailings-EC weeks 1-28 Champion minesite.

Source	D.F.	ANOV SS.	M.S.	F-Value
Time	17	20.48	1.205	156.8*
Treatment	1	.3135E-01	.3135E-01	4.079*
Time x Treatment	17	.3760	.2212E-01	2.878*
Residual	72	.5533	.7685E-02	

Factor	LSD Analysis Ident.	Mean-EC
Lime	No Lime	.5194 B
	2.27 MT/ha	.4854 A

Asterisk (*) indicates significance at p=.05. Same letter next to mean-EC indicates no significant differences between means.

Table 22. Analysis of variance and least significant difference of acid waste rock - pH weeks 1-12 Champion minesite.

ANOV

Source	D.F.	SS.	M.S.	F-Value
Time	11	1.293	.1176	1.754
Treatment	2	371.9	185.9	2775.*
Time x Treatment	22	3.388	.1540	2.298*
Residual	72	4.825	.6701E-01	

LSD Analysis

Factor	Ident.	Mean-pH
Time	No Lime	2.899 A
	13.47 MT/ha	6.127 B
	40.86 MT/ha	7.284 C

Asterisk (*) indicates significance at p=.05. Same letter next to mean-pH indicates no significant differences between means.

Table 23. Analysis of variance and least significant difference of acid waste rock - pH weeks 1-28 Champion minesite.

Source	D.F.	ANOV SS.	M.S.	F-Value
Time	15	1.692	.1128	1.554
Treatment	1	238.0	238.0	3279.*
Time x Treatment	15	2.943	.1962	2.703*
Residual	64	4.645	.7258E-01	

Factor	LSD Analysis Ident.		Mean-pH	
Lime	No Lime		2.950	A
	13.47 MT/ha		6.099	B
Time (13.47 MT/ha)	Week	3	5.65	A
		2	5.81	AB
		29	5.93	ABC
		7	5.95	ABC
		25	6.02	ABC
		21	6.04	ABC
		9	6.07	BC
		17	6.07	BC
		8	6.10	BC
		6	6.10	BC
		5	6.11	BC
		11	6.15	BC
		13	6.18	BC
		10	6.27	C
		4	6.27	C
		1	6.86	
Time (No Lime)	Week	1	2.71	A
		9	2.77	A
		2	2.81	AB
		8	2.81	AB
		4	2.94	BC
		3	2.95	DBC
		11	3.00	D CE
		13	3.01	D CE
		10	3.03	DFCE
		17	3.04	DFCE
		5	3.09	DF E
		29	3.10	F E
		7	3.11	F E
		21	3.12	F E
		25	3.16	F
		6	3.17	F

Asterisk (*) indicates significance at p=.05. Same letter next to mean-pH indicates no significant differences between means.

Table 24. Analysis of variance and least significant difference of acid tailings-pH weeks 1-12 Champion minesite.

Source	D.F.	ANOV SS.	M.S.	F-Value
Time	11	2.550	.2318	2.141*
Treatment	2	332.6	166.3	153.6 *
Time x Treatment	22	5.418	.2463	2.275*
Residual	72	7.794	.1083	

Factor	LSD Analysis Ident.	Mean-
Lime	No Lime	3.433 A
	2.27 MT/ha	3.689 A
	27.24 MT/ha	7.277 C

Asterisk (*) indicates significance at p=.05. Same letter next to mean- indicates no significant differences between means.

Table 25. Analysis of variance and least significant difference of acid tailings-pH weeks 1-28 Champion minesite.

Source	D.F.	ANOV SS.	M.S.	F-Value
Time	15	6.704	.4469	1.722
Treatment	1	.6650	.6650	2.562
Time x Treatment	15	4.596	.3065	1.181
Residual	64	16.61	.2596	

Factor	LSD Analysis Ident.	Mean-pH
Lime	No Lime	3.455 A
	2.27 MT/ha	3.621 A

Asterisk (*) indicates significance at p=.05. Same letter next to mean-pH indicates no significant differences between means.

Table 26. Analysis of variance and homogeneity of regression analysis for acid generation in acid waste rock and mill tailings material - weeks 1-28 Champion minesite.

A N O V.

Source	D.F.	SS	M.S.	F-Value
Treatment	1	520.30	520.30	.54**
Error	34	32721.63	962.40	
Total	35.	33241.93		

Homogenety of Regression

Log Regression Acid Tailings:

Log Acidity ($mgCACO_3$) = 56.43 + (-21.03) week $r^2 = .65$

Log Regression Acid Waste Rock

Log Acidity ($mgCACO_3$) = 79.46 + (-28.36) week $r^2 = .77$

$$t = \frac{b_1 - b_2}{\sqrt{S^2 P[1/\Sigma/x_{ij} - \bar{x}1.)^2 + 1/\Sigma(X_{zj} - \bar{x}_{2.})^2]}}$$

$t = .877^{**}$ $t,01,32 = 2.74$

Double asterisk (**) indicates no significance at p = .01.

Table 27. Analysis of variance and least significant difference of acid waste rock. No lime titratable acidity weeks 1-28 Champion minesite.

A N O V.

Source	D.F.	SS	M.S.	F-Value
Time	17	.5551E+05	3265	47.31*
Residual	36	2484.	69.01	

LSD Analysis

Factor		Ident	Mean-T.A.
Time	Week	6	3.90 A
		25	4.37 A
		17	5.22 A
		21	5.38 A
		15	5.98 A
		11	6.44 A
		29	6.62 A
		14	7.03 A
		9	8.13 A
		13	11.11 A
		8	12.33 A
		5	12.50 A
		7	13.79 A
		10	14.29 AB
		4	15.89 AB
		3	27.67 B
		2	51.58 C
		1	143.90 D

Asterisk (*) indicates significance at p = .05. Same letter next to Mean T.A. indicates no significant differences between means. Std. error mean over 3 reps. = 4.80.

Table 28. Analysis of variance and least significant difference of acid tailings. No lime titratable acidity weeks 1-28 Champion minesite.

A N O V.

Source	D.F.	SS	M.S.	F-Value
Time	17	.4269E+05	2511	38.67*
Residual	36	2338.	64.93	

LSD Analysis

Factor		Ident	Mean-T.A.
Time	Week	3	-3.57 A
		29	1.78 AB
		25	2.20 AB
		21	2.27 AB
		14	2.37 AB
		17	3.05 AB
		15	3.42 AB
		13	3.86 AB
		9	3.91 ABC
		10	4.21 ABC
		11	4.60 ABC
		8	4.74 ABC
		6	5.85 ABCD
		7	7.77 ABCD
		2	10.97 BCD
		4	17.21 CD
		5	18.53 D
		1	126.10 E

Asterisk (*) indicates significance at p = .05. Same letter next to Mean-T.A. indicates no significant differences between means. Std. error mean 3 reps. = 4.65.