

CHEMICAL AND PEDOGENETIC EFFECTS OF SIMULATED PRECIPITATION ON STRIP MINE SPOIL¹

by

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Abstract: Pyritic coal mine spoil was leached with simulated precipitation adjusted to pH values of 5.6, 5.0, 4.6, 4.2, and 3.8 using sulfuric and nitric acid. After being brought to field capacity (32% by weight) with distilled water, 3 replicates of spoil were leached weekly using simulated precipitation at each pH level with a volume equivalent to 2.54 cm depth, and leachates were collected and analyzed. After 156 1-week (3 years) leaching and drying cycles, the spoils released approximately 3.3 g Fe, 35 g SO₄, 0.6g Al, 1.4 g Ca and smaller amounts of other elements per kilogram of spoil. With the exception of sodium, potassium, and pH, the concentration of all elements measured in the leachate followed an exponential equation. Large amounts of each element were released at the beginning of the study. As the study progressed, the concentration of each element in the leachate decreased each week, but the amount of decrease in concentration decreased as the study continued. The same exponential pattern existed for all of the simulated precipitation solutions.

For all elements the differences between the 5 acid precipitation solutions was very small or zero. The most common trend was the pH 4.6 simulated precipitation extracted a slightly higher concentration of certain elements. This trend was only statistically significant for certain elements at randomly occurring weeks during the study. The weight of spoil in each column was weighed at the end of the study and compared to the weight at the beginning of the study. The weight of all dissolved ions summed over the three years of the study averaged 93 percent of the weight of spoil lost.

During the three year span, the spoil changed from a highly toxic material to essentially nontoxic spoil. At the beginning of the study concentrations of Mn, Al, and Fe in the spoil were 99, 52, and 1287 ppm respectively, and after 156 leachings the concentration of Mn, Al, and Fe were reduced to 0.61, 4.1, and 4.68 ppm of spoil, respectively as measured in a water extract.

Additional Key Words: acid mine drainage, acid deposition, soils, pH

Introduction

Precipitation percolating through mine spoil dissolves and transports a variety of materials in the leachate water (Doepker 1988). The dissolved constituents may remain on-site and become part of the ion balance of soil water and eventually affect plant establishment and growth. The dissolved material also can have off-site effects, either

through addition to groundwater, or by addition to surface runoff from the area. When the percolate enters the surface water system it may be called mine drainage, and if acidic, acid mine drainage.

Mine drainage is often severely contaminated, but the contaminant concentration can vary widely among different sources. Watzlaf (1988) worked with several mine waters with pH values as low as 2.0 and iron concentrations ranging from 7 to 7000 mg/L. In general, contaminant concentration increased as pH decreased.

In most of the studies of natural mine drainage or leaching, attention has centered on leachate chemistry and neglected the chemistry of the water used to leach the spoil. This procedure assumes the acid and contaminant potential in the spoil is so great that precipitation chemistry would not

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be important. In this study, we used a leachant liquid with a chemistry similar to natural precipitation that was pH adjusted to the range normally expected in rainfall. The objective of this study was to determine if the chemistry of the leaching water, primarily pH, affected the chemistry of the spoil and the leachate after the water percolated through a mine spoil.

Materials and Methods

Leaching Materials

The leaching solutions were made from distilled water to which reagent grade chemicals were added to approximate the composition of natural rainfall. The compounds used to approximate rainfall chemistry, the mass of each chemical used, and the ion concentration of the leaching material rather than compound concentration are described in a preliminary paper (Gentry et al. 1991). Solution pH was adjusted to treatment levels by controlling the mass of sulfuric and nitric acids used in the formulation.

Spoil Materials

Fresh spoil material was collected from an active coal mine in south-central Kentucky. The material was derived from shales located immediately above the coal. The spoil was acidic and contained significant amounts of pyritic sulfur (Table 1). The high values for potential acidity are similar to values derived for other Appalachian spoils (Ammons and Shelton 1988). The comparatively high values for organic carbon and sulfur likely indicate the pres-

ence of coal wastes in the spoil material. The acid base account suggests that leachate from the spoil should be quite acidic.

Agricultural Soil

The soil used in this study was Blago silty clay loam, a class one soil of high fertility which came from a field that had been cropped for many years and most recently was cropped to soybeans. The organic content was measured using the Walkley-Black method and found to average 5.8 percent with a standard deviation of 0.2 percent. The soil type is silty clay loam consisting of 51 percent silt, 37 percent clay, and 12 percent sand.

Experimental Design

The spoil material was sieved (< 2mm) to remove coarse fragments, and the spoil material was mixed according to accepted procedures (Sobek et al. 1978). In each of 16 separate polyethylene leaching cylinders (10.4 cm diameter by 20.3 cm in length) 1.5 kg of the mixed spoil was placed and retained by an inert fiberglass mat at the bottom of each cylinder. Leaching columns were chosen above alternative methods because the technique has been shown to be the most representative of field conditions (Caruccio and Geidel 1986).

After the columns were filled, 15 cylinders were randomly assigned to 5 treatments in groups of 3 replications per treatment. The remaining cylinder was used to check the response of the spoil material to an initial leaching with unmodified distilled water at a pH of 6.4. In addition to the 16 cylinders filled with spoil, one more cylinder was filled with 1.5 kg of agricultural soil which was treated using a procedure identical to that used for the spoil. The spoil and soil in the treatment columns were wet with the distilled water to bring the material to field capacity.

Treatments

The treatments consisted of leaching the material with artificial precipitation with pH adjusted to 5.6, 5.0, 4.6, 4.2, and 3.8. Each of the 3 replications was irrigated at weekly intervals with 2.54 cm of water and allowed to drain freely. Leachate water from each column was collected in a new polyethylene bottle each week, usually on Thursday, and analyzed the following day. Treatments began in August of 1988 and continued until August 1991. A total of 156 weeks (3 years) was included in this experiment.

The treatment columns were covered with a watchglass during the six-day period between irrigations to prevent excessive drying of the spoil. Although the columns were

Table 1. Properties of spoil material used in leaching study based on total sulfur and pyritic sulfur.

Variable	Value
Values based on total sulfur	
pH, paste method	3.84
Neutralization Potential*	11.73 t
Potential acidity*	41.25 t
Net Acid-Base Account*	-29.55 t
Total sulfur	1.32 %
Total carbon	11.34 %
Values based on pyritic sulfur	
Neutralization Potential	11.73 t
Potential Acidity	26.88 t
Net Acid-Base Account	-15.15 t
Sulfate	0.09 %
Pyritic Sulfur	0.86 %
Organic Sulfur	0.37 %

*CaCO₃ equivalent per 1000 tons spoil material

protected, the seal was not complete. Since many spoil and soil pores drained and air was introduced into the columns between leachings, a definite drying cycle was established. Approximately 50 ml of solution was required to restore the spoil to field capacity prior to leaching. Channel formation in the sample was prevented during percolation by a second fiberglass pad used to distribute the irrigation water over the spoil surface. Also, the columns were rotated 90° with each treatment. Treatment columns were located in a climate controlled area to remove any effects of temperature changes.

Chemical Analyses

The leachate samples were taken to the U. S. Forest Service laboratory immediately after collection and analyses were normally performed the next day. Each leachate sample was analyzed for 18 different ions plus acidity, alkalinity, pH, and specific conductance as described in a preliminary report of this study (Gentry et al. 1991). In addition, total dissolved solids (TDS) was determined by adding the mass of all ions that were measured.

Results and Discussion

Changes in Leachate Concentration With Time

The effects of the various simulated precipitation solutions were compared by passing them through columns of spoil, collecting the leachate and measuring the concentration of 18 different ions plus pH conductivity, sulfate, acidity and alkalinity. This was done once a week for 156 weeks or 3 years. The concentration of each ion, except sodium, potassium, and pH, obeyed an inverse relationship in which the concentration of the ion decreased very rapidly at the beginning and then at a much slower rate as the study progressed. After 1 to 2 years had passed, the concentration of an element was almost constant but at a much higher level

than in the leachant being applied to the column. When the concentration of the element in the leachate was plotted as a function of time, both exponential and hyperbola types of equations were found to give a good fit with the hyperbola fitting slightly better. Examples of this behavior are shown in Figure 1. The data points are shown as dots and the proposed equation is shown as the curve. Similar results were found by Doepker (1988). It is believed that the reason the concentration of each ion decreased rapidly at the beginning of the study is because of easily exchangeable ions being flushed from the column. When the plot of concentration versus time becomes nearly constant, approximately 20 to 40 weeks after the study began, it was assumed that the easily exchangeable ions had been removed. Any ions that were still being leached were being extracted as a result of weathering or decomposition of the spoil. The weathering was evidenced by the decrease in total sulfur, which changed from 1.32 % at the beginning of the study to 0.58% at the end of the study, and the weight of the spoil which decreased 6.1% of the initial weight (Table 2).

Unlike the other elements, for which the concentration in the leachate obeyed an inverse relationship with time, the sodium concentration in the leachate gradually increased with time beginning at approximately 0.8 ppm and rising to approximately 1.0 ppm at the end of the study.

The potassium concentration in the leachate remained relatively constant at 0.5 ppm for the first 1.5 years. Then it gradually increased at a rate that depended on the pH of the leachant. The leachants having pH 4.2 and 5.6 had a potassium concentration in the leachate that was significantly higher than any of the other leachants (Table 3).

The pH of the leachate for each of the simulated rain solutions gradually increased from a pH of 2.1 to a pH of 2.4 representing a two fold decrease in hydrogen concentration.

Table 2. Weight loss of the column compared to total dissolved solids summed over 3 years of leaching.

Column Contents	pH of Leachant	Weight Loss of Column (grams)	TDS Totaled Over 3 Year	Total TDS as % of Weight Loss
Spoil	5.6	76	64	84
Spoil	5.0	83	61	74
Spoil	4.6	109	67	61
Spoil	4.2	98	63	64
Spoil	3.8	92	57	62
Spoil	Dist. Water	132	55	41
Ag. Soil	4.2	27	2.3	9

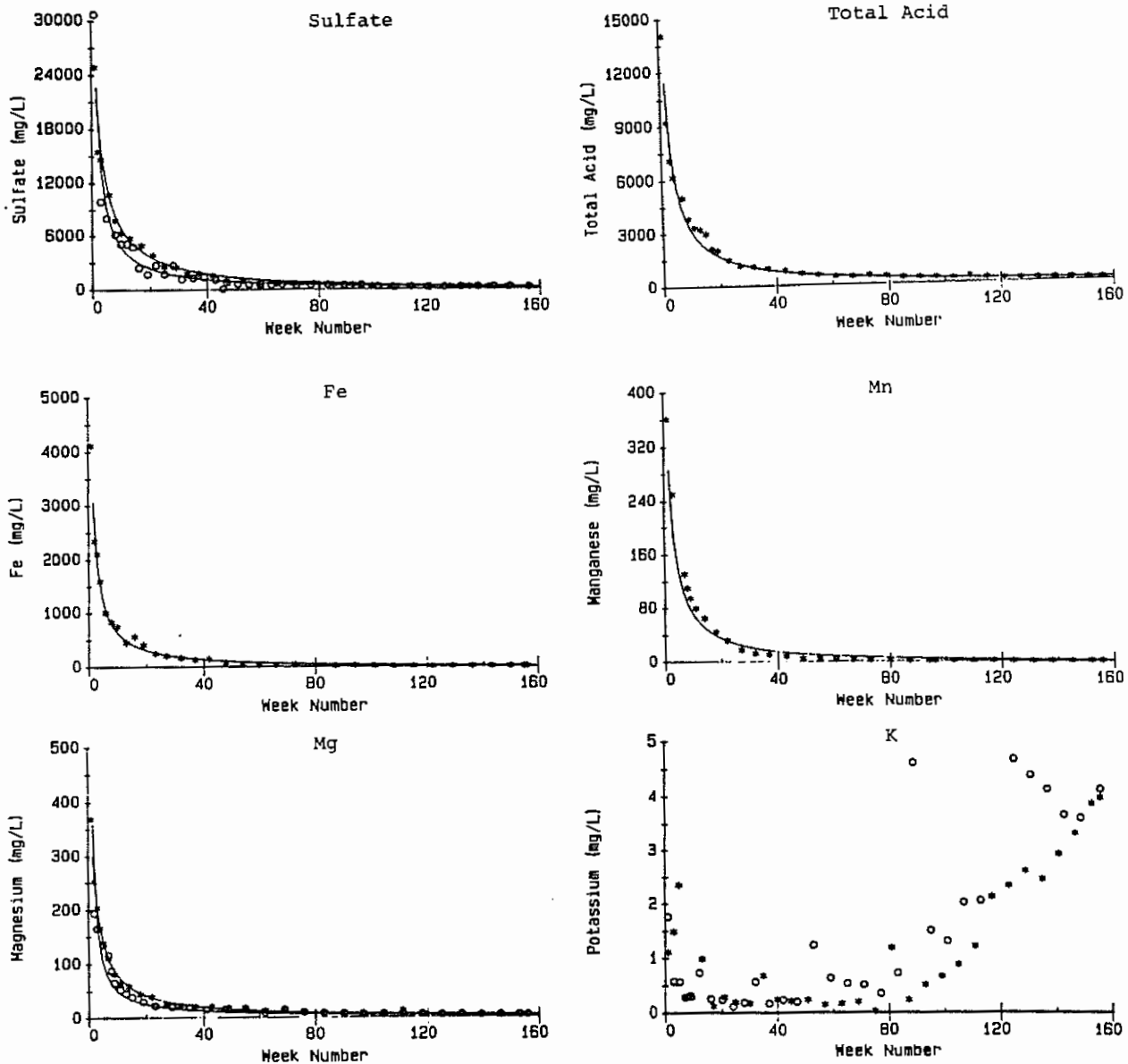


Figure 1. Plot of concentration versus week number. A, B, and C, are coefficients for the equation: $Y = A + B(1/(X - C))$.

Sulfate: Asterisks represent concentration using pH 4.6 leachant;

A = -397.3, B = 93202, C = -2.689;

Circles represent distilled water leachant. A = -144.3, B = 52389, C = -.6985.

Fe: pH 4.6 leachant A = -45.19, B = 7264, C = -.744

Mg: Asterisks represent pH 4.2 leachant; A = -3.202, B = 964.5, C = -1.594.

Circles represent distilled water leachant; A = 0.644, B = 479.9, C = 0.268

Total Acid: pH 4.6 leachant; A = 84.8, B = 37044, C = -1.6199

Mn: pH 4.6 leachant; A = -5.31, B = 865.7, C = -1.36

K: Asterisks represent pH 4.6 leachant; circles represent distilled water leachant

Table 3. Average potassium concentration in last 8 leachate solutions.*

pH of Leachant	Potassium Conc. in Leachant
3.8	4.69 ^b
4.2	5.82 ^a
4.6	3.72 ^c
5.0	4.71 ^b
5.6	5.94 ^a

*Value with a different letter are statistically different bases on Duncan multiple range test (0.05).

Two controls were used in this study. The first control was pH 4.2 extract applied to agricultural soil as described in the methods section of this paper. The second was distilled water applied to the spoil. For both of the controls, the concentration of each ion in the leachate obeyed about the same type of curve as for the extract applied to surface mine spoil. For the soil control there were two differences. The first difference was the concentration of each ion in the leachate approached an approximately constant level much earlier than the spoil leachate. The second difference was the one exception to the inverse relationship which was the variable pH. In this case, the pH stayed at a fairly constant value, which was 6.3 to 6.5, for the entire three years. This pH was higher than the pH of the solution before passing through the column, indicating the soil had a high buffer capacity and was neutralizing most incoming hydrogen ions. The spoil also had a high buffer capacity, as indicated by the change in pH which was 3.8 to 5.6 in the solution applied to the column and 2.1 to 2.4 as it emerged from the column. The same observations were made in studies by Lilholm and Feagley (1988), James and Riher (1986), Brown (1987), and Dethier (1988) in the case of soils, and Doepker (1988) in the case of silver mine tailings.

Comparison of Leachates for Leachants of Different pH

The leachates from columns subjected to leachants of different pH were compared in two ways. The concentration in the leachate of a given element for each column was totaled over the three year span of the study and the totals for the solutions of different pH were compared (Table 4). In this case, there was not enough difference to be statistically significant. In the second method of comparison, the concentration in the leachate was compared with the concentration of the same element for a leachate from a column subjected to a leachant of different pH. In some cases, a

significant difference existed for one to three weeks for a certain element between two of the five possible extractants. There was no consistent difference that lasted several weeks. With the exception of potassium as described above, it was concluded that there was no significant difference for extracting solutions of different pH.

When comparing leachates from the control consisting of distilled water applied to spoil and leachates from the other columns, there were significant differences. With the exception of sodium, boron, and potassium, the ion concentration in the simulated precipitation leachate was higher than that of the distilled water leachate. Examples of these differences are shown in Figure 1.

Changes in the Spoil

At the conclusion of the study, the columns of spoil were weighed and the weight loss calculated by comparing it to the beginning weight of 1500 grams. The weight loss of the spoil was compared to the total of the weekly measurements of total dissolved solids (Table 2). The average of the

Table 4. Total amounts of constituents extracted and average concentration of each in the leachate for the last 8 weeks of the study.

Constituent	Total Extracted	Av. Conc. in Leachate Last 8 Weeks, ppm
	-- g/Kg --	
TDS	41.7	202.00
SO ₄	34.7	202.00
Total acid	21.0	173.00
Fe	3.27	1.51
Ca	1.44	6.48
	-- mg/Kg --	
Si	566	12.20
Mg	505	4.19
Al	390	5.78
Mn	366	.29
K	31	4.80
Zn	24	.08
P	22	.26
Na	21	1.14
Ni	15	.09
Pb	8.7	.041
Cu	7.2	.039
Co	6.0	.023
B	2.3	.08
Cr	2.1	.011
Ti	1.9	.0031

total dissolved solids was 69% of the weight lost by the columns during the 156 weekly leachings. Eighty-five percent of the total dissolved solids were extracted the first year, 10% the second year, and 5% the third year. In contrast to the results of 69% using spoil, the control consisting of Blago soil extracted with pH 4.2 simulated precipitation had a much lower result. In this case, the total dissolved solids was only 9% of the weight loss of the column. For the control consisting of spoil extracted with water, the total dissolved solids was 41% of the weight loss of the column. Apparently, one or more ions being extracted from the soil were not among the 22 variables being measured by this study.

The organic content of the soil could be the source of unmeasured ions. This is evidenced by the low ratio of anions to cations measured and the high organic content of the soil used in the control. In this study, the average ratio of anions to cations for leachate from agricultural soil was 0.30. The corresponding ratio for leachate from columns containing spoil was 1.19. Hazlett and Foster (1989) measured dissolved organic carbon in the percolate from soil in a forest of sugar maple and yellow birch. The organic acids accounted for approximately half of the total anions in the study. If the same ratio held true in this study, it would account for the missing anions that were apparently not measured.

The spoil was then separated into top, middle, and bottom thirds. Ten grams of each section was extracted with 100 ml of distilled water, and the filtrate analyzed for the same 22 variables as the leachates. When comparing the top, middle, and bottom of all fifteen columns that had been subjected to simulated precipitation, it was found that the top generally had a higher concentration of any given ion than the middle or bottom. There were no significant differences between the columns extracted with simulated precipitation solutions of different pH values (Table 5). However, when the filtrate at the end of the study was compared to the filtrate at the beginning of the study, all element concentrations with the exception of hydrogen were significantly less (Table 6). The change was sufficient to transform the spoil

Table 6. Analysis of spoil leachant before and after 156 leachings with simulated precipitation and distilled water.

Element	Concentration in mg/Kg spoil*		
	Before	After Extraction with Simulated Precipitate	After Extraction Distilled Water
Ca	1507	32	15
Mg	433	2.4	4.3
K	20.9	5.1	27
Na	67.9	26.	67
B	.4	.08	.09
Si	5.7	4.3	8.7
Zn	13	.2	.3
P	2.6	.5	.1
Fe	1290	3.1	.8
Cu	4.6	.4	2
Mn	99	.6	.05
Co	5.5	.08	.03
Al	52	3.1	.6
Ni	13	.1	.1
Ti	3.8	.1	.04
Cr	.14	.1	.02
Pb	1.2	.1	.04

from toxic to nontoxic material based on the concentration of Mn, Al, and Fe. The concentration of these 3 ions began at 9, 52, and 1290 micrograms per gram of spoil and were reduced to 0.61, 4.1, and 4.7 micrograms per gram, respectively. The only ion that did not decrease in concentration was the hydrogen ion as shown by a beginning pH of 3.6 and a final pH of 2.9.

Table 5. Concentration of water extractable ions in different sections of column.

Section of Column	Element, (mg/g Spoil)*						
	Ca	Mg	Zn	Cu	Mn	Al	pH
Top	58 ^{a**}	7.9 ^a	49 ^a	1.21 ^a	88 ^a	5.31 ^a	2.93 ^a
Middle	19 ^b	5.7 ^b	.38 ^b	.76 ^b	.62 ^{ab}	4.68 ^a	2.95 ^a
Bottom	16 ^b	5.1 ^b	.32 ^b	.70 ^b	.32 ^b	2.41 ^b	2.83 ^b

*Column means with the same letter are not significantly different using Duncan's multiple range (0.05).

**Concentrations are the average of 15 replication

Conclusions

These results imply that readily available ions are quickly leached from fresh spoil into the ground water. As time passes, the percent of readily available ions greatly decreases but ions continue to be leached, coming from weathering and breakdown of the spoil.

Chemistry of the leachate produced by simulated acid precipitation was dissimilar to that produced by distilled water. Evidence from this study does not identify which parameter causes the different leachate chemistry, although it does show that it is not pH. This study shows that spoil has a very high buffering capacity which results in a pH of the leachate being constant for a long period of time and at a very different pH than the pH of the leachant.

For the spoil columns there were a very small percentage but for soil a very large percentage of the ions being extracted that were not among the ions being measured in this study. In spoil a small percentage of the ions extracted were not identified during the study. The reverse was true for soil as a large fraction of the extracted ions were not identified. It is assumed these ions are organic ions. It was also shown that, in the case of soil, there were many more anions not being measured than cations.

Further studies need to be done to determine if there are any differences in the chemistry of the leachate for spoils of different composition. Studies also need to be done to measure the nature and quantity of the organic ions being extracted from mine spoil and agricultural soil. Work on this problem has already begun.

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