LONG-TERM LEACHING OF MINE SPOIL WITH SIMULATED PRECIPITATION [1]

by

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and

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Abstract. Fresh mine spoil at a pH of 3.84 was collected and transferred to leachate columns in early August 1988. The spoil was leached weekly with simulated precipitation at pH values of 5.6, 5.0, 4.6, 4.2, and 3.8. Control samples of mine spoil were simultaneously leached with distilled water at a pH of 6.47. Leachate was collected and analyzed by standard methods for cations, anions, conductivity, and pH. The cations and anions of major interest were iron, aluminum, manganese, and sulfate. The leachate initially was pH 2.1, with a conductivity of about 10,000 micromho and had concentrations of Fe, Al, Mn, and S04 greater than 4,000, 300, 400, and 24,000 mg/L, respectively. Contaminant levels in the leachate dropped rapidly early in the leaching regime. After four weeks, pH increased slightly to 2.2, conductivity declined to about 7,000, and the ionic concentrations declined to averages of 1,300 for Fe, 170 for Al, 175 for Mn, and 16,000 for SO_4. In the following weeks, contamination in the leachate continued to decline but at a lesser rate. At 20 weeks, pH remained near the 2.0 to 2.2 level; conductivity continued to decline to 4,500; and the ionic concentrations in the leachate were Fe at 325, Al at 55, Mn at 35, and S04 at 3,800 mg/L. After 46 consecutive weeks of leaching, the concentrations in the leachate had declined to lower levels. The leachate pH held steady at a value of about 2.1 and conductivity declined to 3,500. Ionic concentrations were Fe at 70, Al at 20, Mn at 6, and S04 at 900 mg/L. The companion control samples leached with distilled water showed a similar declining pattern, but the absolute values of contamination were always lower than those derived with acidified leaching materials. Except for the control leach material at pH 6.4, the lower pH levels - - 5.6 and below - - all seemed to leach contaminants from the spoil with equal efficiency.

Additional key words: pH, acid mine drainage

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Introduction

Precipitation percolating through mine spoil does dissolve and transport 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, or 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 7,000 mg/L. In general, contaminant concentration increased as pH declined. Mine drainage is often contaminated, but the water chemistry tends to be consistent with time (Halverson and Wade 1988).

In each of the studies of natural mine drainage or leaching, attention has centered on leachate chemistry rather than the properties 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 be important. In this study we used a leaching liquid with a chemistry similar to natural precipitation and a pH adjusted to the range normally expected in rainfall. The objective of the work was to determine if the chemistry of the leaching water, primarily pH, affected the leachate after the water percolated through a mine spoil.

Materials and Methods

Leaching Materials

The leaching solutions were based on distilled water to which reagent grade chemicals were added to approximate the composition of natural rainfall. The compounds used to approximate rainfall chemistry and the mass of each chemical used are given in Table 1. Table 2 lists the ion concentration of the leaching material rather than compound concentration. 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 3). 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 presence of coal wastes in the spoil material. The acid base account suggests that leachate from the spoil should be quite acidic.

Experimental Design

The spoil material was sieved (< 2 mm) to remove coarse fragments, and the spoil material was mixed well according to accepted procedures (Sobek et al. 1978). The mixed material was placed in 16 separate polyethylene leaching cylinders (10.4 cm diameter by 20.3 cm in length) 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 five treatments in groups of three 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. The spoil in the treatment columns was wet with the same water to bring the material to a consistent starting moisture content.

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 three 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 mid-July 1989. A total of 50 weeks 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 protected, the seal was not complete so many soil pores drained and a definite drying cycle was established and air was introduced into each column between leaching treatments. 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. 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 USDA Forest Service laboratory immediately after collection, and analyses were normally performed the next day. Each leachate sample was subjected to a thorough analysis using standard methods and appropriate reference standards. Details of the methods are presented in Table 4. Data analyses were captured in a data file and formatted for statistical analysis with a computer system dedicated to laboratory control.

Table 1. Chemical Composition of Rain Simulants (mg/L)

Compound	Formula wt	Leaching Solution 5.6	5.0	4.6	4.2	3.8
NaCl	58.42	0.176	Same for all solutions			
$CaSO_4 \cdot 2H_2O$	172.17	0.709				
$MgSO_4 \cdot 7H_2O$	246.47	0.355				
K_2SO_4	174.27	0.069				
$NaNO_3$	84.99	0.368				
$(NH_4)_2SO_4$	132.14	0.746				
NH_4NO_3	80.04	0.243				
H_3PO_4 (85.2%)	97.975	0.0084				
H_2SO_4 (96.5%)	98.07	0	0.383	0.987	2.451	5.948
HNO_3 (70%)	63.00	0	0.221	0.554	1.377	3.460

Table 2. Ion Concentrations for Precipitation Simulants (mg/L)

pH	H^+	Ca^{++}	Mg^{++}	K^+	Na^+	NH_4^+	NO_3^-	$SO_4^=$	Cl^-	PO_4^{-3}
5.6	0.0025	0.165	0.035	0.031	0.169	0.258	0.457	1.114	0.107	0.007
5.0	0.010	Same for all solutions					0.610	1.476		
4.6	0.025						0.839	2.015		
4.2	0.063						1.406	3.422		
3.8	0.158						2.841	6.737		

Table 3. Properties of Spoil Material used in Leaching Study Based on Total Sulfur and Pyritic Sulfur

Variable	Units	Value
	Values based on total sulfur	
pH, paste method	pH units	3.84
Neutralization Potential	$CaCO_3$ equivalent per 1000 parts material	11.73
Potential Acidity	$CaCO_3$ equivalent per 1000 parts material	41.25
Net Neutralization Potential		-29.55
Total Sulfur	Percent	1.32
Total Carbon	Percent	11.34
	Values based on pyritic sulfur	
Neutralization Potential	$CaCO_3$ equivalent per 1000 parts material	11.73
Potential Acidity	$CaCO_3$ equivalent per 1000 parts material	26.88
Net Neutralization Potential		-15.15
Sulfate	Percent	0.09
Pyritic Sulfur	Percent	0.86
Organic Sulfur	Percent	0.37

Statistical Analyses

Data analyses were accomplished by utilizing available statistical subroutines (Wilkinson 1988). The primary method was an analysis of covariance. Covariance techniques were used to evaluate the effect of treatment pH while removing the effect of the sequential leachings. The effect of sequential leaching was isolated by using both week number and log week number as covariates. This technique identified both linear and curvilinear week effects. The model expressed each variable as a function of a constant, the treatment, log of the week number, the interaction, and error. Interactions, when significant, suggest that coefficients for slope due to treatment are different.

Factor analysis procedures were used to identify groups of contaminants that responded to the treatments in a similar fashion. Factor analysis does not identify the factors causing the response but can be used to suggest reasons for an observed result. Factor analysis is not based on a model.

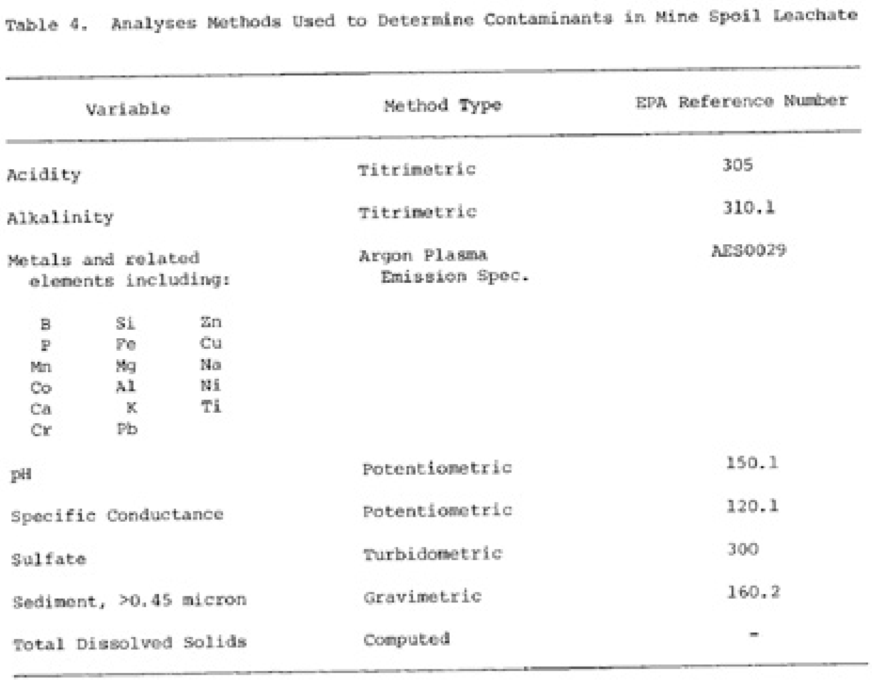

Table 4. Analyses Methods Used to Determine Contaminants in Mine Spoil Leachate

Variable	Method Type	EPA Reference Number
Acidity	Titrimetric	305
Alkalinity	Titrimetric	310.1
Metals and related elements including: B Si Zn P Fe Cu Mn Mg Na Co Al Ni Ca K Ti Cr Pb	Argon Plasma Emission Spec.	AES0029
pH	Potentiometric	150.1
Specific Conductance	Potentiometric	120.1
Sulfate	Turbidometric	300
Sediment, >0.45 micron	Gravimetric	160.2
Total Dissolved Solids	Computed	-

Results and Discussion

Early results from the leaching treatments illustrate some important effects of sequential irrigations of the columns. A single column was leached with fresh distilled water at pH 6.4. The water was not allowed to equilibrate with CO_2 in the air. The leachate chemistry with fresh distilled water was compared periodically with the percolate from leachings with water at the lower pH values, and a few variables of interest are presented in Table 5. These results do not indicate a statistically significant difference among treatments but do illustrate a pattern of high outputs early in the leaching cycle followed by declining values in succeeding weeks. Conversely, values for pH did not change with successive leachings and were not responsive to acidity of the irrigating solution.

The statistical analyses provided more detailed information on the effects of leaching. The results are summarized by main effects, time, treatment, and the interaction (Table 6). Time was transformed to log of treatment week to normalize the data. Treatment, the pH of the leaching solution, and time, log of the sequence member of a leaching, as well as the interaction, significantly affected the concentration of each variable in the leachate in almost all instances.

There were two important exceptions to the significant impacts of treatment and time on leachate chemistry. The pH of the leachate, although treatment showed significant effects, showed little variation during the sequences of leachings, possibly due to buffering. However, less than 5 percent of the variance in pH was explained, so treatment had little total impact. Silicon, a relatively resistant mineral, showed no response to treatment, but the analyses indicated a gradual dissolution over time. Two other elements, Na and Ti, showed treatment effects but were present only in low concentrations seldom exceeding 1 ppm in the leachate. The remaining constituents in the leachate all showed significant effects with treatment, time, and interaction.

Factor analysis was used to group the contaminants in the leachate into categories of materials with a similar response. Factor analysis isolates groups with a similar response but does not identify the factor causing the response. Factor analysis indicated that Mn, Al, Mg, Fe, Zn, Ca, Si, and S04 formed a group that seemed to be correlated with the number of leachings. The computed variables acidity, conductivity, and total dissolved solids (TDS) were also in this group. The response curve had a reverse "J" shape when plotted against leaching number. The computed variables, as expected, were in the group with the highest concentrations in the leachate. The second group included Pb, P, Cu, B, Co, Ni, and leachate pH. The second grouping seemed to be sensitive to the pH of the leaching solution implying acid-induced dissolution as the response curve was more closely related to treatment. The remaining variables, including pH, Na, Cr, K, and Ti all acted independently of the first two groups and each other. The concentration of Na, Cr, and Ti were too low and consistent to show a definite response to the treatment. The remaining variable, K, may have been released from between layers in the clay lattice structure during alternate wetting and drying cycles and actually increased with time. The leachate pH showed no response to treatment or number of leachings.

The analyses indicate that precipitation chemistry and the number of leaching events are important factors in determining spoil leachate chemistry. However, the concentration of materials in leachate declines rapidly during the first few leachings of fresh spoil indicating some resistance to weathering. The leachate chemistry tended to stabilize after about 20 leaching events and continued at the same levels for the next 30 weekly leachings. Leaching materials with pH values 5.6 and below apparently leached contaminants with equal efficiency.

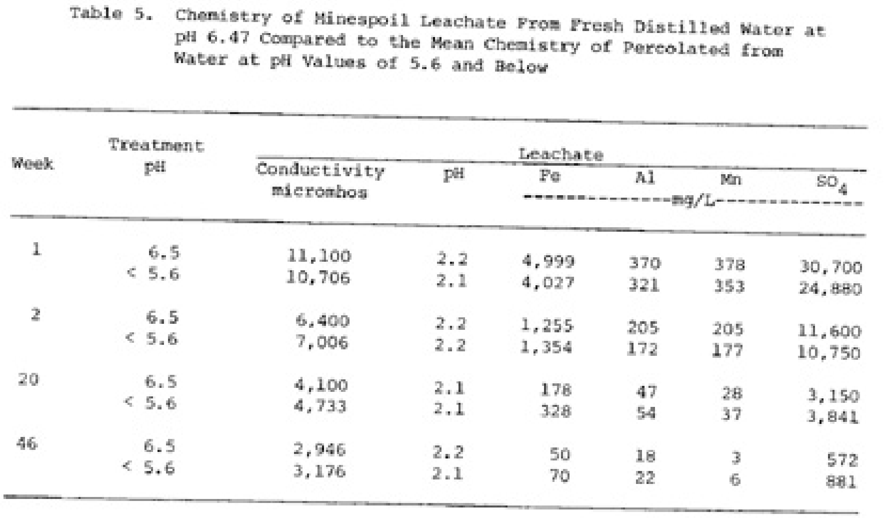

Table 5. Chemistry of Minespoil Leachate From Fresh Distilled Water at pH 6.47 Compared to the Mean Chemistry of Percolated from Water at pH Values of 5.6 and Below

Week	Treatment pH	Leachate					
		Conductivity micromhos	pH	Fe	Al	Mn	SO_4
				mg/L			
1	6.5	11,100	2.2	4,999	370	378	30,700
	< 5.6	10,706	2.1	4,027	321	353	24,880
2	6.5	6,400	2.2	1,255	205	205	11,600
	< 5.6	7,006	2.2	1,354	172	177	10,750
20	6.5	4,100	2.1	178	47	28	3,150
	< 5.6	4,733	2.1	328	54	37	3,841
46	6.5	2,946	2.2	50	18	3	572
	< 5.6	3,176	2.1	70	22	6	881

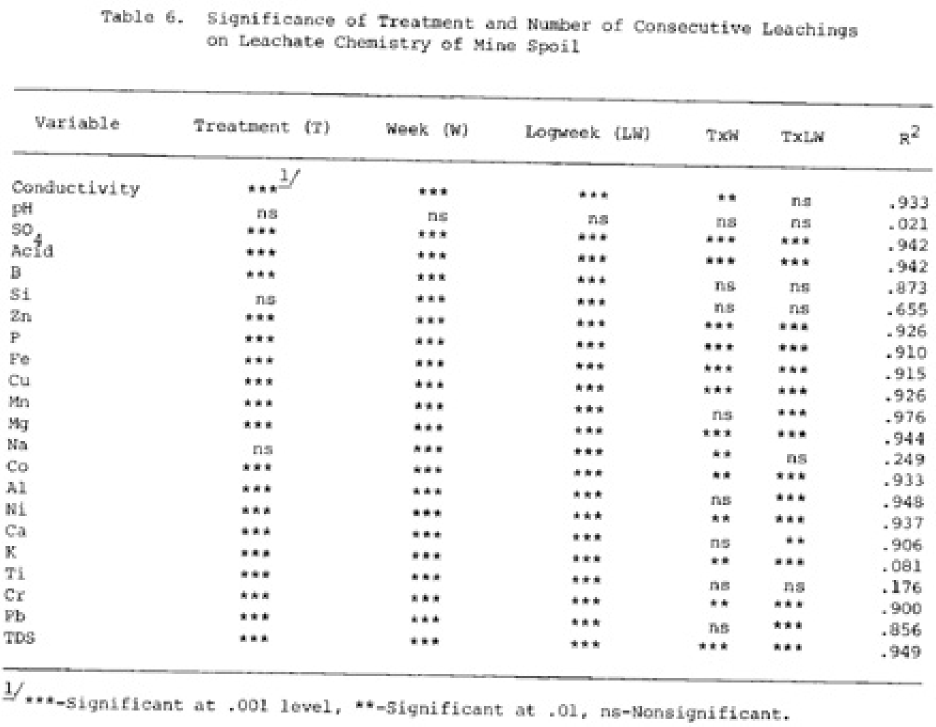

Table 6. Significance of Treatment and Number of Consecutive Leachings on Leachate Chemistry of Mine Spoil

Variable	Treatment (T)	Week (W)	Logweek (LW)	TxW	TxLW	R^2
Conductivity	***[1/]	***	***	**	ns	.933
pH	ns	ns	ns	ns	ns	.021
SO_4	***	***	***	***	***	.942
Acid	***	***	***	***	***	.942
B	***	***	***	ns	ns	.873
Si	ns	***	***	ns	ns	.655
Zn	***	***	***	***	***	.926
P	***	***	***	***	***	.910
Fe	***	***	***	***	***	.915
Cu	***	***	***	***	***	.926
Mn	***	***	***	ns	***	.976
Mg	***	***	***	***	***	.944
Na	ns	***	***	**	ns	.249
Co	***	***	***	**	***	.933
Al	***	***	***	ns	***	.948
Ni	***	***	***	**	***	.937
Ca	***	***	***	ns	**	.906
K	***	***	***	**	***	.081
Ti	***	***	***	ns	ns	.176
Cr	***	***	***	**	***	.900
Pb	***	***	***	ns	***	.856
TDS	***	***	***	***	***	.949

[1/] ***-Significant at .001 level, **-Significant at .01, ns-Nonsignificant.

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