

**ESTIMATING AGRICULTURAL LIMESTONE NEEDS AND  
OBSERVED RESPONSES FOR SURFACE MINED COAL SPOILS**

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## ABSTRACT

Potential acidity in the form of non-oxidized  $\text{FeS}_2$  frequently exists in surface-mined coal spoils. Conventional pH determinations in water, salt, or prepared buffers fail to predict total lime requirement if appreciable quantities of  $\text{FeS}_2$  exist. Total potential acidity as determined by oxidation with  $\text{H}_2\text{O}_2$ , is one method which may be used to predict lime requirement for coal spoils containing sulfide minerals such as pyrite. Field and greenhouse experiments were conducted in order to determine the relative accuracy of the  $\text{H}_2\text{O}_2$  total potential acidity method.

A site was chosen in western Kentucky on acid sandstone spoils which had a SMP buffer lime requirement of  $9.0 \text{ Mg ha}^{-1}$  and a total potential acidity of  $44.8 \text{ Mg ha}^{-1}$  for a field study. Lime rates of 11.2, 22.4, 44.8 and  $89.7 \text{ Mg ha}^{-1}$  of "Ag" limestone were used. Spoil samples were collected from each plot over a period of two years and analyzed for various chemical properties.

An acidic siltstone, an acidic black shale, and an equal mixture of siltstone and black shale were utilized for a greenhouse study. These materials had total potential acidity lime requirements of 20, 250, and  $135 \text{ Mg ha}^{-1}$ , respectively. These spoil materials were limed rates representing 0, 50, and 100 percent of the lime requirement predicted by the  $\text{H}_2\text{O}_2$  total potential acidity method. The spoils of the greenhouse study were subjected to two leaching treatments. After each leaching treatment, the spoils were sampled and the leachate analyzed.

Results from the field study revealed that the pH of the acid sandstone spoil increased from pH 3.0 to pH 4.8, 5.6, 6.5, and 6.8 by the addition of 11.2, 22.4, 44.8, and 89.7 Mg ha<sup>-1</sup> of "Ag" limestone, respectively, after one month. The pH was maintained at acceptable levels for all plots except for the 11.2 Mg ha<sup>-1</sup> lime rate. Lime recommendations based on the total potential acidity test should be sufficient to maintain a proper pH for several years.

Results from the greenhouse study revealed that the prediction of lime requirement by H<sub>2</sub>O<sub>2</sub> total potential acidity method underestimated actual lime needs of the highly acidic black shale sample. However, had a safety factor of a 50% increase in lime rate been used in this greenhouse study, to account for the normally less than pure CaCO<sub>3</sub>, coarseness of limestone grind and improper incorporation or mixing, then the total potential acidity lime requirement should have predicted the proper rates.

## Introduction

Problems can arise when estimating total lime requirement of surface-mined coal spoils which contain appreciable amounts of  $\text{FeS}_2$ . Buffer pH methods do not take into account various iron sulfide minerals. Sulfide minerals, particularly framboidal pyrite and marcasite, can oxidize once exposed to weathering and ultimately produce acidic conditions. In severe cases, plants cannot be established on acidified spoils or continue to grow if spoils become acidic. In addition, severe acid conditions within exposed coal spoils can lead to degradation of both ground and surface waters quality.

Prompt establishment of permanent vegetation is difficult to achieve if adequate amounts of agricultural limestone are not applied. One must formulate a lime recommendation for both the present acidity as well as future potential acidity from oxidation of sulfide minerals. Several experiments have been conducted that show the beneficial effects of liming acid surface-mine coal spoils before establishment of permanent vegetation (1,2,3,4,5,6). However, little research has been reported on the amount of lime needed to stabilize a spoil to a pre-determined pH value for a given period of time.

The nature, amount, and fate of intermediate liming products have not been thoroughly investigated on highly acidic or highly potentially acidic surface-mined coal spoils. Due to the variability in amount and type of spoil materials, it is difficult to predict these lime reaction products. Iron disulfide minerals can vary in crystalline form and particle size. Naturally-occurring neutralizing agents, such as carbonates, can be variable in extent also. Despite the difficulty in predicting lime requirement, total potential acidity analysis may be used as a method for predicting lime needs.

Once a spoil material has been identified as being acidic or if it has a high total potential acidity, it must be either properly limed, or buried with non-acid producing spoil materials or by topsoil. The above is a requirement of the Surface Mining Control and Reclamation Act of 1977.

Determination of the lime requirement of abandoned surface-mined coal lands is another formidable challenge. Redisturbance due to grading of the materials will in all likelihood expose additional iron disulfide materials that had not been subjected to weathering. Prediction of lime requirement, will be an important step in the restoration process.

These studies were undertaken with the following objectives: (1) to determine if the hydrogen peroxide total potential acidity test correctly estimates lime requirement, and (2) To determine the effect of lime on the chemical properties of acidified spoil materials.

#### Methods and Materials

Field Study: The field study was established during May of 1976 on River Queen Mine in Muhlenberg County, KY. The spoil type was predominantly orange to brown sand and weakly-cemented sandstones with lesser amounts of grey shale materials of middle Pennsylvanian age. The spoil material was extremely low in plant-available nutrients with a water pH of 3.6, SMP Buffer pH lime requirement of  $9.0 \text{ Mg ha}^{-1}$ , and a  $\text{H}_2\text{O}_2$  total potential acidity of  $44.8 \text{ Mg ha}^{-1}$  (7). Individual plots were arranged in a randomized split block design with four replications. Finely ground calcitic limestone was applied in May 1976 to each plot at its appropriate rate with an "E-Z Flow®" fertilizer spreader which had been pre-calibrated to deliver the desired lime rates of 11.2, 22.4, 44.8, and  $89.7 \text{ Mg ha}^{-1}$ . The applied limestone was then

incorporated with a John Deere® 1640 disc harrow to a depth of approximately 18 cm. Due to the droughty nature of the sandy spoil, the plots were not seeded until August 20, 1976. Fertilizer applied at seeding time equaled 125, 448, and 370 kg ha<sup>-1</sup> of N, P<sub>2</sub>O<sub>5</sub>, and K<sub>2</sub>O, respectively. A fresh seedbed had been prepared with a disc harrow and KY 31 tall fescue (Festuca arundinacea Schreb.) was broadcast seeded at a rate of 28.1 kg ha<sup>-1</sup>.

Spoil samples were periodically taken over a two-year period in order to monitor the effects of the various liming rates. All samples were taken with a tile spade to a depth of 10-12 cm.

Laboratory analyses performed included pH measurements in H<sub>2</sub>O, KCl, and SMP buffer according to Shoemaker et al. (8). Bray-1 phosphorus (9) was determined on all samples. Extractable K, Ca, and Mg were determined using neutral ammonium acetate (10), flame photometry was used to determine K and Ca, and atomic absorption spectrophotometry for Mg.

Yields of tall fescue were determined in 1978 by harvesting 4.2 m<sup>2</sup> areas of each plot with a Snapper® rotary lawn mower in June and these same areas in August.

Greenhouse Study: The greenhouse study was performed on freshly-exposed (non-weathered) shale materials. One sample was predominantly siltstone and the other black shale. The siltstone was a mixture of the entire overburden materials, as cast by surface mining operations. The black shale was collected discriminately from the strata that immediately overlies the coal bed. Both the black shale and the siltstone were geographically associated in western Kentucky, but from different surface mine operations which were mining the No. 9 coal bed of middle Pennsylvanian age.

The spoils were air dried, and screened to pass a sieve with 1.27 cm openings. Three spoil materials were then evaluated in the greenhouse: black shale, siltstone, and a 50:50 mixture of the black shale and siltstone spoil materials (mixed spoil). Enough spoil to fill 3.3 liter polyethylene pots for each treatment was mixed with appropriate amounts of agricultural grade limestone at rates equaling 0, 50, and 100 percent of the lime requirement, as predicted by the  $H_2O_2$  total potential acidity test. The siltstone had a potential acidity of  $20 \text{ Mg ha}^{-1}$ , mixed spoil was  $135 \text{ Mg ha}^{-1}$ , and black shale was  $250 \text{ Mg ha}^{-1}$ . The containers of spoil materials were maintained at field capacity, but each month an excess of water was applied and allowed to drain through a polyethylene tube in the bottom of each pot so that leachate could be collected and analyzed. Two leaching intensities were used. In one case, approximately 100 ml leachate was collected and this amount of water was equivalent to a water depth of 5 mm. A second leaching treatment consisted of collecting 200 ml of leachate or a water depth of 10 mm. There were five replications of all lime rates and leaching treatments.

After each leaching treatment had been completed, a small amount of material was removed from each pot, air dried, ground to pass a 24 mesh sieve, and analyzed for pH in  $H_2O$ ,  $H_2O_2$  total potential acidity, Bray-1 extractable P, and extractable K, Ca, and Mg. Collected leachates were filtered and analyzed for pH, Ca, Mg, K, Na, Fe, Mn, Al, and total S. These cations were determined by atomic absorption spectrophotometry. Total S was determined by taking a known aliquot and evaporating it to dryness in a crucible analyzed with a Leco furnace.

## Results and Discussion

Field Study The data on which the lime treatments and other fertilizer amendments were based are given in Table 1. These data are a part of a larger study in which phosphorus and tillage variables were investigated (11). Very low pH values were obtained when measured in both water and a KCl salt solution. Also note the very low Bray-1 phosphorus value, as well as low values for exchangeable Ca, Mg, K, and Na for these sandy spoil materials. Data for the SMP lime requirement test indicate that the needed "Ag" lime for this site would be about  $9.0 \text{ Mg ha}^{-1}$ , whereas the total potential acidity test gave a lime requirement of  $44.8 \text{ Mg ha}^{-1}$ . These data indicate a substantial amount of unoxidized sulfide minerals were present in this material. The lowest of the four lime rates,  $11.2 \text{ Mg ha}^{-1}$ , approximates the lime requirement based on the SMP method, whereas the  $44.8 \text{ Mg ha}^{-1}$  was that for the total potential acidity test currently used by the Ky. Agr. Exp. Sta. Soil Testing Laboratory (7). This method was modified from that given by Smith et al. (12) by: (a) not removing any of the existing carbonates or acidity that may be in the sample prior to  $\text{H}_2\text{O}_2$  digestion, and (b) the entire sample is then titrated with standardized base.

The means of the pH measurements made in 1 N KCl for samples taken during this study are presented in Table 2. Salt pH values are given here since they were more sensitive to changes in acidity than those obtained in a water suspension. Such salt pH values are about 0.5 to 0.7 pH units lower than those measured in water. This salt depression in pH is due to hydrolysis of exchangeable  $\text{Al}^{3+}$  and the displacement of exchangeable H to the solution phase (13, 5). There were significant increases in pH for all plots as a

result of liming between the May and June 1976 sampling. There were also significant differences in pH among lime treatments for both the 0.05 and 0.01 alpha levels for the LSD test of significance. For example, the 11.2 Mg ha<sup>-1</sup> lime rate treatment had a significantly lower pH than the other three treatments, and the 22.4 Mg ha<sup>-1</sup> pH value was significantly lower than the pH for the 89.7 Mg ha<sup>-1</sup> lime treatment. The highest mean pH value for all lime rates was obtained for the June 1978 samplings.

The pH readings for the 11.2 Mg ha<sup>-1</sup> lime treatments gradually declined between the June 1976 and December 1977 samplings. This decline most likely resulted from the oxidation of the sulfide minerals in these spoils due to insufficient lime having been applied to these plots. There were essentially no changes in pH for the 22.4, 44.8 and 89.7 Mg ha<sup>-1</sup> lime treatments between August 1976 and December 1977. All three of these lime treatments had appeared to have rapidly reached an equilibrium pH and only the pH from the 22.4 Mg ha<sup>-1</sup> lime treatment decreased between the June and August 1976 samplings.

There were fluctuations in pH within each growing season for both the 1976 and 1977 sampling years. These changes were more pronounced for the 11.2 and 22.4 Mg ha<sup>-1</sup> lime treatments. These fluctuations are most likely a function of the leaching of acidic salts from the sampling zone during the winter and early spring months. Upward movement of acidic salts during the summer months is unlikely since there isn't a water table sufficiently close to the surface for this to occur, hence the drop in pH during the summer is due to the lack of leaching salts and or acids produced from pyrite oxidation.

At the end of this study, only the low lime treatment had pH values below acceptable values (11). The pH values measured in water for the other three treatments averaged 6.5, 7.0 and 7.4 for the 22.4, 44.8 and 89.7 Mg ha<sup>-1</sup> lime treatments, respectively.

SMP lime requirement tests were conducted on all samples collected during this study. However, only the lowest two lime treatments occasionally indicated the need for lime. At the end of the experiment the SMP pH reading for the 11.2 Mg ha<sup>-1</sup> treatment was 6.8, indicating that about 3 Mg ha<sup>-1</sup> lime rate would be needed to raise this treatment to a 6.4 pH reading (when measured in water).

When this experiment was established, we had planned to monitor the pH changes over five or more years. However, due to an error by an equipment operator, these plots were destroyed by the placement of a topsoil stockpile on this location. We can only speculate as to what may have occurred had longer equilibrium periods been possible. Based on work by Ebelhar (5), we feel that the pH from the 22.4 Mg ha<sup>-1</sup> lime rate would have dropped below acceptable values (pH 5.5 in water) in two or three more years, but the pH of plots in which the lime rate was based on the total potential acidity recommendation (44.8 Mg ha<sup>-1</sup>) would have been acceptable for at least five more years.

By adding sufficient lime to raise the salt pH above a 6.0, we feel that there may have been two factors contributing to the stable pH readings observed for the 44.8 and 89.7 Mg ha<sup>-1</sup> lime treatments. The most obvious reason is that sufficient lime had been added to counteract any acids that may have formed through oxidation of sulfide minerals in this spoil material. The second reason is speculative, that the pH had been raised sufficiently high so

that Thiobacillus ferrooxidans or Thiobacillus sulfooxidans were inactive. Nordstrom (14) had noted that these species have an accelerated acid production when the pH (in water) was below 4.5, and Kleinmann (15) indicated that although these bacteria will survive at pH values near 7, they initiate sulfide oxidation at a very low rate. Only the plots with the 11.2 Mg ha<sup>-1</sup> lime treatments had water pH values in the range where accelerated acid production from T. ferrooxidans would be expected.

The application of lime had a pronounced effect on levels of extractable Ca, as expected (Table 3). The level of Ca increased from about 2.0 meq/100g to 8.4 meq/100g for the plots in which 11.4 Mg ha<sup>-1</sup> lime had been applied. Further increases were observed for the 22.4, 44.8 and 89.7 Mg ha<sup>-1</sup> lime applications. These data represent not only exchangeable Ca but also extractable Ca for the following reasons. First of all, calcium carbonate is soluble in NH<sub>4</sub>OAc (approximately 20 meq/100g), hence not all of the Ca reported here is exchangeable if the samples contain free lime. The value for Ca measured prior to liming (Table 1) was most likely exchangeable as well as the Ca values from the 11.2 and 22.4 Mg ha<sup>-1</sup> lime treatments for the August 1978 sampling. Secondly, when CaCO<sub>3</sub> is applied to the acidic spoils, gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O) precipitate may form, which is also extracted by the NH<sub>4</sub>OAc solution. The Ca reported in Table 3 are likely attributed to all three sources: exchangeable Ca, Ca extracted from free CaCO<sub>3</sub>, and CaSO<sub>4</sub>·2H<sub>2</sub>O.

It was also observed that with time, the level of extractable Ca decreased. These changes were most dramatic between the August 1977 and 1978 samplings in which the extractable Ca dropped by 50% for the 11.2 and

22.4 Mg ha<sup>-1</sup> lime treatments. Significant reductions in extractable Ca also occurred for the 44.8 and 89.7 Mg ha<sup>-1</sup> lime treatments.

The dramatic increases in pH which occurred between the Dec. 1977 and June 1978 sampling dates for all lime treatments are believed to be explained by the removal of gypsum by leaching. Prior to this period, the pH had been depressed by the common ion effect. Calcium dissociating from CaSO<sub>4</sub>·2H<sub>2</sub>O was lowering the pH of the system by lowering the solubility of CaCO<sub>3</sub>. When all the CaSO<sub>4</sub>·2H<sub>2</sub>O was removed, the pH increased as the result of a greater solubility of CaCO<sub>3</sub>.

There was a similar change in K and Mg levels extracted from this series of samples between the August 1977 and 1978 sampling. These differences in extractable K and Mg were also probably related to the leaching of soluble sulfate salts.

The levels of Bray-1 phosphorus are also given in Table 3. The high levels extracted from samples collected in October 1976 are the result of a uniform application of about 200 kg ha<sup>-1</sup> of P made in August. The decline of extractable phosphorus as a function of lime rate is related to the neutralization of the HCl in this extractant by the free CaCO<sub>3</sub> in the sample, therefore, there was less acid available to extract phosphorus from the sample and the Bray-1 phosphorus level dropped from 155 to 36 kg ha<sup>-1</sup>. Also note, there was a large variation between replications and treatments, as indicated by the relatively large LSD value.

One year following application of P, the Bray-1 P test declined for all lime treatments. None of the lime treatments resulted in significant differences in Bray-1 P. Also note that the P soil test levels from the 11.2,

22.4 and 44.8 Mg ha<sup>-1</sup> lime treatments were essentially equal and these did not change between August 1977 and August 1978. However, the Bray-1 P soil test level from the 89.7 Mg ha<sup>-1</sup> plots declined between 1977 and 1978. A Bray-1 P soil test level of 45 kg ha<sup>-1</sup> is equivalent to a medium soil test level, whereas values below 35 kg ha<sup>-1</sup> would be considered low (16).

Yield data are given in Table 4. As one would expect, the yields for the June harvests were greater than for the August harvest. Tall fescue was in its reproductive or seed production growth stage in June, and these same areas when harvested in August consisted of vegetative regrowth. There were no significant differences in yield as a function of lime rate for either the June harvest or total production, and one yield (1166 kg ha<sup>-1</sup>) was significantly different from one other (1604 kg ha<sup>-1</sup>) for the August harvest. The lack of significance among these lime treatments was a function of several factors. First, the pH values, phosphorus and other plant nutrient levels among the lime treatments were not different enough to result in significant differences in yield. One should not necessarily expect significant yield responses for tall fescue at the pH range which existed in this study. However, had additional harvest years been possible, significant yield differences would have been expected between the low lime rate and the others. The levels of phosphorus and potassium had decreased in 1978 to levels where these nutrients may have been limiting the yield of tall fescue. Hence, the response in yield due to lime treatments could not be adequately expressed to produce significant differences. Second, we had larger than desired variation among replications, and even with four replications significant differences among treatments were not obtained in 1978.

Greenhouse Study The initial pH of these spoil materials was 5.5, 6.1 and 5.9 for the black shale, siltstone and mixed spoil, respectively. Spoil samples were taken at the end of each leaching period from each pot periodically during this period, and these data are given in Table 5. Initially the black shale sample had a pH of 5.9, but the pH dropped rapidly in the pots which did not receive lime. By the end of the first month, the pH had dropped to pH 3.95 for the 5 mm leaching rate and pH 4.45 under the system receiving the 10 mm. When samples have pH values below pH 4, free acid or acid in excess of the CEC would be expected (17). With time, the pH of the unlimed black shale spoils continued to drop for both 5 and 10 mm leaching intensities as the sulfide materials in this sample underwent oxidation. The pH of the leachate solutions collected are given in Table 6. For the unlimed black shale systems, the pH of the leachate reached a value of 1.5 by the end of the study.

When lime was applied at a rate equal to 50% of the potential acidity, pH values were significantly higher for both suspensions of the spoil and the leachate solutions and the pH of both the spoil and leachate decreased significantly for both leaching rates. Frequently the pH of the leachate was much lower than that for suspensions of the spoil materials.

The series of pH measurements of spoil suspensions was made from the pots receiving a lime rate equal to the total potential acidity and they always exceeded a value of pH 6. There was not the rapid general trend for a decline in pH with time that was observed for the other two lime rates. There were no significant differences between spoil suspensions pH readings within either the 5 or 10 mm leaching systems. The pH of the leachate (Table 6) from this high lime rate series was in excess of pH 6 most of the sampling period; however, by

month 7 and especially for the data collected at month 8, the pH of the leachate had declined significantly. Although the pH of this spoil material was above an acceptable value, based on the pH of the leachate, this spoil material may have become acidic had the experiment been carried out longer. Several factors may contribute to this expected decline in pH of the leachate from the black shale spoil material. First of all, in cases where lime rates are needed and where large levels of iron salts are released, lime particles may become coated with iron oxides. These oxide coatings will encapsulate the lime, thus preventing its reaction with the acids produced. The second reason, there may have been an underestimation of the lime rate needed. The lime applied in this study was pure, finely ground, reagent grade  $\text{CaCO}_3$ , and was thoroughly mixed with the sample. Therefore, we did not use the normal adjustment for the lack of fineness of grind in "Ag" limestone, lack of purity, and lack of adequate mixing. Lime recommendations made by the Ky. Agr. Exp. Sta. Soil Testing Lab (1) are adjusted upward for spoils. This adjustment is a 50 percent increase, so that had this spoil been encountered in the field, a lime rate of  $375 \text{ Mg ha}^{-1}$  would have been recommended or burial with non-toxic materials.

The pH values measured from the series of lime and leaching treatments for the siltstone spoil samples are also given in Table 5. This sample had a much lower total potential acidity lime requirement of  $20 \text{ Mg ha}^{-1}$ . The pH of the unlimed siltstone samples gradually decreased with time, reflecting the slower oxidation of the sulfide minerals than occurred for the black shale sample. Initially the siltstone sample had a higher pH as well as a much lower quantity of  $\text{FeS}_2$ . However, by the fifth month, and especially for the last sampling,

the pH of the unlimed siltstone material had dropped to an unacceptably low pH (less than 5.5).

The pH values of the leachate from the siltstone systems, as one would expect, were consistently higher than those for the black shale samples throughout the experiment. For the zero lime treatment, the pH of the leachate dropped to a value of about pH 3.0 by the eighth month. The pH values of the leachate from treatments receiving lime also declined but remained at least 1.0 pH unit greater than the corresponding sample for leachate from either the black shale or mixed spoil samples.

Both series of limed siltstone samples maintained an acceptable pH throughout the study. Samples receiving half the total potential acidity rate had a pH in excess of 6.5 through the seventh month sampling for both leaching treatments, but by the eighth month the pH started to make a noticeable decline of about 0.5 pH unit. This marked decline, even though the pH was greater than 6.0, indicated that the rate of acid production had or was accelerating, and these data correspond with the low pH of leachates from the seventh and eighth month sampling.

The pH data for the mixed spoil samples both with respect to the of the spoil suspension, as well as the pH of the leachate solution, were intermediate to those of the two samples from which they were derived. The pH of the leachate solutions from the mixed spoils reached similar values as the black shale samples, but it required one to two months longer time. A rapid drop in pH of about 4 pH units of the leachate occurred between months 7 and 8 for samples receiving half the total potential acidity lime rate, but the pH of the spoil suspensions dropped only about 0.2 pH units. This series of mixed spoil

material to which half the lime was applied reached an unacceptable pH value at the end of the experiment.

The leachates from the various systems were analyzed for Ca, Mg, K, Na, Al, Mn, Fe and S, in addition to pH, as discussed earlier. Because of the large number of values, we will discuss only the general trends that were observed. If specific values are desired, they may be found elsewhere (18).

The general trends observed for Ca concentrations were dependent upon the lime treatment and less dependent upon spoil type. Leachates from either the 5 mm or 10 mm treatments of all limed samples released a more or less constant level of Ca of about 400 µg/ml. This concentration was within the range expected for systems in which the solubility of gypsum was controlling the Ca levels in solution. It is also possible that the rate of leaching of calcium may have been faster than the rate of iron disulfide oxidation, as mentioned by Trefford et al. (19). In all cases, calcium concentration was only slightly decreased when the spoil was subjected to the 10 mm leachate treatment as opposed to 5 mm. This suggests that the spoils contained gypsum. Calculations based upon the solubility product of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  confirmed these results.

The level of Mg found in the leachate increased with lime rates and leaching intensities for the black shale samples. Initially, the Mg level was about 120 µg/ml. The Mg levels increased with time to about 400 µg/ml for the limed treatments and 250 µg/ml for the unlimed treatments. Little change in Mg concentration occurred for the siltstone samples, with values ranging from about 50 µg/ml to about 100 µg/ml. The trend for the mixed spoil systems was intermediate in their release of Mg, but was more like the black shale material.

There were significant differences between K levels removed by leaching for the limed versus unlimed treatments. The unlimed treatments released approximately 10 µg K/ml, whereas the limed treatments released about twice that amount of potassium. There was a general trend for a decrease in K removed with time, and this was pronounced for all lime treatments and spoil materials between the last two samplings. This drop in K concentration in the leachate may have been the result of the precipitation of jarosite (20), since there were large levels of iron sulfate in these systems. However, we did not analyze the samples for this new mineral phase.

There were significant amounts of Al, Mn, Fe, and S ( $\text{SO}_4^{-2}$ ) in the leachate solutions and these concentrations were a function of both the lime rate applied and the spoil type. Highest concentrations were observed for the unlimed treatments. The leachate from the 50% lime treatments had significantly lower concentrations of these four elements, however as the pH declined, they increased in concentration. The leachate from the systems receiving 100% of the potential acidity lime rate had only trace levels of Al, Mn, Fe, and S for the first seven months. However, the last sampling had higher levels as would be expected from the pH data, but these levels were still below levels considered toxic by drinking water standards.

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Table 1. Chemical Properties of the Acid Sandstone Spoil Material Prior  
Applying the to Lime Treatments.

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|   |                              |
|---|------------------------------|
| pH in Water -----                                 | 3.6                          |
| pH in <u>N</u> KCl -----                          | 3.3                          |
| pH in SMP buffer -----                            | 6.6                          |
| Exchangeable Ca -----                             | 1.9 (meq/100g)               |
| Exchangeable Mg -----                             | 0.98 (meq/100g)              |
| Exchangeable K -----                              | 0.07 (meq/100g)              |
| Exchangeable Na -----                             | 0.02 (meq/100g)              |
| Lime Requirement by SMP buffer -----              | 9.0 (Mg ha <sup>-1</sup> )   |
| Lime Requirement by Total Potential Acidity ----- | 44.8 (Mg ha <sup>-1</sup> )  |
| Bray-1 Extractable P -----                        | 9.1 (kg P ha <sup>-1</sup> ) |

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Table 2. Effect of Lime Rates on pH Levels in  $\bar{N}$  KCl of Plots Seeded to Fescue Sampled from May 1976 to August 1978.

| Lime Rates<br>(Mg-ha <sup>-1</sup> ) | <u>Sampling Dates</u> |      |      |       |       |      |      |      |       |      |      |
|--------------------------------------|-----------------------|------|------|-------|-------|------|------|------|-------|------|------|
|                                      | 5/76                  | 6/76 | 8/76 | 10/76 | 12/76 | 4/77 | 6/77 | 8/77 | 12/77 | 6/78 | 8/78 |
| 11.2                                 | 3.3                   | 5.1  | 4.8  | 4.6   | 4.2   | 4.4  | 4.4  | 4.3  | 4.2   | 5.5  | 4.7  |
| 22.4                                 | 3.3                   | 6.1  | 5.0  | 5.3   | 5.2   | 5.4  | 5.4  | 5.1  | 5.3   | 6.4  | 6.3  |
| 44.8                                 | 3.3                   | 6.6  | 6.6  | 6.6   | 6.3   | 6.7  | 6.1  | 6.6  | 6.1   | 7.1  | 6.9  |
| 89.7                                 | 3.3                   | 7.0  | 6.9  | 6.9   | 6.9   | 7.0  | 7.2  | 7.2  | 6.8   | 7.3  | 7.2  |
| LSD 01                               | ---                   | 1.0  | 1.1  | 0.9   | 0.7   | 0.8  | 0.7  | 1.1  | 1.1   | 1.0  | 1.5  |
| LSD 05                               | ---                   | 0.7  | 0.8  | 0.6   | 0.5   | 0.5  | 0.5  | 0.8  | 0.8   | 0.7  | 1.0  |
| SE                                   | ---                   | 0.31 | 0.34 | 0.28  | 0.21  | 0.20 | 0.20 | 0.35 | 0.35  | 0.30 | 0.42 |

Table 3. Effect of Lime Rates on Neutral  $\underline{N}$   $\text{NH}_4\text{OAc}$  Extractable Ca, Mg, and K and Bray-1 Phosphorus.

| Element* | Sampling Date | Lime Rate ( $\text{Mg ha}^{-1}$ ) |       |       |       | LSD (0.05) |
|----------|---------------|-----------------------------------|-------|-------|-------|------------|
|          |               | 11.2                              | 22.3  | 44.8  | 89.7  |            |
| Ca       | 10/76         | 8.4                               | 10.7  | 11.8  | 13.6  | 3.3        |
| Ca       | 8/77          | 7.4                               | 11.0  | 11.2  | 14.3  | 3.7        |
| Ca       | 8/78          | 4.8                               | 5.5   | 7.6   | 8.8   | 2.2        |
| Mg       | 10/76         | 1.28                              | 1.11  | 1.58  | 1.06  | 0.84       |
| Mg       | 8/77          | 1.54                              | 0.96  | 1.00  | 0.99  | 1.17       |
| Mg       | 8/78          | 0.36                              | 0.27  | 0.24  | 0.31  | 0.27       |
| K        | 10/76         | 0.066                             | 0.081 | 0.110 | 0.090 | 0.028      |
| K        | 8/77          | 0.061                             | 0.077 | 0.087 | 0.096 | 0.022      |
| K        | 8/78          | 0.043                             | 0.038 | 0.058 | 0.058 | 0.022      |
| P        | 10/76         | 156                               | 122   | 110   | 33    | 50         |
| P        | 8/77          | 90                                | 67    | 48    | 18    | 28         |
| P        | 8/78          | 48                                | 45    | 44    | 18    | 31         |

\*Extractable Ca, Mg and K values are expressed as meq/100 g whereas Bray-1 phosphorus levels are in terms of  $\text{kg ha}^{-1}$ .

Table 4. Effect of Lime Rate on Yield of Tall Fescue.

| Lime<br>Rate        | Harvest date        |      |       |
|---------------------|---------------------|------|-------|
|                     | 6/78                | 8/78 | Total |
| Mg ha <sup>-1</sup> | kg ha <sup>-1</sup> |      |       |
| 11.2                | 3379                | 1425 | 4804  |
| 22.4                | 3668                | 1604 | 5272  |
| 44.8                | 3752                | 1286 | 5038  |
| 89.7                | 3579                | 1166 | 4745  |
| LSD <sub>(05)</sub> | 871                 | 441  | 660   |

Table 5. Effect of Lime Rate and Time on the pH of Black Shale, Siltstone, and the Mixture of Black Shale and Siltstone Under Two Intensities of Leaching.

| Spoil Material                              | Lime Rate<br>(% of P.A.) | Month 1 |      | Month 2 |      | Month 3 |      | Month 5 |      | Month 7 |      | Month 8 |      |
|---|--------------------------|---------|------|---------|------|---------|------|---------|------|---------|------|---------|------|
|   |                          | 5 mm    | 10mm | 5 mm    | 10mm | 5 mm    | 10mm | 5 mm    | 10mm | 5 mm    | 10mm | 5 mm    | 10mm |
| Black Shale                                 | 0                        | 3.95    | 4.45 | 2.40    | 2.45 | 2.50    | 2.50 | 2.65    | 2.65 | 2.85    | 2.75 | 2.45    | 2.65 |
| (LSD <sub>05</sub> between<br>rates = 0.36) | 50                       | 6.23    | 6.20 | 6.05    | 5.75 | 5.65    | 5.75 | 5.35    | 5.35 | 5.45    | 4.95 | 4.15    | 3.78 |
|   | 100                      | 6.38    | 6.50 | 6.45    | 6.28 | 6.58    | 6.48 | 6.38    | 6.50 | 6.55    | 6.40 | 6.30    | 6.30 |
| Siltstone                                   | 0                        | 6.19    | 6.59 | 6.68    | 6.18 | 6.38    | 5.99 | 5.38    | 5.48 | 5.69    | 5.39 | 4.45    | 4.35 |
| (LSD <sub>05</sub> between<br>rates = 0.36) | 50                       | 6.70    | 6.80 | 7.09    | 7.00 | 7.00    | 6.70 | 6.80    | 6.80 | 6.70    | 6.70 | 6.29    | 6.20 |
|   | 100                      | 6.85    | 7.00 | 6.29    | 7.10 | 7.19    | 6.90 | 7.32    | 7.00 | 7.20    | 7.00 | 7.10    | 7.00 |
| Mixed Spoil                                 | 0                        | 4.95    | 5.48 | 2.95    | 2.75 | 2.95    | 2.83 | 2.83    | 2.73 | 2.83    | 2.73 | 2.83    | 2.72 |
| (LSD <sub>05</sub> between<br>rates = 0.36) | 50                       | 6.55    | 6.55 | 6.55    | 6.26 | 6.45    | 6.25 | 6.25    | 6.00 | 6.26    | 5.73 | 5.78    | 5.05 |
|   | 100                      | 6.75    | 6.85 | 6.95    | 6.77 | 7.05    | 6.97 | 6.98    | 6.88 | 7.15    | 6.90 | 6.95    | 6.69 |

Table 6. Effect of Lime Rate and Time on the pH of Leachate from Black Shale, Siltstone, and the Mixture of Shale and Siltstone Under Two Intensities of Leaching.

| Spoil Material                             | Lime Rate<br>(% of P.A.) | Month 1 |      | Month 2 |      | Month 3 |      | Month 5 |      | Month 7 |      | Month 8 |      |
|--|--------------------------|---------|------|---------|------|---------|------|---------|------|---------|------|---------|------|
|  |                          | 5 mm    | 10mm | 5 mm    | 10mm | 5 mm    | 10mm | 5 mm    | 10mm | 5 mm    | 10mm | 5 mm    | 10mm |
| Black Shale                                | 0                        | 2.70    | 3.22 | 1.60    | 1.50 | 1.50    | 1.60 | 1.70    | 1.80 | 1.83    | 1.95 | 1.75    | 1.80 |
| (LSD <sub>05</sub> between<br>rate = 0.93) | 50                       | 6.88    | 5.40 | 7.19    | 6.39 | 6.59    | 6.39 | 3.25    | 2.50 | 2.30    | 2.20 | 2.25    | 2.10 |
|  | 100                      | 7.25    | 7.36 | 7.66    | 7.05 | 7.15    | 7.35 | 7.15    | 6.15 | 5.95    | 3.35 | 4.35    | 3.33 |
| Siltstone                                  | 0                        | 7.50    | 7.50 | 6.49    | 4.53 | 6.00    | 4.70 | 3.70    | 4.05 | 2.90    | 2.90 | 3.05    | 2.90 |
| (LSD <sub>05</sub> between<br>rate = 0.93) | 50                       | 7.50    | 7.75 | 8.10    | 7.30 | 8.19    | 8.78 | 6.79    | 6.96 | 4.66    | 3.23 | 4.25    | 3.65 |
|  | 100                      | 7.65    | 7.80 | 8.00    | 7.69 | 8.65    | 8.25 | 7.25    | 6.38 | 5.49    | 6.50 | 4.65    | 5.96 |
| Mixed Spoil                                | 0                        | 3.70    | 5.05 | 2.10    | 2.00 | 1.90    | 2.00 | 2.00    | 2.00 | 1.90    | 2.10 | 2.10    | 2.10 |
| (LSD <sub>05</sub> between<br>rate = 0.93) | 50                       | 7.85    | 7.85 | 7.75    | 7.15 | 7.43    | 7.25 | 3.53    | 2.84 | 2.51    | 2.43 | 2.40    | 2.30 |
|  | 100                      | 7.90    | 7.69 | 8.05    | 7.45 | 7.85    | 8.35 | 7.75    | 6.55 | 6.05    | 5.05 | 5.45    | 4.85 |