A computerized automated rapid weathering apparatus for determining total lime requirements for acid minesoils
by Kevin Christopher Harvey

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Land Rehabilitation
Montana State University
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Abstract:
Acid minesoil problems, similar to those in the eastern coal mining states, are common at western coal and hardrock mine operations. Traditional analytical methods for predicting lime requirements are inadequate for evaluating on-going acid production from the oxidation of sulfides. Manual laboratory weathering methods attempt to rapidly simulate the natural chemical weathering of acid producing minesoils and overburden. These methods can circumvent the problems associated with acid-base account interpretations. However, the manual laboratory weathering method is extremely laborious and time consuming. The primary objective of this study was to develop a computer-ized automated rapid weathering apparatus (CARWA) that could determine a sample's characteristic acid production curve and subsequent lime requirement in 24 hours instead of 6 to 12 weeks. CARWA prototype development was accomplished in association with total lime requirement determinations for acid minesoil sites at the Dave Johnston Mine in Wyoming.

Twelve acid minesoil samples were weathered and logarithmic curve fitting was used to project one-time application lime requirements. Calculations were based on the assumption that three CARWA weathering cycles represent one year of natural chemical weathering in the field.

CARWA acid production curve characteristics were similar to those determined by the more established manual laboratory weathering method. In addition, CARWA determined lime requirement projections were statistically similar to or greater than those determined by manual weathering..

Acid-base account lime recommendations were consistently much higher than CARWA determined lime rates. This may be due to the measurement of non-reactive sulfides and/or the inclusion of organic sulfur in the calculation of the acid producing potential. A linear regression equation (r=.95) was found to predict CARWA type lime rates from standard acid-base account data of acid minesoil samples from the Dave Johnston Mine.

CARWA lime rates were put to the ultimate test by implementing them into field plot tests at the Dave Johnston Mine. Vegetation performance results after one growing season suggest that substantial perennial grass establishment has occurred on non-topsoiled acid spoils amended with CARWA determined lime requirements.

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

of

Master of Science

in

Land Rehabilitation

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Bozeman, Montana

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ABSTRACT

Acid minesoil problems, similar to those in the eastern coal mining states, are common at western coal and hardrock mine operations. Traditional analytical methods for predicting lime requirements are inadequate for evaluating on-going acid production from the oxidation of sulfides. Manual laboratory weathering methods attempt to rapidly simulate the natural chemical weathering of acid producing minesoils and overburden. These methods can circumvent the problems associated with acid-base account interpretations. However, the manual laboratory weathering method is extremely laborious and time consuming. The primary objective of this study was to develop a computerized automated rapid weathering apparatus (CARWA) that could determine a sample's characteristic acid production curve and subsequent lime requirement in 24 hours instead of 6 to 12 weeks. CARWA prototype development was accomplished in association with total lime requirement determinations for acid minesoil sites at the Dave Johnston Mine in Wyoming.

Twelve acid minesoil samples were weathered and logarithmic curve fitting was used to project one-time application lime requirements. Calculations were based on the assumption that three CARWA weathering cycles represent one year of natural chemical weathering in the field. CARWA acid production curve characteristics were similar to those determined by the more established manual laboratory weathering method. In addition, CARWA determined lime requirement projections were statistically similar to or greater than those determined by manual weathering.

Acid-base account lime recommendations were consistently much higher than CARWA determined lime rates. This may be due to the measurement of non-reactive sulfides and/or the inclusion of organic sulfur in the calculation of the acid producing potential. A linear regression equation (r=.95) was found to predict CARWA type lime rates from standard acid-base account data of acid minesoil samples from the Dave Johnston Mine.

CARWA lime rates were put to the ultimate test by implementing them into field plot tests at the Dave Johnston Mine. Vegetation performance results after one growing season suggest that substantial perennial grass establishment has occurred on non-topsoiled acid spoils amended with CARWA determined lime requirements.

INTRODUCTION

Numerous coal and hardrock mine sites throughout the western United States are experiencing acid minesoil problems parallel to those in the eastern states. Acid production from the oxidation of iron sulfides (e.g. pyrite) in overburden materials often inhibit revegetation of minesoils. The reactions involved in pyrite oxidation are complex but can be summarized by the equation:

$$2\ FeS_2 + 7\ O_2 + 2\ H_2O = 2\ Fe^{+2} + 4\ SO_4^{-2} + 4\ H^+$$

Lime application to neutralize minesoil pH seems necessary to provide a suitable growing medium. However, a reliable methodology to determine a one-time total lime requirement for the life of the material is not available.

Traditional agricultural lime requirement tests (Dunn 1943, Woodruff 1948, Shoemaker et al. 1961, Peech 1965, McLean et al. 1966) generally underestimate the total lime requirement for acid producing minesoils. These methods only evaluate exchangeable or soluble acidity and do not consider the total potential acidity generated from long term chemical weathering of sulfide minerals or organic sulfur compounds.

Acid-base accounting (Smith et al. 1974) is used extensively in the United States to assess the long term acid production and base release in minesoil materials. The method can, with 90 percent accuracy (Russell 1984, Russell and Dollhopf 1984) indicate which geologic stratum in overburden will produce acid upon oxidation/hydrolysis and which will not (Caruccio 1980, Sturey et al. 1982).

The method is less reliable when the actual quantity of acid production must be known so that a lime requirement can be calculated. Variations in kinetics between acid and alkaline production indicate that a simple balance of the acid potential against the base potential, to determine the excess of one over the other, is incorrect (Geidel 1979, Caruccio and Geidel 1984). In addition, uncertainties associated with the yield of acid from organic sulfur in minesoils results in difficult interpretations of acid-base account data (Dollhopf 1984).

An alternative method to analytical approaches such as the acid-base account, is to simulate natural chemical weathering of spoil samples using humidity cells (Hanna and Brandt 1962, Caruccio 1968, Sobek et al. 1978). This empirical technique provides simple control over air, temperature, moisture and catalytic microbes to circumvent the problems associated with acid-base accounting and the uncertainties of acid production from organic sulfur.

Russell and Dollhopf (1984), Russell (1984) and Blanton and Dollhopf (1985) utilized a slightly modified laboratory humidity cell apparatus to weather minesoil materials from ten abandoned hardrock and coal mining areas in Montana. Acid production curves, derived from weekly extractions to measure acid generation, were used to calculate one-time total lime requirements for these materials.

It appears that simulated weathering chambers can be used to determine the total lime requirement of minesoil materials. The technique was laborious and required from six to twelve weeks of time for results, making it impractical to process large numbers of samples or to attain rapid results. This was the impetus behind the development of a rapid and reliable method which will determine one-time total lime requirements for acid producing minesoils.

The primary objective of this study was to 1) develop a computerized automated rapid weathering apparatus (CARWA) that could weather a sample in days rather than weeks. Other objectives were to: 2) determine total lime requirements for acid minesoil sites at the Dave Johnston Mine near Glenrock, Wyoming; 3) compare CARWA lime recommendations to those from the manual laboratory weathering (humidity cell) method and acid-base accounting; 4) determine which sulfur components contribute to acidity liberated by CARWA; and 5) field test lime rates recommended by CARWA.

METHODS AND MATERIALS

Experimental Site Description

The Dave Johnston Coal Mine is located in east central Wyoming on the southern edge of the Gillette coal field (Figure 1). Vegetation communities in this semi-arid region are characteristic of the mixed grass prairie. Natural soils in this area generally exhibit a pH ranging from 6 to 8. Overburden/interburden materials at Dave Johnston contain reduced forms of inorganic and residual (organic) sulfur. Oxidation of these sulfur forms has resulted in localized "hotspots" (low minesoil pH) barren of vegetation that are scattered throughout the post-mine landscape.

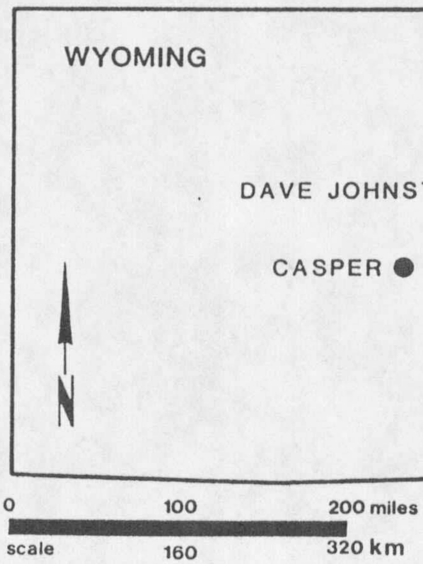


Figure 1. Map of Wyoming showing location of the Dave Johnston Mine.

Two field sites, designated sites A and B, were chosen at the Dave Johnston Mine where existing plant establishment efforts had failed due to low minesoil pH. The area surrounding and including site A was mined in 1967 and recontoured in 1972. The site received 15 cm of top-soil and was seeded with crested wheatgrass (Agropyron cristatum), western wheatgrass (A. smithii) and streambank wheatgrass (A. riparium) at rates of 11, 6 and 6 kilograms pure live seed per hectare, respectively. In addition, 4.5 metric tons per hectare of mulch was applied. Since then acid production from sulfide oxidation left site A devoid of vegetation. The lack of vegetation cover resulted in the erosion and loss of topsoil at this site.

Site B and the surrounding landscape was disturbed in 1958 and regraded in 1966. The site received no topsoil but was seeded with crested wheatgrass and alfalfa (Medicago sativa) at 10 and 3.5 kilograms pure live seed per hectare, respectively. This site was largely without a vegetative cover.

Experimental sites A and B measured 9.1 by 27.4 meters with three plots within measuring 9.1 by 9.1 meters. In the center of each plot, bulk samples of spoil were collected from 0 to 36 cm and from 36 to 102 cm deep. The six samples from each site were air dried, flailed to disaggregate the clods and sieved to attain the less than 2 mm fraction for chemical and physical analyses and for laboratory weathering tests.

Laboratory Analysis of Field Samples

Spoil samples collected from sites A and B 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. Results were interpreted, where applicable, by comparison with the Wyoming Department of Environmental Quality, Land Quality Division Guideline Number 1, Suitability Criteria for Overburden and Topsoil (Table 12 - Appendix A).

Sulfur Fractionation and Acid-Base Accounting

Sulfur fractionation and subsequent acid-base account calculations were performed on two separate size fractions from each air dried sample. One split was sieved to pass a 60 mesh (<.25mm) screen and the other a 9 mesh (2mm) screen. Total sulfur content was determined with a Fisher Sulfur Analyzer. Pyritic sulfur was calculated as the difference between 4.8 N (3:2, $HCl:H_2O$) HCl-extractable and dilute (1:7, $HNO_3:H_2O$) HNO_3-extractable sulfur. The difference between total sulfur minus sulfates and pyritic sulfur was calculated as residual (organic) sulfur (Sobek et al. 1978).

Table 1. Procedures for chemical and physical analysis of minesoil samples.

Parameter	Procedure	Reference
pH	Electrode in water saturated paste.	U.S. Salinity Lab. Staff (1954) p. 102.
Electrical Conductivity (EC)	Water saturated paste extract.	Sandoval and Power (1977) p. 22-24.
Cation Exchange Capacity (CEC)	$BaCl_2$ saturation (acid soil CEC).	Rhoades (1982) p. 154.
Ca, Mg, Na (soluble)	Water saturated paste extract.	Sandoval and Power (1977) p. 24-25.
Sodium Adsorption Ratio (SAR)	Water soluble calculated.	U.S. Salinity Lab. Staff (1954) p. 156.
Ca, Mg, Na, K (extractable)	Ammonium acetate extractable.	Thomas (1982) p. 160.
Exchangeable Sodium % (ESP)	Calculation.	U.S. Salinity Lab. Staff (1954) p. 155.
Base saturation %	Extractable bases - CEC x 100.	U.S.D.A. (1984) p. 31.
Al	KCl extractable.	Barnhisel and Bertsch (1982) p. 282-283.
Cd, Cu, Fe, Mn, Ni, Pb, Zn	DTPA extractable.	Baker and Amacher (1982) p. 331-333.
Mo	Acid Ammonium Oxalate extractable.	Reisenhauer (1965) p. 1056-1057.
As	$NaCO_3$ extractable.	Ganje and Rains (1982) p. 391-398.
B	Hot water extractable.	Bingham (1982) p. 443-444.
SO_4	Precipitation as $BaSO_4$.	Sandoval and Power (1977) p. 29-30.
HCO_3	Water saturated paste extract.	Rand (1976) p. 253-257.
Cl	Water saturated paste extract.	Rand (1976) p. 304-306.
% Total sulfur	Fisher sulfur analyzes.	Sobek et al. (1978) p. 60-62.
% SO_4 - sulfur	(Total-S)-(S after HCl treatment).	Sobek et al. (1978) p. 60-62.
% Pyritic - sulfur	(S after HNO_3 trt)-(S after HCl trt).	Sobek et al. (1978) p. 60-62.
% Residual (organic) - sulfur	[(Total-S)-(FeS_2-S)-(SO_4-S)].	Sobek et al. (1978) p. 60-62.
Acid Producing Potential	(% FeS_2-S + % residual-S)(31.25).	Smith et al. (1974) p. 72.
Neutralization Potential	HCl reaction and titration.	Smith et al. (1974) p. 50-51.
Particle Size Analysis	8 hour hydrometer.	Day (1965) p. 562.
Soil Texture	U.S.D.A. texture triangle.	U.S.D.A. (1951) p. 209.
Organic Carbon %	Dichromate Oxidation.	Nelson and Sommers (1982) p. 570-571.
Saturation %	Water saturated paste.	U.S. Salinity Lab. Staff (1954) p. 84, 107.
Avail, H_2O holding capacity	Pressure plate (.3 bar-15 bar).	Richards (1965) p. 134-137.

The acid production potential (APP) of minesoil samples was determined from sulfur analyses utilizing the following equation:

$$APP = (\%\ \text{pyritic-s} + \%\ \text{residual-s})(31.25)$$

(Smith et al. 1974)

where APP is tons $CaCO_3$ per 1000 tons material. These values were converted to metric tons $CaCO_3$ per hectare 15 cm slice of material in order to present all results in Metric units.

Neutralization potential (in Mt $CaCO_3$/ha 15cm) was determined by treating the samples with a known excess of HCl, heating to ensure complete reaction, and titration with sodium hydroxide (Smith et al. 1974).

The acid production potential was then balanced against the inherent neutralization potential of the sample to obtain the corresponding acid-base account lime excess or deficiency.

Laboratory Weathering Studies

Manual Laboratory Weathering Method

Manual weathering methods are described in detail elsewhere (Russell 1984); but to summarize 200 grams of the less than 2 mm fraction were placed in replicated acrylic weathering chambers (Sobek et al. 1978), inoculated with *Thiobacillus* bacterium and kept moist (Caruccio 1968), aerated, agitated and extracted weekly for six weeks with 200 ml of distilled/deionized water to measure pH and acid generation. Because this method is extremely laborious and time consuming only two samples, one from site A and one from B, were weathered for comparison to the rapid automated method.

Computerized Automated Rapid Weathering Apparatus (CARWA)

Construction of the CARWA required fifteen months of mechanical and electrical engineering. Figure 2 shows a diagram of the CARWA prototype.

Each minesoil sample taken from sites A and B was subjected to CARWA analysis. A bacteria inoculated (see section below on Bacteria Inoculation) 200 gram minesoil sample ($<$2mm fraction) was placed into each of three acrylic weathering compartments. An automated weathering cycle began by spraying 200 ml of distilled/deionized water into each compartment. The minesoil solution was mechanically agitated for one hour, and then the water was extracted into a holding column. The minesoil was aerated for 30 minutes by an overhead fan to encourage oxygenation and partial drying. The extracted water was discharged into a beaker positioned on an automatic turntable, and the next cycle began (Figure 3). The computer control automatically conducted six weathering cycles of approximately 2.5 hours each on the samples. The extracts were monitored for volume, pH and titratable acidity.

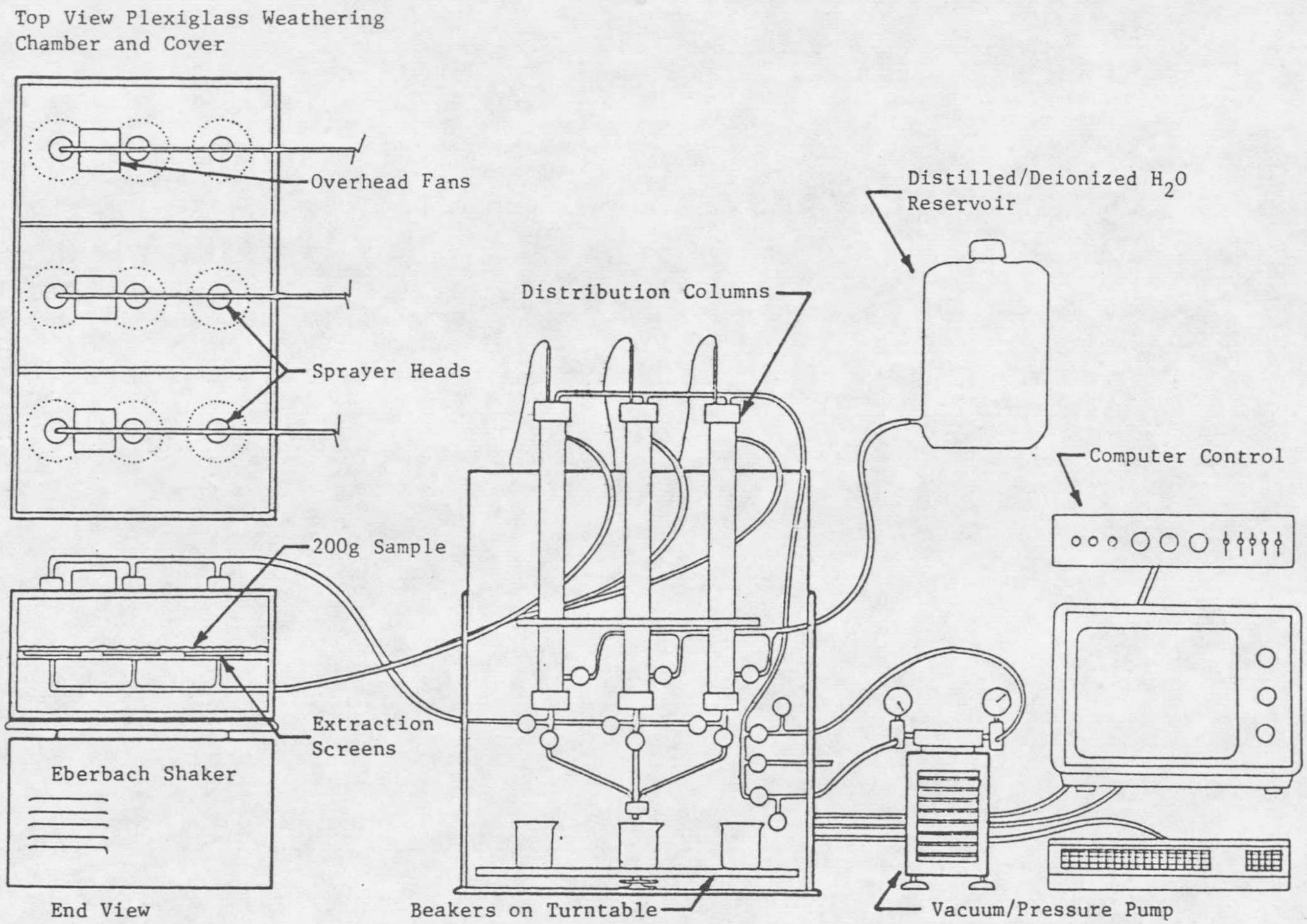


Figure 2. Diagram of the computerized automated rapid weathering apparatus prototype.

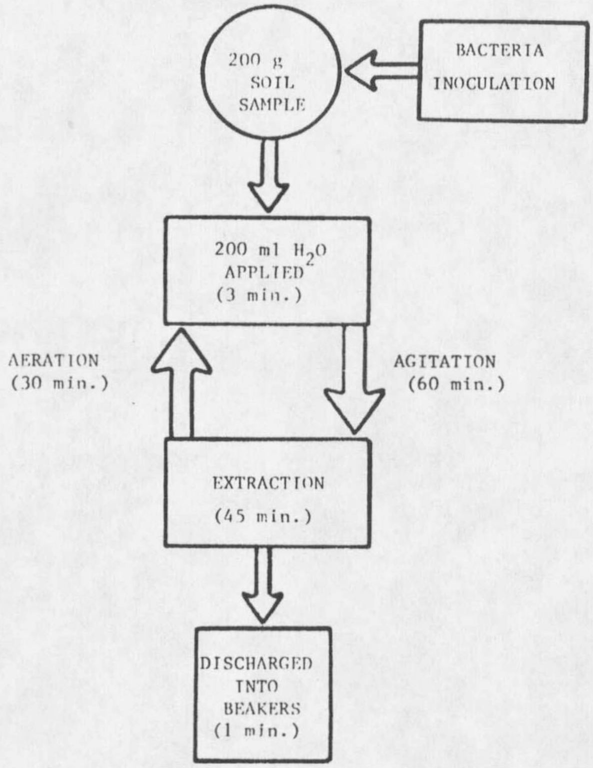


Figure 3. Flow diagram showing the operation of one CARWA weathering cycle.

Each timed mode of CARWA operation (e.g. agitation time) could be easily changed with program prompts prior to the start of weathering. This would allow, for example, the increase of extraction time if a sample turned out to be fine textured, and difficult to extract.

Acid Production Measurement

Titratable acidity and pH were measured on extracts from both manual laboratory weathering and CARWA treatments. Prior to analysis, a portion of each extract was gently boiled for two minutes. This was to ensure complete reaction and hydrolysis of oxidation products (Caruccio 1968). If initial pH was less than 7 then an aliquot was titrated with standardized sodium hydroxide to measure extracted titratable acidity. Titratable acidity was then converted to calcium carbonate equivalents to calculate the amount of lime needed to neutralize the acid generated from each weathering cycle (Table 13 - Appendix A).

Bacteria Inoculation

It has been known for some time that certain bacteria are capable of oxidizing iron and sulfur minerals to produce sulfuric acid. The intent of introducing bacteria populations into the weathering chambers is not to study the effects of bacterial inoculation, but rather simply to imitate the natural environment. This ensures the catalytic effect of microbial populations is not limiting.

Previous weathering studies at Montana State University (Russell 1984, Blanton and Dollhopf 1984) encountered problems with Thiobacillus ferrooxidans inoculation. The use of an acidic growth culture (Silverman and Lundgren 1959) to add bacteria to the minesoil sample contributed significantly to the titratable acidity measured after each weathering cycle. This contribution could not be accounted for, and therefore incorrect lime requirements were calculated.

To remedy these problems a new method of inoculating minesoil samples with bacterium was developed based on a similar procedure by Caruccio (1968). Acid mine drainage samples, known to contain populations of iron and sulfur oxidizing bacteria, were collected from a mine adit discharge that spills into No-Name Creek near Sand Coulee, Montana. Ten drops of acid mine drainage were added to a 200 gram minesoil sample that had already been pre-moistened with 100 ml of distilled/deionized water. Prewetting the samples immediately prior to inoculation would allow the soil-water solution to acidify, thus providing optimum growth conditions for <u>Thiobacillus</u> bacterium. The inoculated minesoil solution was allowed to incubate for 48 hours. The sample was then washed into the weathering chamber with an additional 100 ml of water. This meant that 200 ml of water had already been applied to the sample before the first weathering cycle. The 200 ml of water normally applied during the first CARWA cycle was simply cutoff and the sample was weathered as previously described.

Field Tests

Liming and Seeding

Sites A and B were amended with lime requirements determined by CARWA weathering. In addition, a special 24 hour soil-lime incubation derived lime rate (McLean 1982) was incorporated into minesoils already limed with CARWA rates. One half of each 9.1 by 9.1 meter plot received this special CARWA plus incubation lime rate to 18 cm deep (Figure 4.)

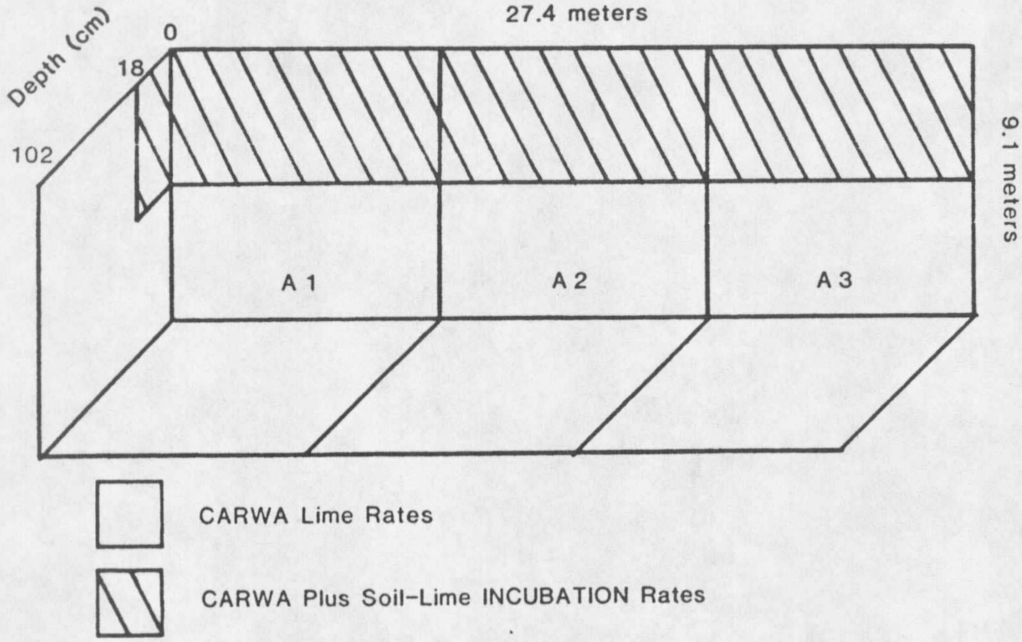


Figure 4. Diagram of field test plots with respect to liming treatments and depths.

The liming agent used was a dolomitic limestone which was obtained from Jirdon Agri Chemicals, Inc. of Morrill, Nebraska. Physical and chemical analyses of this material (Table 2) indicated it would be an excellent liming agent. Actual field application rates were adjusted for the percentage of inert impurities within the liming agent. A correction factor of 25 percent was added to the application rate to adjust for the lack of complete mixing in the minesoil.

Table 2. Physical and chemical analysis of liming agent used in field test.

Particle Size	Chemical Information[1]
< 2 mm 100%	% $CaCO_3$ equivalence = 93
< .42 mm 99%	% $CaCO_3$ = 54
< .25 mm 55%	% $MgCO_3$ = 40
< .15 mm 50%	

[1] $CaCO_3$ equivalence determined by Indicator Titration Method according to AOAC (1975).

Liming and seeding at site A proceeded as follows: 1) The site was deep ripped to a depth of 102 cm with three ripper shanks mounted on a D9H crawler tractor. The 36 to 102 cm CARWA lime rate was incorporated at this time by following behind the ripper and manually pouring the lime into the opening crevice. 2) The 0 to 36 cm CARWA lime rate was applied to the surface and incorporated 36 cm deep with a chisel plow. 3) A roller harrow was employed to mix the surface applied, special incubation lime rate across one half of each plot. The harrow incorporated the lime to 18 cm deep and also prepared the seedbed for the entire site. 4) The site was seeded with a standard seed mix, designed by mine staff, using a Truax seed drill. The seed mix consisted of thickspike wheatgrass (<u>Agropyron dasystachyum</u>), steambank wheatgrass (<u>A. riparium</u>) and slender wheatgrass (<u>A. trachycaulum</u>) applied at rates of 4.5, 2.2 and 4.5 kilograms pure live seed per hectare, respectively.

Site B was limed and seeded the same way as above except that a Patrol was used to rip the site to a depth of 76 cm instead of 102 cm.

Vegetation Performance Measurement

Plant density, an index of germination and initial establishment, was estimated for site A and B immediately after seedling emergence. Density was measured by counting live-rooted plants in 25, 20 x 20 cm quadrats that were systematically located along one diagonal transect within each 9.1 by 4.55 meter subplot. All plants counted were recorded into one of two categories: seeded perennial grasses or weedy species.

Percent canopy cover and above-ground production was measured for both sites during maximum seasonal growth. Canopy cover was estimated in 10, 20 x 50 sampling frames systematically placed along the same diagonal transect in each subplot. Cover for each category, perennial grasses and weedy species, was estimated to the nearest percent, otherwise the techniques were consistent with Daubenmire (1959). Above-ground plant production was measured by clipping all plants at ground level in 6, 50 x 50 cm sampling frames systematically located along the diagonal transect in each subplot. As with density and cover, plants were classified as either perennial grasses or weeds. Samples were oven dried at 65 degrees centigrade for 48 hours before weighing.

RESULTS AND DISCUSSION

Physicochemical Characterization of Acid Minesoil Sites

Results of laboratory chemical and physical analyses for sites A and B are summarized in Table 3. In addition, selected parameters thought to be influenced by the oxidation of sulfides are presented graphically by depth in Figure 5. Site A samples revealed no appreciable differences in texture, which ranged from loam to sandy loam. Site B textures also ranged from loam to sandy loam. A comparison of the laboratory results (Table 3) with the Wyoming Department of Environmental Quality suspect levels (Table 12 -Appendix A) indicated that materials from both sites A and B would be characterized as unsuitable for use as topsoil due to low minesoil pH. As expected, extractable aluminum concentrations were elevated because of the low minesoil pH. However, these analyses did not reveal toxic concentrations of other metals.

Minesoil electrical conductance (EC) was, for most samples, within the acceptable range of salt tolerant vegetation. The dominant anion in all samples was sulfate which suggests that substantial sulfide oxidation has already occurred. High exchangeable acidity is evident by the low base saturation percentage of some of these

Table 3. Summary of physicochemical analysis data for sites A and B.

Parameter	SITE A				SITE B			
	Mean	S.D.	Range Min	Range Max	Mean	S.D.	Range Min	Range Max
pH	2.9	0.48	2.1	3.4	2.7	0.49	2.1	3.2
EC (mmhos/cm)	3.04	2.27	0.66	6.70	6.61	2.83	3.37	10.50
CEC (meq/100g)	14.3	0.66	13.2	15.2	15.8	1.7	13.0	17.4
SAR	0.24	0.12	0.13	0.43	0.12	0.03	0.08	0.16
ESP	1.83	0.37	1.61	2.58	1.53	0.18	1.29	1.76
Ca (meq/L)	17.5	12.3	2.6	29.8	27.5	1.7	25.3	30.5
Mg (meq/L)	11.9	10.9	0.95	27.3	45.8	23.8	12.3	76.8
Na (meq/L)	0.67	0.13	0.48	0.84	0.67	0.15	0.48	0.85
Base Saturation %	53.9	23.1	15.5	79.3	43.8	12.9	20.2	58.2
Ca (meq/100g)	4.89	2.63	0.21	7.31	4.38	1.23	2.83	6.06
Mg (meq/100g)	2.44	.094	1.60	4.17	2.40	1.26	0.26	3.84
Na (meq/100g)	0.27	0.05	0.23	0.37	0.24	0.02	0.21	0.26
K (meq/100g)	0.12	0.09	0.03	0.25	0.05	0.05	0.01	0.15
HCO_3 (mg/L)	0	0	0	0	0	0	0	0
SO_4 (mg/L)	1638.0	1460.0	605.0	2670.0	4550.0	438.0	4240.0	4860.0
Cl (mg/L)	15.0	2.8	13.0	17.0	14.0	2.8	12.0	16.0
B (mg/L)	0.22	0	0.22	0.22	0.27	0.07	0.22	0.32
Al (mg/L)	15.2	4.7	11.9	18.5	33.4	4.7	30.1	36.7
As (mg/L)	0.21	0	0.21	0.21	0.18	0.01	0.17	0.18
Cd (mg/L)	0.09	0.04	0.06	0.11	0.14	0	0.14	0.14
Cu (mg/L)	2.32	0.19	2.18	2.45	2.19	0.39	1.91	2.46
Fe (mg/L)	75.9	5.02	72.4	79.5	88.0	3.3	85.7	90.3
Mn (mg/L)	8.1	2.7	6.2	10.0	16.1	0.1	16.0	16.1
Mo (mg/L)	0.20	0.02	0.18	0.21	0.19	0.05	0.15	0.22
Ni (mg/L)	2.1	1.1	1.3	2.8	2.8	0.4	2.5	3.0
Pb (mg/L)	0.9	0.3	0.7	1.1	0.6	0.4	0.3	0.8
Zn (mg/L)	5.14	2.76	3.18	7.09	5.04	0.39	4.76	5.31
% Sand	51.2	5.7	45.6	61.1	44.5	11.4	29.5	56.7
% Silt	31.0	4.1	23.8	36.4	35.8	8.1	27.1	46.1
% Clay	17.8	2.2	15.1	21.6	19.7	3.5	17.1	24.4
Saturation %	31.8	10.2	15.7	42.2	44.4	8.9	37.1	59.9
% Organic Carbon	0.40	0.15	0.21	0.54	0.78	0.67	0.27	1.48
Plant Avail H_2O %	18.4	2.1	14.8	21.2	20.3	1.6	18.1	22.1

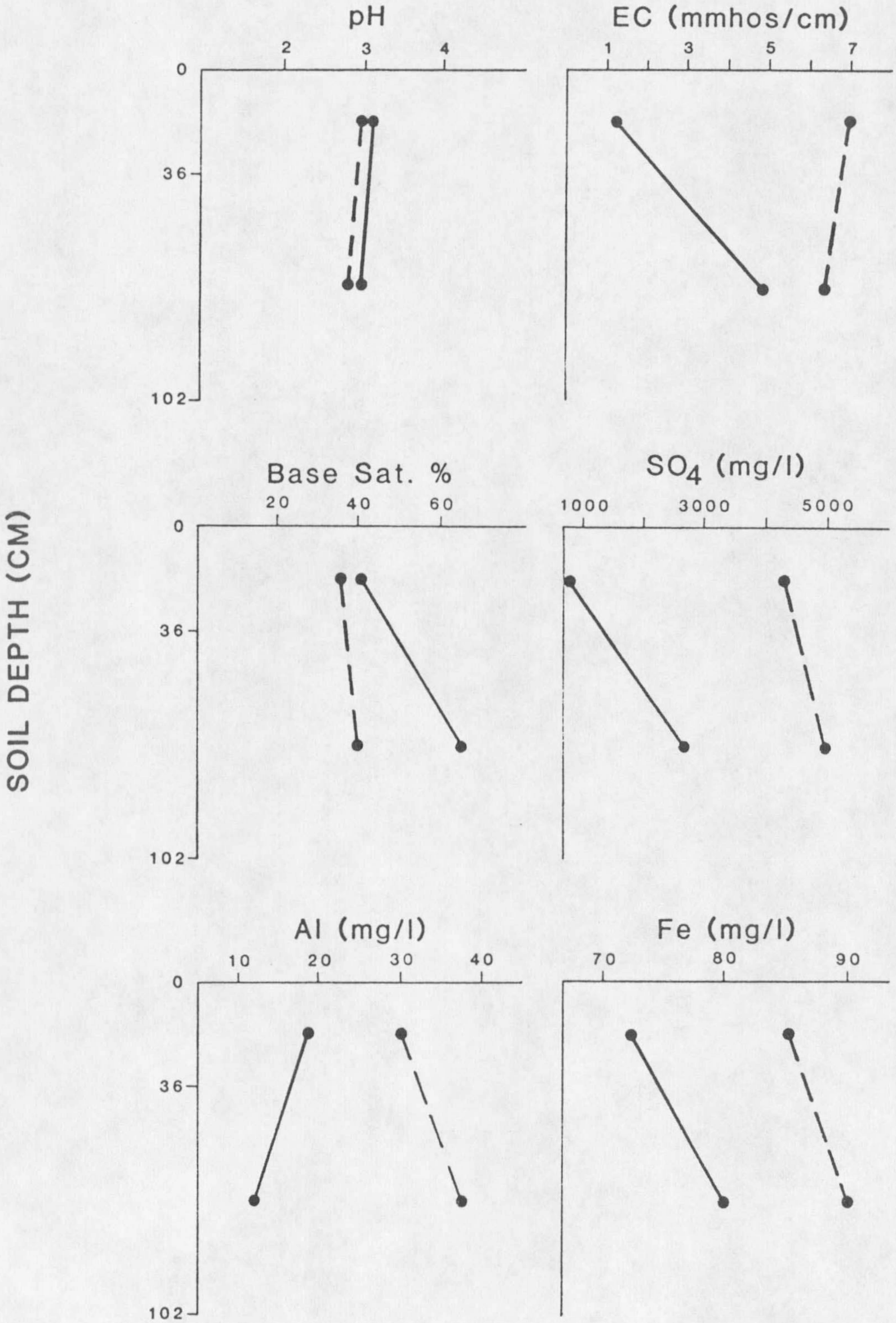


Figure 5. Minesoil profile chemical data for site A (solid line) and site B (dashed line).

minesoils samples. The high level of sulfate ion and the low base saturation percentage are not surprising since these materials have been weathering and producing acid for as long as 18 years.

Other analyzed parameters did not appear to be at toxic or inhibitory levels. Therefore, proper liming practices should be all that is necessary to ameliorate acid conditions and provide a suitable root growth medium.

Acid-Base Accounting

An acid forming potential for a sample exists when the resultant net acid-base account, expressed in metric tons $CaCO_3$ per hectare 15 cm, is less than zero (negative value). Complete sulfur fractionation and subsequent acid-base account results for samples from sites A and B are presented in Table 4. These data indicate that all materials from sites A and B possessed a net acid producing potential. However, only four samples, one from site A and three from B, exceeded the -11 Mt $CaCO_3$/ha 15 cm (-5 Tons $CaCO_3$/1000 tons) suspect level for acid-toxic forming materials established by Smith et al. (1974) and the Wyoming Department of Environmental Quality (1984).

Neutralization potentials are measured by adding a known excess of hydrochloric acid to a minesoil sample and heating to insure reaction between the acid and the inherent neutralizers. The calcium carbonate equivalent of

Table 4. Sulfur fractionation (mean of 3 reps) and acid-base accounting for all samples from sites A and B.

Site/Depth(cm)	% Sulfate Sulfur	% Pyritic Sulfur	% Residual Sulfur	% Total Sulfur	Metric tons $CaCO_3$/hectare 15 cm slice of material: Acid Producing Potential	Neutralization Potential	Acid-base Account
A1 0-36	0.04	0.02	0.03	0.08	-3.50	-3.2.5	-6.75
A1 36-102	0.15	0.01	0.06	0.27	-4.90	-1.10	-6.00
A2 0-36	0.09	0.02	0.05	0.15	-4.90	0.31	-4.59
A2 36-102	0.30	0.04	0.09	0.42	-9.11	-12.98	-22.09
A3 0-36	0.04	0.02	0.04	0.10	-4.20	-3.90	-8.10
A3 36-102	0.10	0.02	0.05	0.17	-4.90	-1.46	-6.36
B1 0-36	0.27	0.05	0.15	0.47	-14.01	-16.41	-30.42
B1 36-102	0.31	0.03	0.05	0.39	-5.61	-14.89	-20.50
B2 0-36	0.26	0.02	0.09	0.38	-7.71	-7.26	-14.97
B2 36-102	0.12	0.01	0.06	0.20	-4.90	-3.90	-8.80
B3 0-36	0.11	0.02	0.06	0.19	-5.61	-1.39	-7.00
B3 36-102	0.14	0.01	0.08	0.22	-6.31	-1.77	-8.08

the sample is obtained by determining the amount of unconsumed acid by titration with standardized sodium hydroxide (Sobek et al. 1978). A negative neutralization potential results when a sample already contains appreciable soluble acidity and no longer has any inherent neutralizing capability. Therefore, more equivalents of titrant (NaOH) would be required to account for the known amount of added acid plus any soluble acid already present in the sample. The amount of excess soluble acid is the amount of $CaCO_3$ equivalents that must be added to the acid-base account as a negative value. A negative value represents a deficiency of calcium carbonate. When a negative neutralization potential is added to a negative acid producing potential, to obtain the acid-base account, the result is a greater lime deficiency.

Negative neutralization potentials, measured in all but one sample, suggest that these sites have already produced much acid and that they no longer possess any inherent alkaline producing materials with which to buffer additional acidity. The relatively high percent sulfate sulfur values also imply that these minesoils have been weathering a long time since sulfate is an end product of pyrite oxidation.

Analysis of variance (ANOV) and least significant differences (LSD) were calculated to determine the variability of acid-base account lime deficiencies across each site and by depth. Site A ANOV (Table 14 - Appendix B) revealed significant differences at the 95% level among the three plots (A1, A2, A3) and two sample depths (0-36cm, 36-102cm). LSD analysis indicated that each sample was significantly different from the other. ANOV and LSD tests for site B (Table 15 - Appendix B) produced identical results. These analyses show that there was appreciable minesoil variability over short distances (a few meters) with respect to acid-base account.

Acid-base accounting was, for this study, performed on two size fractions (< .25mm and < 2mm) from each minesoil sample. Analysis of the less than .25 mm fraction is specified by the published procedure (Sobek et al. 1978). However, simulated laboratory weathering is conducted on the less than 2 mm fraction in order to be consistent with the size fraction used for most soil analytical procedures. ANOV and LSD was performed using all acid-base data from sites A and B combined (Table 16 - Appendix B). These results revealed no statistical difference (P=.01) between the less than .25 mm fraction (mean of -5.28) and the less than 2 mm fraction (mean of -5.29) acid-base account. This result indicates that the use of the less than 2 mm fraction is adequate in laboratory weathering experiments.

Acid Generation Analysis from CARWA

Acid Production Curves

Acid production curves, after six CARWA cycles, for all samples from sites A and B are presented in Figure 6. For all samples, acid yield was high during the first few cycles. After cycle three, acid production remained nearly constant with slight decreases over time. These same acid production curve characteristics occurred during manual laboratory weathering studies by Russell and Dollhopf (1984) and by Blanton and Dollhopf (1984). It is thought that the initial acidity released during laboratory weathering is soluble acidity that was produced prior to laboratory weathering. The acidity released in the latter period of weathering is likely due to oxidation of framboidal pyrite and other reactive sulfur compounds.

Analysis of variance (ANOV) and least significant differences (LSD) were performed to evaluate the variability of acid production, after six CARWA cycles, across each site and by depth. ANOV of site A (Table 17 - Appendix B) showed significance (P=.05) differences among the three plots (A1, A2, A3), two sample depths (0-36cm and 36-102cm) and the plot by depth interaction. LSD analyses revealed that sample plot A2 produced significantly more acidity than plots A1 and A3. LSD also showed that the subsurface samples at site A (36-102cm) yielded greater quantities of acidity than the surface samples (0-36cm).

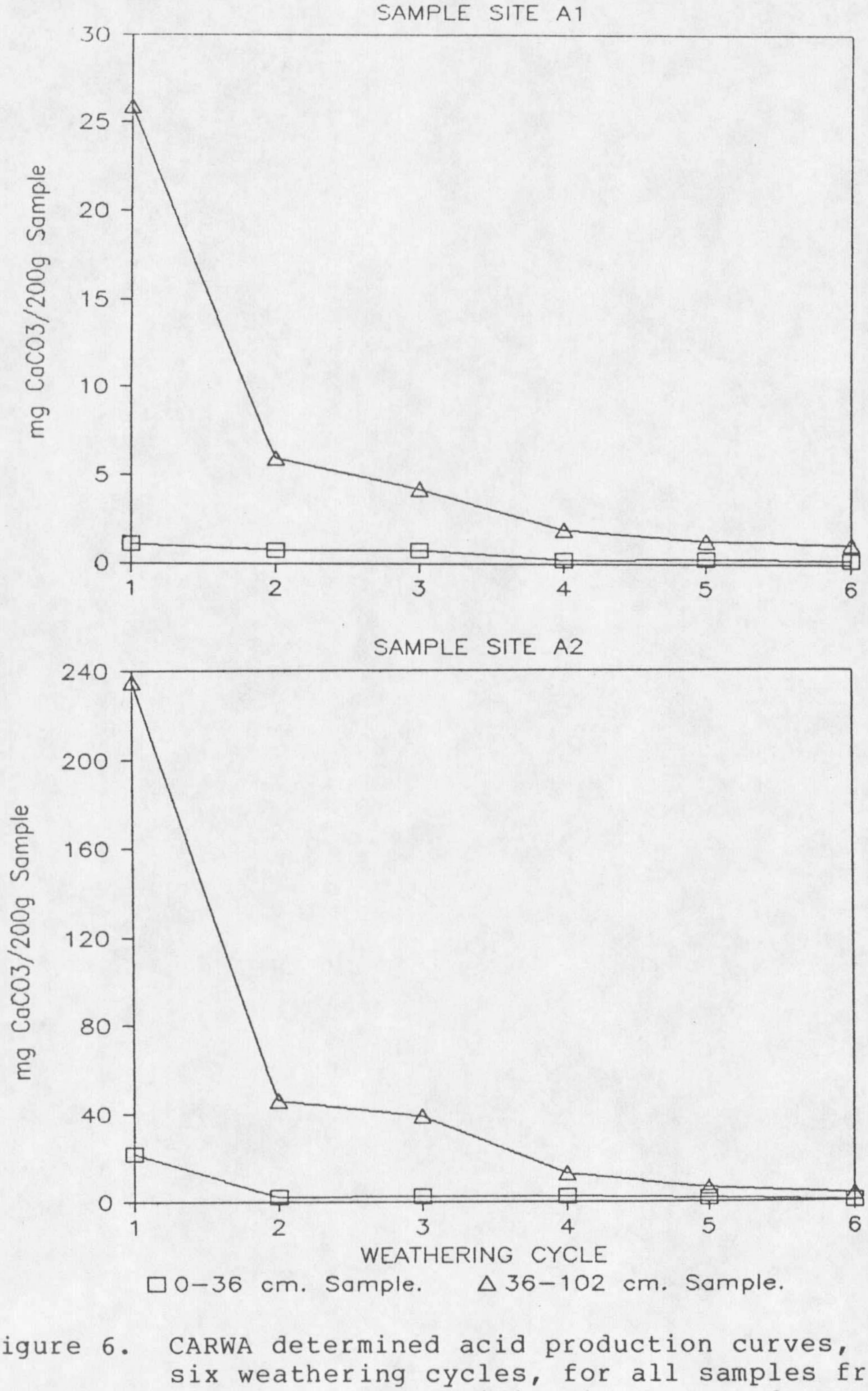
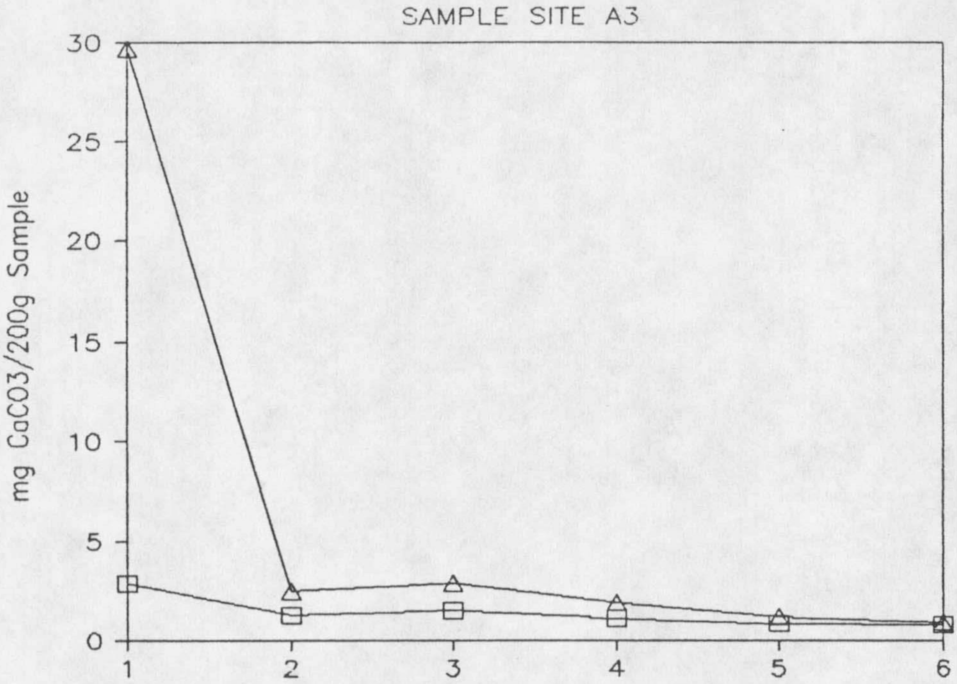


Figure 6. CARWA determined acid production curves, after six weathering cycles, for all samples from sites A and B. Acidity is presented as mg $CaCO_3$/200 g sample.



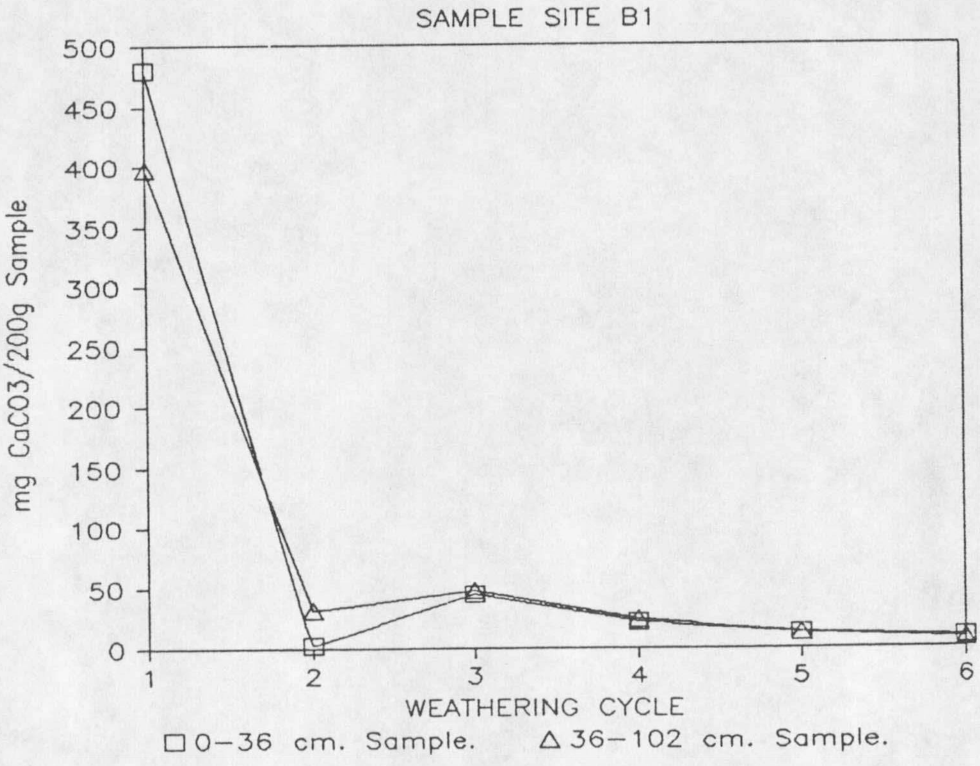


Figure 6. Continued

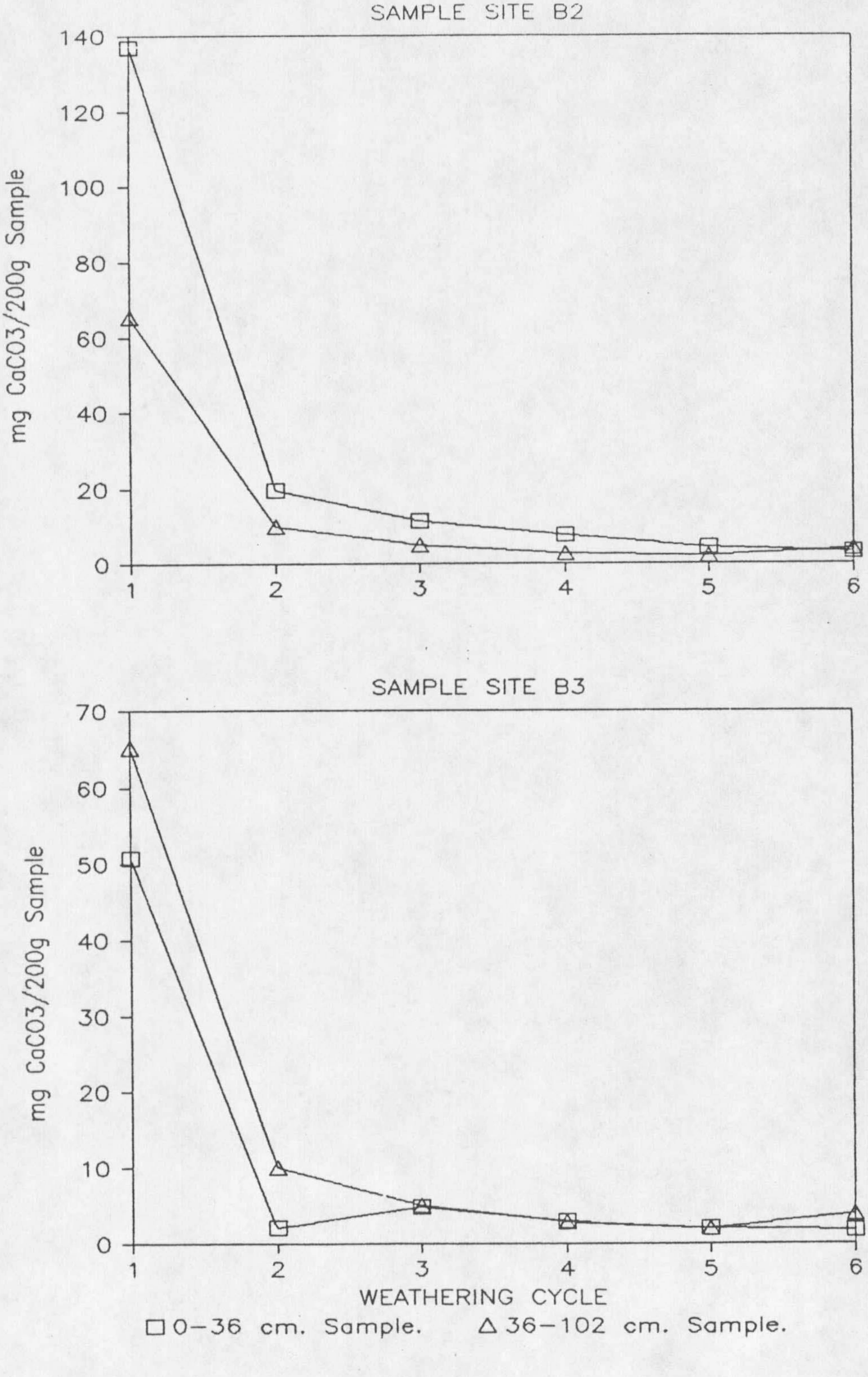


Figure 6. Continued

ANOV of site B acid production (Table 18 - Appendix B) also showed significant (P=.05) differences among the three plots, two sample depths and the plot by depth interaction. LSD calculations revealed a trend of increasing acidity across site B from plot B3 towards B1. Contrary to what was found in site A, LSD indicated that the surface samples produced more acidity than the subsurface samples.

The above statistical analyses indicate, as did tests with acid-base account results, that minesoils can reveal tremendous field variation within only a few meters with respect to acid production.

Lime Rate Determination

The factors influencing acid production in minesoils (pyrite occurrence and morphology, $CaCO_3$ content, soil water pH, oxygen, and bacteria) are all strongly related to the availability of water. Most important is the frequency of contact between infiltrating water and the minesoil material (Geidel 1979). During periods of precipitation or snowmelt, percolating water will rinse the accumulated weathering products from soil particle surfaces. After this wetting front has passed, water retained in contact with the particle surfaces by capillary forces form micro-geochemical environments. These areas of chemical reactivity continue to produce alkalinity and/or acidity until a new front passes, flushing the system to start the process anew. This hypothesis is the basis of rapid laboratory weathering and lime requirement calculation.

An important objective of this study was to determine the total one-time lime requirement for acid minesoil sites A and B at the Dave Johnston Mine. Converting the titratable acidity produced each cycle to metric tons of $CaCO_3$ per hectare 15 cm slice of material allowed a lime rate to be calculated (Table 13 - Appendix A). The logarithmic relationship of cumulative acidity and weathering cycles permitted accurate (high correlation) curve fitting which was used to project the long-term lime requirement. This lime requirement projection is based on the assumption that there are three wet-dry cycles in the natural environment of the Dave Johnston mine site annually. Therefore, three CARWA weathering cycles should approximate one year of chemical weathering in the field. Table 27 (Appendix C) presents the actual logarithmic curve fit equations and their correlation coefficients, used in projecting lime rates for all samples from sites A and B. CARWA projected lime rates needed to neutralize acid production for the next 30 years at sites A and B are shown in Table 5.

Lime application rates are a function of the purity of the lime agent, particle size, reactivity and depth of incorporation. Most liming agents are less than 100 percent pure, therefore, corrections must be made for the percentage of inert impurities within the liming material.

The solubility of the liming agent is also limited by the particle size distribution. Coarse agricultural limestones are less reactive than the fine limestone materials. Meyer and Volk (1952) reported that the most efficient particle size of a liming material was the 60 to 100 mesh (.25mm to .15mm) sized fraction. Liming agents that are of the 100 mesh fraction will react fastest to neutralize the soil pH. Fifty percent of the liming agent used in this study passed a 100 mesh screen. Therefore, half of it should react immediately while the other half will be remaining to neutralize additional acid production. Since not all of the applied lime will be chemically available for neutralization, a correction factor of 25 percent is traditionally added to the field lime rate to adjust for the lack of quantitative displacement of the liming agent in the minesoil. Finally, lime rates determined for a hectare 15 cm slice of material must be corrected for the depth of incorporation in the field. It is important that the lime be thoroughly mixed throughout the expected root zone. With the equipment available today, it is possible to effectively incorporate lime to a depth of approximately 25 cm. Investigations are now under way to develop more effective lime incorporation equipment that will mix lime to a depth of 100 cm or more.

Table 5. CARWA determined 30 year lime requirement projections for all samples from both sites A and B.

	Lime Requirement (Mt $CaCO_3$/ha/15cm)[1]	
	Depth of Sample (cm)	
Site	0-36	36-102
A1	0.08	0.72
A2	0.52	5.87
A3	0.20	0.61
B1	8.05	8.15
B2	2.89	1.39
B3	0.65	0.96

[1] These lime requirements are based on 100% pure $CaCO_3$, therefore, field application rates must be adjusted for the percentage of inert impurities within the liming agent as well as depth. In addition it is customary to add a correction factor of 25% to the application rate to adjust for the lack of quantitative displacement in the liming material.

When determining lime rates for minesoil materials, special consideration should be given to the length of time the materials have been exposed to weathering. Materials that have not been exposed to the atmosphere most likely will yield different acid production curves than those materials exposed for many years. Laboratory weathering of unexposed core samples, for example, theoretically will produce some type of bell-shaped curve as acid production starts from zero. As the framboidal pyrite reacts with water and oxygen, acid production will rise until the pyrite source is depleted after which acid yield will decrease.

Minesoil samples from sites A and B at the Dave Johnston Mine have been exposed to weathering as long as 18 years indicating that much pyrite oxidation has already taken place. Considering the length of exposure and low pH of these samples, the exchangeable acidity is likely to be quite high. Acid cations (i.e. H^{+}, Al^{+++}, Fe^{+++}), which can dominate the cation exchange of acid minesoils, are not removed from the exchange system by leaching with distilled/deionized water (CARWA weathering). The exchangeable acidity of acid minesoil samples can be substantial and should be accounted for when determining total lime requirements. It is recommended that exchangeable acidity of the cation exchange system be determined following CARWA weathering. A simple and inexpensive agricultural lime requirement method such as the SMP-Buffer procedure (Shoemaker et al. 1961) should be adequate. This lime rate in addition to the CARWA 30 year lime requirement projection for potential acidity should greatly enhance vegetation re-establishment on acid minesoils that have been exposed to weathering for a long period of time.

CARWA and Acid-Base Accounting

Acid-base account lime deficiencies for samples from sites A and B (Table 4) were consistently much higher than those lime rates determined by CARWA weathering projections (Table 5). Analysis of the less than 60 mesh (.25mm) size fraction is specified by the standard acid-base account procedure (Sobek et al. 1978). Framboidal pyrite (¼.25 microns diameter), however, is the only form of pyrite considered to be acid producing (Caruccio et al. 1976). Therefore, massive pyritic sulfur and/or other non-reactive sulfides may have been considered acid producing in the acid-base account analyses of these materials. The higher acid-base account lime recommendations may have also been due to the relatively high level of percent residual (organic) sulfur within these samples.

The State of Wyoming requires that organic sulfur be included in the calculation of the acid producing potential. Organic sulfur compounds are generally high in molecular weight, therefore, decomposition may be a long-term process. Frederick et al. (1957) investigated the decomposition of 21 naturally occurring organic compounds in soils and observed that some compounds decomposed and produced acid and some did not. The nature and identity of organic sulfur compounds in minesoils and overburden is not known at this time. It may be that some organic sulfur materials in mine spoils will not readily oxidize or produce acid if they do.

Acid-base accounting does not allow for differences in acid production due to pyrite morphology and to unknown weathering products of organic sulfur compounds. Laboratory weathering can circumvent the uncertainties of acid production from these different sources.

Nevertheless, coal mine operations in Wyoming will continue to use the acid-base account method as it is now definedfor overburden characterization. Therefore, linear regression analysis was used to see if any significant correlations existed between acid-base account recommended lime rates and CARWA 30 year lime rate projections. All data from both sites A and B combined, were used to develop the following regression equation:

$$y = -1.69 + 0.35x$$

where y is the CARWA 30 year lime rate (Mt $CaCO_3$/ha 15cm) and x is the acid-base account lime deficiency (Mt $CaCo_3$/ha 15cm). As hypothesized, the regression revealed a significant ($P=.05$) and strong linear relationship ($r=.95$) between the two lime recommendations. This means that samples taken from materials exposed to weathering for many years at the Dave Johnston Mine can have a CARWA type lime rate predicted from acid-base account data.

The acid-base account theoretically determines the maximum amount of potential acid produced by a sulfide containing minesoil sample. The CARWA method, however, determines a sample's characteristic acid production curve in order to pick a lime requirement for some point in future time. Acid-base account lime deficiencies in this study were consistently much higher than CARWA lime requirement projections but the two correlated extremely well. Perhaps the arbitrary 30 year lime requirement projection only accounts for the readily reactable sulfides such as framboidal pyrite. The higher the total sulfur content, reflected by higher acid-base account values, the higher the framboidal pyrite content. The higher framboidal pyritic sulfur would mean greater acidity produced during CARWA weathering. Thus the high correlation between acid-base accounting and CARWA determined 30 year lime requirements.

Sulfur Fractionation and Acid Production

To further investigate acid generation from CARWA, linear and multiple regression analyses were employed to detect any correlations between total acid production (after six weathering cycles) and individual sulfur components (e.g. pyritic sulfur). All data, from both sites A and B combined, were used to develop the regressions. Table 6 presents the linear regression equations for each of the four sulfur fractions. All of the regression analyses were significant at the 95 percent level.

As expected, a strong correlation (r=.88) between CARWA acid production (dependent) and percent total sulfur (independent) was revealed using linear regression. Percent sulfate sulfur also revealed a strong linear relationship (r=.88) with acid production. Sulfate sulfur is an end product of oxidation/hydrolysis reactions involving sulfides. Therefore, the high correlation of sulfate to acid yield may be linked to soluble acidity that was produced prior to laboratory weathering. A high degree of correlation (r=.85) also resulted when percent pyritic sulfur was related to acid production. Percent residual (organic) sulfur revealed the weakest, but still substantial correlation (r=.66).

Table 6. Linear regression analyses of sulfur fractions and CARWA cumulative titratable acidity (CTA).

Independent	Dependent	Equation[1]	R-value
% Total-S	CTA	$y = -185.4 + 1368.0x$	.88
% SO_4-S	CTA	$y = -131.1 + 1816.0x$	.88
% Pyritic-S	CTA	$y = -133.4 + 13590.0x$	.85
% Residual-S	CTA	$y = -125.7 + 4249.0x$	.67

[1]x = % sulfur form; y = acid production (CTA) after six CARWA cycles in mg $CaCO_3$/200g sample.

Multiple regression techniques were utilized to examine the relative importance of the independent variables (sulfate, pyritic and residual sulfur) on acid production from CARWA. This produced the regression equation:

$$y = -177.7 + 1186(X_1) + 7754(X_2) - 296(X_3)$$

where y is CARWA acid production (mg $CaCO_3$/200g sample) after six weathering cycles, X_1 is percent sulfate sulfur,

X_2 is percent pyritic sulfur and X_3 is percent residual (organic) sulfur. The coefficient of determination (R^2) of this equation is 0.88. This indicates that 88 percent of the factors contributing to acid production have been accounted for by the three sulfur forms. Individual contributions to the total R^2 for sulfate, pyritic and residual sulfur were .49, .38 and .01, respectively.

These results clearly indicate that total acid production, of minesoil samples from the Dave Johnston Mine, determined by CARWA is a measurement of both soluble acidity, which can be linked to the presence of sulfate, and potential acidity located within the pyritic fraction. Apparently, residual (organic) sulfur contributes little, if any, to acid production during CARWA analysis. The insignificance of residual sulfur in the production of acidity is important since the majority (76%) of total reduced sulfur present in these samples was in the residual form. Once again, the question of whether or not residual sulfur should be included in the calculation of acid-base accounts is brought up. If organic sulfur was left out of the acid-base account, a large amount of materials at Wyoming mine sites would then be characterized as suitable overburden. Therefore, less special handling of these materials would be required and mining costs would decrease.

Comparison of Four Lime Requirement Methods

To further evaluate CARWA performance, comparisons were made on four lime recommendation methods that were determined for one sample from site A and one from site B (Table 7). The four lime requirement methods compared were: 1) the less than .25 mm fraction acid-base account; 2) the less than 2 mm fraction acid-base account; 3) the 30 year manual laboratory weathering (MLW) projection and 4) the 30 year CARWA projection.

Table 7. Results of four lime requirement methods performed on one sample from site A and one from site B.

	Lime Requirement (Mt $CaCO_3$/ha/15 cm)	
Method[1]	Site A	Site B
<.25 mm ABA	21.6 a[2]	30.2 a
< 2 mm ABA	21.4 a	31.8 a
MLW	4.4 b	8.1 b
CARWA	5.9 c	8.1 b

[1] <.25 mm ABA is the less than .25 mm fraction acid-base account lime deficiency; <2 mm ABA is the less than 2 mm fraction acid-base account lime deficiency; MLW is a 30 year lime requirement projection from manual laboratory weathering; and CARWA is a 30 year lime requirement projection from a computerized automated rapid weathering apparatus.

[2] Same letter next to value within columns (mean of 3 reps) indicate no significant difference (p= .05) between lime requirements.

Analysis of variance (ANOV) was performed and least significant difference (LSD) calculated to ascertain whether or not statistical difference existed between lime requirement methods (Tables 19 and 20 - Appendix B). ANOV and LSD tests indicated no significant difference (P=.05) between the two acid-base account lime recommendation methods for both samples A and B. These analyses, as expected, did indicate statistical differences (P=.05) between acid-base accounting and laboratory weathering methods. As stated earlier, the higher magnitude of acid-base account lime rates may be due to the measurement of non-reactive (e.g. massive pyrite) sulfur compounds and/or the inclusion of organic sulfur in the calculation of the acid production potential.

For the sample taken from site A, significant difference (P=.05) did exist between MLW and CARWA 30 year lime rate projections. This, however, is a favorable result since the CARWA treatment yielded more acidity from the sample than the established MLW method. No significant difference (P=.05) were detected between CARWA and MLW lime rates for the B sample. This is also a favorable result since the original objective of this experiment was to at least equal MLW acid production with the new CARWA.

The advantages of a computerized automated rapid weathering apparatus over the laborious and time consuming manual laboratory weathering method are two fold. One advantage is the high degree of precision afforded by CARWA. The relative standard deviation between replicated weathering chambers is 3.01 percent. The mechanization of this method eliminates variation due to manual intervention of sample processing. Most importantly, CARWA can determine sample acid production characteristics and lime requirement results in a 24 hour period.

Field Tests

Lime Rates

The 30 year lime requirement projection is based on the assumption that three CARWA weathering cycles equal one year of chemical weathering in the field. The accuracy of this assumption can only be evaluated through field testing. During the week of April 22, 1985, acid minesoil sites A and B at the Dave Johnston Mine were limed and seeded to test the effectiveness of CARWA determined total lime requirements (Table 5) and a special surface applied soil-lime incubation lime rate (see Methods and Materials).

Cost effective reclamation of acidic minesoils will mean liming and seeding the site within a short time period (days). In order for successful seed germination to occur, the surface minesoil (0 to 18 cm) should be near pH 7 immediately prior to seeding. It must be understood that the CARWA recommended lime rate is intended to neutralize the acidity generated by a minesoil over a period of 30 years. Because of the relatively insoluble characteristics of $CaCO_3$, the neutralizing effect is slowly realized. Hence the special surface applied 24 hour soil-lime incubation determined lime rate was developed. This lime requirement method was used to indicate the approximate amount of liming agent necessary to immediately neutralize the pH of acid minesoil sites A and B in the 0 to 18 cm zone. One half of each 9.1 by 9.1 meter plot received this special 24 hour incubation lime rate to a depth of 18 cm in addition to standard CARWA lime requirements. This treatment was compared to subplots with just CARWA limed spoils.

Actual CARWA and CARWA plus incubation field amendment rates were adjusted for lime agent purity, depth of incorporation and lack of quantitative displacement of the lime in the minesoil. Total lime amounts incorporated in the field are presented in Table 8. Note that one half of each plot (9.1 x 4.55 m subplot) received the straight CARWA determined lime rate and the other half received the special CARWA plus surface incubation derived lime requirement.

Vegetation Performance

On June 26, 1985, sites A and B were sampled for plant density to evaluate germination and initial plant establishment (Table 9). These data indicate satisfactory germination had occurred on most of the plots. For comparison, a similar seeding on non-acid spoils at the Dave Johnston Mine with 30 cm of topsoil applied resulted in a perennial grass density of 236 plant/m^2 after one growing season (Glenrock Coal Company 1983). Therefore, initial germination and establishment of grasses on sites A and B was judged to be good considering that the seeding was on acid spoils with no topsoil application. The majority of emerging weedy species seemed to be Russian thistle (_Salsola kali_) and summer cypress (_Kochia scoparia_). These species are considered primary invaders at the Dave Johnston Mine, but they generally do not persist as major components in an establishing plant community after three years.

Table 8. Total lime amounts incorporated to a depth of 102 cm for field test site A and 76 cm for field test site B.

	Total Lime Applied (Mt $CaCO_3$/hectare)	
PLOT	CARWA	CARWA + INCUBATION
A1	4.5	22
A2	38	54
A3	4.5	22
B1	54	76
B2	18	49
B3	9	43

Analysis of variance (ANOV) and least significant difference (LSD) was conducted on plant density data for sites A and B (Table 21 and 22 - Appendix B) in order to analyze the three factors -- plots, lime treatment and vegetative class. ANOV and LSD tests indicated that

Table 9. Initial seedling density for acid minesoil sites A and B at the Dave Johnston Mine.

Plot	Density (plant/m²) CARWA[1] Perennial Grasses	Weeds	CARWA + INCUBATION Perennial Grasses	Weeds	Plot[2] Mean
A1	53	3	94	6	78 a
A2	143	6	185	17	176 b
A3	50	1	171	3	113 a
Lime Trt Mean[2]	85 a		159 b		
B1	112	4	165	13	147 b
B2	70	3	138	9	110 b
B3	0	0	104	6	55 a
Lime Trt Mean[2]	63 a		145 b		

[1]CARWA is the subplot treated with lime rates designed from CARWA recommended lime requirement projections. CARWA + INCUBATION is the subplot treated with an additional surface 0-18 cm soil-lime incubation determined lime rate plus CARWA rates.

[2]Same letter next to mean density indicates no significant difference (P=.05) between means.

density was significantly (P=.05) greater on plots with the highest lime rates. These tests also indicated that plant density on the subplots treated with the CARWA plus incubation rates was significantly (P=.05) greater than the subplots amended with straight CARWA lime rates. Seeded perennial grass density was found to be statistically greater (P=.05) than that of the invading weedy species.

Percent canopy cover and above-ground production was measured for each site at maximum seasonal growth on July 23, 1985 (Tables 10 and 11). As expected, canopy cover and production values obtained during the first growing season were fairly low. For comparison, a similar seeding on non-acid spoils at the Dave Johnston Mine with 30 cm of topsoil applied resulted in a perennial grass cover value of 24% and a production value of 567.8 kilograms per hectare (Glenrock Coal Company 1983).

ANOV and LSD tests were performed on canopy cover and above-ground production for sites A and B (Tables 23 through 26 - Appendix B). As with density, the three factors analyzed were plots, lime treatment and vegetative class.

The hypothesis behind sampling and determining a custom lime requirement for each plot individually was to make sure each plot was neutralized to pH 7. ANOV and LSD tests consistently indicated, as it did with density, that

Table 10. Mean canopy cover during first growing season for acid minesoil sites A and B at the Dave Johnston Mine.

Plot	Canopy Cover (%): CARWA[1] Perennial Grasses	CARWA[1] Weeds	CARWA + INCUBATION Perennial Grasses	CARWA + INCUBATION Weeds	Plot[2] Mean
A1	0.8	0.2	1.5	11.1	6.8 a
A2	4.6	3.4	4.6	7.4	10.0 b
A3	2.1	1.0	6.0	1.6	5.4 a
Lime Trt. Mean[2]	4.0 a		10.7 b		
B1	7.8	1.7	13.8	2.9	13.1 c
B2	2.4	0.7	4.9	0.9	4.5 b
B3	0	0	2.7	0.7	1.7 a
Lime Trt. Mean[2]	4.2 a		8.6 b		

[1]CARWA is the subplot treated with lime rates designed from CARWA recommended lime requirement projections. CARWA + INCUBATION is the subplot treated with an additional surface 0-18 cm soil-lime incubation determined lime rate plus CARWA rates.

[2]Same letter next to mean cover indicates no significant difference (P=.05) between means.

Table 11. First year above-ground plant production for acid minesoil sites A and B at the Dave Johnston Mine.

Plot	CARWA[1] Perennial Grasses	CARWA[1] Weeds	CARWA + INCUBATION Perennial Grasses	CARWA + INCUBATION Weeds	Plot[2] Mean
	Production (kg/ha)				
A1	6.2	1.0	18.1	131.4	78.4 a
A2	51.0	39.5	65.5	88.8	122.4 b
A3	11.8	0.1	42.8	88.0	71.4 a
Lime Trt. Mean[2]	36.5 a		144.9 b		
B1	75.0	14.6	166.1	63.3	159.5 c
B2	36.0	6.3	26.8	48.0	117.1 b
B3	0	0	26.3	20.0	23.5 a
Lime Trt. Mean[2]	44.0 a		116.8 b		

[1]CARWA is the subplot treated with lime rates designed from CARWA recommended lime requirement projection. CARWA + INCUBATION is the subplot treated with an additional surface 0-18 cm soil-lime incubation determined lime rate plus CARWA rates.

[2]Same letter next to mean cover indicates no significant difference (P=.05) between means.

cover and production was significantly (P=.05) greater on plots with the highest lime rates. This is perplexing since presumably the highest lime rates should mean the greatest amount of acid production thus worse conditions for plant growth. This result may be due to a flash of $CaCO_3$ solubility in the plots with the heaviest lime rates. This would cause the pH to rise rapidly towards neutrality resulting in better conditions for plant establishment. This effect may decrease over the next few years.

ANOV and LSD tests of lime treatment consistently indicated that cover and production was significantly (P=.05) greater on subplots amended with CARWA plus the special incubation rates than on subplots amended with straight CARWA lime rates. This result clearly indicated that the application of a 24 hour soil-lime incubation determined lime rate in the surface 0 to 18 cm will increase plant performance if seeding is to be done immediately following liming.

In all but one case, ANOV and LSD analyses of vegetative class revealed that canopy cover and production of seeded perennial grasses was significantly greater (P=.05) than that of the invading weedy species. The invasion of a few weedy species, especially forbs, is characeristic of developing post-mine plant communities in the Northern Great Plains (Rennick and Munshower 1985).

Continued monitoring of plant density, canopy cover and plant production over the next few years is a must in order to fully evaluate CARWA determined lime amendments.

Minesoil pH Monitoring

The primary objective of liming an acidic minesoil is to elevate the pH to near neutrality. Immediately after liming and seeding sites A and B in April, 1985, soil cores were taken from each subplot with a Giddings soil sampler for paste pH determination. Soil core samples were obtained again four months later on July 24, 1985. Results of these pH measurements are graphically presented for each site by subplot and depth in Figure 7.

These data indicate that the greater plant performance on the subplots limed with CARWA plus incubation rates was, as expected, due to the higher surface pH of these subplots. A general trend of decreasing pH with depth was also observed. Therefore, it seems as though complete incorporation of lime was accomplished to a depth of only 15 cm or so. This suggests that efficient incorporation of lime to a depth of 100 cm by pouring lime immediately behind a tractor mounted ripper may not be feasible.

A complete seeding failure occurred on the B3 subplot treated with straight CARWA lime rates. Minesoil pH data for this subplot was quite low indicating that the CARWA method underestimated this lime requirement or minesoil

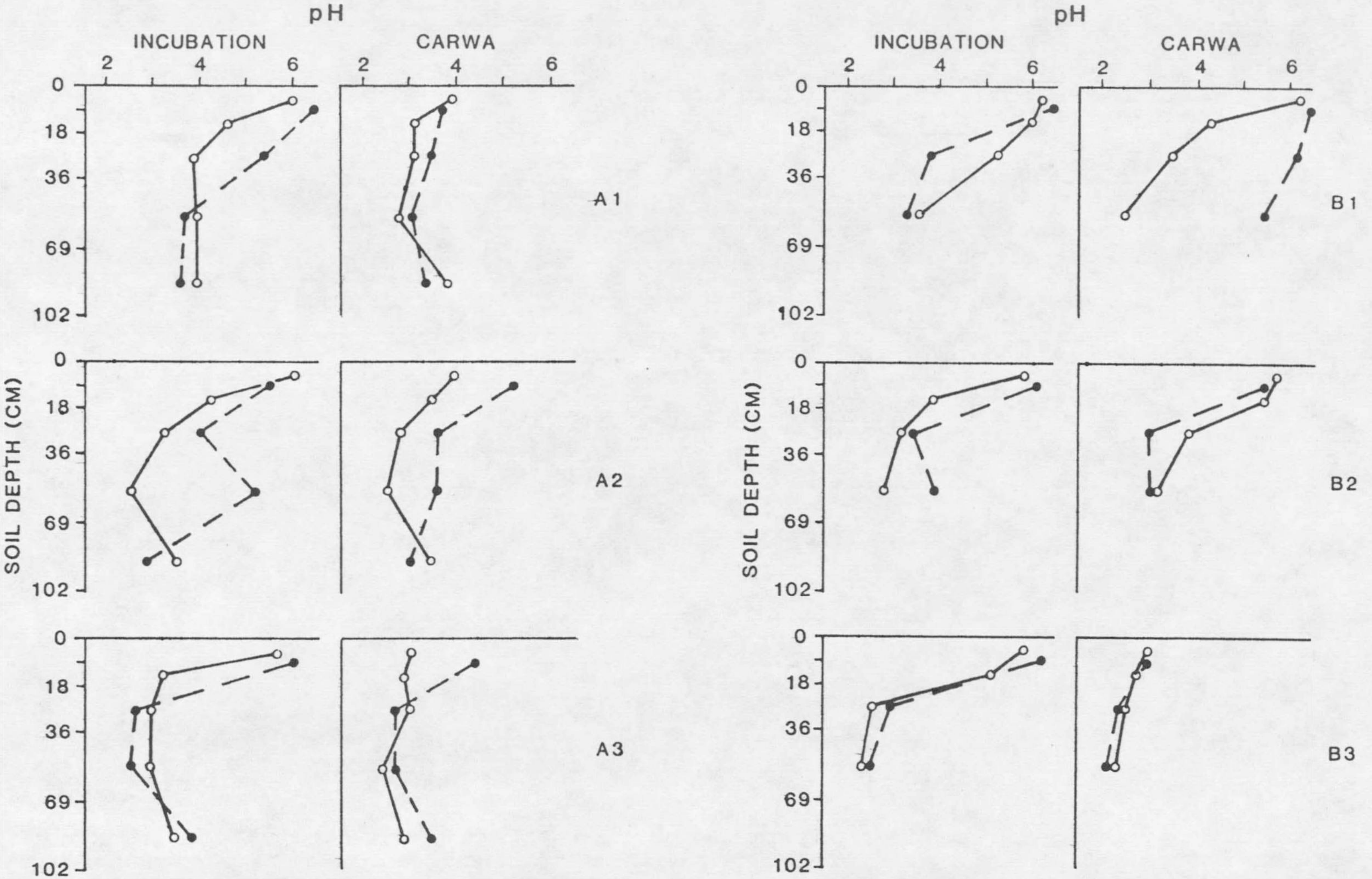


Figure 7. Minesoil paste pH for core samples taken at sites A and B just after liming (dashed line) and four months after liming and seeding (solid lines).

variation was responsible for a sample that produced little acidity upon laboratory weathering. It was noted earlier that minesoil variation, with respect to acid production, was substantial over short distances across sites A and B and by depth.

The most important observation made with these data are the general trend of decreasing pH between the two sampling dates. It is too early to tell if re-acidification is occuring. Continued monitoring of minesoil pH must be done in order to more accurately evaluate CARWA determined lime requirements.

At this point, it looks as though the minesoil pH of sites A and B has yet to be completely neutralized by the lime amendments. The reasons for this are likely to be varied and complex. Perhaps the liming agent has not had enough time to react with the acidity. Calcium carbonate is a relatively insoluble compound and its acid neutralizing effects are slowly realized. Over the next few years the pH of these sites may increase as the lime becomes more available.

Another reason for the minesoil pH remaining low may lie within the calculation of the CARWA lime requirement projection. The assumption that three weathering cycles should equal one year of weathering in the field may be in error. If in actuality ten weathering cycles, for example, represent one year of weathering in the natural environment of the Dave Johnston Mine then lime rates used in this study may be too low. This factor is impossible to evaluate without years of test site monitoring.

A major concern of amending acid producing minesoils is going to be field variation and the sampling problems associated with it. Statistical analyses of results from this study revealed significant variation of acid production across plots and by depth. A more intensive sampling scheme with compositing may have been necessary to accurately determine lime requirements for these plots. However, a sampling intensity any greater than the one utilized in this study would be unrealistic with respect to actual minesoil management plans.

Finally, the persisting low minesoil pH may be due to the exchangeable acidity of these materials. These materials have been exposed to weathering for as long as 18 years which means the exchangeable acidity is probably quite high. Perhaps this exchangeable acidity overwhelmed the CARWA lime rate which was only intended to neutralize remaining potential acidity. It was recommended earlier that this exchangeable acidity be quantified using agricultural lime requirement methods such as the SMP Buffer procedure (Shoemaker et al. 1961). This exchangeable acidity lime requriement plus the CARWA rate for potential acidity will equal a true total lime requirement for minesoils that have already produced much acid.

SUMMARY AND CONCLUSIONS

Acid minesoil problems, similar to those in the eastern mining states, are becoming a problem at western mine sites. Traditional agricultural lime requirement methods do not accurately evaluate on-going acid production from sulfide containing minesoils. Acid-base accounting is widely used to assess the long term acid production and base release in minesoil materials. The method can accurately identify which geologic stratum will generate acid upon weathering and which will not. However, acid base accounting may not be appropriate for determining lime requirements since the kinetics of acid and alkaline production are not parallel. This means a simple balance of the acid potential against the base potential, to determine the excess of one over the other, is incorrect. Laboratory weathering methods have been used successfully to circumvent the uncertainties of acid-base accounting. The manual laboratory weathering method, however, is extremely laborious and time consuming, requiring up to 12 weeks for adequate results. The overall objective of this study was to develop a computerized automated rapid weathering apparatus (CARWA) that could determine total one-time application lime requirements for acid producing minesoils in 24 hours instead of 12 weeks.

Samples were obtained from two acid minesoil sites at the Dave Johnston Mine in Wyoming for physicochemical characterization and laboratory weathering tests. Studies were conducted to compare CARWA lime recommendations to those obtained by the more established but laborious manual laboratory weathering method (MLW) and acid-base accounting. CARWA acid generation was further investigated by evaluating relationships between different minesoil sulfur components and acid production. Finally, CARWA determined lime rates for two acid minesites at the Dave Johnston Mine were put to the ultimate test by implementing them into field plot experiments.

Conclusions drawn from these studies were as follows:

1) The mechanics and precision of the CARWA are sound. Three replications each of twelve samples were weathered consecutively without interuption due to mechanical malfunction. The relative standard deviation between replicated samples averaged only 3.0%.

2) CARWA determined acid production curve characteristics were similar to those determined during earlier manual laboratory weathering studies at Montana State University. This meant that accurate curve fitting analysis could be used to project the long term (30 year) lime requirement for each of the acid minesoil samples.

3) Acid production potentials exhibited extreme field variability within only a few meters across acid minesoil sites at the Dave Johnston Mine. This variability may pose problems when attempting to accurately characterize large minesoil areas for acid production potential.

4) Acid-base account lime recommendations were consistently much higher than those determined by laboratory weathering. This was probably due to the measurement of non-reactive (e.g. massive pyrite) sulfur compounds in the minesoil samples. The inclusion of organic sulfur in the acid-base account calculation may also be responsible for the large discrepency between the two lime rates.

5) CARWA determined 30 year lime requirements correlated well ($r=.95$) with acid-base account lime recommendations using linear regression. Therefore, a CARWA type lime rate can be predicted for materials at the Dave Johnston Mine from routine acid-base account results.

6) Multiple regression analysis of CARWA acid production and sulfur fractionation indicated that soluble acidity and potential acidity from the pyritic fraction were responsible for acid yield from samples taken at the Dave Johnston Mine. Apparently, residual (organic) sulfur contributed little, if any, to acid production during CARWA weathering cycles.

7) Thirty year CARWA lime requirements were either statistically similar to or greater than 30 year manual laboratory weathering lime rates.

8) Substantial perennial grass establishment occurred on non-topsoiled acidic plots amended with CARWA datermined lime requirements. A special 24 hour soil-lime incubatoin derived lime rate applied to the surface 0 to 18 cm zone increased seed germination and plant establishment.

The above results suggest that a computerized automated rapid weathering apparatus has the potential to determine total lime requirements of acid producing minesoils in a automated fashion within a 24 hour time frame.

RECOMMENDATIONS

The automated weathering procedure used in this study attempted to optimize conditions for acid production similar to those found in the natural minesite environment. In order to increase the rate of reaction, it is recommended that a heating element be installed within the weathering chambers. This will ensure optimum conditions for the proliferation of catalytic bacteria populations. Russell (1984) recommended that a freeze-thaw cycle be incorporated into manual weathering procedures to enhance physical breakdown and increase the potential oxidation surfaces of minesoil samples. This will better simulate mineosil weathering processes, however, iron and sulfur oxidizing bacteria populations may suffer.

In order to fully test the ability of CARWA to expedite the oxidation of sulfides, fresh un-oxidized core samples, known to contain substantial levels of reduced sulfur, should be obtained for analysis. Acid production from these samples during CARWA cycles will confirm that rapid weathering is indeed occurring. In addition, complete sulfur fractionation determined before and after laboratory weathering will aid in the understanding of acid yield from CARWA. A decrease in pyritic sulfur content and an increase in sulfate sulfur after weathering, for example, would indicate without a doubt that sulfides were decomposing during CARWA cycles.

Organic sulfur is still an uncertain component of the total sulfur content in western overburden and minesoil materials. Caution should be used in interpreting acid-base account data when organic sulfur is present in the sample. Further research is needed to better quantify the contribution of organic sulfur to acid production in western minesoils.

Minesoil materials that have been weathering in the field a long time and are acidic may have a cation exchange system saturated with acid cations. Therefore, substantial exchangeable acidity, which is not leached with distilled/deionized water, will be present in minesoil samples after laboratory weathering is completed. It is recommended that agricultural lime requirement methods be used at the end of laboratory weathering to account for the exchangeable acidity of the cation exchange system. The lime requirement of the exchangeable acidity in addition to a potential acidity lime requirement determined by CARWA will equal a true total lime rate for acid producing minesoils.

The extrapolation of laboratory results to anticipated field responses is always the most difficult element of overburden analysis. Acidic minesoil sites at the Dave Johnston Mine ammended with CARWA determined lime rates have been evaluated after only one growing season. Continued monitoring of vegetation performance and minesoil pH is necessary if the assumption that three weathering cycles represent one year of weathering in the field is to be fully tested. This assumption can be further evaluated by monitoring profile moisture throughout the year with a neutron probe. This will reveal how many wetting fronts are passing through the profile during a year at the Dave Johnston Mine.

LITERATURE CITED

LITERATURE CITED

AOAC. 1975. Agricultural liming materials. Pages 1-7 in W. Horwitz, ed. Official Methods of Analysis of the Association of Official Analytical Chemists. 12th edition. Washington D.C. 1094 pp.

Baker, D.E. and M.C. Amacher. 1982. Nickel, copper, zinc, and cadmium. Pages 323-336 in A.L. Page, ed. Methods of Soil Analysis. American Society of Agronomy Monograph No. 9, Part 2, 2nd. edition. Madison, WI. 1159 pp.

Barnhisel, R. and P.M. Bertsch. 1982. Aluminum. Pages 275-300 in A.L. Page, ed. Methods of Soil Analysis. American Society of Agronomy Monograph no. 9, Part 2, 2nd. edition. Madison, WI. 1159 pp.

Bingham, F.F. 1982. Boron. Pages 431-447 in A.L. Page, ed. Methods of Soil Analysis. American Society of Agronomy Monograph No. 9, Part 2, 2nd. edition. Madison WI. 1159 pp.

Blanton, F.Y. and D.J. Dollhopf. 1985. Technique development for determining total lime requirement for acid minesoils. Unpublished Mont. State Univ. Reclamation Research Unit Research Report to Montana Abondoned Mine Reclamation Bureau, Helena, MT.

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

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

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

Caruccio, F.T. and G. Geidel. 1984. The prediction of acid mine drainage from coal strip mines. Proceedings of the Conference on Reclamation of Abandoned Acid Spoils. Missouri Dpet. of Natural Resources, Land Reclamation Commission.

Daubenmire, R. 1959. A canopy-coverage method of vegetational analysis. Northwest Sci. 33:43-64.

Day, P.R. 1965. Particle fractionation and particle-size analysis. Page 545-567 in C.A. Black, ed. Methods of Soil Analysis. American Society of Agronomy Monograph No. 9, Part 2. Madison, WI. 801 pp.

Dollhopf, D.J. 1984. Acid minesoil problems in the northern plains states. First Meeting on Reclamation of Lands Disturbed by Surface Mining: American Soc. for Surface Mining and Reclamation. July 10-13. Owensburo, KY. pp. 292-301.

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

Frederick, L.R., R.L. Starky and W. Segal. 1957. Decomposability of some organic sulfur compounds in soil. Soil Sci. Soc. Am. Proc. 21:287-292.

Ganje, T.J. and D.W. Rains. 1982. Arsenic. Pages 385-402 in A.L. Page, ed. Methods of Soil Analysis. American Society of Agronomy Monograph No. 9, Part 2, 2nd edition. Madison, WI. 1159 pp.

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

Glenrock Coal Company. 1983. Dave Johnston Vegetation Monitoring and Research Activities Annual Report. Glenrock Coal Company, Glenrock, WY.

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

McLean, E.O., 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.

McLean, E.O. 1982. Soil pH and lime requirement. Pages 199-224 in A.L. Page, ed. Methods of Soil Analysis. American Society of Agronomy Monograph No. 9, Part 2, 2nd edition. Madison, WI. 1159 pp.

Nelson, D.W. and L.E. Sommers. 1982. Total carbon, organic carbon, and organic matter. Pages 539-579 in A.L. Page, ed. Methods of Soil Analysis. American Society of Agronomy Monograph No. 9, Part 2, 2nd edition. Madison, WI. 1159 pp.

Peech, M. 1965. Lime requirement. Pages 927-932 in C.A. Black, ed. Methods of Soil Analysis. American Society of Agronomy Monograph No. 9, Part 2. Madison, WI. 1572 pp.

Rand, M.C. (ed.). 1975. Standard Methods for the Examination of Water and Wastewater, 14th edition. American Public Health Association, Washington, D.C. 1193 pp.

Reisenhauer, H.M. 1965. Molybdenum. Pages 1050-1058 in C.A. Black, ed. Methods of Soil Analysis. American Society of Agronomy Monograph No. 9, Part 2. Madison, WI. 1572 pp.

Rennick, R.B. and F.F. Munshower. 1985. Season of seeding and plant community structure on surface mined land in southwest Montana. Reclamation Research Unit Report to Western Energy Co., Butte, MT. Mont. Ag. Exp. Sta. Special Report 15, Bozeman, MT.

Rhoades, J.D. 1982. Cation exchange capacity. Pages 149-157 in A.L. Page, ed. Methods of Soil Analysis. American Society of Agronomy Monograph No. 9, Part 2, 2nd edition. Madison, WI. 1159 pp.

Richards, L.A. 1965. Physical condition of water in soil. Pages 128-152 in C.A. Black, ed. Methods of Soil Analysis. American Society of Agronomy Monograph No. 9, Part 1. Madison, WI. 1572 pp.

Russell, L.J. 1984. Technique development for determining total lime requirement for acid-mine sites. M.S. Thesis, Reclamation Research Unit, Montana State University, Bozeman, MT.

Russell, L.J. and D.J. Dollhopf. 1984. Lime requirement determination of minesoil materials in the Butte-Anaconda areas. Unpublished Montana State University, Reclamation Research Unit Report to Anaconda Minerals Co., Butte, Mt.

Sandoval, F.M. and J.R. Power, 1977. Laboratory methods recommended for chemical analysis of mined-land spoils and overburden in western United States. U.S. Dept. of Agric., Agric. Handbook No. 525.

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 Ferrobacilus ferro-oxidans. I. And improved medium and harvesting procedure for securing high cell yields. Journal of Bacteriology, 77:642-647.

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., 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.

Sturey, A.S., J.R. Freeman, T.A. Keeney and J.W. Strumm. 1982. Overburden analyses by acid-base accounting and simulated weathering studies as a means of determining the probable hydrological consequences of mining and reclamation. Symp. on Surface Mining Hydrology, Sedimentology and Reclamation, Univ. of Kentucky, Lexington. pp. 163-179.

Thomas, G.W. 1982. Exchangeable cations. Pages 159-165 in A.L. Page, ed. Methods of Soil Analysis. American Society of Agronomy Monograph No. 9, Part 2, 2nd edition. Madison, WI. 1159 pp.

U.S. Department of Agriculture. 1984. Procedures for collecting soil samples and methods of analysis for soil surveys. Soil Survey Investigations Report No. 1. Soil Conservation Service. 68 pp.

U.S. Salinity Laboratory Staff. 1954. Diagnosis and improvement of saline and alkali soils. Agricultural Handbook No. 60. U.S. Dept. of Agriculture. Washington D.C.

Woodruff, C.M. 1943. Lime requirement determination of soils by means of titration curves. Soil Science, 56:341-351.

Wyoming Department of Environmental Quality. 1984. Guideline No. 1: Topsoil and Overburden. Wyoming DEQ, Land Quality Division.

APPENDICES

APPENDIX A

TOPSOIL AND OVERBURDEN SUITABILITY CRITERIA AND LIME REQUIREMENT CALCULATION

Table 12. Wyoming Dept. of Environmental Quality, Land Quality Divison criteria to establish topsoil and overburden suitability.

	Suitability Levels		
Parameter	Suitable	Marginal	Unsuitable
pH	5.5-8.5	5.0-5.5 8.5-9.0	< 5.0 > 9.0
EC (mmhos/cm)	0-8	8-12	> 12
Saturation %	25-80	< 25 > 80	
Texture		C, SIC, S	
SAR	0-10	10-15	> 15
Boron (ppm)	< 5.0		> 5.0
Molybdenum (ppm)	< 1.0	>1.0	
Acid-base account	> -5 tons $CaCO_3$/1000 tons		< -5 tons $CaCO_3$/1000 tons
Arsenic (ppm)	< 2.0	>2.0	
% Organic Carbon	< 10		> 10

Table 13. Calculation of lime requirement for one laboratory weathering cycle.

$$ETA = \frac{Vt \times Nt}{Va} \times 50{,}000 \times Ve$$

$$TA = \frac{ETA}{\%Ve} = \frac{x}{100}$$

$$RA = TA - ETA$$

$$LR_X = (TA_X - RA_{X-1}) \times 10 - 2000$$

Where X = weathering cycle.

Legend:

ETA = Extracted titratable acidity (mg $CaCO_3$)

Vt = Volume of Titrant used (ml NaOH)

Nt = Normality of Titrant (NaOH)

Va = Volume of Aliquot Titrated (ml)

Ve = Volume extracted from Chamber (L)

TA = Total Acidity (mg $CaCO_3$)

%Ve = % of Total Water Added to Chamber Extracted

RA = Residual Acidity (mg $CaCO_3$)

LR_X = Lime Requirement for One Weathering Cycle (Tons $CaCO_3$/A/6 in.)

Tons $CaCO_3$/A/6in. x 2.242 = Mt $CaCO_3$/ha/15cm.

APPENDIX B

ANOV AND LSD TABLES

Table 14. Analysis of variance and least significant difference of site A - acid-base account (ABA).

Source	D.F.	ANOV S.S.	M.S.	F-value
Blocks	2	.1281	.6407E-01	
Plots	2	31.13	15.57	485.9*
Depth	1	22.38	22.38	698.5*
Plots x Depth	2	69.96	34.98	1092.0*
Residual	10	.3204	.3204E-01	

Factor	LSD ANALYSIS Identity	Mean ABA
Plots	A1	2.742 A
	A3	3.230 B
	A2	5.743 C
Depth (cm)	0-36	2.790 A
	36-102	5.121 B

Table 15. Analysis of variance and least significant difference of site B - acid-base account (ABA).

Source	D.F.	ANOV S.S.	M.S.	F-value
Blocks	2	.1412	.7062E-01	
Plots	2	206.1	103.0	2030.*
Depth	1	24.59	24.59	484.3*
Plots x Depth	2	16.28	8.138	160.3*
Residual	10	.5078	.5078E-01	

Factor	LSD ANALYSIS Identity	Mean ABA
Plots	B3	3.205 A
	B2	5.512 B
	B1	11.25 C
Depth (cm)	36-102	5.488 A
	0-36	7.826 B

Asterisk (*) indicates significance at p = .05. Same letter next to Mean ABA indicates no significant difference between means.

Table 16. Analysis of variance and least significant difference of <.25 mm fraction acid-base account and <2 mm fraction acid base account (ABA).

		ANOV		
Source	D.F.	S.S.	M.S.	F-value
Blocks	2	.1877E-01	.9384E-02	
Method	1	.1800E-02	.1800E-02	.1344E-03
Residual	68	910.8	13.39	

	LSD ANALYSIS	
Factor	Identity	Mean ABA
Methods	<.25 mm fraction	5.281 A
	<2 mm fraction	5.291 A

Asterisk (*) indicates significance at p = .05. Same letter next to Mean ABA indicates no significant difference between means.

Table 17. Analysis of variance and least significant difference of site A - mean cumulative titratable acidity (CTA) after six CARWA weathering cycles.

		ANOV		
Source	D.F.	S.S.	M.S.	F-value
Blocks	2	61.39	30.70	
Plots	2	.1078E+06	.5392E+05	1887.*
Depth	1	.7149E+05	.7149E+05	2502.*
Plots x Depth	2	.7759E+05	.3879E+05	1358.*
Residual	10	285.7	28.57	

	LSD ANALYSIS	
Factor	Identity	Mean CTA
Plots	A1	21.72 A
	A3	23.25 A
	A2	186.7 B
Depth (cm)	0-36	14.20 A
	36-102	140.20 B

Table 18. Analysis of variance and least significant difference of site B - mean cumulative titratable acidity (CTA) after six CARWA weathering cycles.

		ANOV		
Source	D.F.	S.S.	M.S.	F-value
Blocks	2	48.09	24.05E-01	
Plots	2	.8504E+06	.4252E+06	3537.*
Depth	1	7817.	7817.	65.03*
Plots x Depth	2	.1127E+05	5635.	46.87*
Residual	10	1202.	120.2	

	LSD ANALYSIS	
Factor	Identity	Mean CTA
Plots	B3	51.31 A
	B2	136.1 B
	B1	548.9 C
Depth (cm)	36-102	224.6 A
	0-36	266.3 B

Asterisk (*) indicates significance at p = .05. Same letter next to Mean CTA indicates no significant difference between means.

Table 19. Analysis of variance and least significant difference of four lime recommendation methods performed on one sample from site A.

Source	D.F.	ANOV S.S.	M.S.	F-value
Blocks	2	.2610	.1305	
Method	3	160.8	53.61	1529.*
Residual	10	.2104	.3506E-01	

Factor	LSD ANALYSIS Identity	Mean Lime Requirement
Method	MLW	1.953 A
	CARWA	2.617 B
	<2 mm ABA	9.540 C
	<.25 mm ABA	9.643 C

Table 20. Analysis of variance and least significant difference of four lime recommendation methods performed on one sample from site B.

Source	D.F.	ANOV S.S.	M.S.	F-value
Blocks	2	.1343	.6716E-01	
Method	3	312.3	104.1	498.8*
Residual	6	1.252	.2087	

Factor	LSD ANALYSIS Identity	Mean Lime Requirement
Method	CARWA	3.600 A
	MLW	3.687 A
	<.25 mm ABA	13.47 B
	<2 mm ABA	14.20 B

Asterisk (*) indicates significance at p = .05. Same letter next to Mean lime requirement indicates no significant difference between means.

Table 21. Analysis of variance and least significant difference of site A seeding density - plot, lime treatment and vegetative class.

ANOV

Source	D.F.	S.S.	M.S.	F-value
Blocks	26	18.46	.7098	
Plots	2	11.29	5.647	13.79*
Treatment	1	13.05	13.05	31.86*
Plots x Treatment	2	1.215	.6077	1.484
Veg. Class	1	120.0	120.0	293.0*
Plots x Veg. Class	2	9.447	4.724	11.54*
Treatment x Veg. Class	1	5.213	5.213	12.73*
Plots x Trt x Veg. Class	2	3.173	1.586	3.875*
Residual	286	117.1	.4904	

LSD ANALYSIS

Factor	Identity	Mean seedling density
Plots	A1	1.165 A
	A3	1.305 A
	A2	1.612 B
Lime Treatment	CARWA	1.160 A
	CARWA + INCUBATION	1.562 B
Veg. Class	Weeds	.7524 A
	Grasses	1.969 B

Asterisk (*) indicates significance at p = .05. Same letter next to Mean seedling density indicates no significant difference between means.

Prior to analysis all data were transformed using the square root of (x + 3/8) to adjust from a skewed to a normal distribution.

Table 22. Analysis of variance and least significant difference of site B seeding density -plot, lime treatment and vegetative class.

ANOV				
Source	D.F.	S.S.	M.S.	F-value
Blocks	26	18.46	.7098	
Plots	2	11.29	5.647	13.79*
Treatment	1	13.05	13.05	31.86*
Plots x Treatment	2	1.215	.6077	1.484
Veg. Class	1	120.0	120.0	293.0*
Plots x Veg. Class	2	9.447	4.724	11.54*
Treatment x Veg. Class	1	5.213	5.213	12.73*
Plots x Trt x Veg. Class	2	3.173	1.586	3.875*
Residual	286	117.1	.4904	

LSD ANALYSIS			
Factor	Identity	Mean seedling density	
Plots	B3	1.165	A
	B2	1.305	B
	B1	1.612	B
Lime Treatment	CARWA	1.160	A
	CARWA + INCUBATION	1.562	B
Veg. Class	Weeds	.7524	A
	Grasses	1.969	B

Asterisk (*) indicates significance at $p = .05$. Same letter next to Mean seedling density indicates no significant difference between means.

Prior to analysis all data were transformed using the square root of $(x + 3/8)$ to adjust from a skewed to a normal distribution.

Table 23. Analysis of variance and least significant difference of site A canopy cover - plot, lime treatment and vegetative class.

ANOV				
Source	D.F.	S.S.	M.S.	F-value
Blocks	9	6.357	.7063	
Plots	2	8.033	4.017	3.956*
Treatment	1	14.69	14.69	14.47*
Plots x Treatment	2	4.720	2.360	2.324
Veg. Class	1	.6115	.6115	.6022
Plots x Veg. Class	2	12.83	6.414	6.317*
Treatment x Veg. Class	1	2.269	2.269	2.235
Plots x Trt x Veg. Class	2	9.700	4.850	4.777*
Residual	99	100.5	1.015	

LSD ANALYSIS			
Factor	Identity	Mean canopy cover	
Plots	A1	1.485	A
	A3	1.487	A
	A2	2.029	B
Lime Treatment	CARWA	1.314	A
	CARWA + INCUBATION	2.013	B
Veg. Class	Weeds	1.592	A
	Grasses	1.735	A

Asterisk (*) indicates significance at p = .05. Same letter next to Mean canopy cover indicates no significant difference between means.

Prior to analysis all data were transformed using the square root of (x + 3/8) to adjust from a skewed to a normal distribution.

Table 24. Analysis of variance and least significant difference of site B canopy cover - plot, lime treatment and vegetative class.

ANOV

Source	D.F.	S.S.	M.S.	F-value
Blocks	8	5.536	.6919	
Plots	2	33.81	16.90	34.99*
Treatment	1	6.805	6.805	14.08*
Plots x Treatment	2	.2755	.1378	.2851
Veg. Class	1	30.04	30.04	62.16*
Plots x Veg. Class	2	8.049	4.024	8.329*
Treatment x Veg. Class	1	2.893	2.893	5.988*
Plots x Trt x Veg. Class	2	.4849	.2424	.5018
Residual	55	1.320	.2945E-01	

LSD ANALYSIS

Factor	Identity	Mean canopy cover	
Plots	B3	.8980	A
	B2	1.432	B
	B1	2.258	C
Lime Treatment	CARWA	1.278	A
	CARWA + INCUBATION	1.780	B
Veg. Class	Weeds	1.002	A
	Grasses	2.057	B

Asterisk (*) indicates significance at p = .05. Same letter next to Mean canopy cover indicates no significant difference between means.

Prior to analysis all data were transformed using the square root of (x + 3/8) to adjust from a skewed to a normal distribution.

Table 25. Analysis of variance and least significant difference of site A plant production - plot, lime treatment and vegetative class.

ANOV

Source	D.F.	S.S.	M.S.	F-value
Blocks	5	.2377	4754E-01	
Plots	2	.3848	.1924	6.533*
Treatment	1	1.046	1.046	35.52*
Plots x Treatment	2	.9343E-01	.4672E-01	1.586
Veg. Class	1	4810E-01	.4810E-01	1.633
Plots x Veg. Class	2	.1309	.6547E-01	2.223
Treatment x Veg. Class	1	.2961	.2961	10.05*
Plots x Trt x Veg. Class	2	.7464E-01	.3732E-01	1.267
Residual	55	1.620	.2945E-01	

LSD ANALYSIS

Factor	Identity	Mean plant production
Plots	A3	.2203 A
	A1	.2309 A
	A2	.3804 B
Lime Treatment	CARWA	.1567 A
	CARWA + INCUBATION	.3977 B
Veg. Class	Weeds	.2514 A
	Grasses	.3031 A

Asterisk (*) indicates significance at p = .05. Same letter next to Mean plant production indicates no significant difference between means.

Prior to analysis all data were transformed using log(x + 1.1) to adjust from a skewed to a normal distribution.

Table 26. Analysis of variance and least significant difference of site B plant production -plot, lime treatment and vegetative class.

ANOV

Source	D.F.	S.S.	M.S.	F-value
Blocks	5	.5201	1040	
Plots	2	1.301	.6504	26.76*
Treatment	1	.5478	.5478	22.53*
Plots x Treatment	2	.1101E-01	.5504E-01	2.264
Veg. Class	1	.3684-01	.3684E-01	15.15*
Plots x Veg. Class	2	.3355	.1678E-01	6.902
Treatment x Veg. Class	1	.5724E-02	.5724E-02	.2355
Plots x Trt x Veg. Class	2	.1007E-01	.5034E-01	2.071
Residual	55	1.337	.2431E-01	

LSD ANALYSIS

Factor	Identity	Mean plant production
Plots	B3	.1188 A
	B2	.2280 B
	B1	.4424 C
Lime Treatment	CARWA	.1758 A
	CARWA + INCUBATION	.3503 B
Veg. Class	Weeds	.1915 A
	Grasses	.3346 B

Asterisk (*) indicates significance at p = .05. Same letter next to Mean plant production indicates no significant difference between means.

Prior to analysis all data were transformed using log (x + 1.1) to adjust from a skewed to a normal distribution.

APPENDIX C

LOGARITHMIC CURVE FITTING EQUATIONS FOR PROJECTING LIME REQUIREMENTS

Table 27. Logarithmic curve fitting analysis equations for projecting lime requirements on samples from sites A and B.

Sample[2]	Log Curve Fit Equation[1]	R-Value
A1 0-36	$y = 0.011 + 0.014 \ln x$	.99
A1 36-102	$y = 0.294 + 0.092 \ln x$	.99
A2 0-36	$y = 0.234 + 0.062 \ln x$	.98
A2 36-102	$y = 2.70 + 0.705 \ln x$	.98
A3 0-36	$y = 0.029 + 0.038 \ln x$	.98
A3 36-102	$y = 0.329 + 0.062 \ln x$	.99
B1 0-36	$y = 5.23 + 0.627 \ln x$	.95
B1 36-102	$y = 4.40 + 0.833 \ln x$	.99
B2 0-36	$y = 1.54 + 0.297 \ln x$	.99
B2 36-102	$y = 0.739 + 0.142 \ln x$	.99
B3 0-36	$y = 0.285 + 0.081 \ln x$	.99
B3 36-102	$y = 0.555 + 0.086 \ln x$	.98

[1] x = number of CARWA weathering cycles; y = lime requirement in Mt $CaCO_3$/ha/15cm.

[2] Depth of sample in centimeters.

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