DEVELOPMENT OF A COMPUTERIZED AUTOMATED RAPID WEATHERING APPARATUS FOR DETERMINING TOTAL LIME REQUIREMENTS FOR ACID MINESOILS[1]

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Abstract.--Traditional analytical methods for predicting lime requirements are inadequate for evaluating on-going acid production from acid minesoils. The primary 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 minesoils in a 24 hour time frame. Comparisons of CARWA lime recommendations to those determined by the laborious, time consuming manual laboratory weathering method indicate that rapid weathering is feasible.

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 and residual (organic) sulfurs in overburden materials often inhibit revegetation of mine spoils. 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 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 eastern United States to assess the long term acid production and base release in soil materials. The method can, with 90% 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 additon, uncertainties associated with the yield of acid from organic sulfur in western 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 Brant 1962, Caruccio 1968, Sobek et al. 1978). This empirical technique provides simple control over air, temperature, moisture and 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 weathering cell to weather minesoil

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[1]Paper presented at the second annual symposium of the American Society for Surface Mining and Reclamation. Denver, Colorado, October 9-10, 1985.

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Proceedings America Society of Mining and Reclamation, 1985 pp 54-60

DOI: 10.21000/JASMR85010054

https://doi.org/10.21000/JASMR85010054

materials from fifteen 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. Presently the technique is laborious and requires from four to eight weeks of time for results, making it impractical to process large numbers of samples or to attain rapid results. There is an acute need for a rapid and reliable method which will determine a one-time total lime requirement for acid 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 minesoils at the Dave Johnston Coal Mine near Glenrock, Wyoming; 3) compare CARWA lime recommendations with the manual laboratory weathering (MLW) 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

Site Description and Sampling

The Dave Johnston Coal Mine is located in east central Wyoming on the southern edge of the Gillette coal field (fig. 1). Overburden/interburden materials at this mine contain reduced forms of inorganic and residual (organic) sulfur. Oxidation of these sulfur forms has resulted in localized "hotspots" (low minesoil pH) barren of plant growth that are scattered throughout the post-mine landscape.

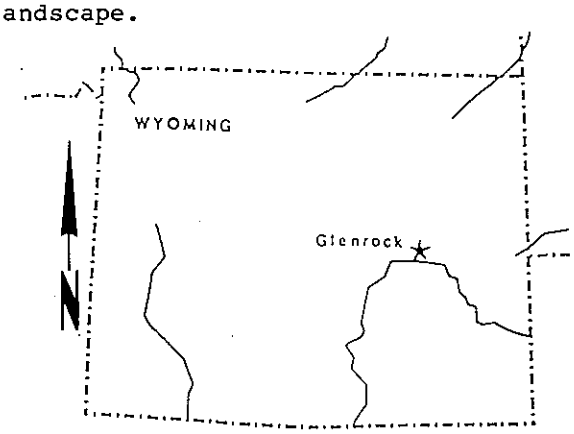

Figure 1. Map of Wyoming showing location of the Dave Johnston Mine near Glenrock.

Two field sites were chosen where existing plant establishment appeared in jeopardy due to low minesoil pH. Each experimental site (Sites A and B) measured 30 by 90 feet with three plots within measuring 30 by 30 feet. In the center of each plot, bulk samples of spoil were collected from 0 to 14 inches and from 14 to 40 inches deep. Each sample was prepared (Sobek et al. 1978) and split for chemical and physical analyses and for laboratory weathering tests.

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 9 mesh (<2mm) screen and the other a 60 mesh (<.25mm) screen. Total sulfur was determined by Fisher Sulfur Analyzer. Pyritic sulfur was calculated as the difference between weak HCl-extractable and concentrated HNO_3-extractable sulfur. The difference between total-sulfur minus sulfates and pyritic sulfur was calculated as residual (organic) sulfur (Sobek et al. 1978). Therefore, the acid production potential (APP, tons $CaCO_3$/1000 tons soil or tons $CaCO_3$/6" Acre slice) of minesoil samples in this study was determined utilizing the following equation:

$$APP = (\%\ pyritic\text{-}S + \%\ residual\text{-}S)\ (31.25)$$
(Smith et al. 1974)

Neutralization potential (NP) determination followed procedures of Smith et al. (1974). APP was then balanced against the inherent NP of the sample to obtain the acid-base account and corresponding 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 plexiglass weathering chambers (3 reps) (Sobek et al. 1978) inoculated with Thiobacillus bacterium and kept moist (Caruccio 1968), aerated, agitated and extracted weekly with distilled, deionized water to measure acid generated.

Computerized Automated Rapid Weathering Apparatus (CARWA)

Construction of the CARWA required 15 months of mechanical and electrical engineering. Detailed descriptions of its functions will not be presented at this time. In summary, an inoculated 200 gram minesoil sample (<2mm fraction) was placed into each of three 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, and the next cycle began (fig. 2). The computer automatically conducted six weathering cycles of approximately 2.5 hours each on the minesoils. The extracts were monitored for volume, initial pH and titratable acidity per 200 gram sample.

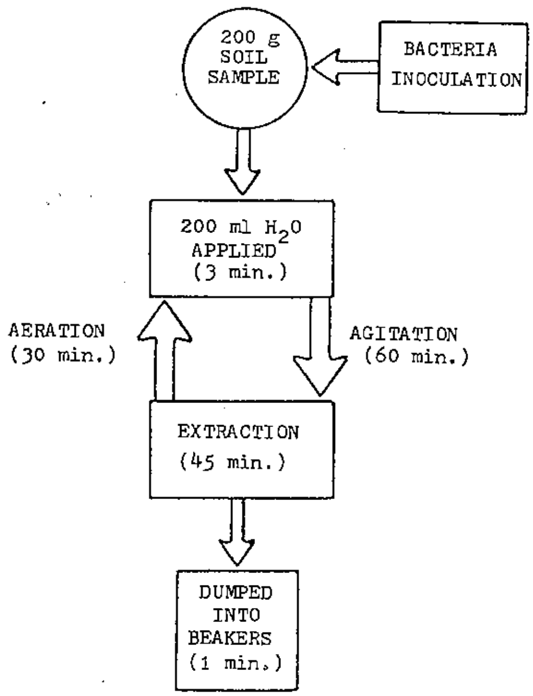

Figure 2. Flow chart showing the operation of one CARWA cycle.

RESULTS AND DISCUSSION

Site Characterizations

The area surrounding and including Site A was disturbed in 1967 and recontoured in 1972. The site received six inches of topsoil and was seeded with three wheatgrass (Agropyron) species. Since then acid production from sulfur containing materials has left Site A devoid of vegetation. The lack of vegetation cover resulted in the erosion and loss of topsoil at this site. Site A minesoil was non-saline and non-sodic, loamy in texture and had a pH (paste) ranging from 2.1 to 3.4.

Site B and the surrounding landscape was mined in 1958 and recontoured in 1966. The site received no topsoil and was seeded with crested wheatgrass (A. cristatum). Presently this site is without a vegetative cover. Site B minesoil was non-saline and non-sodic, loamy in texture and had a pH ranging from 2.1 to 3.2.

Acid-Base Accounting

An acid forming potential for a sample exists when the resultant acid-base value is less than -5 tons $CaCO_3$ per 1000 tons of material (Smith et al. 1974, WDEQ 1984). Acid-base account (<.25mm fraction) lime deficiencies for Site A ranged from 1.8 to 9.6 tons $CaCO_3$ per 1000 tons material. Site B lime deficiencies ranged from 3.1 to 13.5 tons $CaCO_3$ per 1000 tons material.

Acid-base accounting was, for this study, performed on two size fractions (<2mm and <.25mm) from each minesoil sample. Analysis of the less than .25 mm fraction is specified by the established procedure (Sobek et al. 1978). However, simulated laboratory weathering is conducted on the less than 2 mm fraction in order to best represent what is occurring in the field. Analysis of variance and least significant difference was performed using all acid-base data from sites A and B combined. These tests revealed no statistical difference ($P=.01$) between the less than 2 mm fraction ($\bar{x}= -5.29$) and the less than .25 mm fraction ($\bar{x}= -5.28$) acid-base account. This result indicates that the use of the less than 2 mm fraction in laboratory weathering experiments is satisfactory.

Acid Generation Analysis From CARWA

A typical acid production curve during six cycles of CARWA weathering for one minesoil sample is presented in figure 3. For all samples, acid yield was high during the first few cycles. After cycle two, 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). The logarithmic relationship of cumulative acidity and weathering cycles permitted accurate curve fitting which was used to project the long-term lime requirement. This lime requirement projection is based on the assumption that three weathering cycles equal one year of weathering in the field. CARWA lime rates needed to neutralize acid production for the next 30 years at Site A for all six samples (3 plots, 2 depths) ranged from 0.03 to 2.63 tons $CaCO_3$ per acre six inch slice. Lime requirements for all six samples at Site B ranged from 0.29 to 2.65 tons $CaCO_3$ per acre six inch slice.

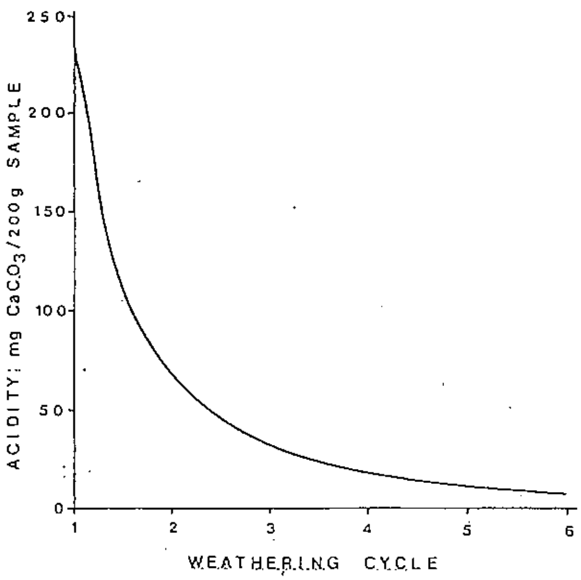

Figure 3. Typical acid production curve of one acid minesoil sample after six cycles of CARWA weathering.

Sulfur Fractionation and Acid Production

To further investigate acid generation from CARWA, linear and multiple regression analyses were employed to detect any correlations between acid production (after 6 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. Sulfur fractionation was performed on all samples in order to calculate an acid-base account.

As hypothesized, a strong correlation (r=.88) between 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 acid production that had occurred prior to laboratory weathering. When percent pyritic sulfur was related to acid production, a significant (P=.05) linear relationship resulted (r=.85). Percent residual (organic) sulfur revealed the weakest, but still substantial correlation (r=.66).

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

$$y = -0.889 + 5.93X_1 - 1.48X_2 + 38.8X_3$$

where y is acid production, X_1 is % sulfate, X_2 is % residual (organic) sulfur and X_3 is % pyritic sulfur. The coefficient of determination (R^2) of this equation is 0.88. This indicates that 88% 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 organic sulfur were .49, .38 and .01, respectively.

These results clearly indicate that total acid production determined by CARWA is a measurement of both available 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.

Comparison of Four Lime Recommendation Methods

To further evaluate CARWA performance, comparisons were made on four lime recommendation methods that were determined for one sample collected at a depth of 14 to 40 inches from Site A and one sample collected at a depth of 0 to 14 inches from Site B (table 1).

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 projection and 4) the 30 year CARWA projection.

Analysis of variance (ANOV) were performed and least significant differences (LSD) calculated to ascertain whether or not statistical differences existed between lime requirement methods. 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 was expected, did indicate statistical differences (P=.05) between

Table 1. Results of four lime requirement methods performed on one sample from site A and one from site B at the Dave Johnston Mine.

	Lime Requirement (tons/acre 6 inches)	
Method[1]	Site A[2]	Site B
<.25mm ABA	9.64 A[3]	13.47 A
<2mm ABA	9.54 A	14.20 A
MLW	1.95 B	3.69 B
CARWA	2.62 C	3.60 B

[1]<.25mm ABA is the less than .25mm fraction acid-base account; 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]No statistical comparisons were made between site A and site B lime requirements.

[3]Same letter next to lime requirements (mean of 3 reps) indicates no significant difference (P=.05) between requirements.

acid-base accounting and laboratory weathering methods. The higher magnitude of acid-base account lime rates may be due to the measurement of non-reactive (e.g. massive pyrite) sulfur compounds in the minesoil samples.

For sample A2, significant differences 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 differences were detected between CARWA and MLW lime rates for sample B1. This is also a favorable result since the original objective of this experiment was to at least equal MLW acid production with CARWA.

The advantages of CARWA over the MLW method are two-fold. One advantage is the high precision of CARWA (3.01% RSD). Most importantly, CARWA can produce sample acid production and lime requirement results in a 24 hour period.

Field Tests

The 30 year lime requirement projection is based on the assumption that three CARWA cycles equal one year of chemical weathering in the field. The accuracy of this assumption can only be evaluated through field testing. During the Spring of 1985, acid minesoil plots at the Dave Johnston Mine (Sites A and B) were limed and seeded to test the effectiveness of CARWA determined total lime requirements. At Site A total lime, incorporated to a depth of 40 inches, for the 30 by 30 foot plots A1, A2 and A3 was 2, 17 and 2 tons $CaCO_3$ per acre, respectively. Site B received 4, 8 and 4 tons $CaCO_3$ per acre 30 inch depth for plots B1, B2 and B3, respectively.

The liming agent used was dolomitic limestone, which was obtained from Jirdon Agri Chemicals, Inc. of Morrill, Nebraska. The neutralizing value of this material was determined to be 93% $CaCO_3$ equivalence. Mechanical analysis (fineness) of this material indicated that it would be quite reactive since 100%, by weight, passed a 9 mesh (<2mm) screen and 55% passed a 60 mesh (<.25mm) screen. Therefore, this material was judged to be an excellent liming agent. Actual field application rates were adjusted for the percentage of inert impurities within the liming agent. In addition, a correction factor of 25% was added to the application rate to adjust for the lack of quantitative replacement in the minesoil (U.S. Salinity Laboratory Staff 1954).

The sequence of events at site A for liming and seeding were as follows: 1) The site was first deep ripped to a depth of 40 inches with three ripper shanks mounted on a D9H crawler tractor. The 14 to 40 inch CARWA lime requirement was incorporated at this time by following behind the ripper and manually pouring the lime into the opening crevice. 2) The 0 to 14 inch CARWA lime rate was then applied to the surface and incorporated 14 inches deep with a chisel plow. 3) A roller harrow was then employed to further mix the lime to a depth of 7 inches and also to prepare the seedbed. 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 (*Agropyron dasystachyum*) streambank wheatgrass (*A. riparium*) and slender wheatgrass (*A. trachycaulum*) applied at a rate of 4, 2 and 4 pounds pure live seed per acre, 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 30 inches instead of 40. This meant that lime incorporation was to a depth of 30 inches rather than 40.

To evaluate inital plant emergence on these sites, density data were collected in late June, 1985 along diagonal transects across each plot. Density was measured by counting live-rooted plants in 25, 20 by 20 cm quadrats. All plants counted were recorded into one of two categories: perennial grasses or weedy species. Initial density data for sites A and B are presented in table 2. These data indicate satisfactory germination has occurred on most of the plots. More in-depth plant performance analyses (cover, production, etc.) will follow once the vegetation has had an opportunity to establish.

Table 2. Initial plant density for acid minesoil sites A and B at the Dave Johnston Mine.

	Density (plants/M^2)	
Plot	Perennial Grasses	Weedy Species
A1	53	3
A2	143	6
A3	50	1
B1	112	4
B2	70	3
B3	0	0

SUMMARY AND CONCLUSIONS

Acid minesoil problems, similar to those in the eastern states, are becoming increasingly familiar at western minesites. Traditional analytical methods to predict lime requirements do not accurately evaluate on-going acid production from sulfide containing minesoils. The overall objective of this study was to develop a computerized automated rapid weathering apparatus (CARWA) that could determine total one-time lime requirements for acid minesoils. Studies were conducted to compare CARWA lime recommendations to those obtained by the more laborious manual laboratory weathering method (MLW) and acid-base accounting. In addition, CARWA acid generation was further investigated by evaluating relationships between different minesoil sulfur components and acid production. Finally, CARWA lime recommendations for two field sites at the Dave Johnston Mine were put to the ultimate test by implementing them into field plot experiments.

Conclusions drawn from the above studies were as follows:

1) The mechanics and precision of CARWA are sound.
2) Multiple regression analysis of CARWA acid production and sulfur fraction ation indicate that available acidity and acidity from the pyritic fraction are responsible for the majority of acid production from samples taken at the Dave Johnston Mine.
3) Thirty year CARWA lime recommendations were either statistically similar to or greater than 30 year MLW lime requirements.
4) Acid-base account lime (requirements) deficiencies were significantly greater 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 sample by the acid-base account technique.
5) Substantial perennial grass establishment occurred on acidic plots limed with CARWA recommended rates.
6) These results suggest CARWA can determine total lime requirements of acid minesoils in an automated fashion within a 24 hour time frame.

ACKNOWLEDGEMENT

The authors wish to express their sincere thanks to the NERCO Mining Company for providing funds to conduct this investigation. In particular, Mr. Chet Skilbred, Dave Johnston Mine, Glenrock, Wyoming, has provided valuable assistance in the operations of this study.

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