ACID MINESOIL PROBLEMS IN THE NORTHERN PLAINS STATES

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ABSTRACT--At numerous surface mine sites in the Northern Plains the acid minesoil problems parallel those experienced in eastern states. The problem is most acute within the Gillette Coal Field in Wyoming. Oxidation/hydrolysis of exposed sulfur-bearing rocks is the source of the acid production. Unlike the situation at eastern mine sites, most of the sulfur in these materials may not be present in the form of pyrite (HNO_3 extractable). This residual sulfur (not extractable with HNO_3) is often assumed to be organic sulfur and generally constitutes 50% to 80% of the total sulfur in overburden.

Little is known about acid generation from organic sulfur when these materials are uncovered and oxidized during mining. Stoichiometrical analysis indicates one mole of organic sulfur can yield two moles of H^+ which is similar to the yield of a mole of pyrite sulfur upon complete oxidation. However, not all soil organic sulfur compounds decompose upon weathering. Our laboratory weathering tests indicate little or no acid is generated from residual sulfur. Uncertainties associated with the yield of acid from organic sulfur make laboratory weathering methods a desirable alternative for lime requirement determination compared to existing analytical laboratory approaches.

INTRODUCTION

We were taught in our first soil science course that soils in the western United States had a basic pH due to the semiarid climate. This stereotype is misleading on mine disturbed lands. If land rehabilitation soil problems in the Northern Plains states could be rated, it is probable that acid producing sites would be ranked number one. The past 100 years has resulted in literally thousands of abandoned coal, silver, and gold mines in this region. A common denominator at each has been the exposure of geologic materials which upon weathering have yielded both low pH minesoils and acid mine drainage. Fortunately about half the *active* large surface coal mines in the region have to date not encountered acid producing strata. Others such as those in the extensive Gillette Coal Field of Wyoming have spoil acid generation problems comparable to sites in the eastern United States.

The need to neutralize acid producing materials with a one-time application of lime is a technical problem. By comparison, common agricultural liming practices permit annual application of this amendment within the framework of tillage and seeding operations. When reacidification of soil occurs it is a relatively simple matter to apply a new dose of lime to amend the pH to near neutrality. However, administration of disturbed lands reclamation requires that an acid soil

be permanently amended to near neutrality with a one-time appliction of lime.

Industry and regulatory agencies (i.e., Abandoned Mines Program) have made large capital investments reclaiming acidic tailing ponds, waste dumps, gob piles, and other minesoil materials only to see reacidification occur in a few years and the long-term viability of the site become jeopardized.

A loss in confidence in minesoil liming methodology has erupted. In this study the sources of minesoil acid production are reviewed and prediction of the total lime requirement utilizing weathering procedures is presented.

ACID-BASE ACCOUNTING

Acid-base accounting (15) is used extensively in the eastern United States to assess the long-term acid production and base release in soil materials. The method has, with 90% accuracy (11, 12) indicated which geologic stratum in overburden will produce acid upon oxidation/hydrolysis and which will not (18, 1). The method is less reliable when the actual quantity of acid production must be known so that the material can be limed to near neutrality. The potential for errors associated with the analytical approach is great and difficult to overcome; therefore, quantitative accuracy on acid production is often poor.

For example, Smith et al. (15) suggested the potential acidity of a material could be determined by oxidizing reduced sulfur (e.g., pyrite) with H_2O_2 followed by titration with a standard base. However, this method can artificially overestimate potential acid production in western overburden (Figure 1). Overestimation of total sulfur content may result in much overburden being falsely categorized as acid producing. The phenomenon can be attributed to the presence of organic matter in samples. As shown in Figure 1, the total sulfur by H_2O_2 analysis correlated closely (r=.86) to overburden sample organic matter content. O'Shay (9) indicated organic matter may form intermediate acid products if there is an insufficient amount of H_2O_2 to completely oxidize the sample. Sulfur fractionation analysis on western overburden strata generally shows more than 50% of the total sulfur is present in organic compounds rather than in sulfides (Figure 1).

This was further demonstrated when 13 overburden samples from the Northern Plains region were analyzed for potential acidity by both the H_2O_2 method and the LECO sulfur analysis method (Figure 2). Results from the two methods were related by linear regression and it was shown that the H_2O_2 method grossly overestimated the potential acidity compared to the analysis by LECO sulfur furnace. It is probable that the H_2O_2 method for determining potential acidity is unreliable for use in western overburden analysis work.
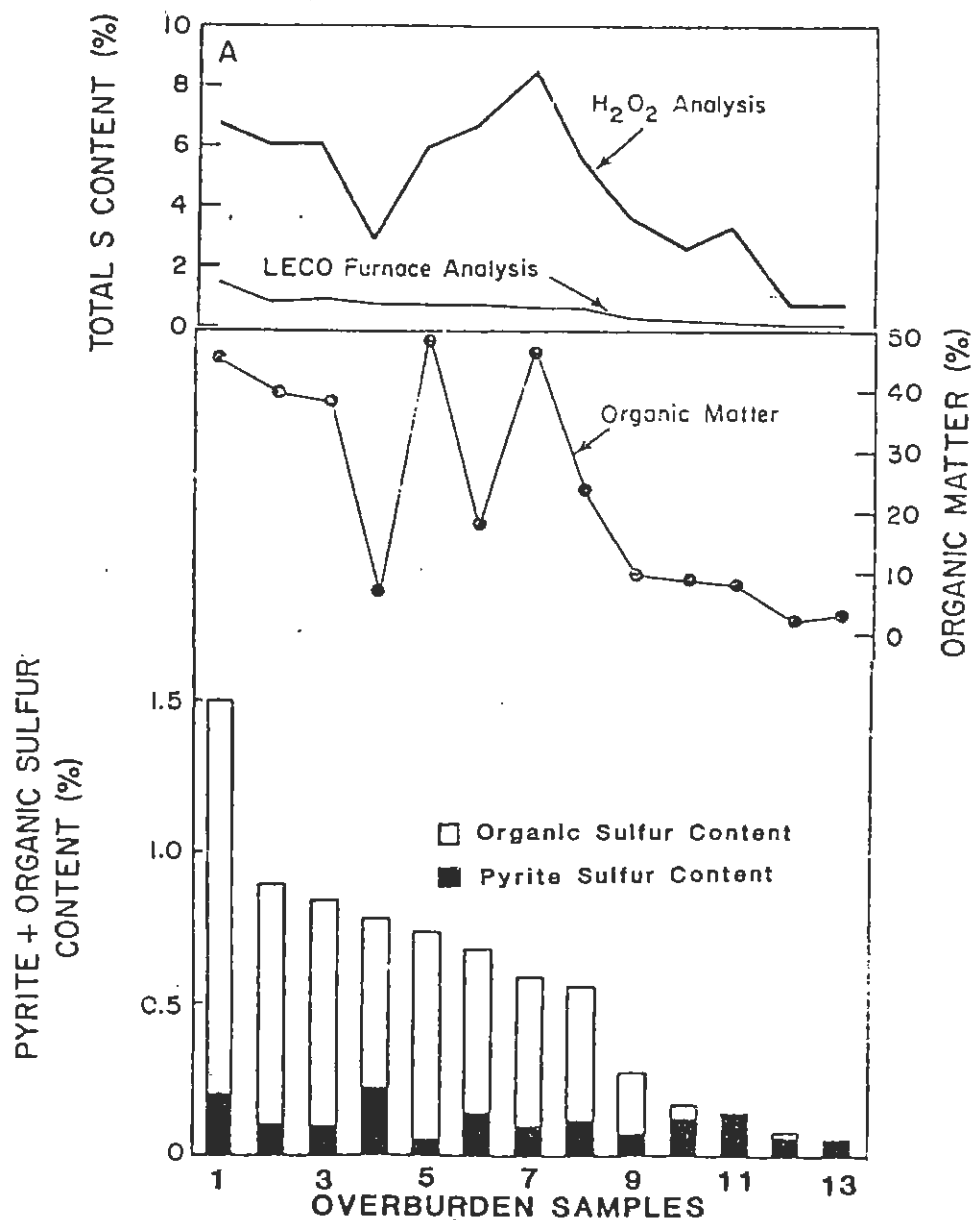
Figure 1. Influence of laboratory method on total sulfur content for 13 overburden samples from the Northern Plains.

ACID PRODUCTION FROM ORGANIC SULFUR

Some organic sulfur compounds can produce acid in soil (4). Knowledge of this phenomenon is very important since most of the sulfur in western overburden and mine waste material is commonly present as organic sulfur rather than sulfide sulfur (pyrite). No researcher has compiled a list of all the organic sulfur compounds present in soil, but it is likely that the list would be extensive. Frederick et al. (4) weathered 20 organic sulfur compounds in soil and found only five decomposed. The others remained relatively inert after five months of weathering.
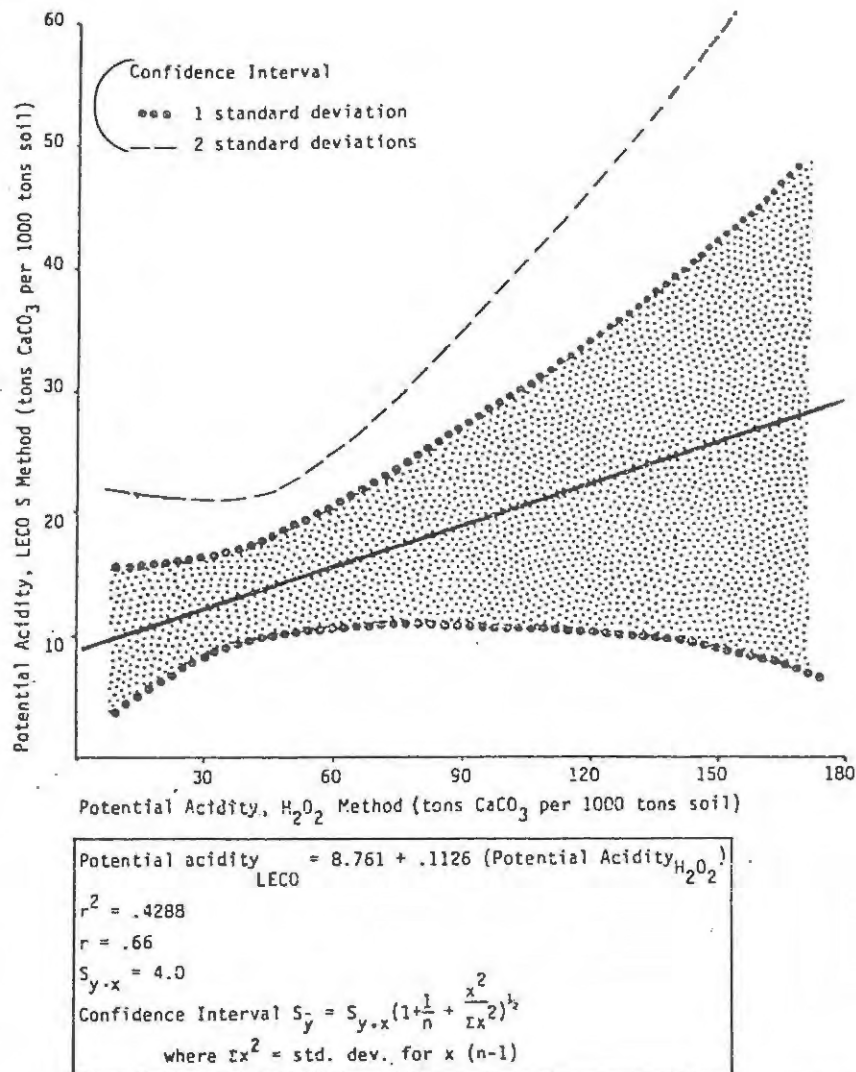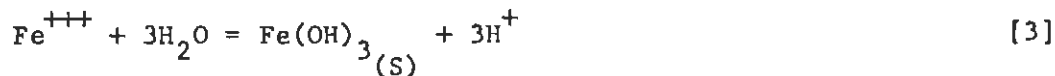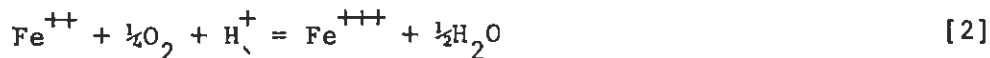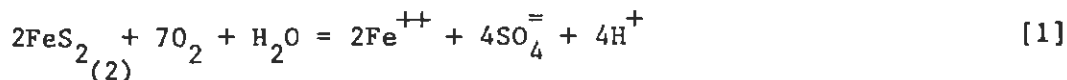
Figure 2. Linear regression relationship between potential acidity by H_2O_2 oxidation and LECO S-furnace on samples from overburden in the Northern Plains.
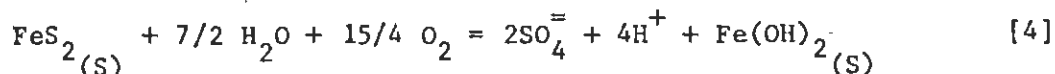
The organic sulfur compound cystine (($SCH_2CH(NH_2) - COOH)_2$) weathered very rapidly and yielded sulfate upon oxidation. When cystine constituted 1% of the soil mass (by stoichiometry, sulfur was 0.25%), the soil pH decreased from 6.1 to 4.3 in 10 weeks. Other organic sulfur compounds that did not decompose upon weathering had no effect on soil pH. Western overburden and mine waste material may have an organic sulfur content of several percent. If all the organic sulfur were present as cystine (unlikely), it is possible that a very acid soil would result which could jeopardize reclamation success. Presumably at some field sites all the organic sulfur could be composed of compounds that do not weather rapidly and therefore have no effect on soil pH.

Given the same quantity (i.e., moles) of pyrite sulfur and organic sulfur, it is possible that more acid could be generated from organic sulfur upon complete oxidation. However, with other assumptions it can be argued that organic sulfur can generate only one quarter as much acid
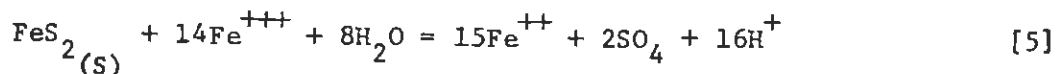
as pyrite. Stoichiometrical analysis demonstrates this phenomenon.
Classical reactions for acid generation from pyrite follow:

$$2FeS_{2(2)} + 7O_2 + H_2O = 2Fe^{++} + 4SO_4^{=} + 4H^+ \qquad [1]$$

$$Fe^{++} + \tfrac{1}{4}O_2 + H^+ = Fe^{+++} + \tfrac{1}{2}H_2O \qquad [2]$$

$$Fe^{+++} + 3H_2O = Fe(OH)_{3(S)} + 3H^+ \qquad [3]$$

which can be summarized as:

$$FeS_{2(S)} + 7/2\ H_2O + 15/4\ O_2 = 2SO_4^{=} + 4H^+ + Fe(OH)_{2(S)} \qquad [4]$$

Therefore one mole of pyrite produces 4 moles of H^+ (acid), or one mole
of sulfur generates two moles of H^+ upon complete oxidation and
hydrolysis. However, in minesoils or in anaerobic settings, (e.g., deep
overburden/spoil sites) the pyrite sulfur could generate much more acid
by an alternate process [5] if the pH of the environment is low (<4.5)
and the microbial population of _T. ferrooxidans_ is active. Reaction [5]
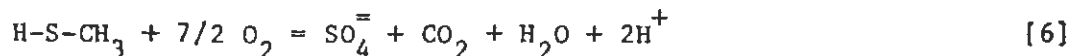is often associated with acid mine drainage settings but it seems

$$FeS_{2(S)} + 14Fe^{+++} + 8H_2O = 15Fe^{++} + 2SO_4 + 16H^+ \qquad [5]$$

probable that in very acid and moist minesoils the production of 16
moles of H^+ (acid) from one mole of pyrite is possible (or $8H^+$ per mole
of S). It has been shown that when the pH decreases to 4.5, Fe^{+++}
becomes more soluble and begins to act as an oxidizing agent, and below
pH 3.0 it is the only important oxidizer of pyrite (13). This means at
pH ≤3.0 acid production by reactions [1] through [4] may be insig-
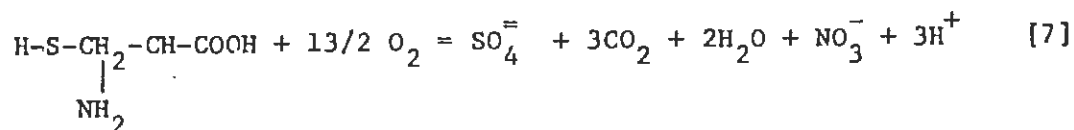nificant compared to reaction [5].

Note that acid minesoil reclamation in the Northern Plains utilizes
the stoichiometrical result, presented by Smith et al. (15), that a soil
with 0.1% sulfur, all as pyrite, will yield by reactions [1] through [3]
above, a quantity of acid that will require 3.125 tons of $CaCO_3$ to
neutralize 1000 tons of soil (6 inch acre slice). We have confirmed
this stoichimetrical result which is widely used by laboratories in our
region to convert sulfur analytical results into a lime requirement
value. However, if minesoil pH is ≤3.0, there is potential that four
times as much acid could generate from a mole of pyrite (by reaction
[5]) as compared to that recognized by Smith et al. (15). In this case,
12.5 tons of $CaCO_3$ would be required to neutralize a soil containing
0.1% pyrite sulfur. Northern Plains minesoil liming efforts based on
acid base account which experienced field reacidification may have been

due to more acid generation by pyrite than stoichiometrically acknowledged by the lab sulfur analysis procedure.

Many soil organic sulfur compounds have complex formulas with corresponding high molecular weights. However, stoichiometrical analyses of relatively simple compounds demonstrate the potentian acid production from organic sulfur upon oxidation. One mole of methyl-mercaptan [6] can upon complete oxidation yield 2 moles of H^+ (acid):

$$H-S-CH_3 + 7/2 \ O_2 = SO_4^= + CO_2 + H_2O + 2H^+ \qquad [6]$$

If the organic sulfur compound is linked to an amine (NH_2) group, an additional mole of H^+ is produced. Consider the oxidation reaction of one mole of cysteine (or 1 mole of sulfur) which yields 3 moles of H^+ [7]:

$$H-S-CH_2-CH-COOH + 13/2 \ O_2 = SO_4^= + 3CO_2 + 2H_2O + NO_3^- + 3H^+ \qquad [7]$$
$$\underset{NH_2}{|}$$

Stoichiometrical analysis of these compounds and others reveals that one mole of organic sulfur will always yield either two moles or three moles of H^+ upon complete oxidation depending on whether an amine linkage is associated with the sulfur unit. Potentially a mole of organic sulfur can yield ($2H^+$) shown in reaction [4] above. If an amine group is present, a mole of organic sulfur can yield ($3H^+$) 150% as much acid as a mole of pyrite sulfur ($2H^+$). However, if low pH minesoils yield acid from pyrite by reaction [5] above with Fe^{+++} as the oxidant, then a mole of organic sulfur will yield ($2H^+$ or $3H^+$) only 25% or 38% as much acid as a mole of pyrite sulfur ($8H^+$).

To summarize, it seems that organic sulfur has the potential to produce as much, or more, soil acidity as pyrite sulfur when soil pH ≥ 4.5. At lower soil pH levels, especially pH ≤ 3, the organic sulfur may produce only about one third as much acid as pyrite sulfur.

However, as stated earlier, research shows that many organic sulfur compounds do not decompose during weathering. Although laboratory methods exist to determine total organic sulfur content in soil, we cannot presently estimate how much will actively oxidize and produce acid. Since western overburden and mine wastes contain sulfur mostly in the organic form, our ability to assess acid production in project areas is weak at best unless weathering methods are employed.

WEATHERING STUDIES

Because of the uncertainty associated with organic sulfur acid production in western minesoil materials, analytical approaches such as the acid-base account may never work satisfactorily. Reclamationists

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need to know the total lime requirement for their project areas now, and it would appear uncertainties associated with lab analytical schemes will remain for many years.

Laboratory attempts to simulate natural chemical weathering (acid production) of overburden and mine waste materials have merit. In effect, weathering studies circumvent uncertainties associated with sulfur analysis methods, stoichiometrical interpretations, and organic sulfur decomposition.

The Soxhlet extractor apparatus has been used for a long time to simulate weathering of geologic materials and, more recently, for soils (10, 7, 19, 14). The high operating temperature of the Soxhlet unit did not permit introduction of microbial populations into the weathering process until Sobek et al. (17) modified the design. Hanna and Bryant (6) developed a simpler approach utilizing a single chamber in which microbes, oxygen, and water levels could be varied to quantify acid production from overburden materials. Other investigators have utilized this chamber design to study acid mine drainage problems (3, 1, 2, 5, 18).

Russell and Dollhopf (12) have weathered minesoil materials from a dozen hardrock mining areas in Montana. Weathering methods are described in detail elsewhere (11); but to summarize, the soil materials were inoculated with _Thiobacillus ferrooxidans_, kept moist, aerated, and extracted weekly with distilled water to measure acid generated. Results from two samples are shown in Figure 3. In the beginning much
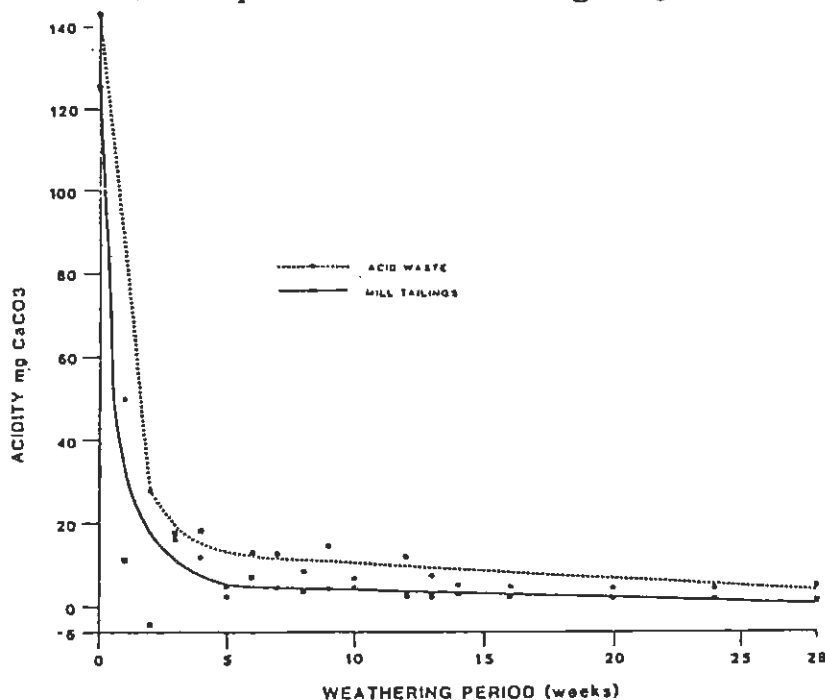

Figure 3. Acid generated over 28 weeks of simulated weathering of acid mine waste materials from the Champion minesite in Montana. The y-scale represents the milligrams $CaCO_3$ needed to neutralize acid produced each week from 200g of soil.

acid was produced each week, but after five weeks of laboratory weathering and acid generated from soil materials remained nearly constant. The flattening out of these curves indicated that an indefinitely long time may be required to completely weather all the acid producing components from these spoil materials. This supports the work of Hanna and Bryant (6) who reported that the weathering of sulfur containing materials is a long degradation process, and that acid production may continue from such degradation for a very long time. All soil materials from Montana that were weathered in this manner revealed similar characteristic curves as that shown in Figure 3. This logarithmic relationship permitted accurate curve fitting which was employed to project the long-term lime requirement (Figure 4). In this example it was determined that 4.7 MT CaCO$_3$/ha/15 cm soil depth would be needed to neutralize the minesoil acid production for the next 30 years. Hopefully after that time the site would be well stabilized with vegetation and the small amount of acid generated would not impact the site. It was assumed that the natural environment underwent three major wet-dry cycles annually which corresponded to three weeks of laboratory weathering.

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 at least six weeks of time per sample. However, we are presently studying methods to expedite the analysis.
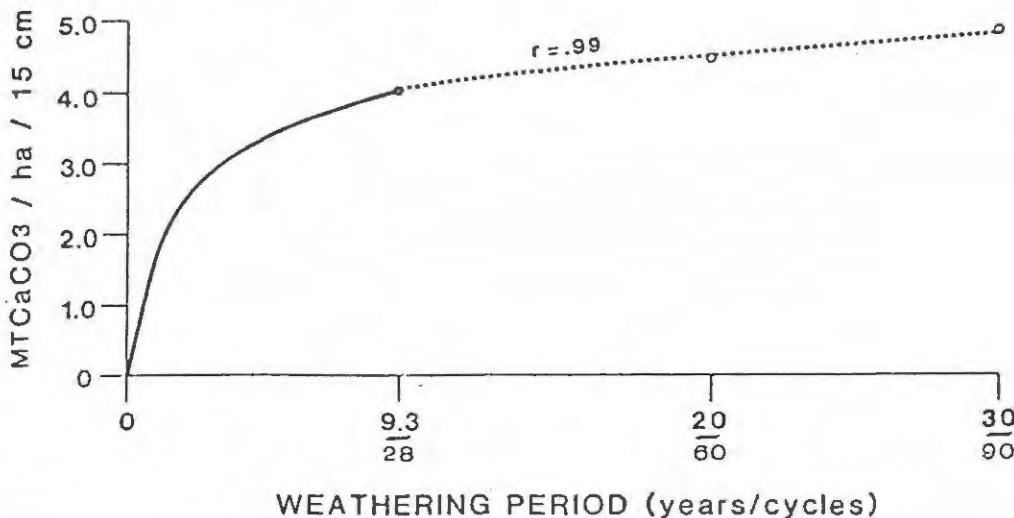

Figure 4. Lime rate requirement through 28 weeks of laboratory weathering and projected lime rate (30 years) for acid waste materials from the Champion minesite in Montana.

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