WATER QUALITY AND HYDROLOGIC IMPACTS

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A METHOD TO QUANTIFY TOPOGRAPHIC EFFECTS ON WATER REDISTRIBUTION AND SPRING WHEAT YIELDS[1]

by

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and
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Abstract. Spring wheat yields and water use were monitored at two locations for five years. At each location, soil series were selected that were representative of different topographic positions in the landscape. The objective of this study was to quantify how topography affects wheat yields and water use. Topographic (topo) factors were calculated at each site by measuring the slope in four directions, 90 degrees apart and adding the slopes together. If a slope was downward toward a site it was considered positive. If the slope was upward toward a site it was considered negative. The topo factor, if positive, would indicate that runon water would be added to a site and if negative, water would be lost from the site due to runoff. When the topo factor was added in to the regression of yield versus water use, the coefficient of determination (R^2) increased in the first three years. The last two years of the study were drought years and the topo factor accurately reflected the lack of water redistribution in those years. Measurements of actual soil water content following rainfall events showed that the topo factor did accurately reflect the actual redistribution of water in the landscape. Topo factors were calculated for measurements 3, 6, 15 and 30 m from each site. Topo factors measured 15 m from the site gave the highest R^2 values in the regression of yield versus water use. The topo factor can be used to help determine the successful reestablishment of productivity on mined-land in a complex landscape.

Additional Key Words: productivity, landscape, slope, wheat, water use.

Introduction

Topographic position in the landscape has been shown to influence crop yields (Ciha, 1984; Simmons et al, 1989; Stone et al, 1985; and Douglas et al, 1985). Some studies have emphasized how erosional losses in productivity are landscape-dependent (Stone et al, 1985; Jones et al, 1989; and Daniels et al, 1985). Hanna et al (1982), among others, have documented how topography redistributes water in the landscape. In a semi-arid area such as the northern Great Plains this becomes important because water is so limiting to crop production. Bauer (1972) showed that stored water at planting or soil-water loss during the growing season plus the growing season precipitation are well correlated with yield of small grains. Because of runoff and runon of precipitation as well as saturated and unsaturated flow in the soil profile, water is not evenly distributed in the landscape.

Regulations in North Dakota require that land disturbed by mining be reclaimed to productivity equal to or greater than the pre-mine land. Since the landscape is severely disrupted during mining, it is difficult to compare land productivity before and after mining without a good understanding of how topography affects crop yields. Doll et al (1984) summarized several studies in North Dakota where landscape position had an important influence on crop production on mined land. Wollenhaupt and Richardson (1982) presented evidence that even microtopographic differences can be an important

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factor in determining crop yields on reclaimed land.

In general, the studies of the influence of topography have been quantitative in nature and have categorized sites only by their morphologic landscape position. Very few have attempted to quantify the landscape effects on crop production. Sinai et al (1981) calculated a soil surface curvature factor that correlated very well with soil moisture content. Simmons et al (1989) used a modification of this method to calculate curvature and slope, which was then found to be significantly related to crop yields.

A study was undertaken to quantify the relationships of landscape to water distribution and crop yields. The ultimate goal of this research is to model and to predict crop yields on unmined and reclaimed land based on such factors as soil water and landscape position which are important to crop production in the northern Great Plains.

Methods and Materials

Two locations were selected for this study. The first was located 5 km west of the town of Underwood, North Dakota. Some preliminary yield data was collected in 1984 and a more intense study began in 1985. The location consisted of 3 fields that encompassed about a half-section, or 130 ha. The second location was about 10 km north of Beulah, North Dakota. Detailed measurements at this site began in 1985. This location consisted of 2 fields which, in total, consisted of about 65 ha.

Soils at both sites were derived from glacial till. At the Underwood site, soil series were identified which represented different topographic positions in the landscape. The Zahl soil (fine-loamy, mixed Entic Haploboroll) is located on hilltops and shoulder positions in the landscape. The Williams soil (fine-loamy, mixed Typic Argiboroll) is located on hilltops and sideslopes. The Bowbells soil (fine-loamy, mixed Pachic Haploboroll) is found in footslope or toeslope positions. The Tonka soil (fine-montmorillonitic, frigid Argiaquic Argialboll) is located in small depressional areas. The Tonka soil series was not present at the Beulah location. Four sites of each soil series were located in each field. In 1986 1 to 3 additional sites of each soil series were located in each field.

Soil water was determined gravimetrically from core samples to a depth of 1.2 m in 0.3 m increments taken approximately every 3 weeks during the growing seasons of 1985-1988. Wheat grain yields were determined from 5 subsamples taken at each site. Each subsample consisted of wheat from two drill rows, 0.91 m long.

The topographic (topo) factor was determined at each site. The slope was measured in four directions, 90 degrees apart from each other. If the slope in any one direction was downward away from the site, it was designated as negative. If the slope was upward from the site, it was designated as positive. Slope measurements from four directions were then added together to give one number, designated as the topo factor. This topo factor should be positive in landscape positions where a net increase in water would be expected from runon water or movement downslope within the soil profile. The topo factor should be negative in landscape positions where a net loss of water should occur from runoff and downslope movement of water in the soil profile. Topo factors were determined for measurements made at distances of 3, 6, 15 and 30 m from the site.

Water use was calculated from the difference in available soil water to a depth of 1.2 m at planting and at harvest plus the total precipitation. Wheat yields were regressed against water use. The topo factor was used to adjust the water use for topographic effects using the equation:

$$AWU = WU\ [(\text{Topo factor} \times CH) + 1] + b \qquad (1)$$

where WU = water use, AWU = adjusted water use, CH is %CH ÷ 100 where % CH is the percent change in water use caused by topo factor of ± 1 at a given site. The % CH which gave the highest R^2 value was selected for the calculation of AWU. The calculated AWU was identical to the AWU which would have been calculated if the topo factor had been added into the WU equation using multiple regression techniques. The additional constraint that the intercept of the AWU equation had to be negative was also imposed on the regression.

Results and Discussion

Highest mean yield of spring wheat was obtained from the Tonka soil sites at the Underwood location (see Table 1). These yields were not significantly different from the spring wheat yields on Bowbells sites. Yields from the Zahl soil sites were lowest of the soils studied and were significantly lower than yields from the Tonka in all years except 1989. Mean yields from the Williams soil were intermediate

Table 1. Yield of spring wheat from the Underwood and Beulah, ND locations.

Soil Series	Wheat Yield				
	1985	1986	1987	1988	1989
	----------Mg ha^{-1}----------				
	Underwood				
Bowbells	3.9a[+]	2.9a	1.7ab		0.7a
Tonka	5.0a	3.0a	2.2a	----	1.4a
Williams	3.1ab	2.4ab	1.2b	----	0.6a
Zahl	2.6b	2.0b	1.0b		0.7a
	Beulah				
Bowbells	5.1a	3.0a	3.9a	1.4a	2.5a
Williams	4.7ab	2.7ab	3.2a	1.6a	2.1a
Zahl	3.6b	1.8b	2.0b	1.3a	1.7a

[+]Mean values in the same column within each location followed by the same letter are not significantly different at the (.05) level according to Tukey's honestly significant difference test.

between Bowbells and Zahl. Spring wheat yields from the Beulah location followed the same pattern between soils. Wheat yields from the Beulah location were higher and did not vary as much from year to year as they did at Underwood. This is probably due to higher stored soil water in the fallowed fields at Beulah compared to the continuously cropped fields at Underwood. Significant differences between soils existed for all growing seasons except 1988 and 1989 which were very hot and were considered drought years. No yields were taken from the Underwood location in 1988 because of a total crop loss due to drought.

Water use was not consistently different between soils at both locations (see Table 2). At the Underwood location, highest water use was recorded at sites with Tonka soils for the years 1985-1987. In a semi-arid climate water use by a growing crop can be considered a measure of water availability. Water use at the Beulah location was generally higher than at the Underwood location. Again this is probably a result of the additional stored water in the fallowed fields at Beulah.

Topo factors varied considerably with the distance the measurement was taken from a given site (see Table 3). The Tonka soils would be expected to have a positive topo factor, since they are located in depressional areas. Similarly, the Bowbells soils located on footslope or toeslope positions would be expected to have positive topo factors. With one exception topo factors for Tonka soils were positive at all measuring distances. Bowbells soils had numerous negative topo factors measured at 3 and 6 m from the site. All topo factors measured at 15 to 30 m were positive for Bowbells soils. The Zahl soils would be expected to have all negative topo factors because of their location on hilltops and shoulders. Surprisingly, topo factors measured at a distance of 3 m were all positive in this field, while those measured at 15 m were all negative. The Williams soils which are located on sideslopes should be intermediate between Bowbells and Zahl. Some of the topo factors for the Williams soils were positive and some were negative when measured 15 or 30 m from the site. Overall, topo factors measured at 15 m from the site seem to give the best values qualitatively matching their topographic position. Topo factors measured at 30 m were almost as good. Just why 15 m worked out best is not clear, but was probably related to the scale of the topographic features in this landscape. A landscape with different topographic characteristics could produce optimum topo factors at other distances.

Table 2. Water use calculated from the difference in soil water content at the beginning of the growing season minus the soil water content at the end of the growing season to a depth of 1.2 m.

Soil Series	Wheat Yield 1985	1986	1987	1988	1989
		----------mm----------			
			Underwood		
Bowbells	151a+	60a	23b	----	52a
Tonka	155a	90a	140a	----	----
Williams	107a	65a	28b	----	43a
Zahl	93a	71a	39b	----	61a
Precipitation	93	139	260		191
			Beulah		
Bowbells		100a	52a	108a	165a
Williams	----	88a	93a	152a	150a
Zahl	----	64a	64a	130a	108b
Precipitation		109	220	101	213

+Values in the same column within each location followed by the same letter are not significantly different at the (.05) level according to Tukey's honestly significant difference test.

The relationship between wheat yield and water use varied considerably, and overall was only fair (see Table 4). At Underwood the coefficient of determination (R^2) in 1985 was 0.70, while the R^2 at Beulah in 1987 was only 0.04. The topo factor increased the R^2 values for both locations for the years 1985-1987 when added into the regression equations. For example, the R^2 from Underwood in 1985 increased from 0.70 to 0.80. The R^2 at Beulah in 1987 increased from 0.04 to 0.62.

Wheat yields on different soils were not significantly different in 1988 and 1989 and the topo factor correctly reflected this (Table 4). Inclusion of the topo factor in the yield versus water use regression at the Beulah location in 1988 and at the Underwood location in 1989 did not improve the regression. At Beulah in 1989 the topo factor increased the regression only slightly.

The 1988 and 1989 growing seasons were unusually hot and dry. That rainfall which did fall usually fell in amounts of 0.015 m or less. Under these conditions very little chance for rainfall redistribution in the landscape occurred.

Soil water content data was analyzed to determine the actual redistribution of water in the landscape following specific rainfall events. Most rainfall events were not of sufficient magnitude for any redistribution to occur or else evaporation and transpiration were too great by the time the measurements were made for the data to be useful. However, reasonably good data was obtained from the rainfall events in the period July 7 - July 28, 1987 (see Table 5). A regression of the topo factor versus change in soil water content produced a poor correlation at the Underwood location and a significant correlation at the Beulah location. Based on these correlations, a change in topo factor of ±1 would cause a change in water content of 24.3 mm at the Underwood location and 7.2 mm at the Beulah location. This represents a 7.7% change in total water use at the Underwood location and a 2.5% change at the Beulah location, which is very similar to the percent change of 7% and 3% calculated in Table 4.

Table 3. Topo factors for slopes measured 3, 5, 15, and 30 meters in a field at the Underwood station.

Soil series	Site	Distance from site (m)			
		3	6	15	30
Bowbells	1	-0.30	-1.10	0.68	0.58
	2	-1.20	0.40	0.98	1.73
	3	2.50	-0.70	1.60	3.61
	4	4.90	0.20	0.80	1.28
	5	-0.60	-2.60	0.28	1.00
	6	3.40	1.05	2.26	2.97
Tonka		2.00	-0.50	1.06	1.99
	2	0.80	2.20	2.02	1.76
	3	5.20	5.20	6.08	5.94
	4	2.80	0.70	1.68	1.12
Williams	1	-1.00	0.55	1.90	1.46
	2	-0.30	-0.60	-1.38	-6.07
	3	-2.90	-4.10	-2.90	-3.96
	4	-1.00	-2.40	0.90	0.40
	5	-0.50	-1.05	-1.26	-1.56
	6	-1.80	-1.35	-0.65	-2.13
Zahl	1	1.10	-1.25	-0.92	-1.33
	2	0.30	-0.25	-3.20	-0.74
	3	0.30	-1.50	-1.58	-3.02
	4	3.20	-0.45	-2.22	0.69
	5	0.20	1.00	-4.02	-4.33
	6	0.30	-2.15	-2.08	-2.82

Conclusions

Yields of spring wheat were higher on soils in lower slope and depressional areas than on hilltops or shoulder positions. In the semi-arid climate of the Northern Great Plains, an important factor causing these topographic differences in yield is the redistribution of water in the landscape. The topo factor was developed to quantify this redistribution of water. Adding the topo factor into the regression of yield versus water use improved the regression in 3 years of the study. In the other 2 years, which were considered drought years, the topo factor correctly reflected the lack of water redistribution in the landscape. Measurement of actual water redistribution in the field following a rainfall event in 1987 provided evidence that the topo factor correctly estimated water redistribution in the landscape. The optimum distance for the slope measurements for the topo factors seemed to be 15 m from a given site.

Table 4. Regression equations of the form yield = a(WU) +b where WU is water use.

Year	Location	a	b	R^2	% change in WU for a topo factor of ± 1.0
			Unadjusted		
1985	Underwood	0.024	-1.49	0.70*	
	Beulah				
1986	Underwood	0.013	-0.43	0.23	
	Beulah	0.019	-1.08	0.62*	
1987	Underwood	0.007	-0.79	0.43*	
	Beulah	0.007	0.96	0.04	
1988	Underwood	-----		----	
	Beulah	0.004		0.12	
1989	Underwood			0.17	
	Beulah			0.22	
1985	Underwood				5
	Beulah				
1986	Underwood	0.015	-0.63	0.58**	4
	Beulah	0.014	-0.13	0.68*	3
1987	Underwood	0.005	-0.05	0.61**	7
	Beulah	0.014	-0.62	0.62*	3
1988	Underwood	-----	-----	----	
	Beulah	0.004	0.60	0.12	0
1989	Underwood	0.006	-0.95	0.17	0
	Beulah	0.007	-0.17	0.40	

* Significant at the .05 level.
** Significant at the .01 level.

Table 5. Relationship between redistribution of rainfall in the landscape during the period July 7 - July 28, 1987, and topo factors using the regression: Topo factor = a (▲ water content) + b.

Location	Rainfall	a	b	R^2	▲ water content ± 1 topo factor
	(mm)				
Underwood	126	-0.041	-3.13	0.17	
Beulah	129	-0.137	-8.48	0.85**	7.2

Literature Cited

Bauer, A. 1972. Effect of water supply and seasonal distribution on spring wheat yields. North Dakota Agricultural Experiment Station Bulletin 490.

Ciha, A. J. 1984. Slope position and grain yield of soft white winter wheat. Agronomy Journal 76:193-196.

Daniels, R. B., J. W. Gilliam, D. K. Cassel, and L. A. Nelson. 1985. Soil erosion class and landscape position in the North Carolina Piedmont. Soil Science Society Journal. 49:991-995.

Doll, E. C., S. D. Merrill, and G. A. Halvorson. 1984. Soil replacement for reclamation of stripmined lands in North Dakota. North Dakota Agricultural Experiment Station Bulletin No. 514. 24 p.

Douglas, C. L., R. R. Allmaras, and P. E. Rasmussen. 1984. Soil productivity on different landscape positions in the Columbia Plateau of Oregon and Washington. Agronomy Abstracts p. 247.

Hanna, A. Y., P. W. Harlan, and D. T. Lewis. 1982. Soil available water as influenced by landscape position and aspect. Agronomy Journal. 74:999-1004.

Jones, A. J., L. N. Mielke, C. A. Bartles, and C. A. Miller. 1989. Relationship of landscape position and properties to crop production. Journal of Soil and Water Conservation. 44:328-332.

Simmons, F. W., D. K. Cassel, and R. B. Daniels. 1989. Landscape and soil property effects on corn grain yield response to tillage. Soil Science Society of America Journal. 53:534-539.

Sinai, G., D. Zaslavsky, and P. Golany. 1981. The effect of soil surface curvature on moisture and yield - Beer Sheba observation, Soil Science 132:367-375.

Stone, J. R., J. W. Gilliam, D. K. Cassel, R. B. Daniels, L. A. Nelson, H. J. Kleiss. 1985. Effect of erosion and landscape position on the productivity of Piedmont soils. Soil Science Society of America Journal. 49:987-991.

Wollenhaupt, N. C. and J. L. Richardson. 1982. The role of topography in revegetation of disturbed lands. In: Mining and Reclamation of Coal Mined Lands in the Northern Great Plains, Proceedings, Montana Agricultural Experiment Station Research Report. 1984.

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GEOCHEMICAL EVOLUTION OF ACIDIC GROUND WATER AT A RECLAIMED SURFACE COAL MINE IN WESTERN PENNSYLVANIA[1]

by

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Abstract. Concentrations of dissolved sulfate and acidity in ground water increase downflow in mine spoil and underlying bedrock at a reclaimed surface coal mine in the bituminous field of western Pennsylvania. Elevated dissolved sulfate and negligible oxygen in ground water from bedrock about 100 feet below the water table suggest that pyritic sulfur is oxidized below the water table, in a system closed to oxygen. Geochemical models for the oxidation of pyrite (FeS_2) and production of sulfate (SO_4^{2-}) and acid (H^+) are presented to explain the potential role of oxygen (O_2) and ferric iron (Fe^{3+}) as oxidants. Oxidation of pyrite by O_2 and Fe^{3+} can occur under oxic conditions above the water table, whereas oxidation by Fe^{3+} also can occur under anoxic conditions below the water table. The hydrated ferric-sulfate minerals roemerite [$Fe^{2+}Fe_2^{3+}(SO_4)_4 \cdot 14H_2O$], copiapite [$Fe^{2+}Fe_4^{3+}(SO_4)_6(OH)_2 \cdot 20H_2O$], and coquimbite [$Fe_2(SO_4)_3 \cdot 9H_2O$] were identified with FeS_2 in coal samples, and form on the oxidizing surface of pyrite in an oxic system above the water table. These soluble ferric-sulfate "salts" can dissolve with recharge waters or a rising water table releasing Fe^{3+}, SO_4^{2-}, and H^+, which can be transported along closed-system ground-water flow paths to pyrite reaction sites where O_2 may be absent. The Fe^{3+} transported to these sites can oxidize pyritic sulfur. The computer programs WATEQ4F and NEWBAL were used to compute chemical speciation and mass transfer, respectively, considering mineral dissolution and precipitation reactions plus mixing of waters from different upflow zones. Alternative mass-balance models indicate that (a) extremely large quantities of O_2, over 100 times its aqueous solubility, can generate the observed concentrations of dissolved SO_4^{2-} from FeS_2, or (b) under anoxic conditions, Fe^{3+} from dissolved ferric-sulfate minerals can oxidize FeS_2 along closed-system ground-water flow paths. In a system open to O_2, such as in the unsaturated zone, the aqueous solubility of O_2 is not limiting, and oxidation of pyrite by O_2 and Fe^{3+} accounts for most SO_4^{2-} and Fe^{2+} observed in acidic ground water. However, in a system closed to O_2, such as in the saturated zone, O_2 solubility is limiting; hence, ferric oxidation of pyrite is a reasonable explanation for the observed elevated SO_4^{2-} with increasing depth below the water table.

Additional Key Words: acid mine drainage; pyrite oxidation; ground-water flow modeling; sewage sludge; ferric-sulfate minerals.

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Introduction

Acidic ground water and acid mine drainage (AMD) can result from the accelerated oxidation of iron-sulfide minerals, such as pyrite, that are exposed during coal mining. The acidic water typically contains large concentrations of sulfate, iron, and other solutes that are dissolved from the reactive minerals in the mined coal and overburden. AMD can degrade the aquatic habitat and the quality of water supplies.

The U.S. Geological Survey (USGS), in cooperation with the Pennsylvania Department of Environmental Resources (PaDER) and with help from a private mining company, conducted an investigation of the factors affecting water quality at a surface-coal mine in western Pennsylvania that was reclaimed partly by application of composted municipal sewage sludge. Incorporation of sewage sludge with mine spoil creates a nutrient-and-moisture-rich medium that supports reestablishment of vegetation on the disturbed landscape (Sopper and Seaker 1984; Seaker and Sopper 1988a,b). It was hypothesized that the decay of organic matter from the sludge and perennial vegetation would deplete oxygen in recharge waters and thus slow or inhibit acid-forming, pyrite-oxidation reactions in the sludge-reclaimed mine spoil. However, unexpected increases in concentrations of sulfate and acidity were measured in ground water downflow from the sludge-treated mine spoil. Negligible concentrations of dissolved oxygen (DO) suggest that acidic ground water evolves by sequential interactions with pyrite and other minerals under oxygen-limited conditions. This paper (1) reviews geochemical reactions that are likely to produce acidic, mineralized ground water, and (2) evaluates if anoxic conditions limit oxidation of pyrite and production of acid below the water table. Geochemical mass-transfer models are presented to quantify the chemical evolution of water and rock along selected flow paths through the mine spoil and bedrock.

Geochemistry of Acid Mine Drainage

Production of Acid

AMD results from the interactions of oxygen, water, bacteria, and sulfide minerals (Temple and Koehler 1954; Singer and Stumm 1970a,b; Nordstrom et al. 1979; Kleinmann et al. 1980; Cathles 1982; Nordstrom 1982). Pyrite (FeS_2), and less commonly marcasite (FeS_2), are the principal sulfur-bearing minerals in bituminous coal (Davis 1981; Hawkins 1984), and because of its wide distribution, pyrite is recognized as the major source of AMD in the eastern United States (Stumm and Morgan 1981, p. 469).

The following overall stoichiometric reactions may characterize the oxidation of pyrite and other iron disulfide minerals exposed to oxygen and water (Stumm and Morgan 1981, p. 470):

$$FeS_2 + 3.5\ O_2 + H_2O \Longrightarrow Fe^{2+} + 2\ SO_4^{2-} + 2\ H^+, \qquad (1)$$

$$Fe^{2+} + 0.25\ O_2 + H^+ \Longrightarrow Fe^{3+} + 0.5\ H_2O, \qquad (2)$$

$$Fe^{3+} + 3\ H_2O \Longrightarrow Fe(OH)_3 + 3\ H^+. \qquad (3)$$

The oxidation of 2 mol of sulfide in pyrite to sulfate (SO_4^{2-}) (reaction 1) consumes 3.5 mol of oxygen (O_2) and releases dissolved ferrous iron (Fe^{2+}) and acid (H^+) into the water. In acidic, aerobic environments, the autotrophic, iron-oxidizing bacteria, Thiobacillus ferrooxidans, can catalyze the oxidation of Fe^{2+} to ferric iron (Fe^{3+}) (reaction 2) (Colmer and Hinkle 1947; Colmer et al. 1949; Temple and Colmer 1951; Temple and Delchamps 1953; Temple and Koehler 1954; Singer and Stumm 1970a,b). However, as acid is neutralized, Fe^{3+} tends to hydrolyze forming relatively insoluble ferrihydrite [$Fe(OH)_3$] (reaction 3) (Whittemore and Langmuir 1975). The overall combination of reactions 1 through 3 may be written

$$FeS_2 + 3.75\ O_2 + 3.5\ H_2O \Longrightarrow Fe(OH)_3 + 2\ SO_4^{2-} + 4\ H^+. \qquad (4)$$

In reaction 4, 3.75 mol of oxygen are consumed to oxidize 1 mol of pyrite and to produce 2 mol of sulfate, 4 mol of acid, and 1 mol of ferrihydrite.

However, other iron minerals, especially ferric-sulfate compounds may form in addition to, or instead of, ferric-oxyhydroxide compounds in acidic weathering environments (Nordstrom et al. 1979; Nordstrom 1982; Karanthanasis et al. 1988, 1990). For example, roemerite may form by the oxidation of pyrite

$$3\ FeS_2 + 11\ O_2 + 16\ H_2O \Longrightarrow Fe^{2+}Fe_2^{3+}(SO_4)_4 \cdot 14H_2O + 2\ SO_4^{2-} + 4\ H^+. \qquad (5)$$

The oxidized minerals roemerite [$Fe^{2+}Fe_2^{3+}(SO_4)_4 \cdot 14H_2O$], copiapite [$Fe^{2+}Fe_4^{3+}(SO_4)_6(OH)_2 \cdot 20H_2O$], and coquimbite [$Fe_2(SO_4)_3 \cdot 9H_2O$] (Palache et al. 1951, p. 520, 532, 623) were identified with pyrite in high-sulfur coal samples collected for this investigation (see discussion of mineralogy below). These hydrated ferric-sulfate salts are highly soluble (Nordstrom 1982) and probably are produced above the water table. They can form in situ, as efflorescences, by the oxidation of iron-sulfide minerals in dewatered, cleated coal seams and (or) in stockpiled or reclaimed overburden. They also can be

precipitated from oxidizing and evaporating iron-and-sulfur-rich solutions at AMD discharge zones or at the capillary fringe in the unsaturated zone (similar to mode of formation of caliche). Such minerals are not likely to be produced below the water table by the oxidation of pyrite, because extreme concentrations of acid, iron, and sulfate are required (D. K. Nordstrom, U.S. Geological Survey 1991, written commun.); however, Baker (1971) reported the presence of ferric sulfate and hydroxide on biologically oxidized, submerged pyrite surfaces that were analyzed under about 0.1 inches (in) of water.

AMD also can form in the absence of O_2. Relatively small amounts of DO may be available below the water table, where O_2 solubility, diffusion, microbial consumption, and oxidation reactions limit the supply of the reactant (Champ et al. 1979; Jaynes et al. 1984a,b). However, Fe^{3+} produced by T. ferrooxidans may oxidize the sulfur in pyrite (Temple and Delchamps 1953)

$$FeS_2 + 14\ Fe^{3+} + 8\ H_2O \Longrightarrow 15\ Fe^{2+} + 2\ SO_4^{2-} + 16\ H^+. \quad (6)$$

Kinetic data suggest that Fe^{3+} is the direct oxidant of pyrite in oxic and anoxic acid systems (Garrels and Thompson 1960; Singer and Stumm 1970a,b; McKibben and Barnes 1986; Moses et al. 1987).

The storage of Fe^{3+} in the unsaturated zone and its subsequent release into ground water is an important aspect of pyrite oxidation below the water table. For example, as the water table rises or as recharge waters percolate through the mine spoil to the water table, previously formed ferric minerals may be transported or decompose releasing Fe^{3+} into ground water and thus providing an oxidant for pyrite. Barnes and Clarke (1964) suggested that because of the absence of DO and limited solubility of Fe^{3+}, O_2 should be discarded as a major reactant in subsurface mine waters and reactions involving only water and minerals should be considered as controls of mine-water quality. Gang and Langmuir (1974) proposed that suspended ferrihydrite colloids could be a source of Fe^{3+} ions

$$FeS_2 + 14\ Fe(OH)_3 + 26\ H^+ \Longrightarrow 15\ Fe^{2+} + 2\ SO_4^{2-} + 34\ H_2O. \quad (7)$$

However, the combination of ferrihydrite dissolution and pyrite oxidation neutralizes acid and produces smaller quantities of sulfate than dissolved iron. Although reaction 7 is thermodynamically feasible, $Fe(OH)_3$ is not a likely source of Fe^{3+} because it normally is formed as acidic water is neutralized downflow from its source.

Another source of Fe^{3+} is the soluble, hydrated ferric-sulfate minerals including roemerite, copiapite, and coquimbite, which can form on the surface of pyrite in weathered zones. Jarosite $[(K,Na,H_3O)Fe_3(SO_4)_2(OH)_6]$ is not a likely source of Fe^{3+} ions because it is relatively insoluble in acidic to neutral waters (Nordstrom et al. 1979; Nordstrom 1982). Although Temple and Koehler (1954) and Zajic (1969, p. 101, 114-116) suggested that ferric-sulfate compounds may oxidize pyrite, they did not expand on the significance of these minerals as reactants in coal-mine spoil, especially on their role in the subsurface evolution of acidic ground water under anoxic conditions. For example, the following overall reaction of pyrite and roemerite generates acid without oxygen:

$$FeS_2 + 7\ Fe^{2+}Fe_2^{3+}(SO_4)_4 \cdot 14H_2O \Longrightarrow 22\ Fe^{2+} + 30\ SO_4^{2-} + 16\ H^+ + 90\ H_2O. \quad (8)$$

Similar reactions may occur between pyrite and copiapite or coquimbite. One can speculate that attempts to stop AMD formation by excluding O_2 after ferric salts have formed in pyritic mine spoil or coal refuse may not be successful because of the potential for release of stored acid, SO_4^{2-}, and Fe^{3+}.

Neutralization of Acid

Acid from the aqueous oxidation of pyrite can be neutralized by reactions with carbonate, silicate, and hydroxide minerals composing the sedimentary rocks in the coal-bearing sequence. Dissolution of these minerals produces elevated concentrations of dissolved cations such as calcium (Ca), magnesium (Mg), sodium (Na), potassium (K), aluminum (Al), and silicon (Si). The following stoichiometric reactions are presented to show mineral sources of major solutes in AMD and to indicate mass-balance relations employed later for the geochemical interpretation of water-quality data.

The most acid-reactive minerals are the carbonates: calcite ($CaCO_3$), dolomite $[CaMg(CO_3)_2]$, and siderite ($FeCO_3$). Carbonates are present in variable quantities as individual mineral grains and as cementing agents in limestone, dolostone, and clastic rocks (sandstone, siltstone, and shale). Dissolution of calcite, dolomite, and other calcium- or magnesium-bearing carbonate minerals neutralizes acid and produces alkalinity (bicarbonate). The dissolution of calcite serves as an example

$$CaCO_3 + H^+ \Longrightarrow Ca^{2+} + HCO_3^-. \quad (9)$$

Reaction 9 shows that 1 mol of calcite will neutralize 1 mol of free acid and produce 1 mol each of dissolved calcium and bicarbonate. However, dissolution of siderite, which is a common mineral in coal-bearing strata, and subsequent oxidation and hydrolysis of iron can produce acid as dissolved carbon dioxide and carbonic acid ($H_2CO_3^*$) (Cravotta et al. 1990)

$$FeCO_3 + 0.25\ O_2 + 2.5\ H_2O \Longrightarrow Fe(OH)_3 + H_2CO_3^*. \quad (10)$$

Cations such as Mn, Mg, and Ca commonly substitute for Fe in siderite (Mozley, 1989; Morrison et al. 1990b). The Ca-Mg-carbonate impurities have neutralizing ability similar to calcite and dolomite; however, like Fe (reaction 3), the hydrolysis of Mn ions will generate acid. Thus, because of its variable composition, the acid-forming or neutralizing potential of siderite is difficult to predict.

Dissolution or hydrolysis of aluminosilicate minerals, which predominate in the clastic overburden rocks, neutralizes acid, but also produces dissolved Al, Si, and major cations such as Mg, Na, and K plus solid phases. Complete solution of aluminum-bearing phases can occur under extremely acid conditions; however, quartz (SiO_2) is resistant to sulfuric acid and is a common residual mineral. For example, chlorite may dissolve incongruently producing solid gibbsite [$Al(OH)_3$] and cryptocrystalline or amorphous silica (SiO_2) plus dissolved magnesium

$$Mg_5Al_2Si_3O_{10}(OH)_8 + 10\ H^+ \Longrightarrow 2\ Al(OH)_3 + 3\ SiO_2 + 5\ Mg^{2+} + 6\ H_2O. \quad (11)$$

Chlorite commonly contains Fe and Mn substituting for Mg. Dixon et al. (1982) report that the weathering of Fe-chlorite in lignite overburden caused preferential leaching of Mg and Fe relative to Si and Al.

Feldspar may hydrolyze producing kaolinite [$Al_2Si_2O_5(OH)_4$], a common clay mineral, plus dissolved silica, potassium, and sodium

$$2\ K_{0.85}Na_{0.15}AlSi_3O_8 + 9\ H_2O + 2\ H^+ \Longrightarrow Al_2Si_2O_5(OH)_4 + 4\ H_4SiO_4^o + 1.7\ K^+ + 0.3\ Na^+. \quad (12)$$

In reaction 12, both K and Na are contained in the feldspar. X-ray diffraction patterns suggest the presence of microcline having this stoichiometry in rock samples collected at the study site (see below).

Elevated concentrations of aluminum are common in AMD because even gibbsite and kaolinite can dissolve in acidic systems (pH less than 4) producing Al^{3+} (Hem 1985), as is shown by the dissolution of kaolinite:

$$Al_2Si_2O_5(OH)_4 + 6\ H^+ \rightarrow 2\ H_4SiO_4^o + 2\ Al^{3+} + H_2O. \quad (13)$$

Reaction 13 shows that the dissolution of 1 mol of kaolinite neutralizes 6 mol of H^+ and produces 2 mol of Al^{3+}. Although acid neutralization is desirable, the leaching of aluminum is not desirable because Al^{3+} can be toxic to aquatic biota (Burrows 1977; Baker and Schofield 1982; Burton and Allan 1986), and the hydrolysis of Al^{3+} produces H^+ and buffers pH to be acid.

Mine Location, Geology, and Hydrology

AMD is widespread in the bituminous coal field of western Pennsylvania where surface mining prevails. A surface coal mine in that region was selected for an investigation of ground-water quality. The mine was reclaimed partly by surficial applications of municipal sewage sludge. The PaDER and USGS wanted to determine potential adverse effects on water quality by leaching of heavy metals and nutrients from the sludge. The

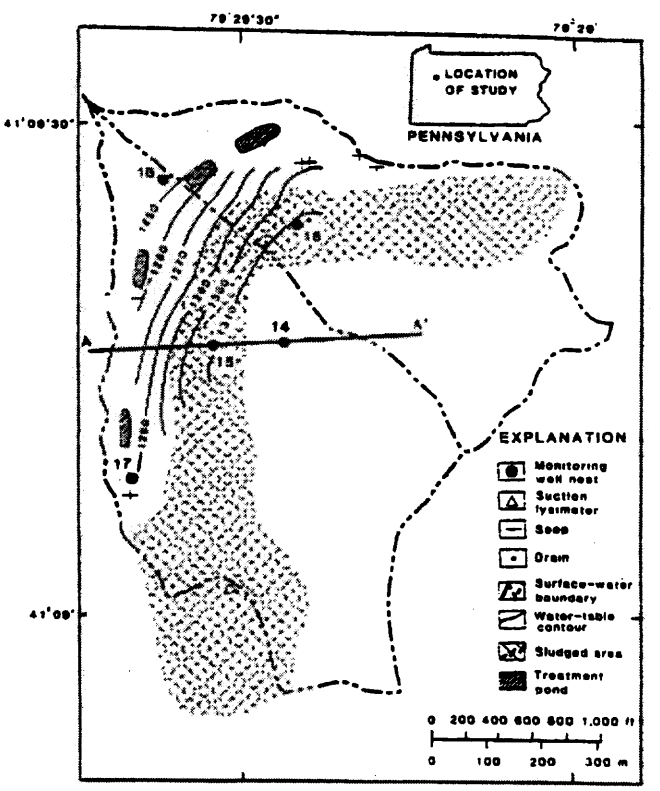

Figure 1.--Location of reclaimed surface coal mine, sewage-sludge-covered area, hydrologic monitoring points, and median water-table configuration. Line A-A' of geologic section in figure 2.

study site also was investigated because AMD had developed during mining and continued to discharge at a number of seeps even though mining and reclamation were completed by enactment of guidelines intended to reduce the effects of mining on the environment.

Mine Location and Description

The study area includes a reclaimed 150-acre surface coal mine about 7 miles (mi) southwest of the city of Clarion in Clarion County, Pennsylvania (see figure 1). The area includes a broad hilltop, surrounded by steep hillsides, and bounded by several small tributaries which flow northward and westward to the Clarion River. Seepage from the mine-spoil banks and outcropping, underlying bedrock flows into these tributaries. Altitudes in the study area range from greater than 1,500 feet (ft) to less than 1,200 ft above sea level.

Prior to 1982, high-volatile bituminous coal of the Allegheny Group was mined by open pit methods. Overburden was removed using a dragline and bucket, and coal was removed by front-end loader and truck. Because roughly half of the area was mined only for the lower Kittanning coal (hilltop) and the other half only for the upper and lower Clarion coals (hillside), a highwall was created separating upper and lower benches (see figure 2). During mining, the mine was backfilled with overburden and coal waste material, and in 1982 at the completion of mining, the mine spoil was regraded into a terraced topographic configuration corresponding to the upper and lower benches. The average thickness of the mine spoil is about 50 ft on the upper bench and 70 ft on the lower bench.

In the spring of 1986, a mixture of composted wood chips and sewage sludge from Philadelphia wastewater treatment plants (Blickwedel and Linn 1987) was spread at a rate of about 60 dry tons per acre over about 60 acres of the mine-spoil surface on the lower bench (see figures 1 and 2). The sludge-covered spoil composes about 40 percent of the reclaimed area. Berms were constructed along the downslope perimeter of the sludge-

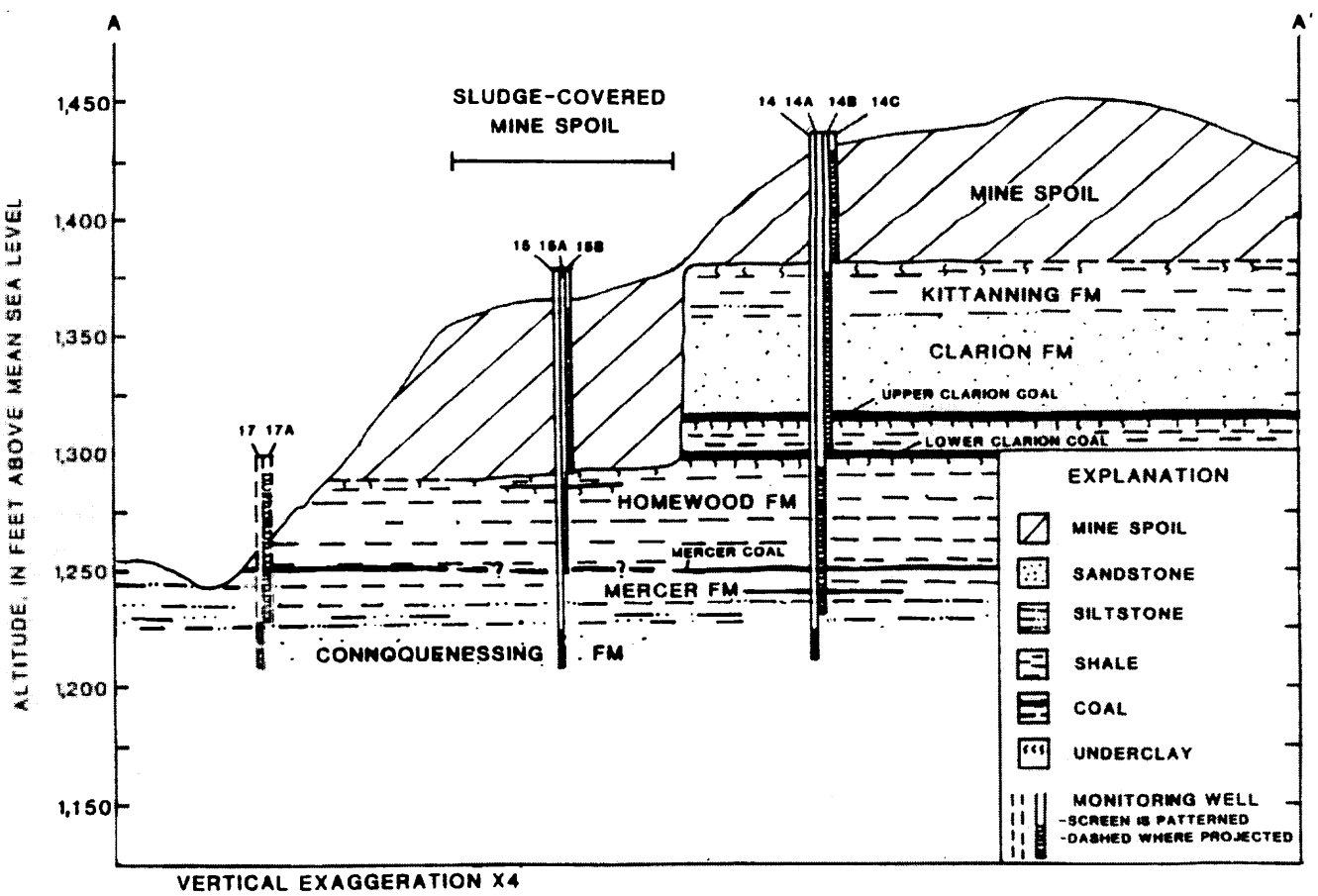

Figure 2.--Geologic section along an east-west traverse through the mine. Line of section shown in figure 1

treated area to prevent the sludge from eroding (before vegetation could be established) and entering nearby surface water. The composted sludge mixture was not applied on the hilltop, which was planted with pine trees, or on the steep "toe-of-spoil" banks below the berms, which remained barren, erodable, and permeable. In contrast, the sludge-treated areas support lush vegetative growth, which was established within months after seeding with perennial grasses.

Geology, Mineralogy, and Rock Chemistry

The study area is underlain by a series of sandstones, shales, and coals that were deposited in brackish and marine environments during the Pennsylvanian Period (Williams 1960). These strata compose (from oldest to youngest) the Connoquenessing, Mercer, and Homewood Formations of the lower and middle Pennsylvanian Pottsville Group; and the Clarion and Kittanning Formations of the middle and upper Pennsylvanian Allegheny Group (Berg et al. 1980, 1983; Buckwalter et al. 1981). A geologic section (see figure 2) was constructed from driller's logs of the rocks encountered during installation of monitoring wells. Fine-grained, white-to-gray sandstone is the predominant overburden lithology, and gray, interbedded shale and siltstone lie above and below the coals. Limestone is sparse to absent in the study area. Bedrock dips approximately 0.5 to 1.0 degree to the northwest.

Mineralogy was determined by x-ray diffraction analysis of crushed rock samples from a 170-ft-long drill core through bedrock from the base of the lower Kittanning coal into the upper part of the Connoquenessing sandstone (well 14 in figure 2). The predominant minerals are aluminosilicates (see table 1): Quartz and kaolinite are present in every horizon; microcline, muscovite, illite, and chlorite are present in most non-coal horizons. Calcite is present only as a trace mineral in the deep shale and siltstone bedrock, and siderite is present in the siltstone and shale horizons above and below the Clarion and Mercer coals. Pyrite and marcasite are present primarily in the coal and secondarily in the shale samples. The ferric sulfates roemerite, copiapite, coquimbite, and jarosite are present, concentrated within several-inch-thick layers in the upper and lower Clarion coals and as trace minerals in the Mercer coals. The sulfate minerals occur as white and yellow efflorescences in cleats and on the surface of the coal samples. Much of the oxidation of pyrite to produce the sulfate minerals probably occurred in situ, prior to core collection, because the Clarion coals in the highwall were dewatered and aerated during mining when the water table was lowered about 25 ft to a level at, or below, the altitude of the base of the lower Clarion coal (see figure 2). However, some ferric sulfates, especially in deeper samples in the Homewood and Mercer Formations also could have formed while the core was in storage. Goethite, the only iron oxide identified, was found in one sandstone sample collected above the upper Clarion coal. Hematite, melanterite, gypsum, dolomite, and pyrolusite were not identified in any samples. The sulfur minerals and calcite are sparse and occur in discrete layers--thus their presence is difficult to confirm by x-ray analysis of composite samples--however, these phases are relatively reactive and are likely to control the quality of ground water.

Chemical analysis of the pulverized rock samples from the drill core (well 14 in figure 2) was performed to confirm and quantify the presence of carbonate, sulfate, and sulfide minerals. The samples were analyzed for neutralization potential (NP), pH of a 1:1 water:rock paste, and concentrations of total sulfur, forms of sulfur (Sobek et al. 1978; Noll et al. 1988), iron, and manganese (see table 2). None of the samples effervesced upon addition of dilute hydrochloric acid (HCl), nor did any have substantial NP (expressed as ppt = tons $CaCO_3$ per thousand tons). The highest NP value is 47.4 ppt for a composite sample from a 0.5-ft-thick horizon, which did not contain detectible calcite. Because the samples did not react visibly with HCl, NP values greater than 30 ppt probably indicate the presence of siderite rather than calcite or dolomite (Brady and Hornberger 1989; Morrison et al. 1990a). The rock samples containing detectible siderite (see tables 1 and 2) have NP values ranging from 1.3 to 47.4 ppt. Negative values of NP indicate production of acid, corresponding with low values of paste pH (less than 4). The rock samples containing iron-sulfide and -sulfate minerals have NP values ranging from -134.9 to -0.3 ppt.

On the basis of the concentration of total sulfur--which consists of sulfide, sulfate, and organic sulfur, generally in order of decreasing abundance--and molar ratios of inorganic sulfur to iron (Sin/Fe) (see table 2), two groups of samples can be distinguished: (1) high-sulfur coal samples containing greater than 2% total sulfur and having Sin/Fe values of 1.2 to 2.1, and (2) low-sulfur, noncoal samples containing less than 0.61% total sulfur and having Sin/Fe values of less than 0.3. Of the high-sulfur group, the Clarion coals and the uppermost Mercer coal are at least 2 ft thick (respective depth intervals: 108.6-111.0; 123.2-126.8; 173.0-175.0), and contain 3.5% to 17% sulfur and 2% to 20% iron. The Sin/Fe values in the original,

TABLE 1.--Minerals identified in drill-core rock samples[1] by x-ray diffraction [● major; O minor; - not detected]

DEPTH INTERVAL[1]	GEO-LOGIC UNIT[2]	LITH-OLOGY[3]	QUARTZ & KAOLINITE	MUSCOVITE & ILLITE	MICROCLINE FELDSPAR	CHLORITE	CALCITE	SIDERITE	PYRITE MARCASITE	ROEMERITE COQUIMBITE COPIAPITE JAROSITE[4]	GOETHITE
46.8- 48.5	KTFM	CL	●	●	●	●	-	-	-	-	-
49.0- 50.0	KTFM	SH	●	●	●	-	-	●	-	-	-
58.0- 60.0	KTFM	ST	●	●	●	-	-	-	-	-	-
66.0- 66.5	VNFM	SS+LS	●	●	●	-	-	●	-	-	-
78.0- 80.0	CLFM	SS	●	●	-	●	-	-	-	-	-
82.0- 84.0	CLFM	SS	●	●	●	●	-	-	-	-	-
90.0- 92.0	CLFM	SS	●	●	●	●	-	●	-	-	-
102.0-104.0	CLFM	SS	●	●	●	●	-	-	-	-	●
108.6-108.9	CLUC	WH	●	-	-	-	-	-	●	●	-
109.5-111.0	CLUC	CO+WH	●	-	-	-	-	-	●	O	-
114.0-116.0	CLFM	SH+SS	●	●	●	O	-	●	-	-	-
123.2-123.4	CLLC	CO+WH	●	●	●	●	-	-	-	O	-
125.5-126.8	CLLC	CO+CL	●	-	-	-	-	-	●	●	-
129.8-131.8	HWFM	CL	●	●	●	-	-	-	-	-	-
137.7-139.0	HWFM	SH	●	-	O	-	-	-	O	-	-
143.5-144.2	HWFM	ST+SH	●	●	-	-	-	O	-	-	-
145.0-147.0	HWFM	ST	●	●	●	-	-	●	-	-	-
153.0-155.0	HWFM	ST	●	●	●	●	-	●	-	-	-
165.0-169.0	HWFM	ST	●	●	●	●	-	●	-	-	-
173.0-175.0	MRFM	CO+WH	●	●	-	●	-	-	●	O	-
175.3-178.0	MRFM	CL	●	●	-	●	O	●	-	-	-
181.9-182.6	MRFM	SH+CO	●	●	O	-	-	-	●	-	-
184.0-185.0	MRFM	CL	●	●	●	-	-	O	-	-	-
188.5-189.0	MRFM	CO	●	●	-	O	-	-	●	O	-
189.5-191.5	MRFM	SH+ST	●	●	●	●	-	-	-	-	-
196.5-199.5	CQFM	SS+ST	●	●	●	●	O	-	-	-	-

[1]Drill core from well 14 location (fig. 2). Composite sample depth interval, in feet below present land surface. The following depth ranges indicate the equivalent position of screened intervals for monitor wells: 0-48 ft = well 14C; 60-127 ft = wells 14B and 15B; 132-195 ft = wells 14A, 15A, and 17A; 197-215 ft = wells 14, 15, and 17.

[2]Geologic units correspond to those in geologic section (fig. 2): KTFM = Kittanning Formation; VNFM = Vanport Formation; CLFM = Clarion Formation; CLUC = upper Clarion coal; CLLC = lower Clarion coal; HWFM = Homewood Formation; MRFM = Mercer Formation; CQFM = Connoquenessing Formation.

[3]Lithology determined by hand-specimen analysis: SS = sandstone; ST = siltstone; SH = shale; CL = underclay; WH = white efflorescence; CO = coal; LS = limestone.

[4]Stoichiometric formulas for ferro-ferric-sulfate minerals are indicated in table 2.

TABLE 2.--Rock sample depth, thickess, neutralization potential (NP), chemical concentrations and ratios
[no data (-); depth in feet below surface (ft); thickness in feet (ft);
weight percent (%) or parts per thousand (ppt); molar ratio (M/M)]

DEPTH INTERVAL[1] (ft)	THICK-NESS (ft)	GEO-LOGIC UNIT[2]	LITH-OLOGY[3]	PASTE pH	NP (ppt)	SULFUR, TOTAL (%)	SUL-FIDE (%)	SUL-FATE (%)	SUL-FUR, ORGN[4] (%)	MANG-ANESE (%)	IRON, TOTAL (%)	S/Fe[4] (M/M)	Sin/Fe[4] (M/M)	Mn/Fe (M/M)
46.8- 48.5	1.7	KTFM	CL	4.4	2.68	0.42	-	-	-	0.047	4.11	0.178	-	0.012
49.0- 50.0	1.0	KTFM	SH	5.2	1.32	.02	0.02	<0.01	<0.01	.007	1.16	.030	0.015	.006
58.0- 60.0	2.0	KTFM	ST	5.7	1.99	.00	-	-	-	.109	9.95	.000	-	.011
66.0- 66.5	.5	VNFM	SS+LS	7.2	47.36	.00	-	-	-	.307	20.40	.000	-	.015
78.0- 80.0	2.0	CLFM	SS	7.0	3.99	.00	-	-	-	.018	1.33	.000	-	.013
82.0- 84.0	2.0	CLFM	SS	7.4	5.88	.00	-	-	-	.022	1.57	.000	-	.014
90.0- 92.0	2.0	CLFM	SS	7.0	6.15	.01	-	-	-	.018	1.45	.012	-	.013
102.0-104.0	2.0	CLFM	SS	6.2	5.49	.06	-	-	-	.026	1.24	.084	-	.021
108.6-108.9	.3	CLUC	WH	1.2	-134.94	17.40	10.61	5.71	1.08	.021	20.32	1.492	1.399	.001
109.5-111.0	1.5	CLUC	CO+WH	2.8	-8.27	3.48	1.88	.27	1.33	.001	1.78	3.413	2.109	.001
114.0-116.0	2.0	CLFM	SH+SS	4.0	5.36	.83	-	-	-	.030	4.65	.311	-	.007
123.2-123.4	.2	CLLC	CO+WH	2.5	-25.44	5.54	4.33	1.11	.10	.075	7.17	1.346	1.322	.011
125.5-126.8	1.3	CLLC	CO+CL	2.4	-27.76	4.35	3.07	1.01	.27	.013	4.51	1.679	1.575	.003
129.8-131.8	2.0	HWFM	CL	6.1	2.08	.11	-	-	-	.004	1.18	.162	-	.004
137.7-139.0	1.3	HWFM	SH	4.2	5.00	.61	.43	.11	.07	.043	3.47	.307	.272	.013
143.5-144.2	.7	HWFM	ST+SH	5.7	15.91	.24	.16	.05	.03	.032	3.97	.105	.092	.008
145.0-147.0	2.0	HWFM	ST	7.3	16.19	.03	-	-	-	.029	3.18	.016	-	.009
153.0-155.0	2.0	HWFM	ST	7.4	45.55	.20	-	-	-	.100	5.64	.062	-	.018
165.0-169.0	4.0	HWFM	ST	6.8	13.06	.17	.12	.02	.03	.077	4.95	.060	.049	.016
173.0-175.0	2.0	MRFM	CO+WH	3.5	-.32	3.44	2.97	.26	.21	.033	4.50	1.332	1.250	.007
175.3-178.0	2.7	MRFM	CL	4.0	-.11	.39	-	-	-	.025	3.11	.218	-	.008
181.9-182.6	.7	MRFM	SH+CO	3.4	-3.48	2.15	1.50	.13	.52	.002	1.64	2.281	1.730	.001
184.0-185.0	1.0	MRFM	CL	7.0	1.00	.12	-	-	-	.005	1.07	.195	-	.005
188.5-189.0	.5	MRFM	CO	2.3	-10.99	4.11	3.13	.49	.49	.009	4.57	1.565	1.379	.002
189.5-191.5	2.0	MRFM	SH+ST	4.3	-.06	.31	-	-	-	.010	1.73	.312	-	.006
196.5-199.5	3.0	CQFM	SS+ST	5.6	.36	.17	-	-	-	.011	1.35	.219	-	.008

[1]Drill core from well 14 location (fig. 2). Composite sample depth interval, in feet below present land surface.

[2]Geologic units correspond to those in geologic section (fig. 2): KTFM = Kittanning Formation; VNFM = Vanport Formation; CLFM = Clarion Formation; CLUC = upper Clarion coal; CLLC = lower Clarion coal; HWFM = Homewood Formation; MRFM = Mercer Formation; CQFM = Connoquenessing Formation.

[3]Lithology determined by hand-specimen analysis: SS = sandstone; ST = siltstone; SH = shale; CL = underclay; WH = white efflorescence; CO = coal; LS = limestone.

[4]Molar ratios of total sulfur to iron (S/Fe) for rock samples include organic sulfur. Fe/S values for the minerals below can be compared with the ratio of inorganic sulfur to iron (Sin/Fe).

pyrite	FeS_2	S/Fe = 2.00	marcasite	FeS_2	S/Fe = 2.00
roemerite	$Fe^{2+}Fe_2^{3+}(SO_4)_4 \cdot 14H_2O$	S/Fe = 1.33	copiapite	$Fe^{2+}Fe_4^{3+}(SO_4)_6 \cdot 20H_2O(OH)_2$	S/Fe = 1.20
coquimbite	$Fe_2(SO_4)_3 \cdot 9H_2O$	S/Fe = 1.50	jarosite	$KFe_3(SO_4)_2(OH)_6$	S/Fe = 0.66

unweathered minerals are unknown; however, values of 1.2 to 2.1 for the coal samples imply the presence iron-sulfide and weathered iron-hydroxide and -sulfate minerals, which have Sin/Fe from 0.66 to 2.0 (see table 2, footnote 3). The ferric-sulfate minerals roemerite, copiapite, coquimbite, and jarosite have Sin/Fe values of less than 2.0. If all iron and sulfur in the unweathered coal samples were in the form of pyrite (+ marcasite), the Sin/Fe ratio would equal 2.0; however, Sin/Fe values substantially less than 2.0 would indicate weathering (oxidation and leaching) because iron generally is less mobile than sulfate. Oxidation of pyrite under unsaturated, nonrecharge (humid air) conditions would conserve the ratio of Sin/Fe = 2.0, which would be expected if the oxidation of pyrite took place while the samples aged in core boxes before analysis. Oxidation of organic forms of sulfur would increase the Sin/Fe ratio. As for low-sulfur, noncoal samples, a combination of pyrite, goethite, siderite, and (or) chlorite will yield Sin/Fe values less than 0.3.

The rock-core chemical data in table 2 also indicate sources of Mn, a major cation in AMD. Manganese is present in all the rock samples, and ranges in concentration from about 0.001% to 0.3%. No dominantly Mn-bearing minerals were identified by x-ray diffraction, which indicates that minerals such as manganite (MnOOH) or pyrolusite (MnO_2) which commonly form coatings within joints and fractures, are not abundant. Manganese is likely to occur in silicate minerals, such as chlorite, which is abundant throughout the section. Although pyrite normally contains trace quantities of Mn (Gang and Langmuir 1974) the coal samples containing detectible pyrite and (or) iron-sulfate minerals have a low molar ratio of manganese to iron (Mn/Fe), ranging from 0.001 to 0.007, which suggests that neither coal nor pyrite is a major source of Mn. However, the higher Mn concentrations (greater than 0.04%) occur in samples containing relatively high Fe, and having a relatively high Mn/Fe, ranging from about 0.01 to 0.02. Most, but not all, the high-Mn samples contain detectible siderite (see tables 1 and 2). Manganese commonly occurs as a trace impurity in siderite, which tends to weather producing iron-manganese oxyhydroxide minerals (Senkayi et al. 1986). The samples containing siderite have Mn/Fe ratios ranging from 0.006 to 0.018, which are consistent with a ratio of 0.012 for a siderite stoichiometry of $(Fe_{0.86}Mn_{0.01}Mg_{0.02}Ca_{0.1})CO_3$, reported by Morrison et al. (1990b).

Ground-Water Hydrology

Three monitoring well nests were installed by the mine operator in a line roughly parallel to the east-to-west direction of ground-water flow (see figures 1 and 2): Nest 14 is in the untreated zone, nest 15 is in the sludge-covered zone, and nest 17 is below the toe of spoil. Nest 14 consists of 4 wells (14, 14A, 14B, 14C), nest 15 consists of 3 wells (15, 15A, 15B), and nest 17 consists of 2 wells (17, 17A). Each well was constructed of 2-in diameter polyvinyl-chloride (PVC) pipe installed in separate drill holes. The annulus above the screen was filled with grout and that below the screen with rock cuttings. Wells 14, 15, and 17 were screened in the Connoquenessing Formation sandstone. Wells 14A, 15A, and 17A were screened in the overlying Mercer Formation coal and shale. Wells 14B and 15B were completed in the lower Clarion coal horizon; well 14B was screened through bedrock and well 15B was screened through sludge-covered mine spoil. Well 14C was screened through the untreated mine spoil at the Kittanning coal horizon on the upper bench.

Static-water levels in the wells were measured monthly from June 1986 through November 1989. The mine spoil on the upper bench forms a perched aquifer with a saturated thickness that has fluctuated seasonally from 6 to 9 ft. However, the mine spoil on the lower bench is part of the water-table aquifer, which is continuous across the site (see figures 1 and 3). The saturated thickness of the mine spoil on the lower bench has fluctuated from about 10 to 21 ft during the period of study. The water table within the adjacent unmined zone (highwall) has fluctuated less than 7 ft, and has remained at least 10 ft above the upper Clarion coal during the post-reclamation period of study. However, during recent mining, the water table probably was lowered to a level about 25 ft below its present location. Such transient hydrologic conditions are ideal for weathering pyrite and forming Fe^{3+} and SO_4^{2-} in the mine spoil (current formation) and unmined coal in the highwall (past formation).

A crude analytical water budget for the period of study includes measured seepage discharge rates and an estimated annual recharge of 45 percent of the cumulative annual precipitation of 43 in. Rainfall data were obtained from records of a National Oceanic and Atmospheric Adminstration (NOAA) weather station at Clarion about 4 mi northeast of the study area (NOAA 1987, 1988). The recharge rate of 45 percent of precipitation (45 % P) assumes 52 % P is lost by evapotranspiration, which is consistent with that for a nearby mine site (Henke 1985), and only 3 % P is lost as runoff because sedimentation ponds prevent most runoff

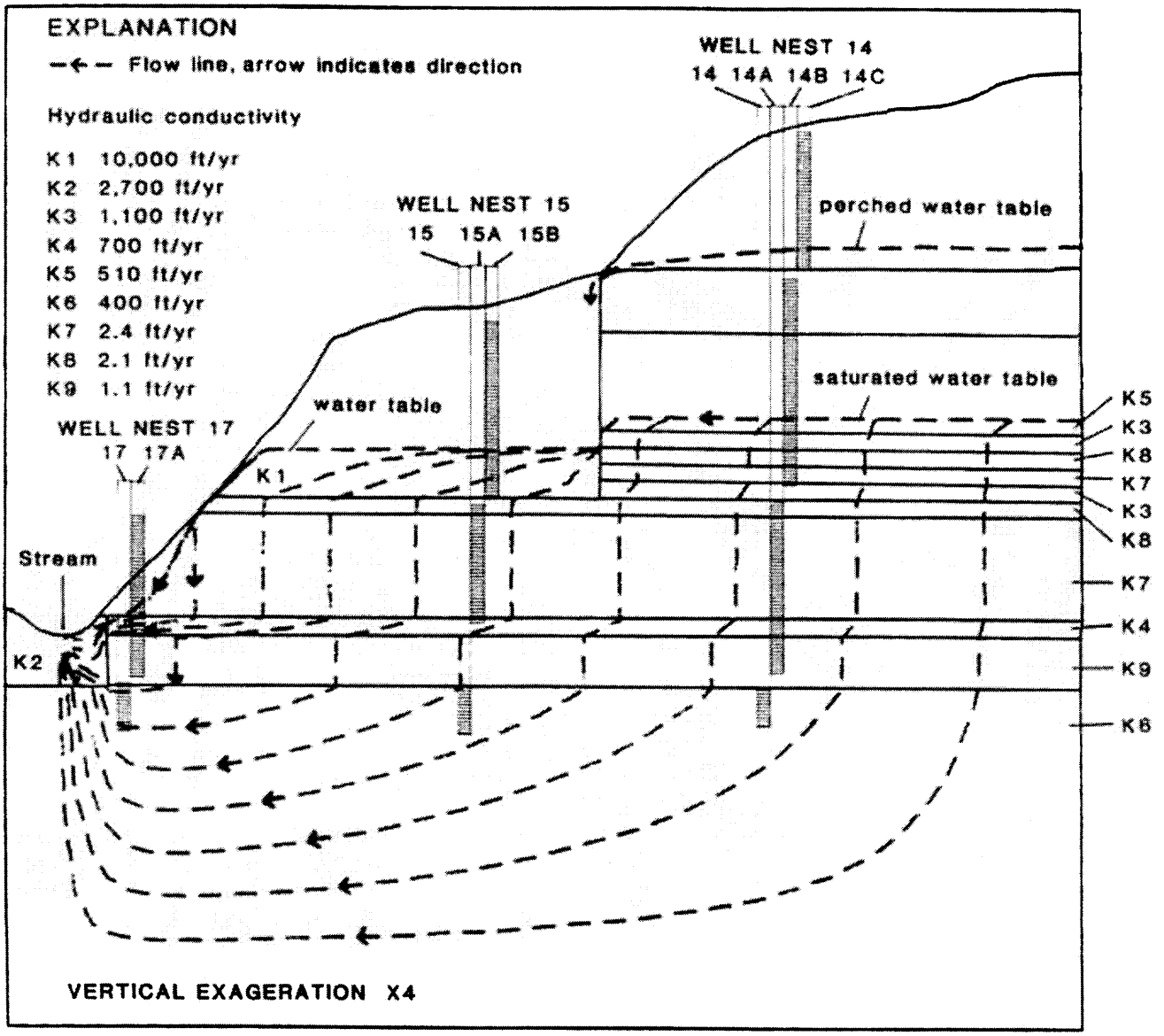

Figure 3.--Ground-water table and flow directions along an east-west section through the mine (Saad and Cravotta, 1991). Model boundaries include: top, constant flux; east, west, and bottom, no flow.

from leaving the mine site. Although the average recharge is 45 % P, the recharge rate to different zones is expected to vary depending on the distribution of mine spoil and occurrence of aquitards (perched aquifer) and seepage areas (toe of spoil).

Geologic and hydrologic data were used to construct a two-dimensional, cross-sectional, layered model of ground-water flow through the mine spoil and underlying bedrock (see figure 3) (Saad and Cravotta 1991). Modeling was conducted using the steady-state option of the finite-difference computer program, MODFLOW (McDonald and Harbaugh 1988) and by simulating a range of boundary conditions and probable hydraulic conductivities. The eastern and western divides and base of the flow system were simulated as no-flow boundaries, and the saturated water table was simulated as a constant-recharge boundary. Different recharge rates were assumed for zones corresponding to the upper bench (below the perched aquifer), lower bench, and toe of spoil to the stream (see figure 3). Seventy-five percent of the recharge to the perched aquifer was assumed to percolate to the underlying saturated bedrock (34 % P), and the remainder was assumed to flow to the highwall and to percolate, in addition to rainfall recharge (45 % P), through mine spoil of the lower bench. Similarly, seepage water from the toe of spoil on the lower bench was added to rainfall recharging the water table between the toe of spoil and the stream. Hydraulic conductivities were varied to reflect three

different hydrogeologic units--spoil, coal and sandstone, and shale and underclay--and were adjusted to match the median static-water levels measured in seven of the nine wells along the cross section. The water levels in wells 14 and 14A were not used because the well casing above the screened intervals is known to leak. The resultant ground-water heads and flow paths were computed and plotted by use the computer programs, CONTOUR (Harbaugh 1990) and MODPATH (Pollack 1989), respectively.

In general, directions of ground-water flow are dominantly horizontal near the water table in the coal and mine spoil, downward through underlying zones across most of the section, and both downward and westward through the deeper underlying bedrock (see figure 3). However, near the stream-discharge zone at the western boundary, ground-water flow is directed upward to the streambed. Flow paths are predominantly horizontal through transmissive units (spoil, coal, and sandstone) and vertical through confining units (shale and underclay). The flow paths through screened intervals of upflow and downflow wells are of particular interest because these define potential reaction paths for water-quality changes.

Conceptual Model of Oxygen Transport

The concept of water-unsaturated, oxygenated zones (open system) versus water-saturated, oxygen-limited zones (closed system) (see figure 4) provides a basis for evaluating where and to what extent oxidation reactions may occur in the subsurface (Champ et al. 1979). The transport of O_2 into unsaturated mine spoil

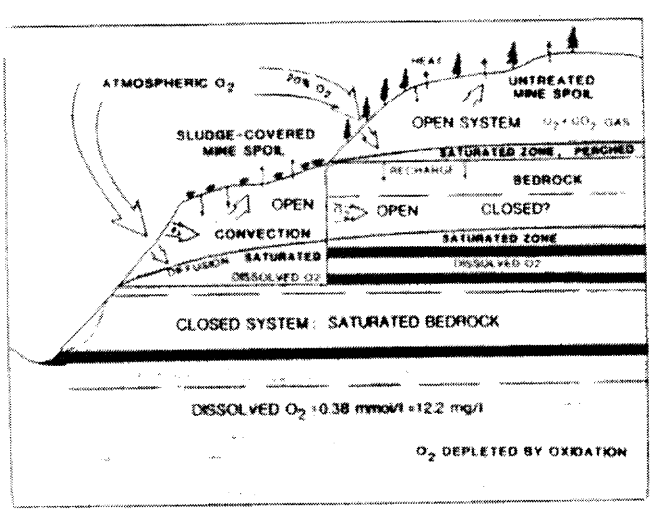

Figure 4.--Conceptual model of oxygen transport into subsurface water-unsaturated and -saturated zones of the mine.

is likely to be driven by thermal convection (Cathles 1982), diffusion (Jaynes et al. 1984a,b), and (or) displacement by recharge waters, depending on unsaturated zone temperature, permeability, pore-gas composition, and moisture conditions. Pyrite oxidation depletes O_2 and warms air within the unsaturated mine spoil. Temperature and gas profiles were not measured in the vadose zone; however, diffusion to O_2-depleted zones will occur, and if the temperature gradients and permeability are large, as expected, convection will predominate as the warm air to rises through the spoil to the surface. In exchange, fresh oxygenated air from the atmosphere flows through the steep, barren slopes into the unsaturated spoil and fractured bedrock. Moisture in the fresh air can condense on mineral surfaces. Thus, water and abundant O_2 are available in the vadose zone (open system) to react with pyrite producing ferric-hydroxide and -sulfate minerals (reactions 4 and 5). Below the water table, however, transport of O_2 is limited by its solubility and time required for diffusion in ground water. Thus, the extent to which oxygenation reactions (such as 1 through 5) occur will be limited by the concentration of DO (closed system). For example, ground water at 6°C can attain a maximum equilibrium concentration of DO of 0.38 millimole per liter (mmol/l) or 12.2 milligrams per liter (mg/l) (Drever 1982, p. 287). As this oxygen-saturated water flows downward from the water table to deeper zones, the oxidation of organic matter, iron, manganese, sulfur, and other reduced elements will deplete DO and produce anoxic conditions at some point along the flow path. Thus, if pyrite oxidation occurs in a closed system by reaction 1, where 1 mol of FeS_2 reacts with 3.5 mol of O_2 producing 2 mol of SO_4^{2-}, then reaction with 0.38 mmol/l of O_2 can produce only 0.22 mmol/l of SO_4^{2-} (= 20.8 mg/l). In contrast, additional and potentially much greater quantities of SO_4^{2-} may be produced in the absence of DO if pyrite oxidation occurs by reactions 6 or 8. However, those reactions still depend on the previous production of Fe^{3+} by reaction 2, which involves O_2.

Geochemical Evolution of Acidic Ground Water

An examination of the geologic and hydrologic data presented in the previous sections shows that certain minerals appear consistently in the rocks of the overburden, coal, underburden, and mine spoil (see table 1), and that the ground water tends to flow from oxic zones near the water table to deeper potentially anoxic zones. The objective of this section is to describe the hydrochemical trends along potential flow paths and to evaluate the formation of acidic ground water by reactions between gaseous, aqueous, and solid phases in systems that are open or closed with respect to O_2.

Hydrochemical Trends

Water-quality data were collected quarterly in December 1986 through September 1989 to characterize hydrochemical trends as affected by surface coal mining and reclamation with sewage sludge. Field measurements and water-quality sampling were conducted after purging stagnant water from wells with PVC bailers. Measurements of pH, DO, platinum-electrode potential (Eh), specific conductance, and temperature were conducted following methods of Wood (1976). DO and temperature were determined by suspending electrometric probes downhole, and specific conductance, pH, and Eh were determined at the well head. Samples for analysis of cations (Fe, Mn, Al, Mg, Ca, Na, K, Si, Ba, Cd, Cu, Ni, Pb, Sr, Zn) were filtered through 0.45-micrometer porosity filters, transferred to acid-rinsed polyethylene bottles, and preserved with nitric acid. Samples for analysis of Fe^{2+} were not filtered, were stored in polyethylene bottles, and preserved with sulfuric acid. Samples for analysis of anions (SO_4, Cl), nutrients (PO_4-P, NO_3-N, NH_4-N), acidity, and alkalinity were not filtered and were stored in polyethylene bottles on ice until analyzed. The water samples were analyzed at the PaDER Bureau of Laboratories facility in Harrisburg, Pa., following methods mainly of Skougstad et al. (1979). Concentrations of cations and silica were determined by inductively coupled plasma emission (ICPE) or atomic absorption (AA) spectrometry; alkalinity and acidity were determined by titration; sulfate was measured by turbidimetry; ferrous iron, phosphorus, nitrogen, and chloride were measured by colorimetry.

Hydrochemical trends, which are apparent as changes in DO, Eh, pH, and solute concentrations (see figure 5), result from interacting physical, biochemical, and geochemical processes. Important physical processes include gas movement, ground-water flow (solute transport), dispersion, dilution, filtration, and evaporation. Biochemical processes include reaction catalysis (iron and sulfur oxidation), cell synthesis (uptake of CO_2 and nutrients), respiration and decay (uptake of O_2 and release of CO_2 and nutrients), and transpiration. Major geochemical processes include ion-complexation, acid-base, oxidation-reduction, precipitation-dissolution, and sorption (ion-exchange) reactions. Modeling to account for hydrochemical variations attempts to relate many of these interacting factors and emphasizes the geochemical interactions between the ground water and solid aquifer matrix.

Most minerals that compose the overburden, coal, and underburden are probable reactants under acid conditions, and minerals that precipitate at seepage zones indicate possible products. To test the thermodynamic potential for dissolution or precipitation of mineral phases, equilibrium speciation and mineral saturation indices were computed using WATEQ4F (Ball et al. 1987). The saturation index (SI) is defined as:

$$SI = \log (IAP/K_T), \qquad (14)$$

where IAP is the measured ion activity product for a solid in water, and K_T is the thermodynamic equilibrium constant for the same solid in the water, at the temperature of interest (Drever 1982; Plummer et al. 1990). If SI is zero, the water is in equilibrium with respect to the mineral. If SI is negative, the water is undersaturated with respect to the mineral and could dissolve it (reactants). If SI is positive, the water is supersaturated and could not dissolve the mineral, but could potentially precipitate it (products). The complete hydrochemical data for the quarterly samples from wells in nests 14 and 15 which were used to calculate median values and corresponding saturation indices are contained in the USGS Quality of Water (QWDATA) data base. The data and SI results judged to be useful in the geochemical mass-transfer models are presented in figures 5 and 6, respectively.

Most mineral phases are not in equilibrium with the ground water; however, SIs for gypsum, $AlOHSO_4$, and amorphous silica are near zero (∓ 0.5) for most water samples (see figure 6). The waters from all wells are supersaturated with respect to chalcedony (cryptocrystalline silica), quartz, jarosite, and goethite. Slight oversaturation of waters with respect to chalcedony and equilibrium with amorphous silica is expected where silicate minerals react in an acidic system. Supersaturation with respect to jarosite and goethite implies that Fe and S are not precipitated as fast as they are produced by the oxidation of pyrite and dissolution of hydrated ferric-sulfate minerals. Kinetic factors favor the precipitation of ferrihydrite instead of goethite or jarosite (Whittemore and Langmuir 1975; Nordstrom et al. 1979); waters from wells 14, 14A, 14B, and 14C are oversaturated and those from wells 15, 15A, and 15B are undersaturated with respect to ferrihydrite. All samples also are undersaturated with respect to calcite, dolomite, siderite, gypsum, epsomite, barite, celestite, melanterite, and many aluminosilicates, most of which are not shown in figure 6. No thermodynamic data are available for roemerite, copiapite, or coquimbite, so that SI values for these minerals could not be calculated; however, a ferric-sulfate phase $Fe_2(SO_4)_3$ included in the WATEQ4F data base is consistently undersaturated ($SI < -22$). Potential solubility control of iron by ferrihydrite, goethite, and possibly jarosite(?) is consistent with

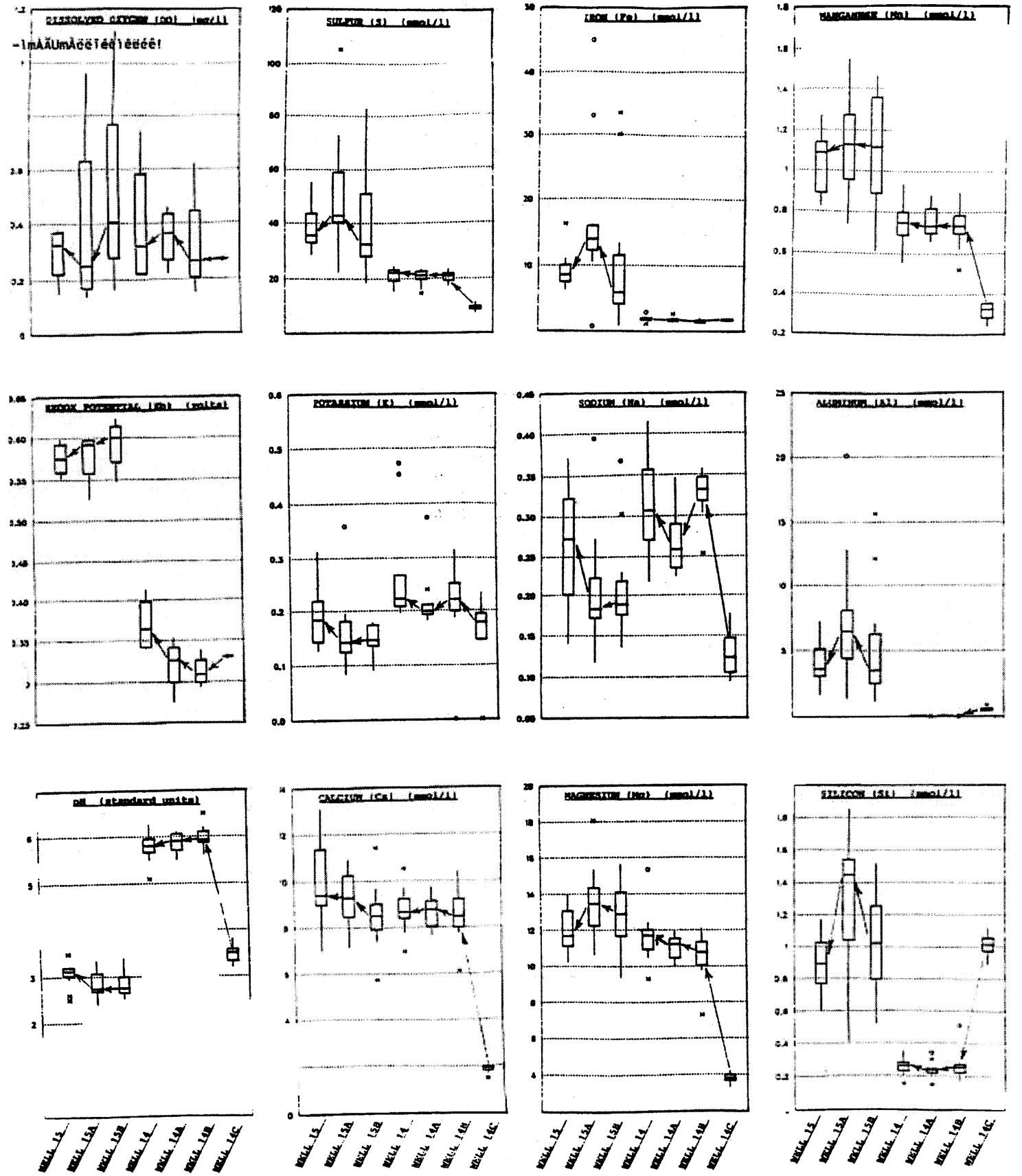

Figure 5.--Boxplots of DO, Eh, pH, and concentrations of major dissolved solutes in waters from well nests 14 and 15. Arrows indicate potential downward flow. Boxes are defined by the interquartile range (IQR = 25th to 75th percentiles). The median (50th percentile) is shown as a horizontal line within the box. Vertical lines are drawn to the data points farthest from the box, yet within a distance 1.5 times the IQR beyond the box. Extreme values beyond this distance are plotted individually (*, o).

results of work by Nordstrom et al. (1979) and Karathansis et al. (1988, 1990).

Figure 5 shows boxplots of the major water-quality data used for equilibrium speciation (mineral SI) and mass-balance calculations. Data for DO, Eh, pH, and major solutes are indicated for samples from well nest 14 beneath untreated spoil (wells 14C, 14B, 14A, and 14) and for samples from well nest 15 beneath sludge-treated spoil (wells 15B, 15A, and 15). Westward ground-water flow from well nest 14 to 15 is indicated in figure 3, which shows that within a given well nest, there also is potential for downward flow. Arrows drawn between medians in the boxes (see figure 5) indicate the downward flow potential within each well nest--wells 14C to 14B to 14A to 14 and wells 15B to 15A to 15. Dissolved SO_4^{2-} (shown as S) is useful as a reaction progress variable, because it is likely that the sulfide and sulfate minerals dissolve irreversibly in most of the system.

The waters from nest 14, generally contain negligible concentrations of DO (< 0.5 mg/l), which are relatively unchanged with depth (see figure 5); however, pH and concentrations of S, Mn, Ca, Mg, Na, and K increase downflow from the untreated mine spoil (well 14C) to underlying bedrock (well 14B). Waters from the bedrock (wells 14B, 14A, and 14) have similar quality. These trends suggest that acid produced in the mine spoil and shallow bedrock is neutralized by reaction with silicate and carbonate minerals in the bedrock. Concentrations of Fe appear to remain level and to be limited to some maximum, probably because of solubility control by precipitation of ferrihydrite or jarosite(?). Concentrations of Si and Al decrease downflow suggesting control by kaolinite and (or) gibbsite.

The waters from nest 15 also contain negligible DO, but relative to equivalent horizons in nest 14 (see figure 2), they have lower pH (< 3), higher Eh (> .5 volts), and generally greater concentrations of major ions (see figure 5). As in nest 14, the ground-water in bedrock beneath the mine spoil is more mineralized than the upflow water; however, the concentrations of S, Fe, Mn, Mg, Al, and Si rise and then fall with increasing depth from wells 15B to 15A to 15. The intermediate depth well 15A has the maximum concentrations of Fe, S, and Al, which may result from acid-generating reactions and partial neutralization by silicates. These waters also exhibit a relative depression in concentration of Na and K. A partial explanation for declines in Na and K downflow from wells 15B to 15A and in S and Fe downflow from wells 15A to 15 is that jarosite could be precipitating at depth. However, considering the data for wells 15A and 15, the ratio of moles of S and Fe presumably lost from solution is greater than that expected considering the stoichiometry of jarosite, and there are corresponding lower concentrations of other solutes including Mg, Mn, Si, and Al in waters from well 15 relative to those from well 15A. These trends suggest the possibility of dilution by mixing of waters from above with less mineralized waters from the west.

Reaction-Path Modeling

The purpose of reaction-path modeling is (1) to explain the spatial hydrochemical changes, (2) to suggest the major reactant and product phases, and (3) to determine the variation in the quantity of each phase entering or leaving the ground-water system. The equations and principles of reaction-path modeling are given elsewhere (Plummer and Back 1980; Parkhurst et al. 1982; Plummer et al. 1983, 1990). Such modeling uses available hydrochemical data and attempts to find a set of mass-transfer reactions that are thermodynamically feasible and satisfy mass-and-electron balance criteria. Mass transfer is indicated

Initial Solution + Reactant Phases
- Product Phases --> Final Solution. (15)

In reaction 15, the initial and final solutions are the molal compositions of water samples from relative upflow and downflow points along a flow path, and the reactant and product phases are minerals and (or) gases that can feasibly react to produce or remove elements and balance electrons. A more complex equation involves the additional mixing of two initial solutions

Initial Solution 1 + Initial Solution 2
+ Reactant Phases - Product Phases -->
Final Solution. (16)

The deeper wells in this study, for example well 15, are likely to sample water that has resulted from mixing of upflow waters as illustrated by the flow paths in figure 3 and water-quality data (see figure 5).

A mass-balance model must contain equal numbers of elements and phases, and for each element in the model, there must be at least one reactant or product phase containing the element. In the special case of a mixing model, one phase is excluded and the proportion of initial waters mixed is included to account for changes in one or more elements. For each chemical element included in the model, a linear mass-balance equation can be written that is the mass-difference between the initial and final solutions plus balancing quantities of reactant and product phases (minerals and gases)

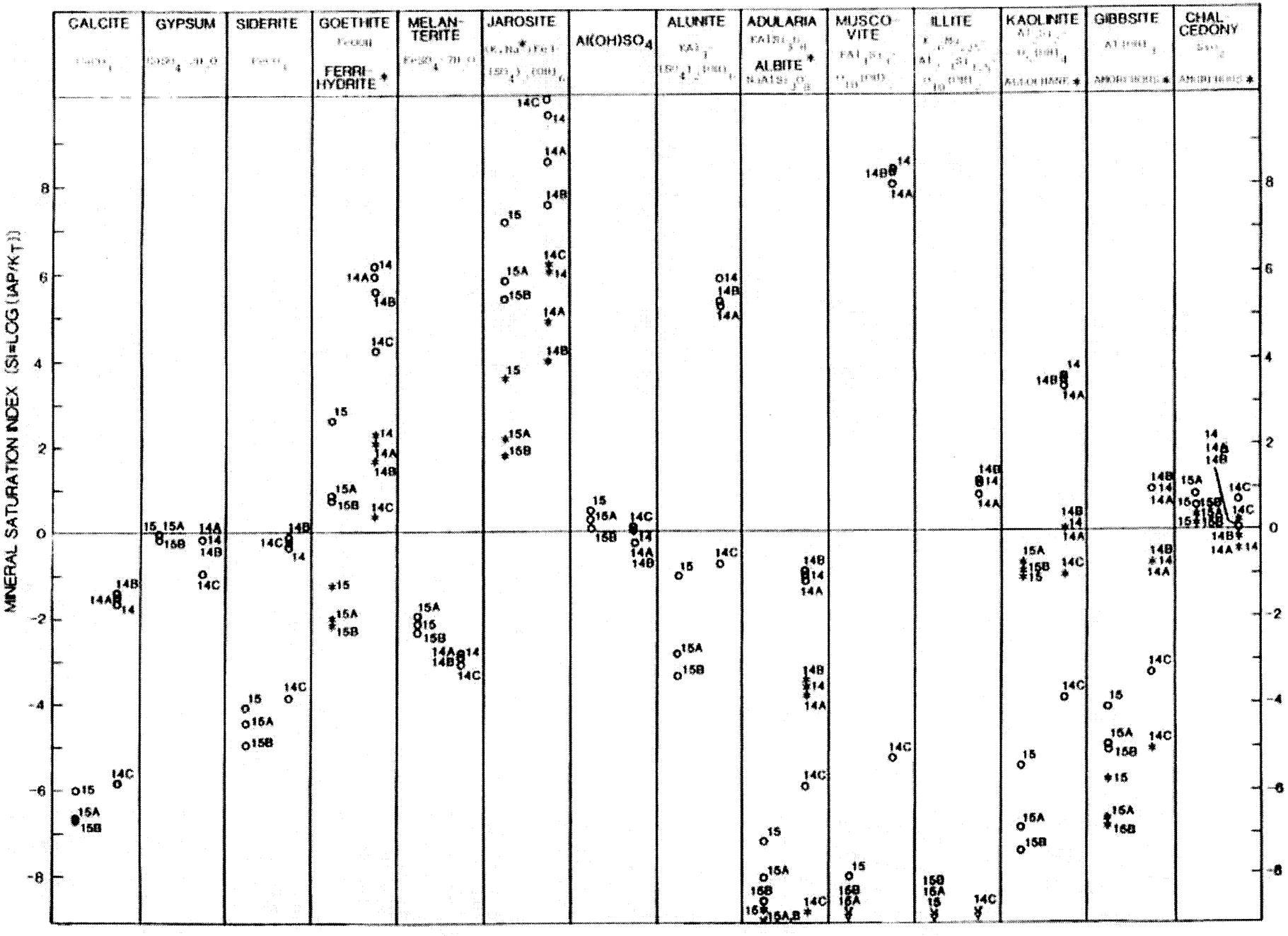

Figure 6.--Mineral saturation indices for median chemical concentrations, pH, Eh, DO, and temperature in ground-water samples. '*' indicates metastable, or less stable, phase relative to 'o'.

containing the element. Stoichiometric coefficients account for the number of moles of the element in the phases and the number of transferable electrons for redox-active species. The quantity of electrons transferred during mass-transfer reactions among the dissolved species and phases is computed by use of an operational "redox state" (RS) that is treated as an additional element (Parkhurst et al. 1982; Plummer et al. 1983, 1990). Thus, a reaction model is a particular choice of phases that react, or mix and react, to produce the measured final water composition.

Four different reaction-path scenarios (see figure 7) are presented to demonstrate the feasibility of pyrite oxidation in systems open and closed with respect to O_2 (see figure 4). The mass-balance models allow the evaluation of the amount of O_2 required to produce measured quantities of dissolved sulfate from pyrite and (or) ferro-ferric-sulfate minerals considering mineral and O_2 solubility constraints, as indicated by the mineral SI (see figure 6) and maximum DO (= 0.38 mmol/l) in a closed system. Additional constraints on "acceptable" models include the absolute change in major solute concentrations and the presence, or absence, of the phases along the flow path(s). The median molal concentrations of the elements and calculated RS for the water samples from nests 14 and 15 that are used as

Possible Reaction-Path Models:

14C --> 14B:	Open system:	Untreated spoil to underlying bedrock
14C + 14B --> 15B:	Open system:	Untreated spoil and unmined coal (highwall) to sludge-treated spoil
	Closed system:	Sludge-treated spoil to underlying bedrock
	Closed system:	Bedrock below untreated and sludge-treated areas to downflow bedrock

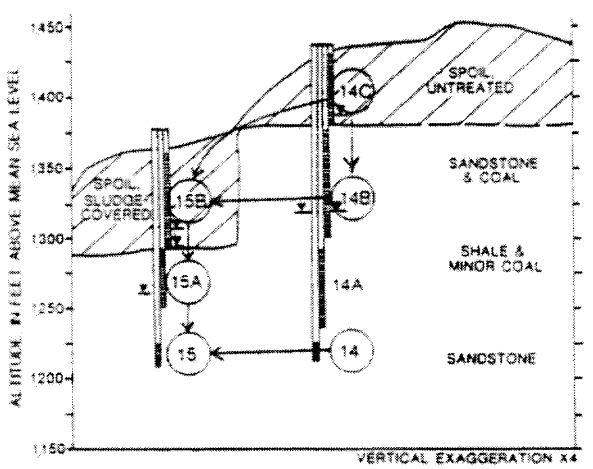

Figure 7.--Diagram showing a summary of potential flow paths for mixing and mass-transfer models. '▼' indicates median static water level.

input data in NEWBAL (Parkhurst et al. 1982) are summarized in table 3. In table 4, reactant minerals are shown with a "+" and product minerals with a "-" considering the SI calculated using the hydrochemical data. Results of the mass-balance calculations are summarized in table 5.

<u>Open system: Downward flow from untreated spoil to underlying bedrock</u>. A 70-ft difference in head between wells 14C and 14B suggests downward flow from the perched ground water in untreated mine spoil (well 14C) to the underlying bedrock aquifer (well 14B) (see figure 7). This system is probably open to O_2 along the flow path because intermediate zones are not saturated with water (see figures 3, 4). The downflow ground water contains greater concentrations of S and major cations except Fe, Si, and Al (see table 3 and figure 5) and is supersaturated with respect to ferrihydrite, jarosite, gibbsite, quartz, and kaolinite (see figure 6), which are potential product phases. Potential reactants include pyrite and roemerite, plus calcite, siderite, pyrolusite, and aluminosilicates to generate the remaining elevated cations. Pyrolusite contains Mn^{4+}, which may have a role similar to Fe^{3+}, in that both ions can oxidize sulfur.

Ten models were generated which satisfy mineral-solubility constraints and explain the changes in water chemistry from well 14C to 14B (see table 5). The major difference among the models is between pyrite or roemerite as the source of S and between siderite and pyrolusite as the source of Mn in solution. Model 5 involves reactions with pyrite, roemerite, and siderite, all of which are sources of Fe. The production of sulfate from pyrite (reaction 4) would require 26.7 to 84.9 mmol O_2; the latter is 223 times the maximum solubility of O_2. However, since the sulfur and most of the iron in roemerite is already oxidized, the same quantity of sulfate can be generated from roemerite with only 0.72 mmol O_2; that is 1.8 times the maximum solubility of O_2 (0.38 mmol/l). Because the system is open to O_2, any model is acceptable. Models 3 and 10 involve the least mass transfer: they react pyrite or roemerite plus pyrite, and pyrolusite, calcite, and aluminosilicate minerals (chlorite, illite, microcline), and produce ferrihydrite, jarosite, kaolinite, amorphous silica, and carbon dioxide (CO_2) gas.

<u>Open system: Mixing of waters from untreated spoil and unmined coal to sludge-treated spoil</u>. An 11-ft difference in head between wells 14B and 15B, screened through the intact and mined Clarion coal horizon, respectively (see figure 7), suggests that flow from the highwall, downdip to the mine spoil occurs. An 80-ft difference in head between wells 14C and 15B also

TABLE 3.--Median values of concentrations of major dissolved solutes and operational redox state[1] (RS) in ground-water samples used in mass-balance computations [units are mmol/kg]

ELEMENT	WELL 14	WELL 14A	WELL 14B	WELL 14C	WELL 15	WELL 15A	WELL 15B
Ca	8.658	8.770	8.471	1.901	9.406	9.294	8.483
Mg	11.333	11.251	10.777	3.747	11.682	13.472	12.896
Na	0.307	0.260	0.332	0.117	0.273	0.182	0.189
K	0.222	0.199	0.220	0.178	0.184	0.142	0.145
Cl	0.085	0.085	0.085	0.085	0.056	0.056	0.056
C	8.360	8.170	9.400	6.780	6.780	6.780	6.780
S	22.168	21.101	20.867	8.890	35.702	42.973	32.558
Fe	1.816	1.771	1.590	1.760	8.648	13.934	5.962
Mn	0.749	0.733	0.732	0.322	1.088	1.130	1.118
Si	0.259	0.235	0.254	1.015	0.896	1.449	1.024
Al	0.013	0.009	0.009	0.537	3.610	6.468	3.506
RS	171.805	164.355	167.330	84.593	258.612	311.356	229.589

[1]Redox state: RS = S*6 + C*4 + Fe(II)*2 + Fe(III)*3 + Mn*2.

TABLE 4.--Stoichiometry[1], reactivity[2], and operational redox state[3] (RS) of potential reactant and product phases used in mass-balance computations [units are mmol]

O2 GAS	+RS 4.00					
PYRITE	+Fe 1.00	S 2.00	RS 0.00			
ROEMERITE	+Fe 3.00	S 4.00	RS32.00			
FERRIHYDRITE	Fe 1.00	RS 3.00				
NA-JAROSITE	-Na 1.00	Fe 3.00	S 2.00	RS21.00		
K-JAROSITE	-K 1.00	Fe 3.00	S 2.00	RS21.00		
PYROLUSITE	+Mn 1.00	RS 4.00				
SIDERITE	+Fe 0.875	Mn 0.015	Mg 0.02	Ca 0.10	C 1.00	RS 5.78
CALCITE	+Ca 1.00	C 1.00	RS 4.00			
CHLORITE	+Mg 5.00	Al 2.00	Si 3.00			
ILLITE	K 0.60	Mg 0.25	Al 2.30	Si 3.50		
MICROCLINE	+K 0.85	Na 0.15	Al 1.00	Si 3.00		
KAOLINITE	Al 2.00	Si 2.00				
SiO2	-Si 1.00					
CO2 GAS	-C 1.00	RS 4.00				

[1]Stoichiometry excludes hydrogen and oxygen (see Parkhurst and others, 1982).

[2]Reactivity defined by saturation index (SI, fig. 6): '+' indicates reactant (SI < 0); '-' indicates product (SI > 0); no sign indicates SI could be positive or negative depending on the particular sample.

[3]Redox state for minerals computed considering redox active components (S, Fe, Mn, O) as defined by Parkhurst and others (1982).

suggests potential flow from the perched aquifer (well 14C). Because the water table defines this mixing flow path (see figure 3), the system is probably open with respect to O_2. The downflow water beneath sludge-treated spoil contains greater concentrations of S, Fe, Mn, Ca, Mg, Si, and Al, and intermediate concentrations of Na and K relative to the upflow sources (see table 3). Downflow waters are supersaturated with respect to amorphous silica, goethite, and jarosite (see figure 6). Jarosite may precipitate and thus account for downflow decreases in concentrations of Na and K. Reactions with pyrite, roemerite, and (or) siderite may produce the observed increases in S, Fe, and Mn. Neutralization reactions with calcite and aluminosilicate minerals such as chlorite, microcline, and kaolinite are probable sources of Al, Mg, Na, K, and Si.

Ten mixing models were generated which satisfy the constraints (see table 5). Although the mixing ratios are different, they all indicate a greater contribution of water from the perched aquifer (67 to 85 percent), which is consistent with the expectation of greater flow rates in mine spoil relative to unmined coal. Some models involve O_2 and some do not; however, all involve reaction with pyrolusite. Models 1, 3, 5, and 7 involve reactions with pyrite and 33 to 51 mmol of O_2. Models 2 and 8 involve equivalent reactions with roemerite and 7 to 10 mmol of O_2 to produce dissolved S and Fe plus ferrihydrite (or goethite) and minor jarosite. Models 4, 6, 9, and 10 do not involve O_2: Models 4 and 6 involve reactions with roemerite and pyrite (reaction 8), and models 9 and 10 involve reactions with roemerite and pyrolusite. Chlorite, calcite or siderite, and microcline or kaolinite, also are reacted in the models. Silica and CO_2 are produced. Because the system is open with respect to O_2 all ten models are acceptable. Models 5 and 6, which involve the least mass transfer, react pyrite or roemerite plus pyrite, and pyrolusite, calcite, chlorite, and kaolinite, and produce ferrihydrite, minor jarosite, silica, and CO_2.

Closed system: Downward flow from sludge-treated spoil to underlying bedrock. A 17-ft difference in head between wells 15B and 15A suggests potential downward flow from the sludge-treated mine spoil to underlying bedrock (see figure 7). The flow path is water saturated and probably closed to O_2. Relative to the water from well 15B, the final water at well 15A contains greater concentrations of S, Fe, Mn, Al, Ca, Mg, and Si, and approximately unchanged, but lesser concentrations of Na and K (see table 3). Reactions with pyrite, roemerite, and siderite can produce the observed increases in Fe and S. Jarosite, which is supersaturated in both upflow and downflow waters can precipitate providing a sink for K and Na. Aluminosilicate minerals and calcite can dissolve producing Ca, Mg, Al, and Si

Four mass-transfer models were generated which satisfied the input constraints (see table 5). The major difference among the models is if pyrite reacts with DO or if roemerite reacts without DO to produce increased iron and sulfate in the downflow solution. All four models include roemerite as a reactant. In model 1, 1 mmol of pyrite is oxidized by 3.5 mmol of O_2 (reaction 1), which is nearly 9 times the maximum O_2 solubility. However, in models 2, 3, and 4, roemerite and small quanitities of pyrite react under anoxic conditions. Model 1 does not meet the closed system criteria for acceptability ($O_2 \leq 0.38$); however, models 2, 3, and 4 do not involve O_2 and can occur in a system closed to O_2. Therefore, if previously formed ferric sulfate or ferric-ions are transported along the flow path, substantial quantities of sulfate can be generated under anoxic conditions, by the dissolution of "stored" ferric salts and by the oxidation of pyrite by Fe^{3+}.

Closed system: Mixing of waters from bedrock below untreated and sludge-treated areas to downflow bedrock. A 25-ft difference in head between wells 15A and 15 suggests a strong potential for downward flow from the bedrock beneath sludge-treated mine spoil (well 15A) to underlying bedrock (well 15), and a 43-ft difference in head between wells 15A and 14 suggests potential for lateral flow to well 15 (see figure 7). Both vertical and lateral flow paths are water saturated and probably closed to O_2. The water at well 15 contains intermediate concentrations of the major ions, except for Ca, which is greater in the downflow water than in the upflow waters (see table 3 and figure 5). Mixing can produce the intermediate concentrations, and reactions with calcite can produce the observed increase in Ca concentration. Jarosite, which is supersaturated in both upflow and downflow waters can precipitate providing a sink for Fe, S, K, and Na.

Oxic and anoxic models were produced for comparison: "oxic" models included O_2 but excluded oxidized minerals (roemerite and pyrolusite), and "anoxic" included oxidized minerals. Six oxic models were generated that involved reactions with 1.39 to 2.23 mmol of O_2 and mixing of waters from wells 15A and 14 to produce the final downflow water (see table 5). Another 13 mixing models were generated which did not involve O_2, but which involved roemerite and pyrolusite. The mixing ratios for the oxic models (1-6) indicate that roughly 80 percent of the volume is from the zone represented by water of well 15A, and 20 percent is from that of well 14. The weighting of water from well 15A is consistent with conservative mixing of sulfate.

TABLE 5.--Summary of mass-transfer results[1]

WELL NAME AND MODEL[2]	MIXING RATIO	O_2 GAS	PYRITE	ROEMERITE	FERRI-HYDRITE	SODIUM JAROSITE	POTASSIUM JAROSITE	PYROLU-SITE	SIDERITE	CALCITE	CHLORITE	ILLITE	MICRO-CLINE	KAOLIN-ITE	SiO_2	CO_2 GAS
WELL 14B																
1	.	84.85	21.03		.		-15.04	.	27.33	3.87	.14	23.10	1.43	-27.69	-30.96	-28.55
2	.	32.87	7.16		-27.72		-1.17	.	27.33	3.84	1.30	.	1.43	-2.28	-4.40	-28.55
3	.	26.68	7.16	.	-3.81		-1.17	0.41	.	6.57	1.40	.	1.43	-2.39	-4.51	-3.95
4	.	33.82	9.07	.	.		-3.08	.41	.	6.57	1.24	3.17	1.43	-5.87	-8.15	-3.95
5	.	66.59	15.93	3.40	.		-16.74	.	27.33	3.84	.	25.93	1.43	-30.80	-34.22	-28.53
6	.	6.90		3.58	-31.30		-1.18	.	27.33	3.84	1.30	.	1.43	-2.28	-4.40	-28.55
7	.	8.84		11.36	-7.96		-16.74	.	27.33	3.84	.	25.93	1.43	-30.80	-34.22	-28.55
8	.	6.99		11.56	.		-17.14	.13	18.92	4.68	.	26.61	1.43	-31.58	-35.03	-20.98
9	.	1.33		6.05	.		-6.10	.41	.	6.57	1.00	8.21	1.43	-11.42	-13.95	-3.95
10	.	0.72		3.58	-7.96		-1.18	.41	.	6.57	1.41	1.43	1.43	-2.39	-4.51	-3.95
WELL 15B	14B:14C															
1	15:85	50.59	11.19	.	-55.05		-.26	.73	55.86		1.39		.26		-4.84	-56.26
2	15:85	10.03	.	5.59	-60.64		-.26	.73	55.86	.	1.39		.26		-4.84	-56.26
3	25:75	36.29	10.52	.	-5.82		-.15	.70	.	4.97	1.49		.13		-4.64	-5.61
4	25:75	.	.51	5.01	-10.82		-.15	.70	.	4.97	1.49		.13		-4.64	-5.61
5	33:67	33.89	9.88	.	-5.48		-.05	.66	.	4.97	1.36		.	.21	-4.24	-5.26
6	33:67	.	.52	4.68	-10.15		-.05	.66	.	4.38	1.36			.21	-4.24	-5.26
7	33:67	43.15	9.88	.	-43.82		-.05	.66	43.82	.	1.18			.39	-4.07	-44.70
8	33:67	7.35		4.94	-48.75		-.05	.66	43.82	.	1.18		.	.39	-4.07	-44.70
9	33:67	.		4.94	-18.30		-.05	.66	9.02	3.48	1.32		.25	.	-4.20	-13.37
10	23:77	.		5.31	-18.76		-.17	.70	8.66	4.20	1.47		.15	.	-4.68	-13.47
WELL 15A:																
1		3.46	1.05	2.08		-0.01	-.00		.80	.73	.11	.	.	1.37	-2.65	-1.53
2			.08	2.73		-.01	-.00		.80	.73	.09	.54	.	.78	-3.27	-1.53
3	.		.08	2.73		-.06	-.28		.80	.73	.11	.	.32	1.21	-3.29	-1.53
4	.		.13	2.55		-.01	-.00	08	.27	.78	.11	.	.	1.37	-2.65	-1.06
WELL 1[illegible]	15A:14															
1	80:20	1.39				-.70	-.91		2.17	.02	.	-5.66	5.09	3.17	-2.12	-2.49
2	80:20	1.39				-1.60	.		2.16	.02	.50	-15.73	11.13	11.22	-2.62	-2.49
3	79:21	1.41			-.44	-.68	-.82		2.43	.	.	-5.59	4.94	3.19	-1.94	-2.75
4	79:21	1.41			-.44	-1.49	.		2.43	.	.45	-14.68	10.39	10.47	-2.40	-2.75
5	79:21	2.23	.22	.	.	-.71	-1.00		2.43	.	.	-5.59	5.16	3.09	-2.38	-2.75
6	79:21	2.23	.22	.	.	-1.71	.		2.43	.	.56	-16.74	11.84	12.00	-2.94	-2.75
7	8:92	.	.32	3.77	.	-.24	-1.68	.31	.	.70		.72	1.43	.	-6.27	-2.15
8	15:85		.15	3.87	.	-.41	-2.26	.26	1.47	.51		.	2.63	.	-7.44	-3.32
9	16:84		.26	3.28	.	-.27	-1.48	.28	.	.64		.	1.71	.42	-5.52	-1.97
10	16:84		.32	2.39	-2.53	-.01	-.02	.28	.	.64		.	.	1.27	-2.10	-1.97
11	17:83		.32	2.36	-2.56	-.01	.	.28	.	.64		-.04	.	1.30	-2.03	-1.96
12	11:89		.	2.84	-7.94	-.02	-.03	.21	5.81	.10		.	.	1.45	-2.39	-7.31
13	12:88			2.79	-7.91	-.02	.	.21	5.74	.10		-.05	.	1.48	-2.30	-7.24
14	13:87			4.64	.	-.59	-3.29	.24	3.40	.32			3.84	-.55	-9.95	-5.09
15	13:87			4.15	-2.18	-.44	-2.40	.23	4.06	.26		.	2.79	.	-7.88	-5.70
16	21:79			3.95	.	-.56	-2.76	.22	2.72	.34		-.61	3.65	.	-8.43	-4.31
17	52:48			1.19	.	-.40	-.61	.14	.	.42		-3.05	2.87	2.19	-2.31	-1.18
18	52:48			1.19	.	-1.01	.	.14	.	.42	34	-9.78	6.91	7.58	-2.64	-1.18
19	55:45			.69	-.93	-.32		.13		.40		-3.30	2.34	1.65	-.78	-1.11

[1]All mineral and gas mass-transfers are in millimoles per kilogram of water; negative for precipitation, positive for dissolution; no value for not reacted. Input data in table 3; mineral stoichiometry in table 4.

[2]Model flow paths shown in figure 7. Well name indicates "final" downflow water: well 14B <-- well 14C; well 15B <-- well 14B + well 14C; well 15A <-- well 15B; and well 15 <-- well 15A + well 14. Model number arbitrarily assigned to facilitate discussion of results.

However, mixing ratios for the anoxic models (7-19) range widely, indicating 8 to 55 percent of the volume is from the zone of well 15A. All 19 models involve reactions with relatively small quantities of pyrite and (or) larger quantities of roemerite plus carbonate and aluminosilicate minerals to produce the dissolved solutes and up to 4 mmol of jarosite. The argument for acid-generating reactions by ferric minerals under anoxic conditions is supported by the anoxic models; however, oxidized minerals such as roemerite and pyrolusite are not likely to occur along the deep flow path. Thus, the oxic mixing models may explain the hydrochemical trends in the deeper aquifer, even though the quantity of O_2 reacted exceeds the solubility maximum of 0.38 mmol/l. Errors in sulfate measurement are likely to cause the computed O_2 to be larger than actually is necessary to achieve mass balance. The error in the analytical charge balance for the samples (well 15A: +12 percent difference; well 15: +3 percent difference; and well 14: -1.23 percent difference) is greater in the high concentration range, suggesting that sulfate may be underestimated in waters from well 15A. A 3 percent error in the measured concentration sulfate in waters from well 15A (43 mmol/l), equates to 2.26 mmol of O_2 considering the stoichiometry of reaction 4. On the basis of this sulfate measurement error, any of the six oxic models (O_2 less than 2.23 mmol) could meet the closed system criteria. All six oxic models react siderite, microcline, and kaoline and produce jarosite, illite, silica, and CO_2. Model 1, which requires only 1.39 mmol of O_2 also involves the least mass transfer.

Discussion

Although DO concentrations were negligible in all samples, one cannot reject a mass-balance model that involves reaction with more O_2 than was measured, because the DO measurement indicates an instantaneous quantity in solution and does not indicate the integrated quantity of O_2 involved in geochemical reactions that produced the oxidized solutes in the water sample. The mass-transfer models indicate the integrated quantities of reactants and products. In an aqueous system closed to O_2, the saturation concentration of O_2 (0.38 mmol/l or less) is the maximum quantity of O_2 available for the integrated reactions, and the measured DO is the absolute limit of O_2 available for reactions downflow. Downflow increases in concentrations of sulfate indicate that sulfur-bearing minerals continued to decompose. Assuming that a closed system is in effect, one can reject mass-balance models that require extreme quantities of O_2 to generate the additional sulfate. Alternative, acceptable mass-balance models indicate that sulfate may be generated by reactions involving ferric-iron minerals (Fe^{3+} ions), lesser quantities of pyrolusite (Mn^{4+} ions), and little or no O_2.

The roles of ferric ions and minerals in the oxidation of pyrite in open and closed systems are clearly important. Fe^{3+} is orders of magnitude more soluble than O_2 in acidic waters. The low pH (less than 3.5) and large quantities of SO_4^{2-} and Fe^{2+} in solution are compatible with the coupled ferric-iron reduction and sulfide-mineral oxidation reactions described by reactions 6 and 8. Thus, as demonstrated in the mass-balance models, SO_4^{2-} is likely to be generated under anoxic conditions in part by reactions with Fe^{3+} and FeS_2, and in part by dissolution of the previously formed ferric-sulfate minerals.

The timing and extent of formation of soluble ferric-sulfate minerals, such as roemerite, copiapite, and coquimbite in the mine spoil and unmined coal seams and the potential for sustained reactions between Fe^{3+} and pyrite is a question that has not been adequately addressed herein. The ferric-sulfate minerals are not the cause of AMD--they are intermediate products of pyrite oxidation. Oxygen must be available for these minerals to form and flowing water must be available to leach the oxidized solutes from the oxic zone(s). AMD formation cannot be prevented unless the oxidation of pyrite and (or) leaching of acid products are controlled. Different methods to remediate or prevent AMD will be necessery depending on whether oxidation products formed "acutely" during the transient effect of mining, or whether they form and leach "chronically" as a result of a continued O_2 convection and diffusion into the mine spoil and periodic leaching by recharge waters or a fluctuating ground water table. At this study site, and at others having similar hydrogeologic conditions, both acute and chronic formation of AMD is likely.

The precipitation of jarosite as a potential sink for Fe^{3+}, SO_4^{2-}, Na^+, and K^+ ions is suggested because it is supersaturated. In controlled systems, substantial quantities of Fe and S can be precipitated as jarosite if large concentrations of Na and (or) K are added (Norton et al. 1991). However, the subsurface precipitation of jarosite has not been confirmed and its supersaturation implies kinetic barriers to precipitation in natural systems (Nordstrom et al. 1979). Furthermore, the solubility of jarosite is such that relatively high concentrations of S and Fe can remain at equilibrium in solutions containing small concentrations of K and Na.

A potential benefit of reclamation with sewage sludge is the potential for stopping the formation of

AMD by excluding O_2 needed by T. ferrooxidans. Pulford et al. (1988) and Backes et al. (1988) provided laboratory evidence that the oxidation of pyrite can be inhibited by organic amendments such as chicken manure and wood waste. Decay of these organic materials consumes O_2, thus preventing the microbial oxidation of iron. However, the opposite trend is observed in comparing water-quality data for samples from nest 14 (unsludged) and nest 15 (sludged). Since the decay of organic matter also will produce CO_2 and release nutrients, it may provide sustenance for T. ferrooxidans. Nitrogen availability has been shown to limit growth of T. ferrooxidans in batch culture experiments (Lau et al. 1970), and ammonium, which predominates over nitrate in sewage sludge (Seaker and Sopper 1988a), is the essential nutrient form (Leathen et al. 1956; Silverman and Lundgren 1959). Thus, unless O_2 is depleted, sewage-sludge amendments could enhance the formation of AMD. At the study site, O_2 transport into the vadose zone was possible because sewage sludge was not spread over critical areas. Perhaps if sewage sludge had been spread over the entire recharge area, including the steep hillsides and toe of spoil, the transport of O_2 into the spoil and consequent oxidation of pyrite could have been reduced more effectively. However, even with more extensive coverage by sewage sludge, AMD can persist because of the presence of previously formed ferric-sulfate minerals and because of the presence of O_2 in recharge during winter months, when cold temperatures inhibit microbial decay of the sludge and soil organic matter.

Mass-transfer modeling is a useful procedure for quantifying the processes that cause water-quality changes and has provided insights into the potential causes and controls of AMD. However, geochemical modeling cannot substitute for basic data collection and hypothesis testing by statistical and other methods. Mass-transfer modeling assumes that the flow paths are well defined and that the stoichiometries of the reactants and products are known. Although the computations are precise, the models are simplified. The ground-water samples are from restricted points within broader flow "channels" defined by flow lines. The defined flow channels are not likely to contain the same water or solutes at upflow and downflow points because the flow of ground water is tortuous, and solutes will disperse. Furthermore, most mineral phases are impure and their stoichiometries are variable. This leads to two problems: (1) Thermodynamic data, which are needed to compute mineral SI's frequently are lacking for uncommon, impure, or amorphous minerals--for example, the necessary data are not available for roemerite, copiapite, or coquimbite. (2) The quantities of reactant and product minerals in a model depend on their stoichiometries--certain phases indicated in the models may not exist along the flow path, and many different minerals may be reacted or produced to achieve the same mass-balance result.

Summary

Despite negligible concentrations of DO (less than 0.5 mg/l = 0.016 mmol/l), concentrations of dissolved sulfate and acidity increased in ground water from bedrock underlying the sewage-sludge-reclaimed mine spoil, suggesting that pyritic sulfur was oxidized below the water table. Furthermore, the waters beneath sewage-sludge-treated spoil were more acidic and contained substantially greater concentrations of dissolved minerals than those from beneath untreated spoil. This paper determined the predominant geochemical reactions that were likely to produce the highly mineralized water and evaluated if anoxic conditions limit oxidation of pyrite along potential ground-water flow paths.

In AMD, the oxidation of iron-sulfide minerals, produces dissolved acid, sulfate, and iron. Neutralization reactions with carbonate and silicate minerals produce elevated concentrations of manganese and aluminum, respectively, and additional dissolved solutes. Geochemical models for the oxidation of pyrite are presented to explain the potential role of O_2 and Fe^{3+} as oxidants under conditions open and closed to O_2, respectively, by reactions (1) and (6):

$$FeS_2 + 3.5\ O_2 + H_2O \Longrightarrow Fe^{2+} + 2\ SO_4^{2-} + 2\ H^+ \qquad (1)$$

$$FeS_2 + 14\ Fe^{3+} + 8\ H_2O \Longrightarrow 15\ Fe^{2+} + 2\ SO_4^{2-} + 16\ H^+. \qquad (6)$$

The iron-oxidizing bacteria, T. ferrooxidans, catalyze the oxidation of Fe^{2+} to Fe^{3+} in oxic systems and increase the rate of pyrite oxidation by reaction 6. Reactions (1) and (6) can occur in oxic systems above the water table, whereas reaction (6) also can occur in anoxic systems below the water table. Secondary minerals such as roemerite $[Fe^{2+}Fe_2^{3+}(SO_4)_4 \cdot 14H_2O]$, copiapite $[Fe^{2+}Fe_4^{3+}(SO_4)_6(OH)_2 \cdot 20H_2O]$, and coquimbite $[Fe_2(SO_4)_3 \cdot 9H_2O]$, which were identified with FeS_2 in coal samples, form on the oxidizing surface of pyrite and precipitate as efflorescences above the water table. These soluble ferric-sulfate "salts" are a source of SO_4^{2-} and Fe^{3+}, which can dissolve in recharge waters, or in ground water during a water-table rise, and can be transported to pyrite reaction sites where DO is absent. For example, the dissolution of roemerite and oxidation of pyrite does not involve O_2

$$FeS_2 + 7\ Fe^{2+}Fe_2^{3+}(SO_4)_4 \cdot 14H_2O \Longrightarrow 22\ Fe^{2+} + 30\ SO_4^{2-} + 16\ H^+ + 90\ H_2O. \quad (8)$$

The computer programs WATEQ4F and NEWBAL were used to compute chemical equilibrium and mass transfer, respectively, considering mineral dissolution and precipitation reactions plus mixing of waters from different upflow zones. Mass-balance models indicate that (a) extremely large quantities of O_2, greater than 100 times its aqueous solubility, can generate observed concentrations of dissolved SO_4^{2-} from FeS_2, and (b) under anoxic conditions, Fe^{3+} from dissolved ferric-sulfate minerals can oxidize FeS_2 along closed-system ground-water flow paths. In a system open to O_2, such as in the unsaturated zone, the aqueous solubility of O_2 is not limiting, and oxidation of FeS_2 by O_2 and Fe^{3+} accounts for most SO_4^{2-} and Fe^{3+} observed in acidic ground water. However, in a system closed to O_2, such as in the saturated zone, O_2 solubility is limiting; hence, ferric oxidation of pyrite is a reasonable explanation for the observed increase in concentration of SO_4^{2-} with increasing depth below the water table.

Conclusions

Mining has disturbed the landscape and has induced changes in the hydrologic system that have promoted the oxidation of pyrite and formation of AMD. Use of sewage sludge in surface-mine reclamation helps to dispose of sludge and to revegetate barren spoil. However, there is still some question regarding potential beneficial effects of the sludge on local ground-water quality. Acidic ground water beneath sludge-treated spoil results from a combination of factors, including: (1) dissolution of pyrite and ferro-ferric-sulfate minerals; (2) lateral flow of gaseous and dissolved O_2 (reactants) into the mine spoil from permeable, unsludged zones; and (3) potential for increased growth of *T. ferrooxidans*, which require O_2 plus CO_2 and nutrients provided by sludge.

DO concentrations are neglible in all the ground water measured, whether from sewage-sludge-treated or untreated zones through mine spoil or bedrock. This implies that the application of sewage sludge did not cause the depletion of DO. Furthermore, the mineralization of the water beneath sludge-treated spoil suggests local addition of sludge did not inhibit, and may have enhanced, the production of acid. The aerobic decomposition of sludge generates carbon dioxide as DO is consumed. Nitrate, ammonium, and phosphate nutrients are likely to be leached and may be utilized by *T. ferrooxidans* in the mine spoil and bedrock. If the bacteria utilize the nutrients, then the concentrations will be reduced and the effect of nutrient leaching will not be obvious by the measurement of dissolved nitrogen or phosphorus concentrations; the bacteria also should be enumerated.

The objective of identifying the reactants and products that control water chemistry cannot be achieved by modeling of water-quality data alone. Hydrological, mineralogical, and rock-chemical data are critically important for describing the geochemical evolution of acidic ground water. Missing data on heat and gaseous fluxes, pyrite distribution, and recharge infiltration through the unsaturated mine spoil would help to define the potential for oxidation of pyrite above the water table. The location and timing of production of ferric-sulfate minerals are uncertain and have not been adequately addressed herein. The inorganic sulfur to iron (Sin/Fe) ratios in rock-core subsamples are compatible with the mineral formulas for pyrite, roemerite, copiapite, and coquimbite, which were found in high-sulfur coal samples collected from a zone that is presently below the water table. Little information exists on the subsurface formation and occurrence of the "sulfate-salts," especially under saturated conditions. Such salts are important as sinks or sources of AMD by providing storage in a solid phase during "dry" periods and by providing an active oxidizing agent when dissolved during "wet" periods.

There are practical implications for the open- and closed-system scenarios for pyrite oxidation and the observed increasing mineralization of ground water with increasing depth below the water table. For example, "special handling" involves the segregation of pyritic materials during surface-coal mining and the subsequent placement of isolated pods of the toxic spoil within the mine backfill. The intent is to prevent reactions that produce acid and prevent the transport of acid from the isolation zones. The PaDER encourages concurrent mining and reclamation with placement of the toxic spoil above the water table--thereby reducing pyrite exposure to air during mining, but increasing its exposure after reclamation. However, others argue that pyritic materials should be placed below the water table where O_2 solubility constraints will limit the extent of acid-forming oxidation reactions (Hammack and Watzlaf 1990). On the basis of results presented herein, neither placement technique is ideal: It is likely that placement of pyrite above the water table will allow the oxidation of pyrite by humid, oxygenated air within the unsaturated zone, and that the placement of pyrite below the water table will allow the oxidation of pyrite both by DO (open system?) and Fe^{3+} ions. Thus unless the material is tightly encapsulated, acid-forming reactions are likely to occur both above and below the water

table. Further study of the problem concerning oxidation of pyrite above and below the water table is necessary to establish the feasibility and success of special-handling techniques.

Additional efforts can be made to establish the mechanisms and rates of acid-forming reactions:

(1) To test if pyrite is oxidized by O_2 or Fe^{3+} ions by reactions (1) or (6), respectively, oxygen isotopes in SO_4, H_2O, and O_2 molecules can be measured. The oxygen atoms in SO_4 should have $d^{18}O$ between atmospheric O_2 ($d^{18}O \cong +23^o/oo$) and meteoric H_2O ($d^{18}O \cong -10^o/oo$) (Taylor et al. 1984a,b), and will approach the meteoric water composition if the ferric-iron oxidation predominates.

(2) To determine if sewage sludge enhances the growth of I. ferrooxidans, ground waters from sludge-treated and untreated mine spoil can be chemically analyzed and bacteria can be enumerated.

(3) To compute kinetics of pyrite oxidation "in the field," ground-water flow velocities can be determined using a calibrated numerical model coupled with the geochemical mass-transfer results.

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Literature Cited

Backes, C. A.; I. D. Pulford; and H. J. Duncan 1988. Treatments to combat pyrite oxidation in coal mine spoil. U.S. Bureau of Mines Information Circular 9183 1:91-96.

Baker, J. P. and C. L. Schofield 1982. Aluminum toxicity to fish in acidic waters. Water, Air, and Soil Pollution 18:289-309.

Baker, R. A. (Mellon Institute) 1971. Evaluation of pyritic oxidation by nuclear methods. U.S. Environmental Protection Agency Water Pollution Control Research Report 14010--F1103/71.

Ball, J. W.; D. K. Nordstrom; and D. W. Zachman 1987. WATEQ4F--A personal computer FORTRAN translation of the geochemical model WATEQ2 with revised data base. U.S. Geological Survey Open-File Report 87-50, 108 p.

Barnes, Ivan and F. E. Clarke 1964. Geochemistry of ground water in mine drainage problems. U.S. Geological Survey Professional Paper 473-A, p. A1-A5.

Berg, T. M. and others 1980. Geologic map of Pennsylvania. Pennsylvania Geological Survey, Fourth Series, Map 1, scale 1:2,500,000, 3 sheets.

Berg, T. M.; M. K. McInerney; J. H. Way; and D. B. MacLachlan 1983. Stratigraphic correlation chart of Pennsylvania. Pennsylvania Geological Survey, Fourth Series, General Geology Report 75.

Blickwedel, R. S. and J. H. Linn 1987. Hydrogeology and ground-water quality at a land reclamation site, Neshaminy State Park, Pennsylvania. U.S. Geological Survey Water-Resources Investigations Report 86-4164, 41 p.

Brady, K. B. C. and R. J. Hornberger 1989. Mine drainage prediction and overburden analysis in Pennsylvania. Proceedings Annual West Virginia Surface Mine Drainage Task Force Symposium, April 25-26, 1989, Morgantown, W.V., 13 p.

Buckwalter, T. F; C. H. Dodge; G. R. Schiner; and H. E. Koester 1981. Water resources of the Clarion River and Redbank Creek basins, northwestern Pennsylvania. U.S. Geological Survey Open-File Report 81-70, 111 p.

Burrows, W. D. 1977. Aquatic aluminum--chemistry, toxicology, and environmental prevalence. CRC Critical Reviews in Environmental Controls 7:167-216.

Burton, T. M. and J. W. Allan 1986. Influence of pH, aluminum, and organic matter on stream invertebrates. Canadian Journal of Fisheries and Aquatic Sciences 43:1285-1289.

Cathles, L. M. 1982. Acid mine drainage. The Pennsylvania State University Earth and Mineral Sciences 51(4):37-41.

Champ, D. R.; R. L. Gulens; and R. E. Jackson 1979. Oxidation reduction sequences in ground water flow systems. Canadian Journal of Earth Science 16:12-23.

Colmer, A. R. and M. E. Hinkle 1947. The role of microorganisms in acid mine drainage--A preliminary report. Science 106(2747):253-256.

Colmer, A. R.; K. L. Temple; and M. E. Hinkle 1949. An iron-oxidizing bacterium from the drainage of some bituminous coal mines. Journal of Bacteriology 59:317-328.

Cravotta, C. A. III; K. B. C. Brady; M. W. Smith; and R. L. Beam 1990. Effectiveness of the addition of alkaline materials at surface coal mines in preventing or abating acid mine drainage--1. Geochemical considerations. Proceedings of the 1990 Mining and Reclamation Conference and Exhibition, Charleston, West Virginia, April 23-26, 1990 1:221-225.

Davis, Alan 1981. Sulfur in coal. The Pennsylvania State University Earth and Mineral Sciences 51(2):13-21.

Dixon, J. B.; L. R. Hossner; A. L. Senkayi; and K. Egashira 1982. Mineralogical properties of lignite overburden as they relate to mine spoil reclamation, in Kittrick, J. A.; D. S. Fanning; and L. R. Hossner, eds., Acid sulfate weathering. Soil Science Society of America, p. 169-191.

Drever, J. I. 1982. The geochemistry of natural waters. Englewood Cliffs, N.J., Prentice-Hall, Inc., 388 p.

Gang, M. W. and D. Langmuir 1974. Controls on heavy metals in surface and ground waters affected by coal mine drainage--Clarion River and Redbank Creek watershed, Pennsylvania. National Coal Association/ Bituminous Coal Research Inc., 5th Symposium on Coal Mine Drainage Research, Louisville, Ky., p. 39-69.

Garrels, R. M. and M. E. Thompson 1960. Oxidation of pyrite in ferric sulfate solution. American Journal of Science, 258:57-67.

Hammack, R. W. and G. R. Watzlaf 1990. The effect of oxygen on pyrite oxidation. Proceedings of the 1990 Mining and Reclamation Conference and Exhibition, Charleston, West Virginia, April 23-26, 1990, v. 1, p. 257-264.

Harbaugh, A. W. 1990. A simple contouring program for gridded data. U.S. Geological Survey Open-File Report 90-144, 12 p.

Hawkins, J. W. 1984. Iron disulfide characteristics of the Waynesburg, Redstone, and Pittsburgh coals in West Virginia and Pennsylvania. Morgantown, W.V., West Virginia University, M.S. thesis, 195 p.

Hem, J. D. 1985. Study and interpretation of the chemical characterisics of natural water (3d). U.S. Geological Survey Water-Supply Paper 2254, 263 p.

Henke, J. R. 1985. Hydrogeologic characterization of a surface mining-impacted watershed with implications for acid mine drainage abatement, Clarion County, Pennsylvania. Pennsylvania State University, unpublished M.S. thesis, 171 p.

Jaynes, D. B.; H. B. Pionke; and A. S. Rogowski 1984a. Acid mine drainage from reclaimed coal strip mines--2. Simulation results of model. Water Resources Research 20(2):243-250.

Jaynes, D. B.; A. S. Rogowski; and H. B. Pionke 1984b. Acid mine drainage from reclaimed coal strip mines--1. Model description. Water Resources Research 20(2):233-242.

Karathanasis, A. D.; V. P. Evangelou; and Y. L. Thompson 1988. Aluminum and iron equilibria in soil solutions and surface waters of acid mine watersheds. Journal of Environmental Quality 17:534-543.

Karathanasis, A. D.; Y. L. Thompson; and V. P. Evangelou 1990. Temporal solubility trends of aluminum and iron leached from coal spoils and contaminated soils. Journal of Environmental Quality 19:389-395.

Kleinmann, R. L. P.; D. A. Crerar; and R. R. Pacelli 1980. Biogeochemistry of acid mine drainage and a method to control acid formation. Mining Engineering 33:300-306.

Lau, C. M.; K. S. Shumate; and E. E. Smith 1970. The role of bacteria in pyrite oxidation kinetics. Third symposium on coal mine drainage research, Pittsburgh, Pennsylvania, May 19-20, 1970, p. 114-121.

Leathen, W. W.; N. A. Kinsel; and S. A. Braley 1956. Ferrobacillus ferrooxidans--A chemosynthetic, autotrophic bacterium. Journal of Bacteriology 72:700-704.

McDonald, M. G. and A. W. Harbaugh 1988. A modular three-dimensional finite-difference ground-water flow model. U.S. Geological Survey Techniques of Water-Resources Investigations TWRI 6-A1, 586 p.

McKibben, M. A. and H. L. Barnes 1986. Oxidation of pyrite in low temperature acidic solutions--Rate laws and surface textures. Geochimica et Cosmochimica Acta 50:1509-1520.

Morrison, J. L.; S. D. Atkinson; A. Davis; and B. E. Scheetz 1990a. The use of CO_2 coulometry in differentiating and quantifying the carbonate phases in the coal-bearing strata of western Pennsylvania--its applicability in interpreting and modifying neutralization potential (NP) measurements. Proceedings of the 1990 Mining and Reclamation Conference and Exhibition, Charleston, West Virginia, April 23-26, 1990, v. 1, p. 243-248.

Morrison, J. L.; S. D. Atkinson; and B. E. Scheetz 1990b. Delineation of potential manganese sources in the coal and overburdens of western Pennsylvania. Proceedings of the 1990 Mining and Reclamation Conference and Exhibition, Charleston, West Virginia, April 23-26, 1990, v. 1, p. 249-256.

Moses, C. O.; D. K. Nordstrom; J. S. Herman; and A. L. Mills 1987. Aqueous pyrite oxidation by dissolved oxygen and by ferric iron. Geochimica et Cosmochimica Acta 51:1561-1571.

Mozley, P. S. 1989. Relationship between depositional environment and the elemental composition of early diagenetic siderite. Geology 17:704-706.

National Oceanic and Atmospheric Administration 1987. Climatological data annual summary, Pennsylvania 1987. NOAA 92:(13) Clarion 3 SW.

National Oceanic and Atmospheric Adminsitration 1988. Climatological data annual summary, Pennsylvania 1988. NOAA 93:(13) Clarion 3 SW.

Noll, D. A.; T. W. Bergstresser; and J. Woodcock 1988. Overburden sampling and testing manual. Pennsylvania Department of Environmental Resources Bureau of Mining and Reclamation, 78 p.

Nordstrom, D. K. 1982. Aqueous pyrite oxidation and the consequent formation of secondary iron minerals, in Kittrick, J. A.; D. S. Fanning; and L. R. Hossner, eds., Acid sulfate weathering. Soil Science Society of America, p. 37-63.

Nordstrom, D. K.; E. A. Jenne; and J. W. Ball 1979. Redox equilibria of iron in acid mine waters, in Jenne, E. A., ed., Chemical modeling in aqueous systems--Speciation, sorption, solubility, and kinetics. American Chemical Society Symposium Series 93, p. 51-79.

Norton, G. A.; R. G. Richardson; R. Markuszewski; and A. D. Levine 1991. Precipitation of jarosite compounds as a method for removing impurities from acidic wastes from chemical coal cleaning. Environmental Science and Technology 25:449-455.

Palache, Charles; H. Berman; and C. Frondel 1951. System of mineralogy (7th). New York, John Wiley and Sons, 1124 p.

Parkhurst, D. L.; L. N. Plummer; and D. C. Thorstenson 1982. BALANCE--a computer program for calculating mass transfer for geochemical reactions in ground water. U.S. Geological Survey Water-Resources Investigations Report 82-14, 29 p.

Plummer, L. N. and W. Back 1980, The mass balance approach--application to interpreting the chemical evolution of hydrologic systems. American Journal of Science 280:130-142.

Plummer, L. N., J. F. Busby; R. W. Lee; and B. B. Hanshaw 1990. Geochemical modeling of the Madison aquifer in parts of Montana, Wyoming, and South Dakota. Water Resources Research 26:1981-2014.

Plummer, L. N.; D. L. Parkhurst; and D. C. Thorstenson 1983. Development of reaction models for groundwater systems. Geochimica et Cosmochimica Acta 47:665-685.

Pollack, D. W. 1989. Documentation of computer programs to compute and display pathlines using results from the U.S. Geological Survey modular three-dimensional finite-difference ground-water flow model. U.S. Geological Survey Open-File Report 89-381, 188 p.

Pulford, I. D.; C. A. Backes; and H. J. Duncan 1988. Inhibition of pyrite oxidation in coal mine waste, in Selected papers of the Dakar symposium on acid sulphate soils, Dakar, Senegal, January, 1986. Netherlands, International Institute for Land Reclamation and Improvement, ILRI 44, p. 59-67.

Saad, D. A. and C. A. Cravotta III 1991. Modeling of ground-water flow along a cross section through a reclaimed surface coal mine in western Pennsylvania (abs.). American Association of Surface Mining and Reclamation, 8th Annual National Meeting, May 14-17, 1991, Durango, Co.

Seaker, E. M. and W. E. Sopper 1988a. Municipal sludge for minespoil reclamation--I. Effects on microbial populations and activity. Journal of Environmental Quality 17(4):591-597.

Seaker, E. M. and W. E. Sopper 1988b. Municipal sludge for minespoil reclamation--II. Effects on organic matter. Journal of Environmental Quality 17(4):598-602.

Senkayi, A. L.; J. B. Dixon; and L. R. Hossner 1986. Todorokite, goethite, and hematite--alteration products of siderite in east Texas lignite overburden. Soil Science 142:36-42.

Skougstad, M. W.; M. J. Fishman; L. C. Friedman; and others 1979. Methods for the determination of inorganic substances in water and fluvial sediments. U.S. Geological Survey Techniques of Water-Resources Investigations TWRI 5-A1, 626 p.

Silverman, M. P. and D. G. Lundgren 1959. Studies on the chemolithotrophic iron bacterium Ferrobacillus ferrooxidans--1. An improved medium and a harvesting procedure for securing high cell yields. Journal of Bacteriology 77:642-647.

Singer, P. C. and W. Stumm 1970a. Acidic mine drainage--the rate-determining step. Science 167:1121-1123.

Singer, P. C. and W. Stumm (Harvard University) 1970b. Oxygenation of ferrous iron. U.S. Department of the Interior, Federal Water Quality Administration (U.S. Environmental Protection Agency) Water Pollution Control Research Report 14010--067/69.

Sobek, A. A.; W. A. Schuller; J. R. Freeman; and R. M. Smith 1978. Field and laboratory methods applicable to overburdens and minesoils. Cincinatti, Ohio, U.S. Environmental Protection Agency Environmental Protection Technology EPA-600/2-78-054, 203 p.

Sopper, W. E. and E. M. Seaker 1984. Strip mine reclamation with municipal sewage sludge. U.S. Environmental Protection Agency EPA-600/S2-84-035.

Stumm, Werner and J. J. Morgan 1981. Aquatic chemistry--an introduction emphasizing chemical equilibria in natural waters (2nd). New York, John Wiley and Sons, 780 p.

Taylor, B. E.; M. C. Wheeler; and D. K. Nordstrom 1984a. Oxygen and sulfur isotope compositions of sulfate in acid mine drainage--evidence for oxidation mechanisms. Nature 308:538-541.

Taylor, B. E.; M. C. Wheeler; and D. K. Nordstrom 1984b. Stable isotope geochemistry of acid mine drainage--experimental oxidation of pyrite. Geochimica et Cosmochimica Acta 48:2669-2678.

Temple, K. L and A. R. Colmer 1951. The autotrophic oxidation of iron by a new bacterium, Thiobacillus ferrooxidans. Journal of Bacteriology 62:605-611.

Temple, K. L. and E. W. Delchamps 1953. Autotrophic bacteria and the formation of acid in bituminous coal mines. Applied Microbiology 1:255-258.

Temple, K. L. and W. A. Koehler 1954. Drainage from bituminous coal mines. West Virginia University Bulletin (Series 54, No. 4-1) Engineering Experiment Station Research Bulletin 25, 35 p.

Whittemore, D. O. and D. Langmuir 1975. The solubility of ferric oxyhydroxides in natural waters. Ground Water 13:360-365.

Williams, E. G. 1960. Marine and fresh water fossilferous beds in the Pottsville and Allegheny Groups of western Pennsylvania. Journal of Paleontology 34:908-922.

Wood, W. W. 1976. Guidelines for collection and field analysis of ground-water samples for selected unstable constituents. U.S. Geological Survey Techniques of Water-Resources Investigations TWRI 1-D2, 24 p.

Zajic, J. E. 1969. Microbial biogeochemistry. New York, Academic Press, 345 p.

PROGRESSIVE DEVELOPMENT OF WETLAND HABITATS AT THE AMC WETLANDS CENTRE, CAPEL, WESTERN AUSTRALIA[1]

by

Denis R. Brooks[2]

Abstract. A series of freshwater lakes was created during mining for heavy mineral sands at Capel, 125 miles south of Perth, in Western Australia. The lakes intercept the ground water table and have a total surface area of about 110 acres. In recognising the potential conservation value of the site, especially for waterbirds, the company established the AMC Wetlands Centre in 1987. Comprehensive research and site development programmes were implemented. Baseline studies of the hydrology, lake chemistry, algae, invertebrates, vegetation, and the waterbirds indicated the potential of the lakes for development as a wetland ecosystem whilst identifying the priorities for habitat enhancement. Significant improvements in water quality have been achieved. Extensive earthworks have involved re-shaping the banks, creating islands, channels, loafing peninsulas and shallow feeding areas. A wet woodland is being created for colonial nesting waterbirds. A variety of vegetation types is being established to provide habitat for a wide range of birds. Ongoing studies have revealed that the diversity of algae, diatoms, and invertebrates, important components of the food chain, is improving as the habitat develops. Waterbird usage of the lakes is increasing and their breeding success is improving. The site has considerable potential for public recreation and education.

Additional Key Words:mineral sands, waterbirds, aquatic invertebrates, algae, macrophytes, food chain.

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Introduction

Wetlands are a valuable and diminishing resource in the south-west of Western Australia. It has been estimated that the values of more than 2/3 the wetlands on the Swan Coastal Plain have been reduced or destroyed by various forms of land use (Anon,

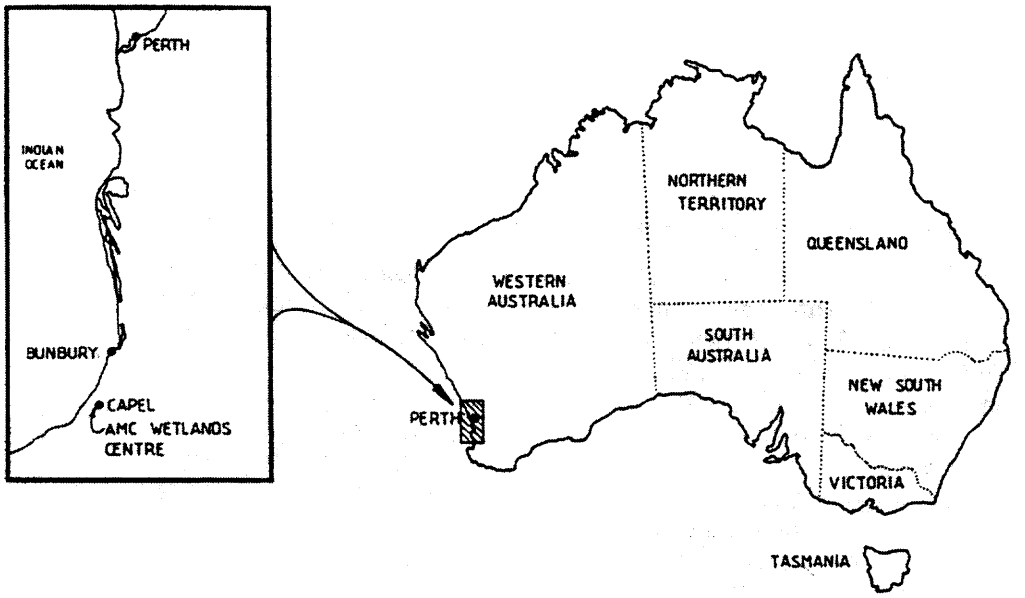


Figure 1. — LOCATION OF AMC WETLANDS CENTRE AT CAPEL WESTERN AUSTRALIA

1991). Permanent freshwater bodies, being important summer refuges for waterbirds in the south-west (Jaensch, et al., 1988), are particularly scarce as in this mediterranean climate (AAR 830mm, 32.5 in) many wetlands dry up during the summer months.

Under such circumstances, the creation of new wetlands, including permanent freshwater bodies, is a valuable contribution to the State's environmental effort, especially as the south-west is important for migrating birds (Lane, 1987). Whilst mining for mineral sands at Capel, 200km (125 mi) south of Perth (see Figure 1), AMC Mineral Sands Ltd., (AMC), created a series of permanent freshwater lakes. The establishment of a wetlands project on the site has been described previously (Brooks, 1988). This paper discusses the progressive development of the project at what is now known as the AMC Wetlands Centre.

Background

Mining for mineral sands, principally ilmenite, has continued at the site since 1956. At times, mining of very high grades resulted in significant backfill deficits, which created lakes where the pits intersected the groundwater table. The available tailings were used to restore the contours of the surrounding areas.

The lake system comprising the AMC Wetlands Centre was formed between 1975 and 1979. There are 12 lakes in the system, mostly interconnected, with a total water surface of about 44 ha (110 acres). Prior to mining, most of the area supported a pine plantation of low productivity (State Forest), with the balance being private grazing land. Following mining, the newly formed lakes served as the mine water supply until 1988, and they have continued to receive treated effluent from the mineral

processing plants enroute to the discharge point.

Initially, reclamation of the area mined concentrated on re-establishing pastures on the surrounding land and on planting trees and shrubs around the banks of the lakes for aesthetics and to attract birdlife. Most of this work took place between 1977 and 1983. Meanwhile, the lakes became partially colonised with wetland flora, and waterbirds were frequently observed to visit them.

In 1984, the company commissioned the Royal Australasian Ornithologists Union (RAOU) to advise on the potential of the lakes for development of self-sustaining wetland ecosystems for the benefit of waterbird conservation.

Jaensch (1985) reported that with a number of development techniques the lakes had potential to achieve the stated objective, as well as providing considerable opportunities for research, education and passive public recreation. On this basis, the company initiated a wetlands project in 1986, over and above the regulatory requirements of its mining lease.

The AMC Wetlands Centre was established with the following objectives:

1. To develop self-sustaining wetland ecosystems for the conservation of waterbirds in lakes created by mining at Capel.

2. To facilitate research into wetland ecosystems including their development and management.

3. To develop the potential and facilities for public education and recreation at the Capel wetlands.

4. To develop and demonstrate rehabilitation technology for wetlands created by human activities.

A management committee for the Centre was established to advise the company on future directions of research and management, including budgets, and to review progress. Membership of the committee represents the main expertise in and responsibilities for wetlands and waterbird conservation in the State, thereby forging links between appropriate government authorities, industry, research, and conservation institutions. There is representation from the company, RAOU, Department of Conservation and Land Management, The University of Western Australia, Curtin University of Technology, and Murdoch University. The interaction within this group is proving to be one of the valuable and exciting benefits flowing from the project.

Baseline Studies

One of the first steps was to initiate a series of multi-disciplinary baseline studies to determine the ecological status of the lakes and to indicate priorities for future research and development. Nearby natural wetlands were used as control sites. These studies were completed in 1987.

Hydrology studies of the lake system and surrounding areas revealed that water levels in the lakes were being maintained artificially high by 0.5-1.0m because of an effluent stream and management of the lakes for mine water supply (Nield and Townley, 1987). In addition, the levels did not reflect the seasonal fluctuation of the groundwater table, thereby inhibiting development of the ecosystem, particularly the fringing vegetation and associated invertebrate populations. Subsequently, a water bore was installed in the deep aquifer

to supply the mine with make-up water. The discharge point at the end of the lake system was then set at the estimated winter high water mark to enable a normal seasonal fluctuation to become established.

A preliminary survey of waterbird usage of the lakes, with monthly recordings by volunteer observers, was conducted from November 1984 to November 1986. A total of 24 species of waterbirds was recorded on the lakes system during the survey period (Jaensch, 1986; Bamford and Jaensch, 1987). Whilst the lake system supports an appreciable number of species and individuals, it was not as valuable as natural wetlands in the district. Limitations of the habitat in supplying food and shelter were reported as being the main probable factors. This conclusion was supported by the observation that the older lakes, which had achieved more advanced habitat development, were more heavily utilised by waterbirds. Seasonal patterns of usage revealed that the system was of greatest value as a refuge in the dry season (late spring to late autumn) when seasonal waterbodies in the district dried up. Two species, Pacific Black Duck (*Anas superciliosa)* and Black-fronted Plover (*Charadrius melanops*), were observed breeding on the lakes during the survey.

The breeding success of waterbirds on the lakes was studied during the 1986/87 breeding season (Bamford, 1987). Although 12 species bred on a nearby natural swamp, only 5 bred on the lake system, and with a poor success rate. Most losses occurred within the first 2 weeks from hatching; the major causes apparently being poor nutrition and predation. The Pacific Black Duck, which relies heavily on invertebrates as a protein source, fledged only 2 ducklings from a minimum of 22. On the other hand, the Purple Swamphen (*Porphyrio porphyrio*), which has a more varied diet, fledged 7 chicks out of a minimum of 10. Breeding success was highest on the oldest lakes with better developed emergent vegetation providing more breeding sites and improved nutrition. The species list was increased to 27 during this study, 25 of which could have bred on the lakes given suitable conditions. Thus, these results reflected the early development of habitats on the lake system.

Lack of aquatic invertebrates as a protein source was confirmed as one of the major factors in the poor breeding success of the birds (Cale and Edward, 1987). Whilst a high invertebrate species richness was recorded in the lakes, abundance was low compared with natural wetlands. Eighty-three invertebrate taxa were recorded in the lakes, the most abundant being Coleoptera (18%), Chironomidae (17%) and Crustacea (10%). The oldest lake supported 57% of all identified taxa, and was best in all habitat components (i.e., benthic, macrophyte and plankton). This result correlated strongly with the level of macrophyte cover. The faunal studies confirmed that the lakes had the potential for development as self-sustaining wetlands, although the need to increase their productivity through habitat development was highlighted.

Factors limiting the productivity of the lakes were found by Gordon and Chambers (1987) to include steep slopes, hard substrates, and poor water quality. These factors limited the development of fringing emergent and submerged vegetation and the invertebrate populations they support. The ponds were well oxygenated, lacked temperature and oxygen stratification, and showed small diurnal changes. Water quality limitations included low pH (3-4), extremely high ammonia levels (22,300-82,700 μg/L), low phosphorus concentrations (4-120 μg total P/L), and high iron and

manganese levels that could give rise to phosphorus complexing. Sediments were also low in inorganic and organic phosphorus. This study demonstrated the need for extensive landscaping of the existing system to provide shallow areas with wide, flat banks of soft sandy substrate to encourage the development of vegetation and the need to improve water quality.

The poor water quality was reflected in the algal populations of the lakes, which were diatom-dominated with a well established benthic diatom community of low diversity (John, 1988). The assemblage of diatoms in the lakes was indicative of low pH with little biological symptom of eutrophication. Conversely, the assemblage of algae in a nearby natural wetland sampled at the same time indicate it is an eutrophic system. Of the 67 taxa recorded, 55 were diatoms. A nearby natural wetland displayed the maximum species richness with 62 taxa. The maximum species richness in the Centre's lakes occurred in the oldest, best developed lake, with 40% (25 species) of the species present in the natural wetland. These results confirmed that the lake system was in a relatively undeveloped state.

Habitat Development

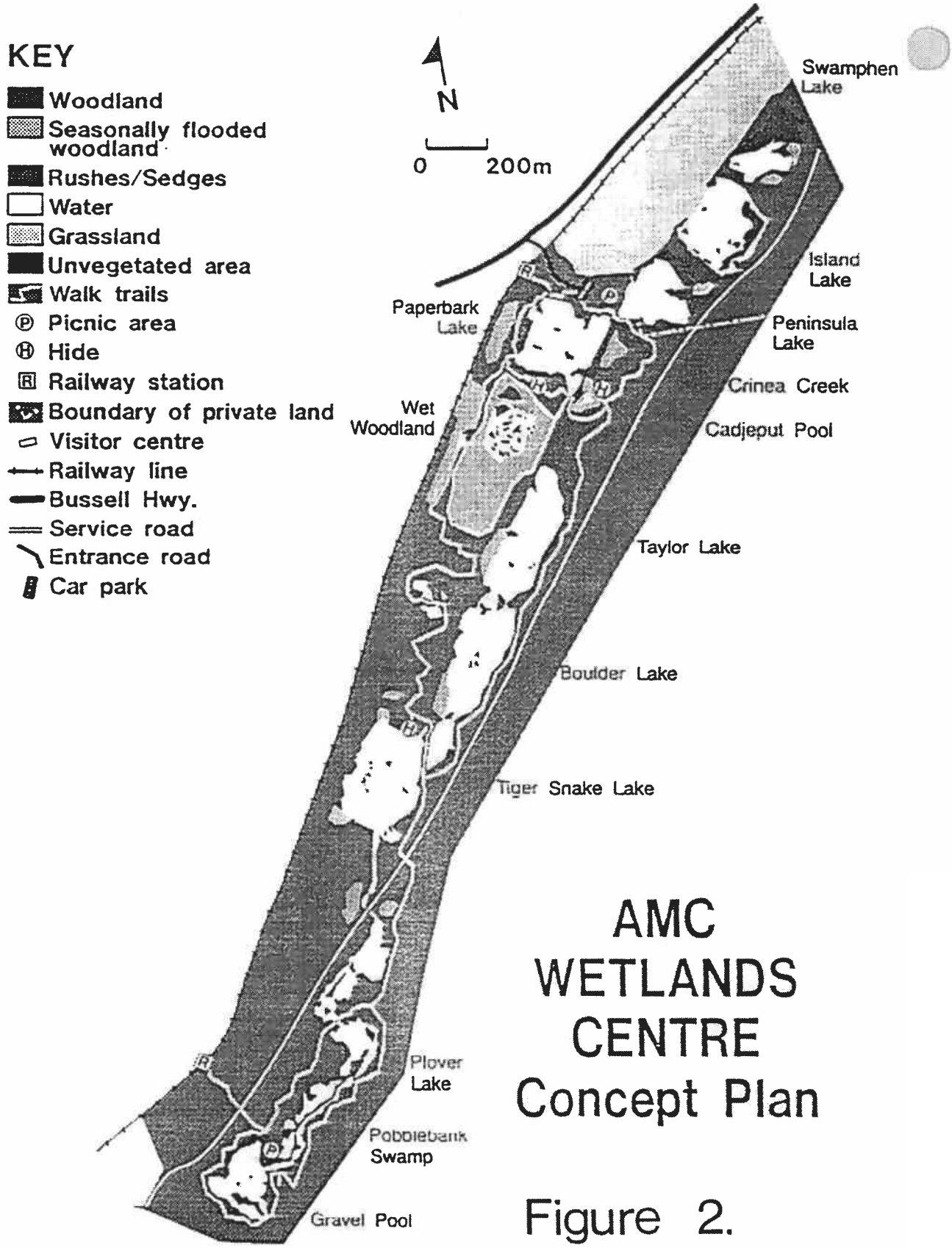
Whilst the baseline studies indicated that the lakes had potential for development as a wetland ecosystem, productivity needed to be improved substantially at all levels of the food chain. Priority attention was to be given to water and sediment chemistry, re-shaping of shorelines, vegetation establishment, and development of the specific habitat needs of fauna, including invertebrates, birds, and other vertebrates.

A concept plan was prepared for the Centre to set the direction of its long term development (see Figure 2). In addition to planning the habitat development of the lakes and surrounding uplands, the concept plan also set out potential development of facilities for public usage of the Centre, including visitor's centre and carpark, picnic areas, walk trails, viewing hides, and tower.

Site development works commenced during the 1987/88 summer and have since concentrated on enhancement of the habitat. Development of the public facilities is envisaged at a later stage when the ecosystem has developed to a satisfactory level of productivity. Project funding was established on a 5 year basis to cover project management, research, and development, with a review at the end of that period.

The baseline studies had indicated that poor water quality was one of the main constraints on development of the ecosystem. These problems had arisen because the mineral processing plant's effluent treatment facilities were not performing adequately. These facilities were progressively upgraded between 1987 and 1989 for operational reasons and the wetlands subsequently benefited. Water quality at the end of the lake system has improved markedly (see Table 1). Iron, manganese and pH levels are now all within acceptable limits, and sulphate levels continue to improve. Nitrogen and phosphorus levels remain out of balance, because of release of ammonium in the effluent stream.

In planning the habitat development programme, it was recognised that each species of waterbird has particular habitat requirements for breeding, feeding and loafing (Nicholls and Davies, 1990). For example, ibis and other colonial nesting birds need wet woodlands. Dabbling ducks usually nest in hollow trees, while shovellers and black



AMC WETLANDS CENTRE Concept Plan

Figure 2.

Table 1 - Quality of water discharging from the lake system averaged over the October - December quarter for 1987/90 (Galloway, pers. comm.).

Parameter	1987	1988	1989	1990
pH	3.64	6.82	7.53	7.42
Fe (ppm)	1.4	0.4	0.3	0.5
Mn (ppm)	22	9.4	0.3	0.1
SO_4 (ppm)	1,033	866	1,360	856

ducks will nest on the ground under shelter. Swans, diving ducks and marsh harriers breed in reed beds. Grebes and rails require emergent vegetation and waders prefer bare shores.

Swans and coots feed on benthic macrophytes and graze on grassland. Diving ducks, cormorants, grebes and most ducklings feed on aquatic invertebrates. Herons and waders feed in shallow water on invertebrates and small vertebrates. Dabbling ducks feed on seeds in shallow water, often in seasonally inundated areas. Swamphens feed on macrophyte rhizomes. Reed warblers feed on upland invertebrates, while marsh harriers feed on small vertebrates around the lakes.

All waterbirds need to be able to loaf and roost in safety. Islands are ideal for this activity. Ducks need sands spits, bare rocks and islands. Cormorants need exposed sites to dry their wings and use dead trees and poles for this purpose.

To ensure adequate resources for waterbird feeding, other links in the foodchain are essential. The specific habitat needs for algae and diatoms, invertebrates, small vertebrates and vegetation have to be provided. Thus, in order to develop a self-sustaining ecosystem, the project team aimed to develop all stages of the foodchain.

Extensive earthworks have been carried out on the site to improve the topography of the lakes. Shorelines have been modified to create gentle, sloping banks and shallow water, as well as to make them more irregular to increase the length of shoreline. Islands have been created by excavating channels across peninsulas. Bare sand spits have been created to provide loafing areas for a range of bird species and nesting grounds for waders. A number of small ponds have also been excavated as breeding sites for frogs.

A low-lying area occupying 8 hectares (20 acres) adjacent to the lakes has been excavated to below winter water level. The objective was to establish a series of islands and channels of varied dimensions on one end, and a shallow area for winter flooding on the other. A wet woodland for colonial nesting birds is being established on the islands and channels, and the shallow winter flooded part will provide feeding sites. The area is surrounded by a bank and moat for protection against predators, and to minimise disturbance by visitors.

The specific habitats being developed at the Centre can be grouped structurally into woodlands, fringing vegetation, and water (Nicholls and

Davies, 1990).

In the wet woodland, a number of *Melaleuca* spp. are being established in zones relative to their individual water level preferences. Sedges and rushes are being similarly planted in some of the channels.

A larger range of species is being used to establish fringing woodland communities on the original lakes. In addition to the *Melaleuca* spp., Flooded Gum (*Eucalyptus rudis*), She-oak (*Allocasuarina obesa*), Swamp Banksia (*Banksia littoralis*), and wattles (*Acacia* spp.) are being planted because their individual attributes have specific value to the ecosystem.

A mosaic of plant communities is being established on the surrounding uplands to enhance the habitat for vertebrates such as reptiles and small mammals, and to provide further breeding and feeding sites for birds. The communities are grouped into four structural types (forest, woodland, heath, and grassland) representative of vegetation in the region. It is also expected that this mosaic will become a valuable educational resource.

Fringing vegetation provides important breeding and shelter habitat for waterbirds as well as habitat for the aquatic invertebrates which constitute a valuable component of waterbird diets (Nicholls and Davies, 1990). Sedgelands are being established in shallow waters and reed beds of *Typha* and *Baumea* spp. are developing in slightly deeper water. Seasonally-flooded areas are being sown as water meadows to provide grazing and seeds for some of the birds.

While the fringing vegetation is developing, straw is being added to shallow water to provide a carbon source and habitat for invertebrates. Street and Titmus (1982) found that the addition of straw to lakes at Great Linford in the United Kingdom improved the invertebrate populations substantially, and the breeding success of birds using invertebrates as a protein source improved as a result. Observations at Capel support these findings and quantitative data are being collected.

Areas of deep water are important for diving birds such as cormorants, grebes, and diving ducks, as well as providing loafing areas for ducks and swans. These areas are not being planted, although some natural colonisation is occurring.

Open shallow-water areas are being retained as important feeding sites. Such areas, if sheltered, are usually highly productive for algae and invertebrates because of the high light and oxygen levels, and are valued by the wading birds.

Areas of bare shoreline are also being retained as loafing and nesting sites for a number of species.

Additional roosting sites are being provided for cormorants, herons, and ducks by the placement in the lakes of whole, dead trees cleared from the mine path. Aquatic invertebrates also benefit from this technique.

As the habitat enhancement programme is now well advanced, attention is being turned to developing landscaping plans for the public facilities to be established in the longer term. Carparks, picnic areas, walking trails, and viewing sites are being planned so that screening vegetation can be established early, principally on the uplands. This will minimise disturbance of the waterbirds by visitors. Whilst planting of the screening vegetation has commenced, it is likely the infrastructure will be

phased in over a number of years.

Research Programme

A multi-disciplinary research programme, co-ordinated by the Management Committee, is an integral part of the project, and focuses on the development of the foodchain. The programme is measuring changes in the biota of the lakes over time, investigating methods of nutrient enhancement, and studying inter-relationships between various components of the ecosystem. Studies are being conducted into water ecology, algae, invertebrates, vertebrates, macrophytes, and birds.

Water Ecology

In the early stages of the project, the following four factors in the water chemistry were limiting the productivity of the system (Gordon and Chambers, 1987):

1. Low pH (≈ 4)
2. High ammonium concentrations (≈ 50,000 μg/L)
3. Low phosphorus concentrations (0-15 μg/L)
4. High concentrations of iron, manganese, and sulphate.

As the productivity of the lakes was low, the amount of utilisable carbon to establish a foodchain was presumed to be low.

Initially, benchtop studies of intact water/sediment columns were conducted to examine the effect of improving water quality on the plant and invertebrate productivity (Chambers, 1991). It was found that the buffering capacity of the microsystem was very high, although the mechanism is unknown; daily additions of alkali were necessary to maintain the pH near neutral. When phosphate was added to the microsystem, a large proportion was immediately removed from solution, most likely through bonding to particulate material and complexes in the water column. Additional experiments showed that the sediment has a large capacity for uptake of phosphorus, probably due to its high iron and manganese content. However, the phosphorus bonded to the sediment is still available to algae for growth, provided the phytoplankton is in close proximity to the sediment. Results from phytoplankton cultures showed that pH was not a barrier to algal productivity, but did affect species assemblage.

Addition of phosphorus and carbon together rapidly produced a bacterial bloom which gave rise to a reducing environment in the sediments. However, the anaerobic conditions did not bring about a marked increase in free phosphate in the water. Algal blooms followed the collapse of the bacterial bloom.

While these experiments were being conducted, water quality in the lakes had improved substantially, with pH increasing to near neutral, and iron and manganese being reduced to low levels. Accordingly, field studies that followed the initial benchtop experiments concentrated on effects of added phosphorus.

Initial field experiments examined the effect of added phosphorus on algae and macroinvertebrates in experimental enclosures within a lake (Chambers and Cale, 1991). Phosphorus concentrations up to the maximum rate of 10 mgP/L produced marked increases in chlorophyll concentration within 1 week. Inorganic phosphorus concentrations in the water column dropped to negligible levels within the same time period. Invertebrates (principally micro-crustacea) also responded to phosphorus addition. The density of micro-crustacea in the benthos, copepods in the plankton, and total zooplankton also increased with increasing levels of phosphate

addition. Whilst the experimental techniques had limitations for examining long term effects, the results clearly showed the potential for increased productivity of the lake system with the addition of phosphorus.

Initial results from current research on a whole lake appear to confirm these findings. Phosphorus was added to one of the smaller lakes in the system at a rate comparable to 7 mg/L. A green algal scum on the lake surface formed within 1 to 2 weeks (Chambers and Cale, pers. comm.). Benthic algae increased productivity, and there are indications of species richness also increasing. Approximately 1 month after the phosphorus addition, a bloom of the water flea *Daphnia* sp. was observed, and a second species of *Daphnia* appeared in the second month. *Daphnia* is still present in the lake 8 months later.

Algae

Initial algal studies by John (1988) provided baseline data from only one sampling date (May 1987). Current work involves monitoring the algal populations on a seasonal basis, and quantitative sampling for statistical analysis of similarity and diversity of ponds, as well as quantitative abundance of individual species. Also, further work is in progress on the taxonomy of microalgae in the region, as this information will be an invaluable tool for monitoring water quality.

Since the pH of the water in the lake system increased in 1988, there has been a transition from acidophilus species to a dominance of circumneutral species (John, pers. comm.). Concomitantly, there has been a substantial increase in species diversity, indicating the potential of the system to sustain diverse consumer communities. This increasing species diversity was further illustrated by the observation of a planktonic diatom bloom within the last year.

Invertebrates

Following the initial baseline studies (Cale and Edward, 1987), a detailed monitoring programme was set up in one of the lakes (Boulder Lake) to determine the spatial and temporal distribution of abundance and diversity of the invertebrates.

Major changes in the composition of the benthic and planktonic communities were observed as the pH of the lake water increased in 1988 (Cale and Edward, 1990a). Seasonal diversity and species richness increased, with additional species of Chironomidae, Ostracoda, Cladocera, and Cyclopoida appearing in both the benthos and plankton. Both total abundance and standing biomass in the benthos decreased as the pH increased. As the invertebrate communities are in transition, these effects are not expected to continue long term. The zooplankton of the lake was also affected by rising pH, as micro-crustacea increased and coleopteran plankters decreased. This was seen to be beneficial to the productivity of the habitat, with benefits flowing to waterfowl, as the micro-crustacea have shorter generation times than the coleopteran taxa. The seasonal distribution of abundance and diversity was masked by the rise in pH.

The number of species comprising the benthic fauna at the end of the first study period (December 1988) was comparable with values obtained in studies of other wetlands on the Swan Coastal Plain (Davies et al., 1987). Similarly, the standing biomass observed in the benthos in this study was comparable to values reported from other Australian studies (Maher and Carpenter, 1984). The functional

nature of benthic communities also changed in response to pH. Filter feeders became more abundant, joining the predators and collectors previously recorded. It was concluded that the increased complexity afforded by the addition of functional feeding groups will enhance the stability and productivity of the lakes (Cale and Edward, 1990a). This monitoring is continuing.

In a further study, Cale and Edward (1990b) investigated the benthic macroinvertebrate faunas of 3 different habitats: viz *Typha orientalis*, *Isolepis prolifera*, and open water. The 2 vegetation habitats had significantly higher species richness, abundance, and standing biomass of invertebrates than the open habitat, but were not different from each other. Standing biomass was nearly an order of magnitude greater in vegetated habitats than in the open habitat. A standing biomass of 8 g/m^2 was measured for the *I. prolifera* habitat, a value comparable to that from studies of other Australian wetlands (Maher and Carpenter, 1984).

An additional habitat study is now in progress. Other species of macrophytes are being examined, as well as a mat of straw of comparable surface area (Cale, pers. comm.). This will enable the effects of "shape" of each habitat to be compared to gain a better understanding of the habitat requirements of aquatic macroinvertebrates.

Vertebrates

A monitoring programme studying the status of frogs and reptiles was initiated in September 1988 and is continuing. Trapping revealed that probably all frog species common in the region were present on the wetlands site (Bamford, 1990). Not all species were observed breeding, however, recently metamorphosed frogs of several species, notably *Crinia glauertii* and *C. insignifera*, were found to be widespread in 1988/89. Breeding was restricted to seasonal pools adjacent to the wetlands and to Swamphen Lake and Litoria Swamp. At least 1 species, *C. insignifera*, bred in the wet woodland less than 1 year after construction, indicating the potential for the wetlands as they develop. The presence of the mosquito fish (*Gambusia affinis*) in most of these lakes may well be restricting frog breeding, as this species preys on young tadpoles. However, increased development of fringing vegetation may mitigate this predation.

In 1990, it was found that the continuing colonisation of the site by frogs was being aided by the creation of "frog hollows", which separated them from the mosquito fish-infested lakes. Several species of frogs were found to be breeding in the wet woodland, which is also free of mosquito fish.

Species of reptiles were poorly represented in the initial trapping results, as many species probably present in the region were not recorded (Bamford, 1990). The distribution of reptiles was irregular, with most species recorded close to remnant native vegetation. In 1990, additional species were recorded for the first time, and some of these were associated with the introduction of logs, rocks, and gravel to some upland areas. It is expected that the development of upland vegetation will benefit the reptile species significantly.

Macrophytes

A 3 year research project commenced in 1989 to investigate practical means to propagate and establish a select number of sedges, rushes, and bulrushes, and to

determine their preferred habitat. As there is a paucity of information in the scientific literature on these aspects, this research should provide important information for wetland management and restoration elsewhere.

Transplantation trials have been set up for 12 species where the effect of planting rhizomes at 5 water depths on establishment and tolerance to seasonal flooding will be studied (Chambers, pers. comm.). Some of the species suffered setbacks in the early stages by either wave action or grazing from waterbirds. However, after 15 months, definite trends are beginning to emerge. The trials will continue for another 12 months to consolidate these trends.

To supplement the field trials, a controlled experiment has been set up at Murdoch University to examine the effect of water depth above and below ground surface on 9 species (Chambers, pers. comm.). The species chosen represent 3 size classes: small (<0.5m in height), medium (≈1m), and tall (2-3m). Water depths range from 1m below ground to 0.75m above ground. The plants are being monitored fortnightly for their condition, productivity, flowering, and seed set. Measurements on their physical environment are also being made including redox of the sediment, pH, and temperature of the water, and light intensity both in the air above the plants and at various water depths. After 8 months, definite trends in species survival with water depth are beginning to show. Surprisingly, all species are performing well where water level is up to 1 metre below ground surface, although this may change as the dry summer progresses.

Additional information is being gathered on the phenology and habitat preferences of 13 species. Transects have been set up across the water gradient in natural stands of these species (Chambers, pers. comm.), and monitoring of a range of parameters is conducted monthly. Early data already show differences between species in plant condition and flowering at different parts of the water gradient.

Trials are also being conducted to determine the viability, germinability, and germination requirements of seed of 13 wetland species (Chambers, pers. comm.).

All of these investigations have been designed to obtain a better understanding of the biology of the wetland macrophytes common to the region.

Birds

The research described above is all designed to benefit the waterbirds. Therefore, the monitoring programme initiated during the baseline studies continues to record how the birds respond to changes in their habitat.

The number of bird species recorded at the Centre is steadily increasing (see Table 2). The increase of 14 species from 1987 to 1988 is partly attributable to the presence of a resident observer since December 1987. It may also reflect improving water quality in 1988/89, because the number of bushbird species recorded did not increase to the same extent as the waterbird species.

The pattern of usage of the lakes by the waterbirds varies considerably. The numbers of some species of waterbirds seen on each survey has increased significantly, notably for the Australasian Grebe (*Trachybaptus novaehollandiae*), Black Swan (*Cygnus atratus*), Australian Shelduck (*Tadorna tadornoides*), Pacific Black Duck and Musk Duck (*Biziura lobata*) (Davies, Bamford and Doyle, pers. comm.). Other species have declined in numbers, whereas still others showed

Table 2 - Number of bird species recorded at the AMC Wetlands Centre from 1985 to 1990 (Davies, Bamford and Doyle, unpublished data).

	1985	1986	1987	1988	1989	1990
Waterbirds	23	24	30	42	45	48
Bushbirds	*	*	39	41	42	43
Total			69	83	87	91

* Not recorded

an initial decline followed by a rise.

A number of factors may be affecting the waterbirds including seasonal differences, improvements in water quality, site disturbance during the development programme, and changes in habitat relative to the specific needs of individual species. Seasonal influences can be quite marked. For example, the 1987/88 summer was very dry and many waterbirds used the lakes as a summer refuge. The numbers of Pacific Black Duck increased about threefold in this period.

Further promising trends are being observed in waterbird breeding at the Centre. The number of species breeding and the number of nests recorded at the site rose substantially in the 1990/91 summer (see Table 3). Nest totals may be higher than those shown, as it has been difficult to assign some juveniles to broods. Siteworks may have disturbed some of the birds from 1987 to 1989.

Species observed breeding at the site include Pacific Black Duck, Purple Swamphen, Australian Shelduck, Black Swan, Musk Duck, Grey Teal (*Anas gibberifrons*), Australasian Grebe, and Black-fronted Plover. Of these, the Black Swan was the only species that did not breed on the lakes in 1990/91. It had bred successfully on the lakes in the previous 3 years, but had suffered fox predation in the 1989/90 summer.

Breeding success, as measured by the percentage of fledglings to hatchlings, is difficult to determine at this time. Some broods migrate to neighbouring wetlands before fledging. However, observations indicate that more juveniles are being raised to an older age than previously, presumably because food supplies are improving. Predation remains a limitation to breeding success and it is hoped that this factor may diminish in time as the habitat develops. The wet woodland will certainly be helpful in this respect, as the surrounding moat protects the area from ground predators.

The lakes are in a transitional phase, recovering after extensive siteworks and improvements in water quality. As research on the other components of the ecosystem shows the habitats are developing, and the waterbirds are showing the benefits.

Public Use and Education

Whilst the development of public facilities is still in the planning phase, public interest in the project is increasing. This interest is coming from a wide spectrum of the community, ranging from politicians to school children. Although it is not proposed to open the site to the

Table 3 - Waterbird breeding trends at the AMC Wetlands Centre from 1986 to 1991 (Davies, Bamford and Doyle, unpublished data).

	1986/87	1987/88	1988/89	1989/90	1990/91
No of species breeding	3	3	4	5	7
No of nests	6	4	6	10	22

Table 4 - Visitation to the AMC Wetlands Centre on guided tours during 1990

Month	Tours	Visitors	Month	Tours	Visitors
January	3	29	July	8	21
February	4	9	August	8	38
March	7	52	September	11	179
April	7	157	October	16	241
May	4	117	November	22	753
June	5	200	December	11	205

general public for some years, pre-arranged tour groups are given guided inspections. During 1990, a total of 106 groups containing a total of 2,001 visitors toured the Centre (see Table 4). Of these, 51% of the tours were by local community groups, and 18% were from local schools, the latter contributing 45% of the total visitation.

The visitors' experience from the guided tour is being supplemented by educational folders. The folders contain information on the project, as well as on the ecological aspects of wetlands and waterbirds. These fact sheets are being added to progressively, and are being designed for various target audiences. This activity will grow in significance as the Centre develops.

Technology

From the outset, it was recognised that this project provided an excellent opportunity to further community understanding of wetlands and their reconstruction. Such information is of value to the community only when it is communicated to a wide audience.

This is being achieved in a number of ways. First, findings from the research and monitoring programme are being reported in a Technical Report Series that is lodged in relevant libraries and referenced in this paper. Initial reports in this series are relatively site specific; however, as the research programme focuses increasingly on functional relationships, the reports will have wider application.

Second, the guided tours are educating a wide range of people including politicians, government officials, industry personnel, education specialists, school children, and the general public. We believe it is important that the

community at large understand how our environment can be managed successfully.

Third, the Western Australian Environmental Protection Authority has approached the company with a request to prepare a manual on wetland restoration. The EPA receives numerous requests for such information, and it was considered that the AMC Wetlands Centre provided an excellent base for the preparation of such a manual. The concept is being developed.

Conclusion

When the AMC Wetlands Centre was established in 1987, it was recognised that the lake system had potential for development as a conservation area for waterbirds. At the same time, it was understood that the lakes were in the very early stages of successional development, and a number of limitations had to be overcome.

Over the past 4 years, considerable effort has been put into developing the various habitats needed by a range of bird species. This work has been supplemented by a multi-disciplinary research programme. As a result, the lakes are in a transition phase; various facets of the food chain are increasing in productivity. The waterbirds are responding with increased usage of and breeding on the lake system. It is anticipated that the productivity of the system will increase rapidly over the next few years.

Meanwhile, the emphasis of siteworks will gradually change to development of public facilities, subject to availability of funds. The research programme will continue to be an important part of the project, and will focus increasingly on functional relationships of the wetland ecosystem.

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Literature Cited

Anon. 1991. Draft Environmental Protection (Swan Coastal Plain Wetlands) Policy, 1991, 4pp. Environmental Protection Authority, Perth, Western Australia.

Bamford, M. 1987. Breeding success of waterbirds on ponds formed by sand-mining near Capel, WA, for the 1986/87 breeding season. AMC Wetlands Centre Tech Rep No 3, 12 pp. AMC Mineral Sands Ltd., Perth, Western Australia.

Bamford, M. and Jaensch, R. 1987. Waterbird usage of the Capel sand-pit lakes, November 1985-November 1986. AMC Wetlands Centre Tech Rep No 2, 19pp. AMC Mineral Sands Ltd., Perth, Western Australia.

Bamford, M.J. 1990. The status of frogs and reptiles at Capel, WA. Report on a study from September 1988 to August 1989. AMC Wetlands Centre Tech Rep No 8, 29 pp. AMC Mineral Sands Ltd., Perth, Western Australia.

Brooks, D.R. 1988. Wetlands rehabilitation following mineral sands mining in Australia. Vol II, pp 146-153. In Mine Drainage and Surface Mine Reclamation. Bureau of Mines Information Circular 9184. Pittsburgh, PA.

Cale, D.J. and Edward, D.H.D. 1987. Fauna: Preliminary survey results and recommendations by Aquatic Research Laboratory, Department of Zoology, University of Western Australia. AMC Wetlands Centre Tech Rep No 4, 32pp. AMC Mineral Sands Ltd., Perth, Western Australia.

Cale, D.J. and Edward, D.H.D. 1990a. Macro-invertebrate fauna: A quantitative study of Boulder Lake, Capel, WA from December 1987 to December 1988. AMC Wetlands Centre Tech Rep No 9, 35pp. AMC Mineral Sands Ltd., Perth, Western Australia.

Cale, D.J. and Edward, D.H.D. 1990b. The influence of aquatic macrophytes on marcoinvertebrate communities in Swamphen Lake, Capel, Western Australia. AMC Wetlands Centre Tech Rep No 10, 29pp. AMC Mineral Sands Ltd., Perth, Western Australia.

Chambers, J.M. 1991. Investigations into improving water quality and phytoplankton growth in lakes at Capel, Western Australia, through adjustment of pH, phosphorus and carbon concentrations in wetland microsystems. AMC Wetlands Centre Tech Rep (in prep). AMC Mineral Sands Ltd., Perth, Western Australia.

Chambers, J.M. and Cale, D.J. 1991. The effect of added phosphorus to algal and macroinvertebrate communities in experimental enclosures in Taylors Lake, Capel, Western Australia. AMC Wetlands Centre Tech Rep (in prep). AMC Mineral Sands Ltd., Perth, Western Australia.

Davis, J.A., Rolls S.W. and Balla, S.A. 1987. The role of Odonata and aquatic Coleoptera as indicators of environmental quality in wetlands In The Role of Invertebrates in Conservation and Biological Survey. J.D. Majer (Ed), WA Department of Conservation and Land Management Report, 1987.

Gordon, D.M. and Chambers, J.M. 1987. Water ecology and vegetation of the Capel Ludlow wetlands, Western Australia. AMC Wetlands Centre Tech Rep No 5, 74pp. AMC Mineral Sands Ltd., Perth, Western Australia.

Jaensch, R.P. 1985. A development plan for wetlands formed by the extraction of mineral sands at Capel, Western Australia. 75pp. Unpublished report to AMC Mineral Sands Ltd., Perth, Western Australia.

Jaensch, R.P. 1986. Waterbird usage of the Capel sand-pit lakes, November 1984-October 1985. AMC Wetlands Centre Tech Rep No 1, 21pp. AMC Mineral Sands Ltd., Perth, Western Australia.

Jaensch, R.P., Vervest, R.M. and Hewish, M.J. 1988. Waterbirds in nature reserves of south west Australia. Report No 30. Royal Australasian Ornithologists Union, Perth, Western Australia.

John, J. 1988. A preliminary survey of algae of the Capel-Ludlow wetlands, Western Australia. AMC Wetlands Centre Tech Rep No 7, 40pp. AMC Mineral Sands Ltd., Perth, Western Australia.

Lane, B. 1987. Shore birds in Australia. Nelson, Melbourne.

Maher, M. and Carpenter, S.M. 1984. Benthic studies of waterfowl breeding habitat in south-western New South Wales. ii Chironomid populations. Aust J Mar Freshw Res 35, 97-110.

Nicholls, F.M. and Davies, S.J. 1990. Techniques for developing wetland habitats at AMC Wetlands Centre, Capel, Western Australia. In Environmental Workshop 1990, Vol I, pp 67-83. Australian Mining Industry Council, Wollongong.

Nield, S.P. and Townley, L.R. 1987. Study of water levels in the Capel wetlands. AMC Wetlands Centre Tech Rep No 6, 24pp. AMC Mineral Sands Ltd., Perth, Western Australia.

Street, M. and Titmus, G. 1982. A field experiment on the value of allochthonous straw as food and substratum for lake macroinvertebrates. Fresh-water Biology 12, 403-410.

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MASS OF IONS REMOVED BY LEACHING MINE SPOIL WITH SIMULATED PRECIPITATION[1]

by

Claude E. Gentry, Howard G. Halverson, and Gary L. Wade[2]

Abstract. A pyritic coal mine spoil was leached with simulated precipitation that was adjusted to pH values of 5.6, 5.0, 4.6, 4.2, and 3.8. Each mine spoil column contained 1500 g of recently dug, extremely acid mine spoil material. 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 94 1-week leaching and drying cycles, the spoils released approximately 3.6 g Fe, 35 g SO_4, 0.6 g Al, 1.5 g Ca Kg^{-1} and smaller amounts of other elements. Patterns of release changed during the 94 weeks. Early in the study, sums of leached Fe and Ti showed significant differences among precipitation pH treatments. At the midpoint of the study, sums of leached Al, Ti, and Cr showed significant differences among treatments, but Fe did not. After 94 weeks, only the sums of leached Al, P, and Cr were significantly different among treatments. Leachate of all treatments was consistently about pH 2.1 for most of the 94 weeks, but it rose to about pH 2.3 near the end of this period. These results suggest that fresh spoil quickly contributes readily available ions to groundwater leachate. The pH of incident precipitation significantly affects leaching losses of some elements from mine spoils.

Additional key words: pH, acid mine drainage, acid-rain, mine soils.

Introduction

There has been increasing concern as well as controversy regarding the effect of acid deposition on terrestrial ecosystems, especially on surface mined areas in which ameliorative treatments are unlikely (Krug and Frink 1983; Likens et al. 1989). Neutralization of acid deposition is necessary to prevent acidification of streams and ground water, and creation of elevated, dissolved Al, Fe, and Mn concentrations that are toxic to fish and other animals and plants. Determining the effect of acid precipitation on strip mine spoil is a complex problem because of the heterogeneous composition of the spoil parent material.

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

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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 groundwaters, 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^{1}. 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 on 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, a leaching liquid with a chemistry similar to natural precipitation and a pH adjusted to the range normally expected in rainfall was used. The objective 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

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 southcentral Kentucky. The material was derived from shales located immediately above the coal. The spoil was acidic and contained significant amounts of pyritic sulfur (see Table 3). The high values for potential acidity are similar to values from other Appalachian spoils (Ammons and Shelton 1988). The comparatively high values for organic carbon and sulfur 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 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, 20.3 cm in length) and retained by an inert fiberglass mat at the bottom of each cylinder. Leaching columns were chosen over alternative methods because the technique has been shown to be the most representative of field conditions (Caruccio and Geidel 1986).

After each column was filled with 1.5 Kg^{1} of spoil, 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 spoil material to an initial leaching with unmodified distilled water at a pH of 6.5. Spoil in each treatment column was brought to field capacity with distilled water.

Treatments

The treatments consisted of leaching the material with artificial precipitation adjusted to pH 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

Table 1. Chemical Composition of Rain Simulants (mg L^{-1})

Compound	Formula Wt	Leaching Solution				
		5.6	5.0	4.6	4.2	3.8
NaCl	58.42	0.176				
$CaSO_4.2H_2O$	172.17	0.709				
$MgSO_4.7H_20$	246.47	0.355				
K_2SO_4	174.27	0.069	Same for all solutions			
$NaNO_3$	84.99	0.368				
$(NH_4)_2SO_4$	132.14	0.746				
NH_4NO_3	80.04	0.243				
H_3PO_4 (85.2%)	97.98	0.008				
H_2SO_4 (96.7%)	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^{-1})

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						0.610	1.476		
4.6	0.025		Same for all solutions				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 1,000 parts material	11.73
Potential Acidity	$CaCO^3$ equivalent per 1,000 parts material	41.25
Net Neutralization Potential		-29.55
Total Sulfur	%	1.32
Total Carbon	%	11.34
	(Values based on pyritic sulfur)	
Neutralization Potential	$CaCO^3$ equivalent per 100 parts material	11.73
Potential Acidity	$CaCO^3$ equivalent per 100 parts material	26.88
Net Neutralization Potential		-15.15
Sulfate	%	0.09
Pyritic Sulfur	%	0.86
Organic Sulfur	%	0.37

bottle each week, and analyzed the following day. Treatments began on August 11, 1988, and continued until June 17, 1990, for a total of 94 weeks.

The treatment columns were covered with a watch glass during the 6-day period between irrigations to prevent excessive drying of the spoil. Although the columns were protected, the seal was not complete; so, many spoil pores drained and a definite drying cycle was established with air 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. Also, the columns were rotated each week. 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 (see Table 4). Data analyses were captured in a data file and formatted for statistical analyses with a computer system dedicated to laboratory control.

Statistical Analyses

Data analyses were accomplished by utilizing various statistical subroutines (Wilkinson 1988). The primary method utilized 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 are due to treat-

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

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

ment beyond that expected by chance.

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. Analysis of variance (ANOVA) was used to determine statistical difference among means due to treatment.

Results and Discussion

Mean loads of all chemical constituents in leachates from a toxic strip mine spoil decreased significantly with sequential, simulated acid-rain irrigations (see Table 5). The leachate chemistry with fresh distilled water was compared periodically with percolate from leaching with simulated acid-rain at various acidity levels. The results for the major potential phytotoxic chemical factors do not indicate a highly statistically significant difference among simulated acid-rain treatments, but they do illustrate that significant changes occurred with each leaching. Concentrations of leachate chemical components consistently declined. Other parameters, including the control samples, except pH, also declined in concentrations as a result of sequential leaching with simulated acid-rain irrigations. Patterns of release changed during the 94 weekly leaching cycles. They illustrated a pattern of high output early in the leaching cycle, followed by declining values for succeeding weeks during the first year (Halverson et al. 1990). Thereafter, much smaller declines occurred in chemical composition with each additional leaching.

The leachate mean pH values averaged over 94 weekly applications of simulated acid-rain did not decrease with decreasing solution pH (see Table 6). All leachate pH values were considerably less than the pH of the solutions applied. Lilieholm and Feagley (1988) found the leachate pH values of soil

Table 5. Chemistry of minespoil leachate from fresh distilled water at pH 6.5 compared to the mean chemistry of leachates from simulated precipitation water at pH values of 5.6 and below.

Weeks	Treatment	EC	Leachate pH	Fe	Al	Mn	SO_4	TDS
	pH	ds/m	---------- mg /L-					
1	6.5	11.1	2.2	4,999	370	378	30,700	37,762
	<5.6	10.7	2.1	4,027	321	353	24,880	30,607
2	6.5	6.4	2.2	1,255	205	205	11,600	16,645
	<5.6	7.0	2.2	1,354	172	177	10,750	19,754
20	6.5	4.1	2.1	178	47	28	3,150	3,697
	<5.6	4.7	2.1	328	54	37	3,841	4,528
46	6.5	2.9	2.2	50	10	3	572	665
	<5.6	3.2	2.1	70	22	6	881	1,069
94	6.5	1.8	2.3	10	10	0.41	425	486
	<5.6	2.0	2.2	12	12	0.79	478	554

to be higher than the pH of solution applied. They also found that the leachate pH value from soil decreased with decreasing leaching solution pH. These data indicate that the buffering capacity of the spoil was very low, and that it had been depleted by simulated acid-rain treatments, because it was unable to accept H+ions. Since all leachate pH values in this study were lower than the leaching solutions, the simulated acid-rain solutions brought about additional chemical weathering and leaching. Chemical weathering is a part of natural soil development from spoil material (Struthers 1964).

The lowest leachate pH value was found for the first application of simulated acid-rain solution (see Table 5). The pH of the leachates showed little variation with successive leachings and was not responsive to the acidity of irrigation solutions during the first year. The pH of the leachate for all treatments began to rise gradually with successive leachings during the second year. Leachate pH values were not responsive to acidity of the irrigating solutions but to mine spoil and leachate chemistry.

Mean leachate electrical conductivity (EC) was significantly influenced by leaching solution pH. The pH 4.6 solution had the highest leachate EC value and the 5.6 pH solution the lowest value (see Table 6). This relationship was obtained throughout the greater part of the experiment. A maximum release of ions occurred from spoils receiving the 4.6 pH leaching solution. The pH 4.6 leaching solution produced the greatest EC and the lowest mean pH leachates.

Mean Al concentrations were significantly affected by leaching solutions pH. The 4.6 pH solution produced the highest concentration of Al in the leachates. These responses correlated well with Fe, EC, and leachate pH, and indicate steady mineral dissolution. However, smaller concentrations of Al, Fe, and acidity occurred with the pH 3.8 leaching solution. These factors suggest that mine spoil pH may be lowered by leaching with solutions below pH 5.6 or by acid-rain. Also, mine spoil mineral and chemical composition and weathering properties are contributing factors to leachate chemistry. All leachates contained sufficient concentrations of heavy metals and soluble salts to create potentially toxic conditions, so they would be classified as phytotoxicant for most organisms.

Mean loads of all chemical constituents in mine

Table 6. Mean of leachate pH, electrical conductivity, and aluminum and iron concentrations as influenced by pH leaching solutions for 94 weeks.*

pH		EC ds/m		Al. mg L^{-1}		Fe mg L^{-1}	
pH	Mean	pH	Mean	pH	Mean	pH	Mean
5.6	2.12	5.6	3.78a	5.6	41a	5.6	2.28a
5.0	2.10	5.0	3.82ab	5.0	42a	5.0	2.25a
4.6	2.06	4.6	4.06b	4.6	45b	4.6	2.84c
4.2	2.11	4.2	3.90ab	4.2	49c	4.2	2.49b
3.8	2.14	3.8	3.86ab	3.8	39a	3.8	2.35a

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

spoil leachate increased significantly as the acidity level increased in simulated acid-rains from pH 5.6 to 4.6. Total dissolved solids, (TDS), decreased with leaching solutions less than 4.6 pH (see Table 7). After 94 weekly leachings with 2.54 cm of simulated acid-rain at a pH of 4.6, the spoil released approximately 35 g of sulfate, 3.6 g of iron, 0.6 g Al, 1.5 g Ca, and smaller amounts of other elements per kg of mine spoil. Approximately 42 g of total dissolved solids per kg of spoil were released.

Patterns of release of the chemical constituents changed during the 94 weeks. Early in the study, sums of leached Na, Al, Fe, Ti, Mn, and P showed significant differences among simulated acid-rain treatments. At the midpoint of the study, sums of leached Al, Ti, and Cr showed significant differences among treatments, but iron did not. After 94 weeks, Al, P, Cr, and TDS were significantly different among treatments. The companion control samples leached with fresh distilled water (pH 6.5) showed a similar declining pattern, but the absolute values of chemicals leached were always slightly lower than those derived with acidified leaching materials (see Table 7). Except for the control leach material at pH 6.5, lower pH levels of 5.6 and below, all seemed to accelerate leaching of contaminants from the spoil, with a peak efficiency when the leaching solution was at a pH of 4.6. Leachates from all treatments were consistently about pH 2.1 for most of the 94 weeks, but it rose to about 2.3 near the end of this period. All leachates had

Table 7. Mass of ions removed and chemical composition of leachate from minespoil with 94 simulated acid-rains.*

Parameter	Simulated Rain				
mg Kg $^{-1}$	pH 5.6	pH 5.0	pH 4.6	pH 4.2	pH 3.8
SO_4	33,467	32,080	34,799	32,590	30,173
Acid	18,814	19,052	20,547	19,097	18,354
Fe	2,855	2,820	3,569	3,080	2,952
Mn	377	361	383	359	337
Al	521.ab*	527 ab	566.a	535.a	497.b
Mg	460	469	482	453	431
Ca	1,369	1,312	1,518	1,412	1,169
Si	226	277	270	281	26.3
P	14.2ab	13.0ab	15.2a	12.9ab	12.4b
K	8.3	6.0	5.0	4.2	5.9
B	1.7	1.8	1.7	1.8	1.7
Zn	21.7	22.7	23.6	22.9	24.2
Cu	6.7	6.5	7.0	6.6	6.5
Na	12.3	12.4	10.8	12.3	11.3
Co	5.6	5.6	5.8	6.3	5.8
Ni	14.2	14.4	15.1	15.1	13.8
Ti	1.8	1.8	2.3	1.5	1.79
Cr	2.0ab	2.0ab	2.1ab	2.2a	1.9b
Pb	8.2	8.2	9.0	8.8	8.2
TDS	39,927.ab	38,294.bc	41,669.a	38,788.b	35,906.c

*Values in rows followed by the same letter are not significantly different among acid-rain treatments at the 95% confidence level.

lower mean pH and higher mean acidity levels than the leaching solutions.

Conclusions

These results imply that fresh spoil quickly contributes readily available ions to groundwater leachate. The materials in the leachate are produced by weathering of rock and minerals in the spoil after repeated leaching with simulated acid-rain. The large amount of SO_4, Fe, Al, Mn, and TDS removed by leaching could contaminate and produce phytotoxicity in ground or surface water. Nevertheless, it is clear that the hydrologic regime within mine spoil can also affect leachate and ground water chemistry. Acidification by simulated acid-rain depleted the low buffering capacity of the spoil and increased weathering, resulting in leachate pH values lower than the pH of the applied simulated acid-rain. The pH of incident precipitation modestly, but significantly, affects leaching losses of some elements from mine soils. Further studies in the field and laboratory are needed to fully evaluate the state of spoil (mine soil) - plant - water - environments under the stress of acid precipitation.

LITERATURE CITED

Ammons, J.T. and P.A. Shelton. 1988. A comparison of results from acid-base accounting versus potential acidity measured by the peroxide oxidation of weathered and unweathered soil containing pyrite. p. 206-209. In Mine Drainage and Surface Mine Reclamation, Vol. 1: Mine Water and Mine Waste. (Pittsburgh, Pa., April 19-21, 1988). Bureau of Mines Information Circular IC 9183.

Caruccio, Frank T. and Gwendelyn Geidel. 1986. An evaluation of mine waste overburden analytical techniques. p. 147-153. In 1986 National Symposium on Mining, Hydrology, Sedimentology, and Reclamation. (Lexington, Ky., December 8-11, 1986). University of Kentucky.

Doepker, Richard D. 1988. The interrelation of factors influencing the dissolution of metals in columns of mine tailings. p. 210-219. In Mine Drainage and Surface Mine Reclamation, Vol, 1: Mine Water and Mine Waste. (Pittsburg, Pa., April 19-21, 1988). Bureau of Mines Information Circular IC 9183.

Halverson, Howard G. and Claude E. Gentry. 1990. Long-term leaching of mine spoil with simulated precipitation. Proceedings of 1990 Mining and Reclamation Conference. (April 23-26 Charleston W.V.) Morgantown, W.Va: West Virginia University Vol. 1. 27-32.

Halverson, Howard G. and Gary L. Wade. 1988. Chemical variation in acid mine drainage in southern Kentucky. p. 95-104. In 1988 Symposium on Mining, Hydrology, Sedimentology, and Reclamation. (Reno, Nev., December 5-9, 1988). University of Kentucky.

Krug, E.C., and C.R. Frink. 1983. Acid-rain on acid soil: A new perspective. Sci. 221:520 - 525.

Likens, G.E., R.F. Wright, J.N. Galloway and T.J. Butler. 1979. Acid-rain. Sci. Am. 241:43-51.

Lilieholm, B.C. and S.E. Feagley. 1988. Effects of simulated acid-rain on soil and leachate acidification of a Lexington silt loam. Soil Sci. Vol 146, No. 1: 44-50.

Sobek, A.A., W. A. Schuller, J.R. Freeman and R. M. Smith. 1978. Field and laboratory methods applicable to overburden and minesoils. EPA-600/2-78-0S4. Cincinnati, Oh. pp. 204.

Struthers, P.H. 1964. Chemical weathering of strip-mine spoils. The Ohio Journal of Sci. 64 (2): 125-131.

Watzlaf, George R. 1988. Chemical stability of manganese and other metals in acid mine drainage sludge. p. 83-90. In Mine Drainage and Surface Mine Reclamation, Vol. 1: Mine Water and Mine Waste. (Pittsburgh, Pa., April 19-21, 1988). Bureau of Mines Information Circular IC 9183.

Wilkinson, L. 1988. SYSTAT: The system for statistics. Systat, Inc., Evanston, Ill.

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THE REMOVAL OF NICKEL FROM MINE WATERS USING BACTERIAL SULFATE REDUCTION[1]

by

R W. Hammack and H. M. Edenborn[2]

Abstract. Experiments were done to determine if a mushroom compost-based sulfate reduction system could be used to treat nickel-contaminated mine waters. Sulfate reduction systems were established in columns containing acid-washed mushroom compost. Simulated mine waters containing 2000 mg/L sulfate and 50 to 1000 mg/L nickel were adjusted to pH 4.5 and pumped through the columns at flow rates between 15 and 25 mL/hr. During the first nine days of operation, virtually all influent nickel was removed in the columns by sorption and ion exchange mechanisms. The nickel removal rate then dropped to 18 to 30 mg Ni/day (7.8 to 12.8 nmol/g-substrate/day), probably due to low sulfate reduction rates. When sodium lactate was added to the inflow, a sustained and seven-fold increase in the nickel removal rate was observed. Bacterial sulfate reduction rates measured in mushroom compost-based wetlands exposed to coal mine drainage are 2 to 20 times faster than the rates observed in this study. Low sulfate reduction rates in the columns may have been due to the inhibition of microbial activity by high nickel concentrations and the removal of labile organic compounds from the mushroom compost substrate during acid-washing. Results of this study indicate that bacterial sulfate reduction can effectively treat nickel concentrations up to 500 mg/L if labile carbon is nonlimiting.

Introduction

The sulfide-rich Duluth gabbro deposit in northeastern Minnesota is an important source of nickel, copper, zinc, cobalt, and associated precious metals (Natarajan et al. 1982). Mining of this ore body will inevitably result in the production of contaminated water. Acidic and metal-contaminated leachates now drain from waste rock removed from a test shaft driven into a highly-mineralized zone of the deposit near Babbitt, MN (A and B, Table 1). Other portions of the Duluth Complex are being disturbed by the open-pit mining of underlying taconite orebodies. Currently, this sulfide-rich waste rock is being stockpiled to permit the mining of subjacent taconite orebodies. The

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Table 1 - Water quality[1] of leachates from Duluth Gabbro waste rock

	Concentrations, mg/L						
Sample	pH[2]	SO_4^{2-}	Cu	Ni	Co	An	Fe
A	4.8	2740	63.0	196.0	9.1	10.3	0.10
B	4.2	3430	115.0	198.0	9.8	10.0	0.20
C	6.9	1125	0.02	1.6	0.06	0.02	0.10
D	7.2	1910	0.11	2.2	0.10	0.04	0.10
E	7.1	4000	0.64	50.0	3.4	3.6	0.10
F	5.4	1425	0.46	14.0	0.94	1.6	0.20

[1]Data provided by Kim Lapakko, Divison of Minerals, Minnesota Department of Natural Resources.
[2]Standard units.

water quality of the drainage emanating from these stockpiles exceeds water quality standards by as much as 2 to 3 orders of magnitude (samples C, D, E, and F, Table 1).

Prior to mining the Duluth Complex ore deposit, water pollution control measures must be in place to ensure the protection of the region's environment. A number of options are available for the treatment of metal-contaminated drainages. Chemical treatment plants that add alkaline materials are able to treat water effectively, but they are expensive to build, maintain, and operate. Metal adsorption onto sedge peat (Eger and Lapakko 1988) and polymeric beads containing Sphagnum peat (Jeffers 1990), are both demonstrated, low-cost techniques for treating stockpile drainages with total metal concentrations of less than 100 mg/L. However, the high total leachate metal concentrations from waste rock piles at the Babbitt test shaft (often exceeding 300 mg/L) would tend to saturate the adsorption/absorption capacity of sedge- or Sphagnum-based treatment systems relatively quickly. The required frequency of Sphagnum replacement or acid stripping (in the case of peat-containing beads) could make the use of these treatment methods economically impractical.

The precipitation of metals as insoluble sulfides is another potential treatment method for acidic Duluth gabbro leachates. Crushed limestone and gaseous H_2S have been used previously to treat acid mine waters with a high iron content (Streeter 1970). In this technique, an amorphous iron monosulfide precipitate was formed by the reaction of iron and H_2S. Crushed limestone was used to elevate the pH to about 6, where amorphous iron monosulfide was stable. Nickel, copper, and many other metal ions would both be expected to precipitate more readily than iron in the presence of excess hydrogen sulfide (Ehrlich 1981). Sodium sulfide (Na_2S) has also been added to complex wastewaters to remove Cd, Zn, Pb, and Cu as insoluble sulfides (Bhattacharyya et al. 1979). Oxyanions of selenium and arsenic were also removed by this process, presumably via the formation of elemental selenium and arsenic sulfide minerals.

One advantage of sulfide precipitation over alkali addition as a chemical treatment is that a more compact sludge is produced that can be introduced directly into conventional smelters for metal recovery. However, a sulfide precipitation plant would be expensive to operate because of high H_2S or Na_2S costs. There are also safety concerns when transporting or applying toxic H_2S gas or caustic Na_2S. The high cost of H_2S can be avoided by biologically-generating H_2S via dissimilatory sulfate reduction. Biological sulfate reduction consumes only waste organic material and sulfate,

a major constituent of acid mine waters. Safety concerns would also be lessened because only the amount of H_2S necessary to precipitate metals would be generated in a properly designed system.

Dissimilatory sulfate-reducing bacteria reduce inorganic sulfate or other oxidized sulfur forms to sulfide. This sulfide is not incorporated into the organism but is released as free H_2S. Desulfovibrio and Desulfotomaculum are the two best known genera of these bacteria. They are strict anaerobes and are severely inhibited by even small amounts of oxygen. They will, however, survive long periods of oxygen exposure and become active when anaerobic conditions are restored. In fresh waters, bacterial sulfate reduction is often limited by the availability of sulfate ion (Herlihy and Mills 1985), but this is seldom the case in mine drainages resulting from the oxidation of sulfide minerals. Sulfate reduction activity has likewise been detected at environmental temperatures between 0 and 70° C (Postgate 1979).

Bacterial sulfate reduction does appear to be inhibited in acidic environments below pH 4 (Wakao et al. 1979), a common characteristic of acid mine drainage. This does not preclude the use of sulfate-reducing bacteria in acidic environments, however, because of their ability to generate alkalinity via their metabolic activity. The overall sulfate reduction process can be represented by the following generalized equation:

$$\text{Simple organic compounds} + SO_4^{2-} \xrightarrow[\text{anaerobic}]{\text{bacteria}} \text{acetate} + H_S^- + HCO_3^- \qquad (1)$$

In this reaction, the organic compounds and sulfate are converted to acetate, bisulfide or hydrogen sulfide, and bicarbonate. Application of this process in the treatment of acidic mine effluents may thus help to improve water quality in three ways:

1. sulfide generated as bisulfide or hydrogen sulfide can react quickly with metals to form insoluble precipitates and decrease dissolved metal concentrations,

2. alkalinity generated as bicarbonate and acetate can help neutralize acidity and raise effluent pH, and

3. dissolved sulfate concentrations can be reduced.

This paper presents the results of laboratory experiments designed to determine if bacterial sulfate reduction is a potential treatment technique for nickel-contaminated mine drainage.

Materials and Methods

Sulfate reduction experiments were carried out in 5.1 cm (2 in) I.D. by 45.7 cm (18 in) long columns containing 400 g of mushroom compost. Mushroom compost is a waste product of mushroom farming that consists of composted straw, hay, horse and poultry manure, ground corncobs, gypsum, and limestone. As received, this material contains an intrinsic alkalinity equal to 35 tons $CaCO_3$/1000 tons. Initially, deionized water adjusted to pH 1 with concentrated hydrochloric acid was passed through the columns to remove the intrinsic alkalinity of the compost. When the pH of the column effluents dropped below 2, this treatment was suspended. The columns were then inoculated with leachate from fresh mushroom compost and a circumneutral solution containing 2000 mg/L SO_4^{2-} (as Na_2SO_4) was passed through the columns at a 25 ml/hr flow rate for 2 weeks. After the presence of viable populations of sulfate-reducing bacteria (as growth in Postgate's medium B; McIntire et al. 1990) was demonstrated for each column, pH 4.5 solutions containing 2000 mg/L SO_4^{2-} and 50, 100, 200, 500, and 1000 mg/L Ni (as $NiCl_2 \cdot H_2O$) were passed through the columns at flow rates ranging from 15-25 mL/hr (12.5 hr average residence time).

After 20 weeks, 3500 mg/L lactate, as sodium lactate was added to the influent solutions (pH adjusted to 4.5). No effort was made to deplete the oxygen content of the influent solutions. Therefore, the dissolved oxygen content of solutions entering the columns would be in equilibrium with the atmosphere, a condition likely to be encountered at most mine sites. The effluent from each column was sampled weekly and analyzed to determine pH, acidity/alkalinity, and concentrations of Ni, SO_4^{2-}, and lactate. Nickel was measured by ICP atomic emission spectroscopy; sulfate and lactate were both measured by liquid chromatography. Acidity and alkalinity were determined by titration and expressed as mg/L $CaCO_3$ equivalent. The sulfide content of column effluents was measured by sulfide ion sensitive electrode when hydrogen sulfide odors were detected in effluent reservoirs. At the completion of the experiment, the two columns receiving 500 mg/L nickel inflow were frozen and cut into three equal segments. Acid volatile sulfide (AVS) distillations were performed on each segment (Jorgenson 1978). AVS techniques were originally developed to determine iron monosulfide accumulations in substrates undergoing sulfate reduction. The applicability of AVS techniques to other biogenically-precipitated metal sulfides is currently being evaluated.

Results and Discussion

Adsorption an Absorption Phase

For the first nine days of operation, virtually all influent nickel (fig. 1-4) and some of the sulfate (fig. 5-8) were removed by passage through the mushroom compost column. Sorption mechanisms are thought to be primarily responsible for their removal during this period. The extent that sulfate reduction may have contributed to nickel and sulfate removal during this period cannot be determined accurately. Potential indicators of bacterial sulfate reduction activity, such as increases in pH (fig. 9) and alkalinity (fig. 5-8), are masked by the effects of ion exchange that result in a lowering of pH and alkalinity. The decrease in pH from 4.5 at the inflow to about 3.7 in the effluent (fig. 9) can be attributed to Ni^{2+} displacement of H_3O^+ from ion exchange sites. Based on the

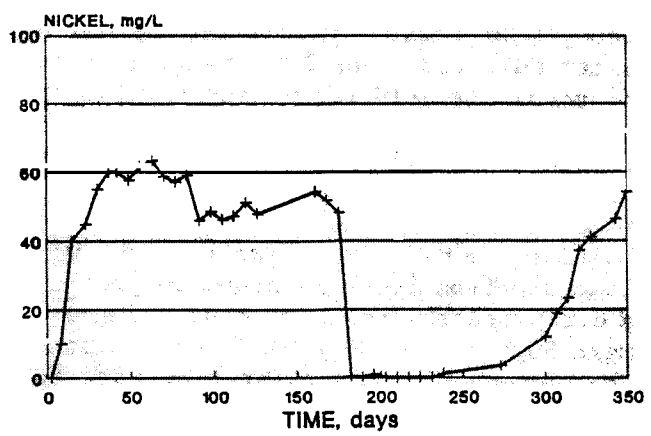

Figure 1. Average effluent nickel concentrations from two columns receiving aqueous solutions containing 100 mg/L nickel and 2000 mg/L sulfate. Lactate supplementation (3500 mg/L) began on day 161 and was suspended on day 198.

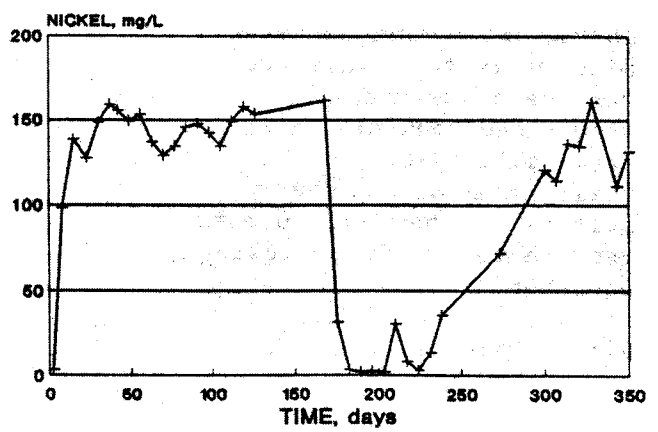

Figure 2. Average effluent nickel concentrations from two columns receiving aqueous solutions containing 200 mg/L nickel and 2000 mg/L sulfate. Lactate supplementation (3500 mg/L) began on day 161 and was suspended on day 198.

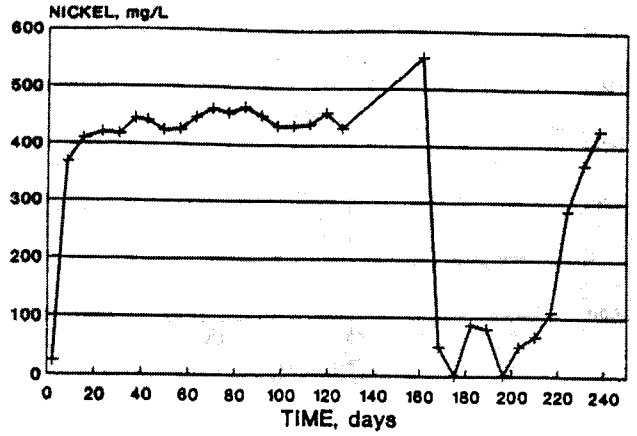

Figure 3. Average effluent nickel concentrations from two columns receiving aqueous solutions containing 500 mg/L nickel and 2000 mg/L sulfate. Lactate supplementation (3500 mg/L) began on day 161 and was suspended on day 198.

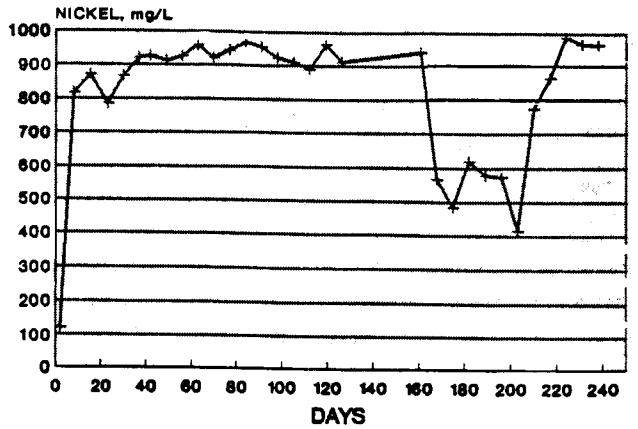

Figure 4. Average effluent nickel concentrations from two columns receiving aqueous solutions containing 1000 mg/L nickel and 2000 mg/L sulfate. Lactate supplementation (3500 mg/L) began on day 161 and was suspended on day 198.

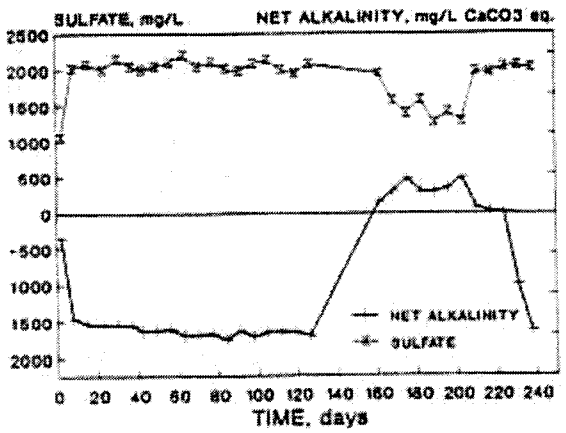

Figure 5. Average net alkalinity and sulfate concentrations in effluents from columns receiving solutions containing 100 mg/L nickel and 2000 mg/L sulfate. Lactate supplementation (3500 mg/L) began on day 161 and was suspended on day 198.

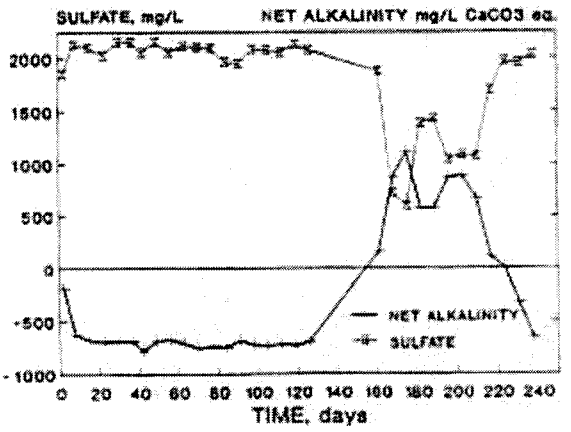

Figure 6. Average net alkalinity and sulfate concentrations in effluents from columns receiving solutions containing 200 mg/L nickel and 2000 mg/L sulfate. Lactate supplementation (3500 mg/L) began on day 161 and was suspended on day 198.

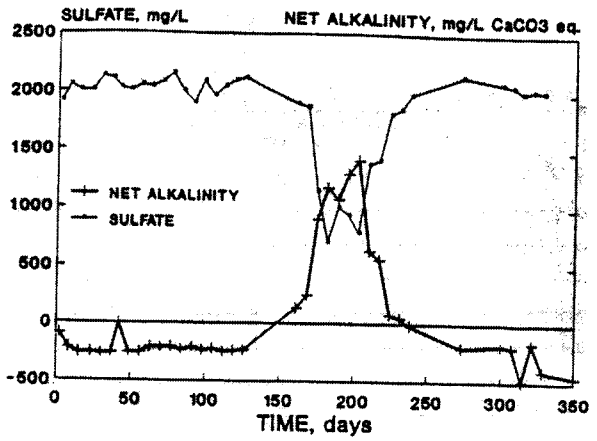

Figure 7. Average net alkalinity and sulfate concentrations in effluents from columns receiving solutions containing 500 mg/L nickel and 2000 mg/L sulfate. Lactate supplementation (3500 mg/L) began on day 161 and was suspended on day 198.

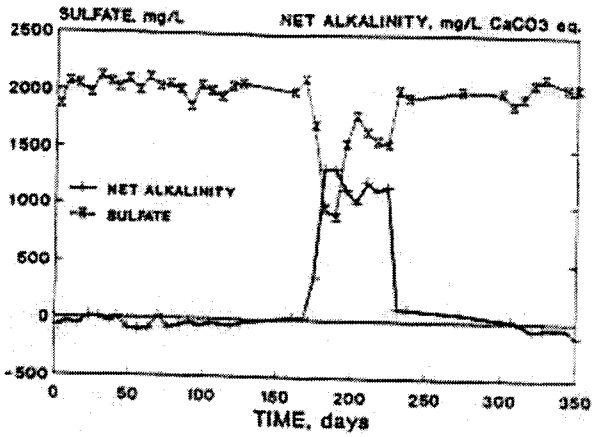

Figure 8. Average net alkalinity and sulfate concentrations in effluents from columns receiving solutions containing 1000 mg/L nickel and 2000 mg/L sulfate. Lactate supplementation (3500 mg/L) began on day 161 and was suspended on day 198.

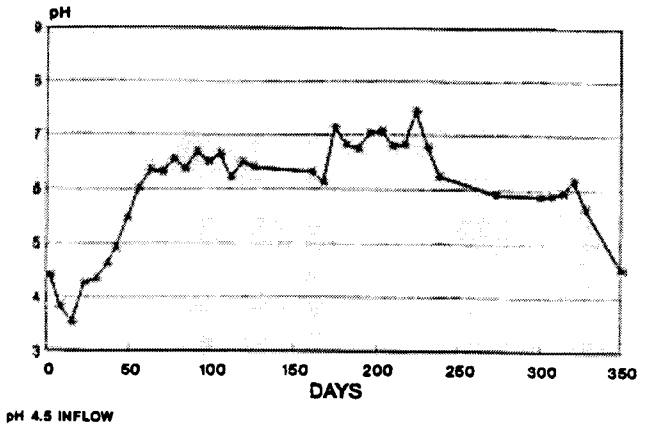

Figure 9. Effluent pH of a column receiving solutions containing 500 mg/L nickel and 2000 mg/L sulfate. Lactate supplementation (3500 mg/L) began on day 161 and was suspended on day 198.

pH decrease, ion exchange can account for the removal of at least 5 mg Ni^{2+}/L, assuming that all cation exchange sites were occupied with H_3O^+ following acid washing of the compost. Nickel removal due to ion exchange may have been higher than indicated, considering that some of the released H_3O^+ may have been consumed subsequently by sulfate reduction.

Sulfate Reduction Phase

After day 9, the rates of nickel removal in the mushroom compost columns fell to 18-30 mg Ni/day (7.8-12.8 nmol/g-substrate/day) (fig. 1-5). These rates remained relatively stable until supplemental carbon was added on day 161. It is unlikely that sorption processes contributed to nickel removal during this time. Otherwise, the rate of nickel removal would have been expected to decrease with time and exhibit a greater dependence on the influent nickel content (fig. 10).

The increases in pH and alkalinity, the long-term and sustained rates of fell to 18-30 mg Ni/day (7.8-12.8 nmol/g-substrate/day) (fig. 1-5). These rates remained relatively stable until supplemental carbon was added on day 161. It is unlikely that sorption processes contributed to nickel removal during this time. Otherwise, the rate of nickel removal would have been expected to decrease with time and exhibit a greater dependence on the influent nickel content (fig. 10).

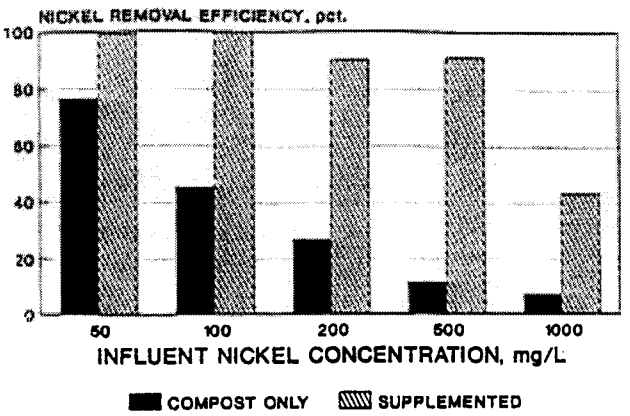

Figure 10. Average nickel removal rate (n = 14) at five influent nickel concentrations.

The increases in pH and alkalinity, the long-term and sustained rates of nickel removal, and the fact that nickel removal rates were only slightly dependent on influent nickel content all imply that sulfate reduction was probably responsible for the nickel removed during this period of time. However, no decrease in effluent sulfate concentration was detected. Nickel removal during this period ranged from 40 to 60 mg/L; about 65 to 98 mg/L of sulfate would have to be reduced to precipitate this amount of nickel as a sulfide. The dissolution of sulfate minerals (eg. gypsum) within the mushroom compost could easily have generated more sulfate than was consumed by these low rates of sulfate reduction. Therefore, it is not surprising that no net loss of sulfate was observed. There is no evidence to suggest that ion exchange processes contributed to nickel removal during this period.

Sulfate reduction rates in this study were estimated from measured rates of nickel removal although, during certain periods, nickel was removed from solution by sorption and ion exchange mechanisms, as well as sulfate reduction. However, nickel removal by mechanisms other than sulfate reduction quickly decreased as sorption and ion exchange sites become saturated. The nickel removal rates used for estimating sulfate reduction rates were determined after sorption and ion exchange mechanisms were no longer significant. These estimates assumed that all sulfide generated by sulfate reduction is precipitated as nickel sulfide. If hydrogen sulfide or bisulfide washed out of the columns without reacting with nickel, the estimated sulfate reduction rate could be significantly lower than the actual rate. Unfortunately, measurements of effluent sulfide concentrations were too infrequent to accurately determine the amount of unreacted sulfide that escaped from the columns. Therefore, estimated sulfate reduction rates are only a rough approximation of the actual rates, but do indicate the capacity of a compost system to precipitate metals. Sulfate reduction rates calculated from the amount of nickel removed were 10-20 times lower than rates measured previously in the mushroom compost substrate of a constructed wetland receiving acid mine drainage (McIntire et al. 1990). If nickel was inhibitory to sulfate-reducing bacteria, higher nickel concentrations would be expected to result in significantly lower sulfate reduction rates. However, sulfate reduction rates increased slightly with increased nickel content (fig. 10). This observation can be explained by the fact that higher metal contents result in lower concentrations of hydrogen sulfide or bisulfide which are known to be inhibitory to sulfate reducing bacteria (Miller 1972). Therefore, nickel toxicity to sulfate-reducing bacteria does not appear to be responsible for the low rates observed during this period. However, sulfate reduction rates may be limited by the ability of mushroom compost to supply labile carbon. The acid-washing of the mushroom compost during column preparation may have both removed labile carbon and destroyed fermentative bacterial populations necessary for the formation of labile carbon. To test this hypothesis, 11 mL of a 60 pct

sodium lactate solution were added to each liter of inflow. Nickel removal and sulfate reduction rates increased seven-fold to a maximum of 216 mg Ni/day (92 nmol/g-substrate/day). Effluent sulfate concentrations dropped dramatically, and pH and alkalinity showed marked increases during the period of sodium lactate supplementation. The positive response of sulfate reduction indicators to the addition of sodium lactate supported the hypothesis that sulfate reduction on mushroom compost was carbon limited. The nickel removal efficiencies for columns operating with and without lactate supplementation are shown in figure 11.

The estimated sulfate reduction rates for the columns in the presence of excess labile carbon were lower than expected. However, because the estimated rates were based on nickel removal, the low rates are partly explained by the fact that some hydrogen sulfide or bisulfide exited the column without reacting with nickel. During the period of supplementation, sulfide concentrations as high as 196 mg/L were measured in column effluents. Increases in net alkalinity (fig. 5-8) corroborate the release of unreacted sulfide from the column because hydrogen sulfide must be removed from solution as a gas in order for alkalinity to increase. There would be no net increase in alkalinity when hydrogen sulfide or bisulfide was precipitated as nickel sulfide. In addition, anaerobic, purple sulfur bacteria were observed growing in the columns during the experiment. These photoautotrophic bacteria use light energy to convert hydrogen sulfide to elemental sulfur and hydrogen gas. The activity of purple sulfur bacteria would reduce the amount of hydrogen sulfide available for metal precipitation. For these reasons, all bacterially-generated sulfide would not be available for nickel precipitation. Therefore, actual sulfate reduction rates in the column may have been comparable to the 150-200 nmol/cc-substrate/day rates measured by McIntire et al. (1990).

Oxygen and pH inhibition of sulfate-reducing bacteria where water entered the mushroom compost columns may be indicated by lower AVS accumulations in these areas (fig. 12). Sulfate reduction cannot occur until all of the dissolved oxygen has been removed from the influent stream. At the influent pH of 4.5, sulfate reduction does occur but is probably greatly inhibited (Wakao

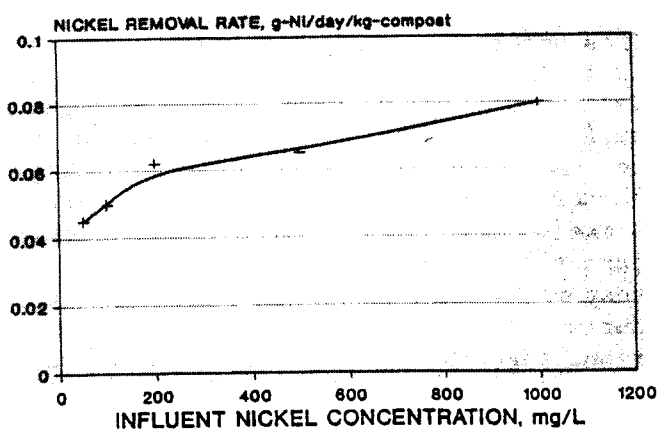

Figure 11. Nickel removal efficiencies for supplemented and unsupplemented columns at influent nickel concentration between 50 mg/L and 1000 mg/L.

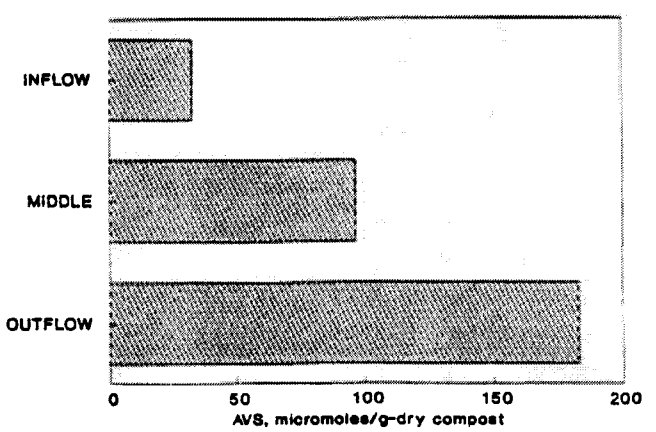

Figure 12. Average acid volatile sulfide accumulations in three segments of columns receiving solutions containing 500 mg/L nickel and 2000 mg/L sulfate.

1979). Results of this study (fig. 10 and 13) imply that nickel does not inhibit the activity of sulfate-reducing bacteria at concentrations at or below 1000 mg/L. Previous studies that evaluated the toxicity of nickel on sulfate-reducing bacteria have reported contradictory conclusions. Miller (1950) observed that nickel inhibited sulfate-reducing bacteria growing on sodium lactate. However, in a later study, Capone et al. (1983) found that the addition of 1000 mg/L nickel had no long-term effect on methanogenesis, sulfate reduction, and carbon dioxide evolution in anoxic salt marsh sediments. McIntire et al. (1990) reported no toxicity at nickel concentrations below 211 ppm. The extent to which nickel inhibits the activity of sulfate-reducing bacteria, if at all, cannot be concluded based on the results of the present study. However, at nickel concentrations less than 1000 mg/L, inhibitory effects appear to be minor and should not significantly impair sulfate reduction treatment methods.

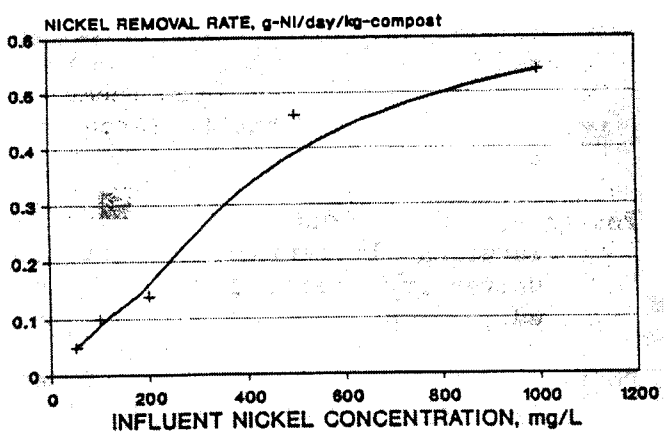

Figure 13. Average nickel removal rate (n = 6) at five influent nickel concentrations during lactate supplementation.

Conclusions

Sulfate reduction is a low-cost, low-maintenance technique capable of treating mine waters with elevated nickel concentrations. Based on 12-hr residence times, sulfate reduction treatment systems using mushroom compost as the primary organic substrate could remove 45-75 mg Ni^{+2}/kg-substrate/day from pH 4.5 wastewaters containing up to 1000 mg/L Ni^{+2}. Supplementation of the influent with 3500 mg/L lactate increased nickel removal to 540 mg Ni^{+2}/kg-substrate/day. Other less expensive industrial organic waste products may be useful in supplementing the nutrient requirements of sulfate-reducing bacteria in environments where their metabolic activity is sub-optimal. Peptone, glucose, and molasses (Wakao et al. 1979; Maree and Strydom 1987) are known to sustain sulfate reduction when fermentative bacteria are also present. Waste products of the food processing industry such as whey, brewery wort, sauerkraut filtrate, and peach peelings (Corrick et al. 1970) are low-cost supplements available in some areas. Anaerobically digested cattle wastes (Ueki et al. 1988) have widespread availability. Research is currently underway to identify other widely-available organic waste products that can be used by sulfate-reducing bacteria and their associated fermentative bacterial populations.

Two potential drawbacks to sulfate reduction-based treatment systems are that their efficiency will be decreased by cold temperature and low pH. Additional capacity must be engineered into systems to compensate for reduced biological activity in winter months. Placing systems underground where temperatures are more constant may result in more uniform performance, for example. Likewise, sulfate reduction treatment systems could be built large enough to provide enough inherent buffering capacity to compensate for short periods of time when the influent pH would normally be inhibitory to

bacteria. These engineering design alternatives are currently being investigated (Dvorak et al. 1991)

Acknowledgements

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Literature Cited

Capone, D.G., D.D. Reese, and R.P. Kiene. 1983. Effects of metals on methanogenesis, sulfate reduction, carbon dioxide evolution, and microbial biomass in anoxic salt marsh sediments. Applied and Environmental Microbiology 45: 1586-1591.

Corrick, J.D., M.J. Rose, J.A. Sutton, and J.M. Carosella. 1970. Microbial conversion of hydrous calcium sulfate to hydrogen sulfide. BuMines RI 7355, 15 p.

Dvorak, D.H., H.M. Edenborn, R.S. Hedin, and P.E. McIntire. 1991. Treatment of metal-contaminated water using bacterial sulfate reduction: results from pilot-scale reactors. Proceedings of the 1991 AIME Annual Meeting, Denver, CO.

Eger, P. and K. Lapakko. 1988. Nickel and copper removal from mine drainage by a natural wetland. p. 305-309. In Mine drainage and surface mine reclamation, volume 1: mine water and mine waste. BuMines IC 9183, 413 p.

Ehrlich, H.L. 1981. Geomicrobiology Marcel Dekker, Inc., New York: 393 p.

Herlihy, A.T. and A.L. Mills. 1985. Sulfate reduction in freshwater sediments receiving acid mine drainage. Applied and Environmental Microbiology 49: 179-186.

Jorgenson, B.B. 1978. A comparison of methods for the quantification of bacterial sulfate reductio in coastal marine sediments. I. Measurements with radiotracer techniques. Geomicrobiology Journal 1: 11-27.

Jeffers, T.H., personal commun., 1991

Manning, P.G., T.P. Murphy, and T. Mayer. 1988. Effect of copper sulfate on pyrite formation in reducing sediments. Canadian Mineralogist 26: 965-972.

Maree, J.P. and W.W. Strydom. 1987. Biological sulphate removal from industrial effluents in an upflow packed bed reactor. Water Research 21(2): 141-146.

McIntire, P.E., H.M. Edenborn, and R.W. Hammack. 1990. Incorporation of bacterial sulfate reduction into constructed wetlands for the treatment of acid and metal mine drainage. p. 207-213. In Proceedings of the 1990 National Symposium on Mining Knoxville, TN, May 14-18, 1990, 275 p.

Miller, L.P. 1950. Formation of metal sulfides through the activities of sulfate-reducing bacteria. Contributions from Boyce Thompson Institute for Plant Research 16: 85-89.

Postgate, J.R. 1984. The sulphate reducing bacteria. Cambridge University Press, New York, 2nd ed., 208 p.

Rossi, G. and H.L. Ehrlich. 1990. Other leaching processes. p. 149-170. In Microbial Mineral Recovery. Ed. by H.L. Ehrlich and C.L. Brierley. McGraw-Hill Publishing Company Co., New York, 454 p.

Streeter, R.C. 1970. Sulfide treatment of coal mine drainage. p. 152-168. In Third Symposium on Coal Mine Drainage Research, Pittsburgh, PA, May 19-20, 1970.

Tomizuka, N. and M. Yagisawa. 1978. Recovery of metals from a bacterial leaching solution with sulfate-reducing bacteria. p. 339-344. In Metallurgical applications of bacterial leaching and related microbiological phenomena. Ed. by L.E. Murr, A.E. Torma, and J.A. Brierley. Academic Press, New York, 526 p.

Ueki, K., K. Kotaka, K. Itoh, and A. Ueki. 1988. Potential availability of anaerobic treatment with digester slurry of animal waste for the reclamation of acid mine water containing sulfate and heavy metals. Journal of Fermentation Technology 66(1): 43-50.

Wakao, N., T. Takahashi, Y. Sakurai, and H. Shiota. 1979. The treatment of acid mine water using sulfate-reducing bacteria. Journal of Fermentation Technology 57(5): 445-452.

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TREATMENT OF METAL-CONTAMINATED WATER USING BACTERIAL SULFATE REDUCTION: RESULTS FROM PILOT-SCALE REACTORS[1]

by

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Abstract. Pilot-scale biological reactor systems were installed to treat metal-contaminated water in an underground coal mine and at a smelting residues dump in Pennsylvania. The reactors consisted of barrels and tanks filled with spent mushroom compost, within which bacterial sulfate reduction became established. Concentrations of Fe, Zn, Mn, Ni, and Cd were lowered by over 95% as these metals were precipitated in the reactors. The formation of insoluble metal sulfides by reaction with bacterially generated H_2S was identified as an important metal retaining process in the reactors. This paper examines the chemistry of the reactor systems and opportunities for enhancing their metal-retaining and alkalinity-generating potentials.

Additional keywords: anaerobic reactors, heavy metal sulfides, spent mushroom compost.

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Introduction

Bacterial sulfate reduction has been identified as a potentially valuable process for removing contaminant metals from coal and metal-mine drainage (Tuttle et al., 1969; Hedin et al., 1988; Wildeman and Laudon, 1989). Under anaerobic conditions, sulfate-reducing bacteria oxidize simple organic compounds with sulfate, and thereby generate hydrogen sulfide and bicarbonate ions:

$$SO_4^{-2} + 2 \text{ lactate} \rightarrow 2 \text{ acetate} + H_2S + 2HCO_3^- \quad (1).$$

Hydrogen sulfide reacts with many contaminant metals to form insoluble metal sulfides:

$$H_2S + M^{+2} \rightarrow MS + 2H^+ \quad (2),$$

where M includes metals such as Fe, Zn, Ni, Cd, Cu, and Pb. Bicarbonate ions can consume protons to raise the pH of acidic water:

$$HCO_3^- + H^+ \rightarrow CO_2 + H_2O \quad (3).$$

Hammack and Hedin (1989) and McIntire et al. (1990) experimented with simple water treatment reactors consisting of carboys and columns filled with organic matter in which sulfate reduction became established. Their reactors lowered iron, nickel, and manganese concentrations in synthetic mine drainage by 60 to 90%. These results led us to construct pilot-scale reactors of a similar design to evaluate their potential for treating metal-contaminated water. The design of these sulfate reduction reactors required:

1) exclusion of oxygen,

2) a source of sulfate (commonly present in contaminated water),

3) a source of simple organic compounds to serve as a bacterial carbon source, and

4) a means by which to physically retain the metal sulfide precipitates.

Low pH (<5) inhibits sulfate-reducing bacteria (Postgate, 1984) and increases the solubility of metal sulfides, which required that the reactors also be designed to generate sufficient alkalinity to raise the pH of acidic inflows.

In this paper we present our initial findings on the performance and chemistry of the pilot-scale reactors, and discuss some strategies for enhancing their performance.

Methods

Two pilot-scale reactor systems were constructed in 1990. The reactors in each system consist of either capped barrels (Pittsburgh system) or covered tanks (Palmerton system), filled with loosely-packed spent mushroom compost. Spent mushroom compost consists of a composted mixture of manure, hay, straw, corn cobs, and wood chips that has been conditioned with gypsum and limestone, and used for

cultivating mushrooms. Since it decomposes readily, the compost serves as a source of organic carbon for bacterial sulfate reduction, and its bulk form serves to physically detain any precipitated solids. The different mushroom composts we used in each system contained 50-60 wt% organic matter and 10-15 wt% pulverized limestone (dry wt basis).

The Pittsburgh reactor system was installed to treat acidic, iron-contaminated drainage within the Experimental Mine at the U.S. Bureau of Mines, Pittsburgh Research Center. This system consists of three 200 L reactor barrels plumbed in series and receiving water from a 1140 L supply tank (see Figure 1[a]). Barrels were used instead of a single large reactor because of height limitations within the coal mine. The underground location of this system maintained a nearly constant temperature of 10°C, permitting operation during the winter.

The Palmerton reactor system was installed to treat metal-contaminated drainage from a smelting residues dump at the former New Jersey Zinc Company plant in Palmerton, Pennsylvania. This system consists of 2 independent, 4,500 L reactor tanks receiving water from a 3,500 L supply tank (see Figure 1[b]). The data presented for this system were collected during summer operation, when average ambient temperature ranged between 18 and 24°C.

Table 1 shows the quantity of compost contained in each system and the mean flow rates and residence times at which each system was operated. As our primary objective was to evaluate the chemistry and water treatment potential of the reactor systems, we used residence times at which we expected significant metals removal to occur. In the Palmerton system, the flow rate through one reactor (reactor 2) was doubled after 10 weeks of operation to observe the effects of a shortened residence time.

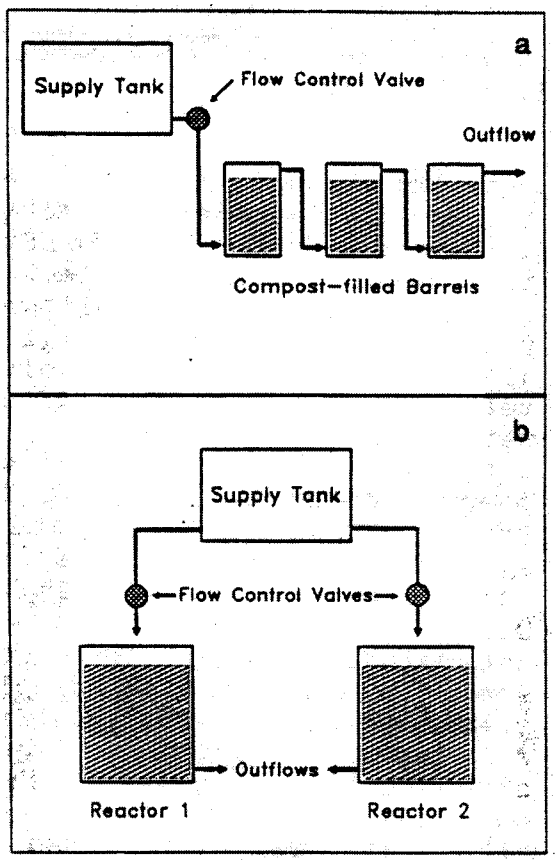

FIGURE 1

Figure 1. Schematics of the Pittsburgh (a) and Palmerton (b) Reactor Systems.

Water Sampling and Analysis

Influent, effluent, and occasional porewater samples

Table 1. Selected physical characteristics of reactor system design and operation

	Pittsburgh System	-- Palmerton System -- Reactor 1	Reactor 2
Volume of compost, L	624	3038	3038
Dry mass of compost, kg	68	572	572
Mean flow rate, ml/min	55	70	70/131[1]
Mean residence time, days	5	17	17/9[1]

Flow rate increased (residence time decreased) four weeks after the leaching phase.

were collected at 1-2 week intervals. Samples for metals analysis were acidified immediately upon collection (total metals) or following filtration through a 1.2 μm glass fiber filter (dissolved metals). Metal concentrations were determined using an ICP atomic emission spectrophotometer, except for Cd (atomic absorption spectrometry) and ferrous iron (titration with $K_2Cr_2O_7$). Dissolved sulfide was determined using an ion-specific electrode on samples preserved with NaOH. Sulfate was measured using a liquid chromatograph coupled with a conductivity detector, and alkalinity was determined by titration with 0.2 N H_2SO_4 to pH 4.5. Whenever possible, dissolved sulfide, alkalinity, and pH were determined on the same day the samples were collected.

Compost Sampling and Analysis

The spent mushroom compost used in each system was sampled before being placed in the reactors, and after 17-18 weeks of system operation. The 18-week samples from the Pittsburgh system were collected from depths of 10 cm and 60 cm in each of the 3 reactor barrels (maximum depth = 75 cm). The 17-week samples from the Palmerton system were collected from a depth of 60 cm (maximum depth = 135 cm) at 2 locations within each reactor. At each depth or location, a composite sample of 3-6 subsamples was collected by hand and immediately sealed in an argon-filled container.

The total content of inorganic cations and anions was determined by ashing subsamples in a muffle furnace at 550°C for 6 hours, and analyzing an HCl extract of the ash. A residual fraction consisting primarily of silica and clay minerals remained undissolved by this procedure. Calcium carbonate content was deduced from discrepancies in the mass and charge balances revealed by a comprehensive analysis of the ash extract. Sample moisture content was determined at 112°C.

The total iron content was expected to consist of a "fixed" fraction, tightly bound within organic matter and resistant clay minerals, and a "labile" fraction, occurring in forms, such as FeOOH, that are soluble under acidic and reducing conditions. Because of its potential solubility, the labile iron would be susceptible to leaching, and would be available for reaction with H_2S. The labile iron content of the compost samples from the Pittsburgh system was determined by extracting subsamples with 4 N HCl under an argon sparge, and analyzing the extract for iron.

A single subsample from the 10 cm depth in the first reactor barrel of the Pittsburgh system was examined by Mossbauer spectroscopy (Willard et al., 1974) to directly identify the iron minerals present.

Acid-volatile sulfide (AVS), present as monosulfides such as FeS and ZnS, and chromium-reducible sulfur (CRS), present as pyrite (FeS_2) and elemental sulfur, were determined by anoxic acid distillation (Cornwell and Morse, 1987). The H_2S was liberated with 6 N HCl, and trapped in 0.2 N NaOH.

Results

Following start-up, both systems underwent an initial phase during which Ca, Mg, Na, K, and sulfate ions were leached from the compost. By the time this phase was completed, effluent color had changed from dark brown to yellow; the effluent acquired a strong hydrogen sulfide odor; effluent concentrations of magnesium, sodium, and potassium had fallen to influent levels; and net sulfate consumption (reduction) and metal retention became discernible. The initial leaching phase was complete for the Pittsburgh system after 3.5 weeks of operation and 3940 L of flow, and for the Palmerton system after 6 weeks of operation and 4140 L of flow.

The results presented below pertain to system performance following the initial leaching phase. For the Pittsburgh system, a 14-week period involving 6110 L of flow is considered, and for the Palmerton system, a 16-week period involving 11,000 L (reactor 1) to 19,300 L (reactor 2) of flow is considered.

Changes in Water Chemistry

Mean influent and effluent water analysis results are shown for the Pittsburgh system in Table 2, and for the Palmerton system in Table 3. Both systems lowered contaminant metal concentrations by greater than 95%, lowered sulfate concentrations by about 30%, and produced circumneutral effluents having high alkalinity. The effluents from both systems contained high concentrations of dissolved sulfide (HS^- and H_2S), which, coupled with the lowering of sulfate concentrations, indicates that bacterial sulfate reduction was occurring.

Both systems continued to release calcium after leaching of the other base cations had

Table 2. Chemical analysis of influent and effluent water for the Pittsburgh reactor system.

	Influent		Effluent
pH	3.7		6.9
	------	mg/L	------
Alkalinity, as $CaCO_3$	17[1]		632
Total Fe	67		<0.2
Ferrous Fe	37		<0.2
Ferric Fe	10		nd
Suspended Fe	20		nd
Dissolved Al	7		<0.2
Ca	294		518
Sulfate	973		712
Dissolved sulfide	nd		34

Values are means of 8 influent and 11 effluent samples;
nd = not detectible;
[1] Alkalinity present only in samples with pH >4.5 (n=2).

Table 3. Chemical analysis of influent and effluent water for the Palmerton reactor system

	Influent		Effluent
pH	6.3		6.9
	------	mg/L	------
Alkalinity, as $CaCo_3$	17		1102
Zn	302		0.42
Mn	24		0.50
Ni	0.85		0.03
Cd	0.29		<0.005
Ca	275		720
Sulfate	2989		2352
Dissolved sulfide	nd		109

Values are means of 9 influent and 18 effluent samples;
nd = not detectible

ceased. Possible origins for this calcium include the dissolution of limestone (a constituent of the spent mushroom compost) and the decomposition of calcium-rich organic matter.

The Pittsburgh system consistently lowered aluminum concentrations to less than 0.2 mg/L. Since aluminum does not form a stable sulfide in the presence of water, this removal likely resulted from its hydrolysis to insoluble $Al(OH)_3$:

$$Al^{+3} + 3H_2O \rightarrow Al(OH)_3 + 3H^+ \quad (4).$$

This reaction is spontaneous at the circumneutral pH prevailing within the reactor barrels (Stumm and Morgan 1981). Ferric iron also hydrolyzes at circumneutral pH, but in the anaerobic environment within the barrels, it apparently was reduced to ferrous iron, which requires a much higher pH for hydrolysis. This reduction probably occurred in conjunction with the microbial oxidation of organic compounds ("CH_2O"):

$$4Fe^{+3} + CH_2O + H_2O \rightarrow 4Fe^{+2} + CO_2 + 4H^+ \quad (5).$$

Ferric iron was never detected in water that had passed beyond 7% of the total system volume, though ferrous iron concentrations usually remained high beyond that point. Also, suspended ferric oxyhydroxide (FeOOH) did not visibly accumulate in the inflow zone of the first reactor barrel, which suggests that influent FeOOH was similarly reduced and dissolved:

$$4FeOOH + CH_2O + 7CO_2 + H_2O \rightarrow 4Fe^{+2} + 8HCO_3^- \quad (6).$$

Analyses of pore water from the Pittsburgh system revealed that essentially all of the influent iron was removed by the first reactor barrel. Also, very little dissolved sulfide and alkalinity left the first barrel, thereby leaving the second and third reactor barrels to generate the high levels of dissolved sulfide and alkalinity observed in the system effluent.

Changes in Compost Composition

Table 4 shows the results of the analyses of Pittsburgh system compost. Total iron content for the second and third reactor barrels did not change significantly during the course of this study. This is consistent with the results of the water analyses, which detected very little iron leaching from the system, and which indicated that the influent iron was being removed entirely in the first barrel. Since little iron left the system, most of the original 63 μmoles of labile Fe/g compost was retained within the reactors.

Comparison of total iron contents indicates that the first reactor barrel accumulated 90 μmoles of Fe/g compost from the influent water. By adding this accumulated iron to the 63 μmoles/g of retained labile iron, a total retained iron content of 153 μmoles/g is

Table 4. Chemical analysis of the Pittsburgh system compost

	Before operation	----After 18 weeks---- Barrel 2-3	Barrel 1
	--------μmoles/g dry wt-------		
Total Fe	136	133	226
Labile Fe	63	nm[1]	nm[1]
AVS	<0.1	69	150
CRS	23	140[2]	140[2]
$CaCO_3$	999	708	547

Values are means of 4 to 12 samples;
[1] Not measured directly--probably equal to corresponding AVS;
[2] System average.

obtained. This closely matches the acid-volatile sulfide (AVS) content of 150 μmoles/g that was found in the first barrel, thus suggesting that iron was retained primarily as ferrous monosulfide (FeS). In agreement with this, Mossbauer spectroscopy identified FeS as the predominant iron form present.

Note that, despite the absence of net iron accumulation in the second and third reactor barrels, AVS still accumulated there, evidently due to the reaction of H_2S with the labile iron in those barrels.

Of the total accumulation of reduced sulfur (AVS and CRS) within the system, an average of 55% was accumulated in the chromium-reducible sulfur (CRS) fraction. Mossbauer spectroscopy failed to detect any pyrite (FeS_2) in the compost, which suggests that elemental sulfur was the CRS form accumulated.

During system operation, the limestone content in the compost decreased by 35% for the entire system, and by 45% in the first barrel. This decrease confirmed the hypothesis that limestone dissolution generated much of the system's net effluent calcium and alkalinity:

$$CaCO_3 + CO_2 + H_2O \rightarrow Ca^{+2} + 2HCO_3^- \qquad 7$$

Limestone dissolution was evident in the second and third reactor barrels, where pore-water pH was circumneutral, as well as in the first barrel, where pore-water pH was often lower. The mean rate of limestone dissolution for the system was 234 mg $CaCO_3$/L of flow.

Table 5. Chemical analysis of the Palmerton system compost

	Before operation	----After 17 weeks---- Reactor 1	Reactor 2
	--------μmoles/g dry wt-------		
Zn	26	308	545
Mn	6	38	25
Fe	98	109	87
AVS	<0.1	259	198
CRS	45	108	184

Values are means of 3 to 4 samples

Table 5 shows the results of the analyses of Palmerton system compost. Note that, in this system, accumulated AVS accounts for only 40-80 % of the retained metals. This indicates that some of the metals were being removed by processes such as hydrolysis, in addition to being precipitated as insoluble sulfides. Chromium-reducible sulfur comprised 29 - 48 % of the total reduced sulfur (CRS + AVS) accumulated by the Palmerton reactors.

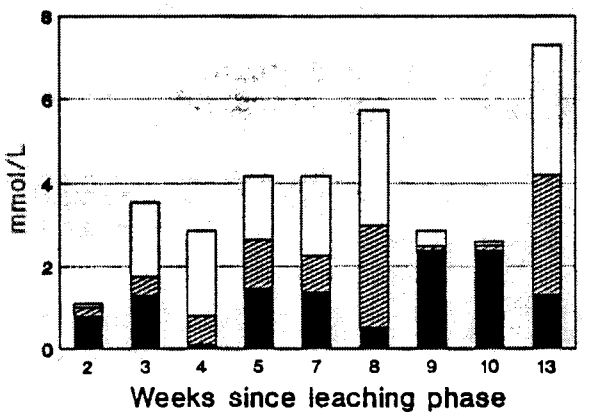

FIGURE 2

Figure 2. Sulfur budget for the Pittsburgh reactor system. Bar height represents total sulfate reduced, and is divided into portions accounted for by retained FeS (black), CRS (white), and effluent sulfide (shaded).

Sulfur Budget

The results of the water and compost analyses identified 3 sinks for the hydrogen sulfide produced by bacterial sulfate reduction: reaction with metal ions to form insoluble metal sulfides (AVS), conversion to CRS forms, and escape from the system in the effluent as unreacted sulfide. Figure 2 shows the mmol/L of sulfate reduced (total bar height) over time for the Pittsburgh system, divided according to the portions accounted for by iron accumulation, effluent sulfide, and CRS (by difference). All

Table 6. Average rates of sulfate reduction, metal retention, and AVS/CRS accumulation for the reactor systems.

Process	Mean Rate ($nmol/cm^3$ compost/day)	
--Pittsburgh system ----------	Entire System ----	First barrel
Sulfate reduction[1]	377	id
Total iron retention[2]	101	170
Retention of influent Fe	31	100
Retention of labile Fe	70	70
AVS accumulation[2]	107	167
CRS accumulation[2]	156	id
---Palmerton system ----------	Reactor 1 ----	Reactor 2
Sulfate reduction[1]	276	235
Zn, Mn, Ni, and Cd retention[1]	168	292

[1,2] Calculated from changes in water chemistry (1) or substrate composition (2); id = insufficient data.

of the sulfate removed from the influent water was assumed to have been reduced to H_2S. Since the influent iron was completely retained by the system, the bar segment representing iron retention also represents influent iron concentration. Note that, for weeks 4 and 8, when influent iron concentrations were less than 0.5 mmol/L (28 mg/L), over 4 times as much sulfide escaped in the effluent as was retained as FeS. In contrast, during weeks 9 and 10, when influent iron concentrations were around 2.4 mmol/L (134 mg/L), nearly all of the sulfur reduced was retained as FeS, and very little effluent sulfide escaped.

Table 6 shows the mean rates of sulfate reduction, metal retention, and AVS/CRS accumulation computed for the 2 reactor systems. The iron retention and AVS/CRS accumulation rates for the Pittsburgh system were computed using compost analysis data:

$$\frac{\text{nmol change in X}}{\text{g dry compost}} \times \frac{\text{g dry compost}}{\text{cm}^3\text{ moist compost}} \times \frac{1}{\text{days}} = \text{nmol/cm}^3\text{/day}$$

Compost analysis data were not used to compute rates for the Palmerton system because the compost sampling method was insufficiently representative.

The other rates were computed from water analysis data:

$$\frac{\text{nmol/L change in X}}{\text{cm}^3 \text{ compost in system}} \times \frac{\text{L of flow}}{\text{day}} = \text{nmol/cm}^3\text{/day}$$

The rates of AVS accumulation almost equal those of total Fe retention for the Pittsburgh system, as would be expected if FeS was being formed. Note that the sulfate reduction rate for the Pittsburgh system exceeds the sum of the AVS and CRS accumulation rates by 114 nmol/cm^3/day. This difference suggests an average effluent sulfide concentration of 37 mg/L, which is close to the measured average of 34 mg/L. By neglecting CRS formation, and similarly computing effluent sulfide from the Palmerton system rates, values of 104 and 0 mg/L sulfide are obtained for reactors 1 and 2, respectively. These concentrations are low in comparison with the measured averages of 149 (reactor 1) and 69 (reactor 2) mg/L. This indicates that more sulfide escaped the Palmerton system unreacted than the metal retention rates suggest, and further indicates that some of the metal removal observed in the Palmerton system occurred through processes other than sulfide precipitation.

Origins of Effluent Alkalinity

Both reactor systems produced effluents having high alkalinity. Equations 1, 2, and 4 - 7, describing the principal reactions consuming or producing alkalinity in the reactors, were used to derive the following equation for predicting effluent alkalinity (meq/L) from the absolute values of measured changes in the concentrations (mmol/L) of SO_4^{-2}, Ca^{+2}, FeOOH, M^{+2}, Al^{+3}, and Fe^{+3}:

$$\text{Alkalinity} = 2SO_4^{-2} + 2Ca^{+2} + 2FeOOH - 2M^{+2} - 3Al^{+3} - 1Fe^{+3} + \text{influent alkalinity} - \text{influent } H^+ \quad (8).$$

The derivation of equation 8 assumes that equations 1, 2, and 4 - 7 are the sole sources of alkalinity and acidity, and that the concentration changes observed for the indicator ions are induced solely by the reactions they indicate.

Figure 3 shows the alkalinity values computed using equation 8, along with the corresponding measured alkalinity values for the reactor system effluents. Correlation of the 2 sets of values gives an r^2 of 0.92 ($P < .01$; $n = 8$) for the Pittsburgh system, and 0.87 ($P < .01$; $n = 18$) for the Palmerton system. This agreement between the 2 sets of values supports the hypothesized origins of effluent alkalinity.

Sulfate reduction (equation 1) and limestone dissolution (equation 7) were the dominant sources of alkalinity for both systems. Of the total computed alkalinity generated by these 2 reactions combined, limestone dissolution contributed an average of 53% for the Pittsburgh system, 58% for Palmerton reactor 1, and 71% for Palmerton reactor 2.

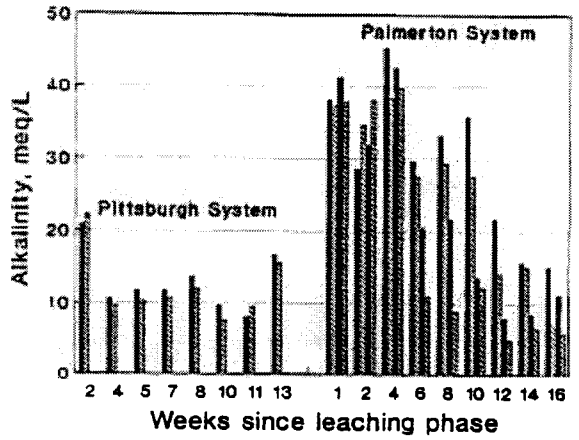

FIGURE 3

Figure 3. Alkalinity of effluents from the 2 reactor systems. Shaded bars depict measured values and solid bars depict computed values.

Discussion

The results presented in this paper confirm that contaminant metals can be precipitated as insoluble sulfides by reaction with biologically-generated hydrogen sulfide. Several strategies for enhancing the metal-retaining and alkalinity-generating effects are suggested by the results.

The maximum quantity of metal that can be precipitated in a sulfide form is dictated by the quantity of H_2S available for reaction. One means of enhancing metal retention, therefore, might be to increase the rate of bacterial sulfate reduction. McIntire et al (1990) found that when lactate, a preferred carbon source for sulfate-reducing bacteria, was added to the metal-contaminated water entering their reactors, sulfate reduction and metal retention increased. This suggests that the type or quantity of organic compounds released by the decomposing spent mushroom compost limits the rate of sulfate reduction. Thus, the rate might be increased by filling the reactors with a different organic material, or by supplementing the compost by adding organic compounds to the influent water. Since sulfate reduction is a microbial process, its rate might also be increased by raising reactor temperature.

Another means of enhancing reactor metal retention would be to modify reactor design or operation so that all of the H_2S produced reacts completely to form metal sulfides and none is lost as effluent sulfide or CRS. For the Pittsburgh system, an inverse relationship was found between influent iron and effluent sulfide concentrations. Similarly, pore-water sulfide concentrations were low where dissolved iron was still present, and high where dissolved iron was absent. These observations demonstrate that excess sulfide, destined for release in the effluent, can be exploited for metals removal, provided the system is fed metal ions at a sufficiently high rate. For metals that are relatively toxic to bacteria, such as cadmium and copper (Postgate 1984; McIntire et al,. 1990), the influent metal load might best be adjusted by modifying flow rate, whereas, for other metals, influent concentration could also be modified. No means can be suggested for exploiting the H_2S converted to CRS forms, since the pathway of this conversion is poorly understood.

If acidic water is to be treated, the reactors must generate net alkalinity to prevent the bacteria from being inhibited and metal sulfides from being dissolved. Limestone dissolution in the reactors generated slightly more alkalinity than did sulfate reduction. When the compost limestone content eventually becomes depleted, or in a reactor built without limestone, sulfate reduction would have to be relied upon as the principal alkalinity generator. Since metal sulfide formation (equation 2) consumes as many moles of alkalinity as are generated by sulfate reduction (equation 1), no net alkalinity will be gained from sulfate reduction if all of the H_2S produced is consumed for metal retention. Thus, sulfate reduction serves as an important alkalinity source only if some H_2S remains unreacted. In the Pittsburgh system, this tradeoff between alkalinity generation and H_2S consumption was observed directly, as most of the net alkalinity and excess H_2S accumulated in the second and third reactor barrels in the absence of iron removal.

This study demonstrates that sulfate reduction reactors of the simple design investigated here are capable of removing Fe, Zn, Mn, Ni, and Cd from contaminated water. Without modifying reactor design, metal retention rates can be increased by providing influent metal loads sufficiently large to completely consume the H_2S generated. The theoretical maximum metal retention rate will equal the sulfate reduction rate. If acidic water is being treated, the reactor interior must be protected from acidification, either by incorporating limestone into the organic substrate, or by operating the reactors at a lower metal retention rate such that H_2S is produced in excess of the amount that will be consumed by metal sulfide formation. Higher rates of metal retention could also be attained by modifying reactor design to encourage higher rates of bacterial sulfate reduction.

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References

Cornwell, J. C. and J. M. Morse. 1987. Characterization of iron sulfide minerals in anoxic marine sediments. Marine Chemistry, Vol. 22, pp. 193-206.

Hammack, R. W. and R. S. Hedin. 1989. Microbial sulfate reduction for the treatment of acid mine drainage: a laboratory study. In: Proceedings, Ninth Annual West Virginia Surface Mine Drainage Task Force Symposium, April 25-26, 1989, Morgantown, WV.

Hedin, R. S., R. W. Hammack, and D. M. Hyman. 1989. Potential importance of sulfate reduction processes in wetlands constructed to treat mine drainage. In: Constructed Wetlands for Wastewater Treatment, D. A. Hammer (ed.), Lewis Publishers, Chelsea, MD, pp. 508-514.

McIntire, P. E., H. M. Edenborn, and R. W. Hammack. 1990. Incorporation of bacterial sulfate reduction into constructed wetlands for the treatment of acid and metal mine drainage. In: Proceedings, The 1990 National Symposium On Mining, May 14-18, 1990, Knoxville, TN. pp. 207-213.

Postgate, J. R. 1984. The Sulphate-reducing Bacteria. Cambridge University Press, New York, NY, 208 p.

Stumm, W., and J. J. Morgan. 1981. Aquatic Chemistry, Second Edition. John Wiley & Sons, New York, NY, 780 p.

Tuttle, J. H., P. R. Dugan, and C. I. Randles. 1969. Microbial sulfate reduction and its potential utility as an acid mine water pollution abatement procedure. Applied Microbiology, Vol. 17, No. 2, pp. 297-302.

Wildeman, T. R. and L. S. Laudon. 1989. The use of wetlands for treatment of environmental problems in mining: non-coal mining applications. In: Constructed Wetlands for Wastewater Treatment, D. A. Hammer (ed.), Lewis Publishers, Ann Arbor, MI, pp. 221-231.

Willard, H. H., L. L. Merritt, and J. A. Dean. 1974. Instrumental Methods of Analysis. D. Van Nostrand Company, New York, NY, 860 p.

THE USE OF BENCH SCALE PERMEAMETERS FOR PRELIMINARY OF METAL REMOVAL FROM ACID MINE DRAINAGE BY WETLANDS[1]

by

Judith L. Bolis, Thomas R. Wildeman, and Ronald R. Cohen[2]

Abstract. Water drainage from abandoned mines in the Central City-Idaho Springs mining district has impacted the water quality of Colorado front-range water systems. To determine metal removal from mine drainage, permeameters with a high-alkalinity organic substrate were designed to operate in downflow and upflow configurations. Mine drainage from the National and Quartz Hill Tunnels were used in the permeameter testing. Initial flow rates were 10 mL/min and 1 mL/min for the National and Quartz Hill Tunnel drainages, respectively. Both drainages were tested in 3 parallel cells under varying initial conditions. One cell was initially dry, 1 was soaked with water for 1 week to attain anaerobic conditions, and 1 was soaked with water for 1 week and inoculated with established wetland substrate containing sulfate-reducing bacteria. Results indicate an increase of water pH from 5.6 to 7.7 and 2.5 to 7.4 at National and Quartz Hill Tunnels, respectively. Metal removal occurred within all cells for both drainages. The National Tunnel drainage contains metal levels of approximately 42 ppm Fe, 19 ppm Mn, 1 ppm Cu, and 7 ppm Zn. Removal of metals was over 95 %. The Quartz Hill Tunnel drainage contains metal levels of approximately 700 ppm Fe, 80 ppm Mn, 60 ppm Cu, and 140 ppm Zn. Results showed metal removal of over 99 %. Loading rates ranged from 2.1 to 3.8 grams per day per square meter (gdm^2) for the National Tunnel and 4.2 to 6.3 gdm^2 for the Quartz Hill Tunnel. Results indicate that bench scale permeameters can be used to evaluate metal removal from mine drainage and to attain design criteria for larger scale wetlands.

Additional Key Words: acid mine drainage, constructed wetland, wetland design, heavy metals remediation

Introduction

In the design of a wetland treatment system for mine drainage, various stages of experimentation can be performed to determine design criteria (Reynolds 1991). Lab analysis of microorganism activity has been successful for studying wetland treatment at the Big Five Tunnel mine drainage in Idaho Springs (Batal 1989, Machemer 1990, Reynolds 1991, Wildeman & Laudon, 1989). Bench scale permeameters were used to evaluate the hydraulic conductivity of specific substrates at the Big Five wetland and were found to be predictive of pilot scale operations (Lemke 1989). From evaluation of metal removal data, loading rates can be determined which provide design criteria for a treatment system (Hedin 1990, Wildeman 1990, Reynolds, 1991).

To evaluate mine drainages in the Central City-Blackhawk area, a part of the Idaho Springs-Central City Superfund area, bench scale permeameters were designed to evaluate metal removals, change in pH,

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system configuration, initial substrate conditions, and substrate loading rates.

The drainages chosen for analysis flowed from the National Tunnel and the Quartz Hill Tunnel. Both represent 2 completely different types of mine drainage in the Central City district (Wildeman 1974). Characteristics of the National Tunnel drainage are a slightly acidic pH of 5.6 and metal concentrations similar to that of the Big Five tunnel. Preliminary metal concentrations for iron, manganese, copper, and zinc were 42, 19, 0.18, and 7 ppm, respectively. Due to the pH, a significant problem with precipitation of iron hydroxide exists. The Quartz Hill Tunnel drainage represents the extremes of acid mine drainage for the area. The pH ranges from 2.3 to 2.7, while metal concentrations are comparatively high. The preliminary metal concentrations for iron, manganese, copper and zinc were 920, 63, 77, and 91 ppm, respectively.

The objectives were: 1) to evaluate metal removal efficiencies and the change in pH over time, 2) to evaluate an upflow configuration compared to a downflow configuration, 3) to evaluate the system by varying initial substrate conditions, and 4) to determine loading rates.

Materials and Methods

The permeameters for this study were constructed of 32 gallon plastic garbage cans fitted with PVC pipe and designed to operate without valve control in both upflow and downflow configurations. Flowrates were adjusted by raising or lowering the output level. Consideration was made for iron hydroxide clogging, adjustability of flowrates, and limited maintenance. Figure 1 is a diagram of the permeameters in the downflow configuration. Further details of the design and operation of this experiment are described in a report by Bolis and Wildeman (1990).

The permeameters for evaluation of the National Tunnel and Quartz Hill Tunnel mine drainages were setup in the field and in the lab, respectively. At each site, 3 downflow permeameters were setup and designated as Cell A, Cell B, and Cell C. Cell A contained the standard substrate and was considered to be a dry cell. This cell was not soaked or inoculated. Cell B contained the standard substrate and was soaked with city water for 1 week prior to operation. Cell C, which contained the standard substrate, was soaked for one week prior to operation, and was inoculated with substrate containing sulfate reducing bacteria from the Big Five constructed wetland (Batal 1989).

Previously, mushroom compost had been utilized as substrate at the Big Five constructed wetland (Batal 1989). After titrating the mixture with HCl, it was concluded that it may not provide sufficient buffering capacity for both mine drainages. The permeameter substrate selected was composed of cow manure and planter soil in a 3:1 ratio to provide a soil pH of approximately 8.7.

The permeameters at the National Tunnel were located near the adit with a PVC pipe running mine drainage to the system. A trough system was designed to feed mine drainage into each permeameter with both the trough and permeameters having an overflow system. Water was hauled from the Quartz Hill Tunnel site to the lab in 50 liter carboys. Each cell had an individual reservoir for mine drainage and an overflow system. Each permeameter had at least 1 inch depth of standing water on top of the substrate at all times.

Operation of both sites began in June 1990 and continued through October 1990. Cell A was changed from a downflow configuration to an upflow configuration at the end of 2-months operation at both sites. Fresh inoculated substrate was added to the permeameter and the flow direction was reversed and operated for approximately 2 months. At both sites, it was necessary to make regular checks on the system to adjust the permeameter flowrates, check the mine drainage, and rid the system of any iron hydroxide clogging.

The permeameters were operated at approximately 10 mL/min for National Tunnel and 1 mL/min for Quartz Hill Tunnel. The flowrates of the permeameters were determined by evaluating metal removal rates of the Big Five pilot treatment system in Idaho Springs, CO. The Big Five wetland operates at about 1/8 gpm/100 ft^2 and has shown to remove metals effectively (Wildeman 1990).

The heavy-metal concentration of the National Tunnel is approximately equal to that of the Big Five Tunnel. Table 1 shows a total of Fe, Mn, Cu, and Zn to be between 80 and 90 ppm for both drainages. Therefore, utilizing an effective flowrate of 1/8 gpm/100 ft^2, and a surface area of 0.204 m^2 for the permeameter, a new flowrate was calculated. The flowrate for the National Tunnel was determined to be approximately 10.0 mL/min.

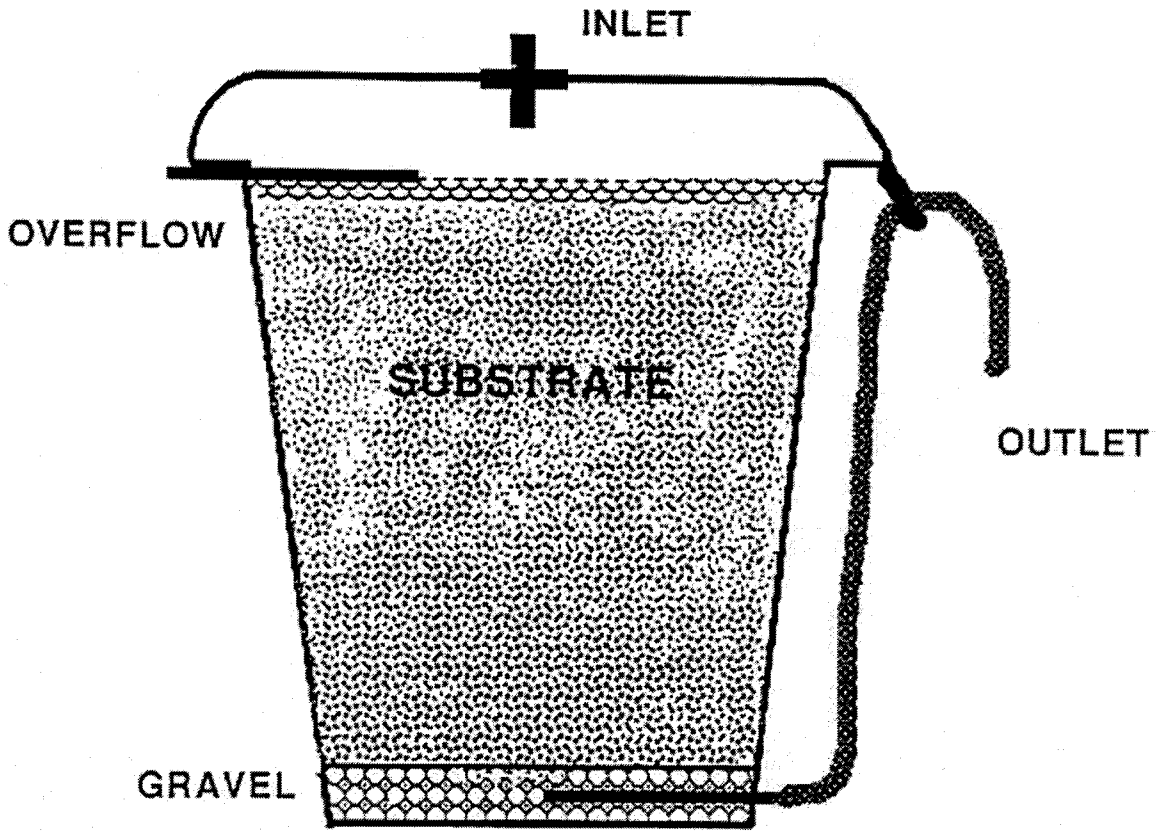


Figure 1. Typical bench scale wetland module in downflow configuration.

Table 1. Concentrations of Metals in Mine Drainage (ppm)

	Big Five	National Tunnel		Quartz Hill Tunnel	
	June, 1990	June, 1973	June, 1990	June, 1973	June, 1990
Eh	700	450	420	450	720
pH	3.0	4.6	5.8	2.6	2.7
Fe	50	50	42	820	920
Mn	32	28	19	80	63
Cu	0.9	1.4	.18	70	77
Zn	10	11	7	130	91

Similarly, the Quartz Hill Tunnel heavy-metal concentration is about 1060 mg/L as shown in Table 1. By comparing these concentrations with those of the Big Five and National Tunnel, the flowrate was reduced by a factor of 10. Therefore, a flowrate of 1 mL/min was selected for Quartz Hill permeameters.

Water sampling and field measurements were done on a weekly basis for the first 10 weeks of the experiment. The schedule was changed to bimonthly sampling when Cell A was changed to the upflow configuration. During sampling, water was filtered and treated with HNO_3. Duplicates of both the mine drainage and the cell outputs were taken on a regular basis. The results of the duplicates were averaged with the original sample for reporting. The Quartz Hill Tunnel mine drainage was sampled in the field and in the lab. There were no significant changes in the measurements of the metal concentrations. These values were averaged for data reporting.

The metal analyses for this project were done by flame atomic absorption and sulfate determinations were made gravimetrically by precipitation of $BaSO_4$.

Results

Tables 2 and 3 show the concentrations of mine drainage influent and permeameter effluent for the National and Quartz Hill Tunnels, respectively. Included in these tables are the percentages of the decrease in the metal concentrations for each permeameter relative to the mine drainage. Also included are the sulfate concentrations, pH's, and the effluent flowrates of each permeameter.

From the metal removal data in Tables 2 and 3, area-adjusted loading rates can be determined (Hedin 1990). Table 4 shows the area-adjusted removal rates for the National Tunnel and Quartz Hill Tunnel mine drainages. Ranges and averages are provided for both iron concentration and total metal concentrations in grams per day per square meter (gdm^2). The following calculation is performed to determine the loading rates (Hedin 1990):

$$\text{Rate} = ([M_{md}] - [M_{cell}])(Q)(CF)/A$$

where:

[M]	=	concentration of metal
md	=	mine drainage
cell	=	permeameter cell effluent
Q	=	flow rate of mine drainage into permeameter
CF	=	conversion factor of 1440 min/day
A	=	area of permeameter = 0.204 m^2

As shown in Table 4, the metal removal rates for the National Tunnel range from 3.0 to 6.0 gdm^2 with an average of 4.3 gdm^2. The average flow for the National Tunnel permeameters was 10 mL/min. The metal removal rates for the Quartz Hill Tunnel range from 5.4 to 8.5 gdm^2 with an average of 6.7 gdm^2. The average flow for the Quartz Hill Tunnel permeameters was 1 mL/min.

Discussion

The pH of the mine drainage and cell output for the National and Quartz Hill Tunnels are shown in Figure 2 for the 19-weeks of experimentation. The pH of the National Tunnel permeameter effluents parallel the fluctuations of the mine drainage from 5.2 to 5.8. The effluent pH's are maintained between 7.0 and 8.0 during the initial 4 weeks of experimentation. However, as the National flowrates cells were varied after week 6, to 2- and 3-times the original flow of 10 mL/min, the pH's show an overall decrease. Between weeks 9 and 13, Cell A was changed from downflow to upflow configuration and the cell maintained a higher pH for about 4-weeks.

For the Quartz Hill Tunnel, as the mine drainage pH fluctuated from 2.3 to 2.8, the permeameter effluent pH ranged from 6.2 to 8.2. An overall decline in pH occurred during the 19 weeks from around 8.0 to 6.5. In later weeks, the flowrate for Cells B and C, was increased from the established rate of 1 mL/min to 2-3 mL/min. After Cell A was changed from a downflow to upflow configuration in week 13, the effluent pH was approximately the same as Cells B and C.

By comparing the pH fluctuations at both sites, the start-up conditions of dry, soaking with water and inoculation show minor variation. Also, comparing the pH change in the upflow and downflow configurations show few differences.

The comparison of iron concentrations in the mine drainage and permeameter effluent for the National Tunnel and Quartz Hill Tunnel is shown in Figure 3. Cells B and C of National Tunnel had a slower start-up removal rate of about 5 to 7 weeks than Cell A. However, in week 13, as Cell A was changed to an upflow configuration, the removal was similar to Cells B and C in weeks 1-6. Note that the upflow Cell A was inoculated while downflow Cell A was not, perhaps indicating that the inoculin impedes immediate iron

Table 2. National Tunnel concentrations of mine drainage and permeameter output in mg/L, flowrate in mL/min.

	Cu	% dec.	Fe	% dec.	Mn	% dec.	Zn	% dec.	SO_4^{2-}	pH	flow rate
Week 1											
MD	.45		50.3		20.5		8.8		938	5.7	
Cell A	--		--		--		--		--	--	
Cell B	.3	33.3	4.7	90.6	1.1	94.6	.6	93.2	3260	7.4	
Cell C	.2	55.5	13.9	72.4	1.6	92.2	.4	95.5	1200	7.0	
Week 2											
MD	.2		40.9		20.3		8.2		899	5.2	
Cell A	.05	97.5	.8	98.0	.9	95.6	.05	99.4	871	7.2	38
Cell B	.2	--	18.8	54.0	1.5	92.6	.5	93.9	825	7.3	7.5
Cell C	.05	75.0	5.9	85.6	1.4	93.1	.2	97.6	462	7.0	7.5
Week 3											
MD	.3		44.0		20.3		8.5		935	5.4	
Cell A	.05	98.3	2.1	95.3	11.0	45.8	0.5	94.1	906	6.6	25
Cell B	.08	73.3	14.7	66.6	1.6	92.1	.3	96.5	341	7.5	10
Cell C	.05	98.3	4.3	90.2	1.9	90.6	.2	97.6	86	7.7	2
Week 4											
MD	.2		39.3		20.8		8.5		926	5.9	
Cell A	.05	75	2.6	93.4	12.4	40.4	.05	99.4	871	7.7	30
Cell B	.05	75	11.1	71.8	1.6	92.3	.2	97.6	197	7.7	15
Cell C	.05	75	2.5	93.6	1.3	93.8	.08	99.1	106	7.7	
Week 5											
MD	.4		42.5		21.6		8.4		947	5.5	
Cell A	.05	87.5	2.4	94.4	14.0	35.2	.08	99.0	687	7.4	22
Cell B	.07	82.5	7.4	82.6	1.3	94.0	.2	97.6	47	7.3	1
Cell C	--		--		--		--		--	--	
Week 6											
MD	.3		41.4		21.0		8.4		936	5.6	
Cell A	.05	83.3	1.4	96.6	17.0	19.0	.07	99.2	778	6.7	25
Cell B	.05	83.3	3.6	91.3	.7	96.7	.1	98.8	417	7.3	15
Cell C	.05	83.3	.7	98.3	1.9	91.0	.06	99.3	710	6.8	1
Week 7											
MD	.3		41.6		19.0		8.0		936	5.4	
Cell A	.05	83.3	2.2	94.7	14.1	25.8	.06	99.2	738	7.1	15
Cell B	.07	76.7	2.1	95.0	.8	85.8	.1	98.8	272	7.0	9
Cell C	.05	83.3	.6	98.6	1.8	90.5	.04	99.5	804	7.0	5
Week 9											
MD	.2		34.1		20.0		8.4		--	5.5	
Cell A	.05	97.5	2.0	94.1	18.5	7.5	.1	98.8	--	6.7	19
Cell B	.05	97.5	1.3	96.2	8.7	56.5	.05	99.4	--	7.0	38
Cell C	.05	97.5	1.2	96.5	7.9	60.5	.05	99.4	--	6.4	24

Table 2. (continued) National Tunnel concentrations of mine drainage and permeameter output in mg/L, flowrate in mL/min.

	Cu	% dec.	Fe	% dec.	Mn	% dec.	Zn	% dec.	SO_4^{2-}	pH	flow rate
Week 11											
MD	.2		39.9		21.8		8.9		995	5.3	
Cell A	--		--		--		--		--	--	
Cell B	.07	65	1.5	96.2	17.2	21.1	.1	98.9	941	6.6	130
Cell C	.05	75	.1	99.7	13.7	37.2	.01	99.9	873	6.5	35
Week 13											
MD	.2		41.9		22.8		9.1		772	5.8	
Cell A	.05	75	7.4	82.3	1.5	93.4	.5	94.5	1317	7.5	12
Cell B	.07	65	.2	99.5	16.0	29.8	.07	99.2	923	6.7	
Cell C	.05	75	.1	99.8	17.8	21.9	.2	97.8	908	6.7	20
Week 15											
MD	.1		42.3		23.1		7.9		860	5.4	
Cell A	.08	20	5.5	87	.3	98.7	.3	96.2	664	7.4	7
Cell B	.05	50	--		--	--	.3	96.2	--	6.3	30
Cell C	.05	50	.3	99.3	13.1	43.3	.01	99.9	507	6.4	26
Week 17											
MD	.1		54.8		24.8		9.5		1027	5.5	
Cell A	.3	--	2.9	94.7	.4	98.4	.1	98.9	752	6.9	9
Cell B	.05	50	1.5	97.3	18.6	25	.07	99.3	929	6.3	24
Cell C	.05	50	.3	99.5	13.1	47.2	.01	99.9	507	6.4	30
Week 19											
MD	.08		49.2		24.4		9.0		1010	5.2	
Cell A	.05	62.5	2.9	94.1	2.6	89.3	.4	95.5	1001	6.2	43
Cell B	.05	62.5	.05	99.9	3.4	86.1	.05	99.4	--	6.2	42
Cell C	.05	62.5	.2	99.6	18.8	23.0	.04	99.6	922	6.5	24

Table 3. Quartz Hill concentrations of mine drainage and permeameter output in mg/L, flowrate in mL/min.

	Cu	% dec.	Fe	% dec.	Mn	% dec.	Zn	% dec.	SO_4^{2-}	pH	flow rate
Week 1											
MD	55.7		672		82.5		136.2		4340	2.7	
Cell A	--		--		--		--		--	--	
Cell B	.3	99.5	7.6	98.9	1.5	98.2	.5	99.6	2410	6.9	[illegible]
Cell C	.2	99.6	15.3	97.7	2.9	96.5	.4	99.7	1300	6.5	
Week 2											
MD	56.2		666		84.2		141.6		4380	2.6	
Cell A	.4	99.3	8.7	98.7	1.4	98.3	.9	99.4	515	8.6	.9
Cell B	.3	99.5	6.8	99.0	1.7	98.0	.6	99.6	188	7.9	.7
Cell C	.1	99.8	4.8	99.3	1.7	98.0	.2	99.9	109	8.2	.7
Week 3											
MD	56.2		680		84.9		143.2		4300	2.6	
Cell A	.3	99.5	2.6	99.6	1.5	98.2	.6	99.6	280	7.5	1.0
Cell B	.12	99.8	4.5	99.3	1.4	98.4	.3	99.8	520	7.4	1.4
Cell C	.05	99.9	3.8	99.4	1.4	98.4	.1	99.9	237	7.3	1.2
Week 4											
MD	47.5		636		79.4		132.6		4190	2.4	
Cell A	.06	99.9	1.6	99.7	.9	98.9	.3	99.8	450	7.4	1
Cell B	.05	99.9	1.9	99.7	.9	98.9	.2	99.8	773	7.5	1.1
Cell C	.05	99.9	1.0	99.8	1.0	98.7	.2	99.8	412	7.4	.8
Week 5											
MD	54		681		78.2		138.0		4280	2.3	
Cell A	.05	99.9	1.2	99.8	.7	99.1	.2	99.9	640	7.5	.6
Cell B	.05	99.9	1.3	99.8	.7	99.1	.2	99.9	812	7.3	.9
Cell C	.05	99.9	.8	99.9	.8	99.0	.2	99.9	306	7.3	.3
Week 7											
MD	48.4		626		78.2		133.3		4300	2.5	
Cell A	.05	99.9	.9	99.9	1.0	98.8	.2	99.9	1080	7.2	1
Cell B	.05	99.9	1.0	99.8	.6	99.2	.2	99.8	660	7.4	.9
Cell C	.05	99.9	.5	99.9	1.6	98.0	.1	99.9	1180	7.2	.9
Week 9											
MD	55.2		628		78.8		160		3800	2.7	
Cell A	.05	99.9	.46	99.9	1.5	98.1	7.4	95.4	1312	7.1	1.3
Cell B	.05	99.9	.43	99.9	.5	99.4	9.1	94.3	995	7.3	1.4
Cell C	.05	99.9	.3	99.9	3.5	95.5	5.2	96.8	1332	6.9	1.4
Week 11											
MD	69.8		806		70.5		101.5		3992	2.9	
Cell A	--		--		--		--		--		
Cell B	.05	99.9	--		.5	99.3	.2	99.8	1067	8.0	.6
Cell C	.05	99.9	--		1.6	97.7	.3	99.7	556	7.9	.7

Table 3. (continued) Quartz Hill concentrations of mine drainage and permeameter output in mg/L, flowrate in mL/min.

	Cu	% dec.	Fe	% dec.	Mn	% dec.	Zn	% dec.	SO_4^{2-}	pH	flow rate
Week 13											
MD	63.5		900.5		82.1		167.9		3829	2.6	
Cell A	.08	99.9	3.0	99.7	.9	98.9	.5	99.7	732	7.5	.4
Cell B	.05	99.9	.3	99.9	1.4	98.3	.2	99.9	1006	7.3	.5
Cell C	.05	99.9	.3	99.9	3.7	95.5	.2	99.9	725	7.2	.6
Week 15											
MD	57.1		692		76.8		159.1		3090	2.5	
Cell A	.4	99.3	3	99.6	.9	98.8	.5	99.7	1777	7.7	.9
Cell B	.05	99.9	.1	99.9	8.5	88.9	.2	99.9	2842	7.0	1.5
Cell C	.05	99.9	.1	99.9	15.7	79.6	.1	99.9	2929	6.8	1.7
Week 17											
MD	54.4		702.9		79.7		177.4		4027	2.5	
Cell A	.04	99.9	1.8	99.7	.6	99.2	.4	99.8	2207	7.7	.7
Cell B	.05	99.9	3.3	99.5	22.0	72.4	.2	99.9	3342	6.6	2.4
Cell C	.24	99.6			--		.1	99.9	3089	6.4	2.9
Week 19											
MD	59		633.8		95.9		190		3438	2.3	
Cell A	.26	99.6	1.6	99.7	1.2	98.7	.1	99.9	3430	7.1	1.2
Cell B	.6	98.9	119.2	82.2	58.9	38.6	.1	99.9	3574	6.4	2.1
Cell C	.8	98.6	38.5	93.9	50.5	47.4	.1	99.9	3340	6.4	1.5

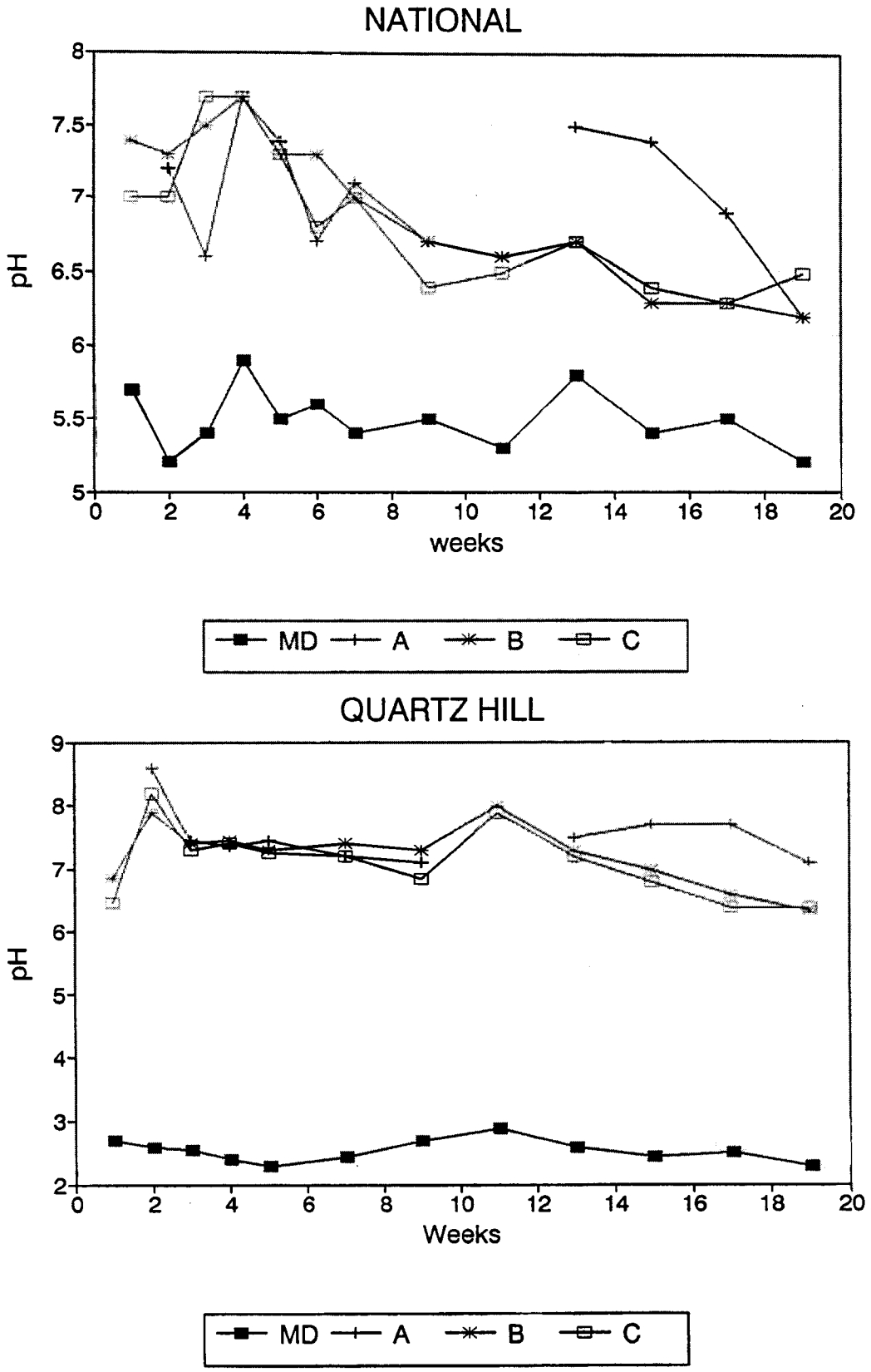
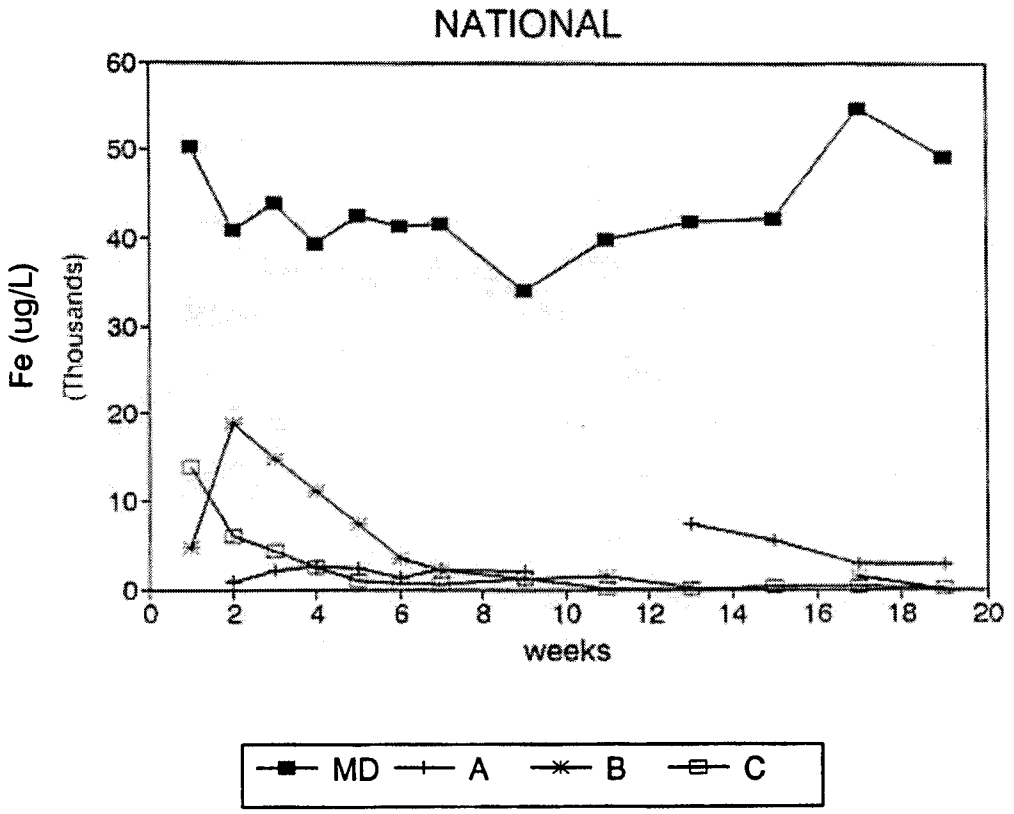


Figure 2. pH of mine drainage and permeameter effluents for National Tunnel and Quartz Hill Tunnel.



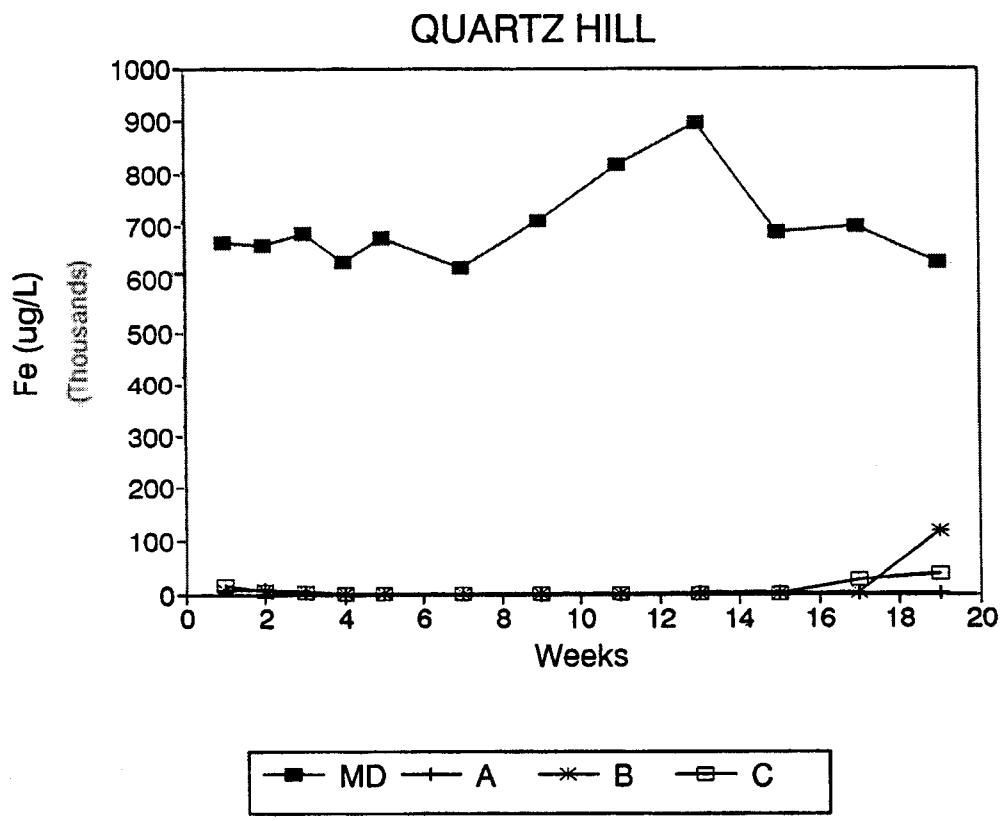


Figure 3. Iron content of mine drainage and permeameter effluents for National Tunnel and Quartz Hill Tunnel.

removal. However, the inoculated and soaked permeameters are expected to work better. This difference in removal may be due to the National Tunnel permeameters being on-site in the field. During the first 4-weeks, flows were found to be quite variable and the removal may have been affected.

Quartz Hill Tunnel iron-removal data shows nearly 100 % removal of iron from all 3 cells during the experimentation. Variations of the flowrate of 1 mL/min showed no apparent effect on the removal of iron. Again, no significant changes are shown by varying substrate conditions and direction of flow. The consistency of this removal pattern, compared with the removal of iron from the National Tunnel permeameters, may be due to the experiments being run in the laboratory and the flows were monitored daily for the first 4 weeks.

Figure 4 shows a comparison of the removal of manganese for the field experiment at the National Tunnel and the lab experiment for the Quartz Hill Tunnel. As the other figures have illustrated, the fluctuations of metal removal in the field are much greater than the lab experiment. For Cells B and C, the removal of manganese from the National Tunnel water was high in the first 7 weeks of the experiment, while it was poor from Cell A. This may be attributed to the variation in the flowrate of Cell A early in the experiment. After week 7, the decrease in the removal of manganese from Cells B and C may be due to the increased flowrate of the system. Note that in week 13, the upflow configured Cell A shows high removal of manganese. The reason for manganese variability in the National Tunnel permeameters is uncertain. However, Machemer and Wildeman (1991) found that Mn can be removed by adsorption onto the substrate in the early stages of wetland operation. After about 8 weeks, when the substrate sites are saturated, Mn concentration in the effluent increases.

Manganese removal for Quartz Hill Tunnel mine drainage was much more consistent. It averaged over 95 % until week 13 when Cells B and C show an apparent decrease. This is best attributed to the increase in permeameter flowrate, which causes a drop in effluent pH, or to the sorption site being saturated by Mn. The change of Cell A to an upflow configuration shows consistent manganese removal for the remaining 6 weeks. Again, this cell was soaked and inoculated and can be compared with Cell C.

For other heavy metals, the National Tunnel permeameter effluent data indicate nearly 4 weeks is needed to attain a less-than detection limit for copper as shown in Tables 2 and 3. The copper removal tended to vary with the amount of copper in the mine drainage. Despite fluctuations in the Quartz Hill Tunnel mine drainage, copper removal was near 100% for the entire 19 weeks. Zinc removal from both mine drainages was very effective, as shown in Tables 2 and 3. The data show no apparent differences between the dry, soaked, and inoculated cells, as well as between the upflow and the downflow configurations.

Summary

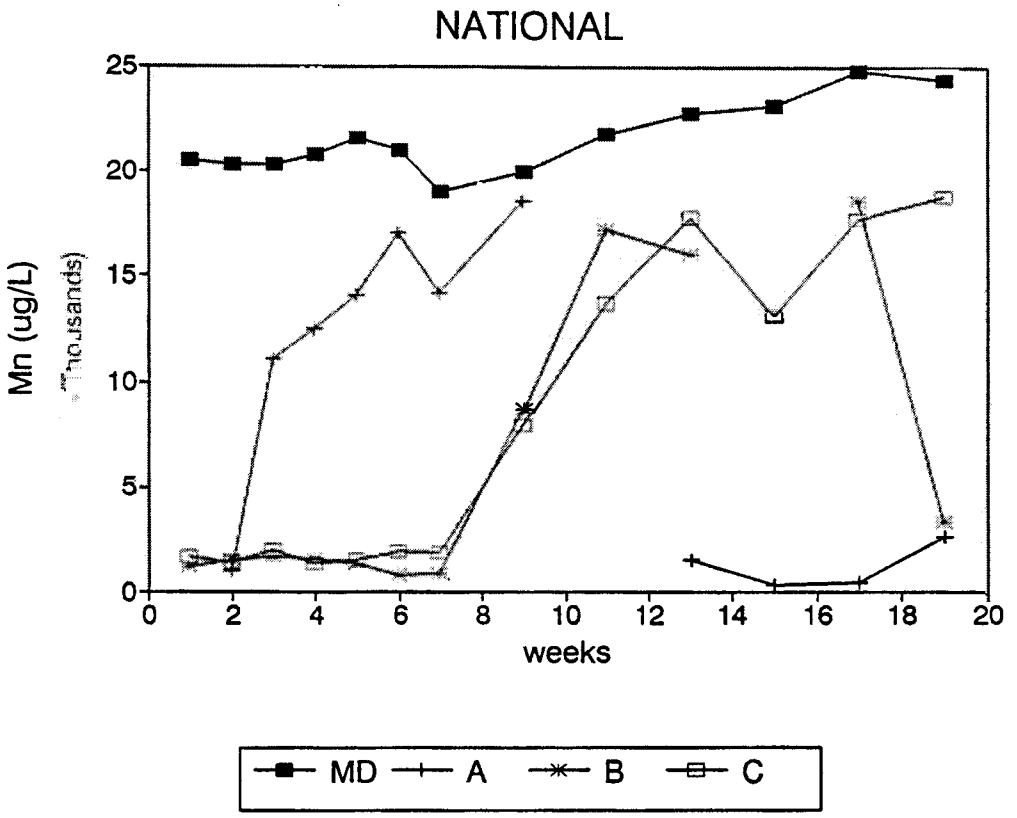
The conditions of the lab were much more favorable than the field for testing due to weather and maintenance problems. The variation in the soaked and inoculated substrate may only be apparent in the iron and manganese removals of the National Tunnel mine drainage. The dry substrate initiated high iron removal immediately, while the soaked and inoculated substrate initiated manganese removal immediately. Both the upflow and downflow configurations showed equally effective removal of metals and increase in pH.

As shown with both drainages, an increase in the flowrate will cause a decrease in the overall pH of the effluent. Total metal removal of Quartz Hill Tunnel mine drainage was not as sensitive to the flowrate change as the National Tunnel mine drainage. Removal of copper, iron, manganese, and zinc from the mine drainages was nearly 100 % throughout the experiment. The exception was manganese removal, which declined in the last 8 weeks. Declines in manganese removal may be explained by an increase in flowrate, decline in pH, and overloading of the system. The flowrates of 10 mL/min for National Tunnel and 1 mL/min for Quartz Hill Tunnel were sufficient to insure an increase in pH and attain a high metal removal.

Finally, loading rates of the substrate were determined. Metal removal rates for the National Tunnel permeameters range from 3.0 to 6.0 gdm^2, with an average of 4.3 gdm^2. The Quartz Hill Tunnel permeameter metal removal rates range from 5.4 to 8.5 gdm^2, with an average of 6.7 gdm^2.

Acknowledgements

The authors would like to acknowledge Camp Dresser & Mckee who funded this project, specifically Susan Morea.



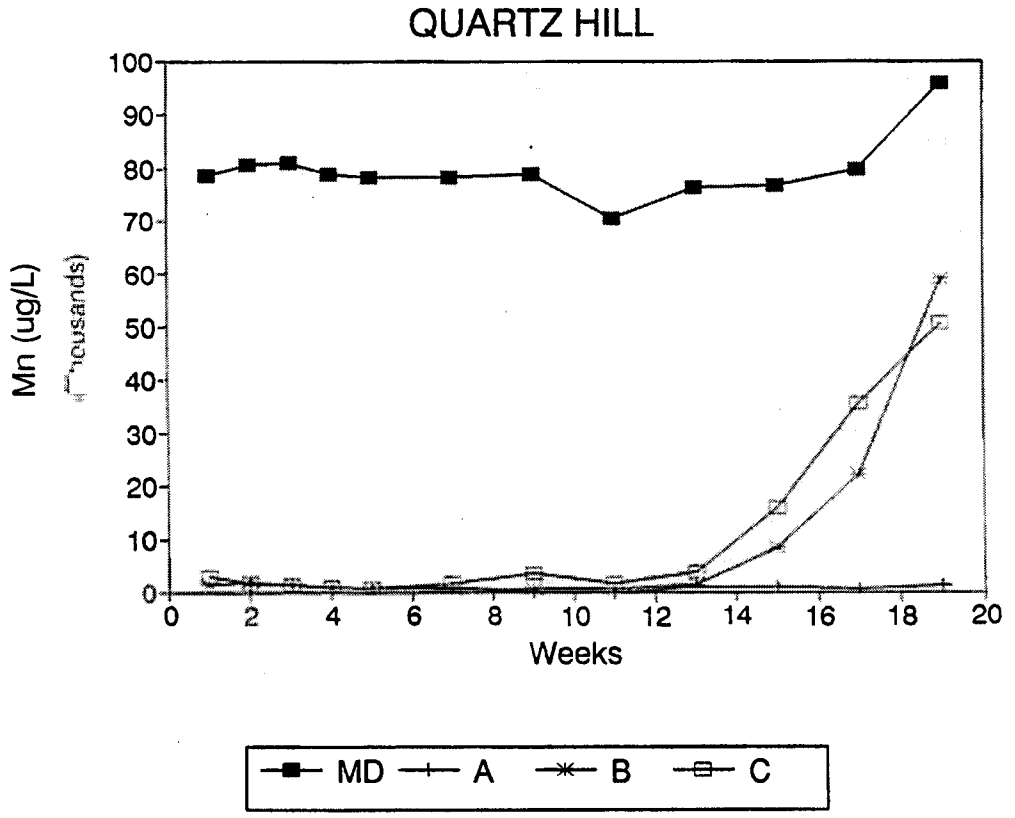


Figure 4. Manganese content of mine drainage and permeameter effluents for National Tunnel and Quartz Hill Tunnel.

Table 4. Area Adjusted Removal Rates for National and Quartz Hill Tunnels (grams/day/meter^2)

		National gdm^2	Quartz Hill gdm^2
Iron	Range	2.1 - 3.8	4.2 - 6.3
	Average	2.8	4.8
Total Metals	Range	3.0 - 6.0	5.4 - 8.5
	Average	4.3	6.7

Literature Cited

Batal, W., T.R. Wildeman, L.S. Laudon, and N. Moodnoordin. 1989. Bacteriological Tests from the Constructed Wetland of the Big Five Tunnel, Idaho Springs, Colorado. In: D.A. Hammer, Ed. Proceedings of the International Conference on Constructed Wetlands for Wastewater Treatment. Lewis Publishing, Ann Arbor, MI. pp. 761-764.

Bolis, J.L. and T.R Wildeman. 1990. Bench Scale Permeameter Testing of Mine Drainage from National and Quartz Hill Tunnels, Clear Creek/Central City Superfund Site, Draft Report to Camp Dresser & McKee.

Hedin, R.S. and R.W. Nairn. 1990. In: Proceedings of the 1990 Mining and Reclamation Conference, West Virginia Univ. Publications, Morgantown, WV. pp. 385-392.

Lemke, P.R. 1989. Analyses and Optimization of Physical and Hydraulic Properties of Constructed Wetlands Substrates for Passive Treatment of Acid Mine Drainage. Master's Thesis No. 3823, Colorado School of Mines, Golden CO. 78 pp.

Machemer, S.D.; P.R. Lemke; T.R. Wildeman; R.R. Cohen; R.W. Klusman; J.C. Emerick; and E.R, Bates. 1990. Passive Treatment of Metals Mine Drainage through use of a Constructed Wetland. In: Proceedings of the 16th Annual Hazardous Waste Research Symposium, U.S. EPA, Cincinnati, OH. EPA Document No. EPA/600/9-90-037, pp. 104-114.

Machemer, S.D. and T.R. Wildeman. 1991. Organic Complexation Compared with Sulfide Precipitation as Metal Removal Processes from Acid Mine Drainage in a Constructed Wetland. Journal of Contaminant Hydrology. In review.

Reynolds, J.S.; J.L. Bolis; S.D. Machemer; and T.R. Wildeman. 1991. Sulfate Reduction in A Constructed Wetland. Preprints Div. Environmental Chemistry, v. 31, No. 1. pp. 504-509.

Wildeman, T.R.; D.L. Cain; and A.H. Ramire. 1974. The Relation Between Water Chemistry and Mineral Zonation in the Central City Mining District, Colorado. In: National Symposium of Water Resources Problems Related to Mining. Proceedings No. 18, American Water Resources Assn. pp. 219-229.

Wildeman, T.R. and L. S. Laudon. 1989. In: Constructed Wetlands for Wastewater Treatment, Lewis Publishers, Chelsea, MI. pp. 221-230.

Wildeman, T.R.; S.D. Machemer; R.W. Klusman; R.H. Cohen: and P. Lemke. 1990. Metal Removal Efficiencies from Acid Mine Drainage in the Big Five Constructed Wetland. 1990 Mining and Reclamation Conference, Charleston, WV. pp. 417-424.

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FLOC LOGS IMPROVE THE EFFLUENT QUALITY ?[1]

by

Dharmvir K. Bhatnagar[2]

Abstract. Enforcement of the U.S. Surface Mining Control and Reclamation Act (SMCRA) of 1977 and the National Pollutant Discharge Elimination System (NPDES) led to the suggestion that flocculant (floc) logs can be utilized to improve the quality of the effluent leaving coal mine sites. The two main pollutants generated from the surface coal mining operations are acid discharge and sediment. At a mine site in Iowa, sediment not acid discharge was the main pollutant. SMCRA design standards for sedimentation ponds require that a pond have adequate capacity to contain from its watershed the sediment and runoff resulting from the design event. The east pond at the Iowa site was not big enough for the 860-acre watershed. Alternatively, as allowed by the regulations, the operator demonstrated using the computer model SEDIMOT II that peak settleable solids in the effluent would meet the NPDES criterion of 0.5 ml/l. However, the regulatory authority contended that the particle size distribution used in the model was not representative. Another computer run for the soil sample taken from the pond exceeded the NPDES limits. Both recognition of the property of the floc logs and increasing the capacity of the east pond contributed to a solution.

REGULATIONS

The Surface Mining Control and Reclamation Act (SMCRA) of 1977 mandates that (1) all surface drainage from the disturbed area shall be passed through a siltation structure before leaving the permit area, (2) discharges of water from areas disturbed by surface mining activities shall be made in compliance with the National Pollutant Discharge Elimination System (NPDES) permit, and (3) sedimentation ponds shall be designed, constructed and maintained to contain or treat the 10-year, 24-hour precipitation event ("design event") unless a lesser design event is approved by the regulatory authority based on terrain, climate and other site-specific conditions and on a demonstration by the operator that the effluent limitations of the NPDES permit will be met. One of the requirements of NPDES permits is that the peak settleable solids in the effluent shall not exceed 0.5 ml/l.

PROBLEM IDENTIFICATION

A pond, known as "east pond" (see figure 1) at American Coals Corporation surface mine number 3 in Mahaska County, Iowa, was the key structure where the runoff left the permit area since the inception of the mine in 1979. The sediment was dredged out of the pond only twice in 8 years for having excessive accumulation in the pond. There had not been any acid discharge problem at the mine site, perhaps because the overburden was not pyritic.

The pond, having a total storage capacity of 10 acre-feet, was identified in 1987 to be too small to contain

[1]Paper presented at the American Society of Surface Mining and Reclamation, Durango, Colorado, May 14-17, 1991.

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the required runoff resulting from the 860-acre drainage area in the design event of a 4.8-inch precipitation. Further, it was suggested that the peak settleable solids in the effluent from the principal spillway for the design event would exceed the limit of 0.5 ml/l, thus violating the NPDES permit conditions. The operator was asked either to enlarge the pond to contain design storm event runoff from or to demonstrate that the effluent would have settleable solids within the allowable limits for the design event.

ANALYSIS

Of the 860-acre drainage area of the east pond the disturbed area according to the mine plan was 100 acres within the 262-acre permit area. The rest of the 860-acre drainage area was in row crop or pasture, excluding ponds, roads, buildings, and drainageways. The east pond was the last in a series of ponds, which were proposed as final pit impoundments and were integral components of the comprehensive sediment and water management plan. The enlargement of the east pond from its 10 acre-feet capacity to the required 60 acre-feet to contain the runoff from the design storm event would submerge a substantial area of land and would require relocation or raising of the county road.

The operator tried the second alternative. Using a computer model SEDIMOT II, developed by the University of Kentucky, the operator demonstrated that without enlarging the pond the effluent would have only 0.16 ml/l peak settleable solids for the design event. However, the Iowa Department of Agriculture and Land Stewardship's Division of Soil Conservation (DSC), the State agency which has primacy to enforce SMCRA, contended that the first soil sample used in the model was not representative of the soils in the drainage area as it was taken from the upstream end of the main drainage. A second run of SEDIMOT II was conducted for a 4.8-inch precipitation event, for a second soil sample from the pond itself. With the pond capacity increased to 17.5 acre-feet, this model projected 1.10 ml/l settleable solids. A third run, differing from the second only for a 3.3-inch precipitation event, projected 0.39 ml/l peak settleable solids. The particle size distribution of the two samples is compared in Table 1. It seemed apparent that soil particle size was a vital factor in this case.

Use of gel flocculants is documented in the literature (e.g., Moore, 1982). Flocculants were used in the form of 9-inch diameter, 20-inch long, 40-pound stiff gel logs. When water flows around the logs, a polymer is released by hydration and erosion to form a solution that first neutralizes the charge on the surface of suspended particles and then agglomerates fine particles into a larger mass.

Theoretically, the settling velocity of a particle increases with the square of its diameter, according to Stoke's law. However, there was no correlation available for the quantitative effect of the flocculant on the particle size. Still, the operator demonstrated the qualitative effectiveness of the flocculants in a jar to both DSC and OSMRE. Equal amount of the same soil was mixed with equal amounts of water in two different jars, turning the water murky. Gel flocculants were added in one jar and the solids started settling immediately, making the water clear at a pretty fast rate.

SOLUTION

The pond was widened and deepened, increasing its capacity to 17.5 acre-feet at the crest level of the emergency spillway; thus assuring that the pond was design-safe for a 3.3-inch precipitation event without any treatment. Additionally, floc logs were placed hoping that they would cause the soil particles to coagulate and settle to such a degree that the peak settleable solids in the effluent would remain within NPDES permit limits.

The number of floc logs was recommended by the manufacturer to expose a certain surface area of the logs for the design discharge. However, it was not known if the flocculants were ever used for such high discharges (710 cft/sec in this case). Thirty-eight logs were cut longitudinally into halves. The 76 half-logs were suspended by steel cables in 13 rows, 10-feet apart; 6 rows in the emergency spillway channel of pond #2 (see figure 2) and 7 rows near the road culvert, which is 1,000 ft. upstream of the east pond dam, in the main drainageway. The half-logs were hung at such a height above the drainage bed that they would be submerged in the runoff resulting from a 3.3-inch or greater precipitation event.

POST-SOLUTION STATUS

By the summer of 1988, a comprehensive sediment and water management plan was implemented in the field. Coal extraction was ceased and backfilling, grading, and seeding were started. The years 1988 and

1989 were drought years. Since then, vegetation was re-established in the disturbed area of the permit. However, the effectiveness of the plan could not be verified since the effluent had not been tested for settleable solids prior to placement of the floc logs.

RECOMMENDATIONS

Some correlation needs to be established between soil particle size before and after the use of flocculants to assess the effective quantity of floc logs with more confidence. The extent of the effectiveness of floc logs should be verified by periodically testing settleable solids in the effluent both before and after using the flocculants. Sediment storage capacity in ponds may have to be increased to accomodate the additional sediment deposit that might be discharged with runoff without the use of flocculants.

Literature

Code of Federal Regulations, Mineral Resources, 30 CFR, sections 816.42, 816.46(b)(2) and 816.46(c)(iii)(C).

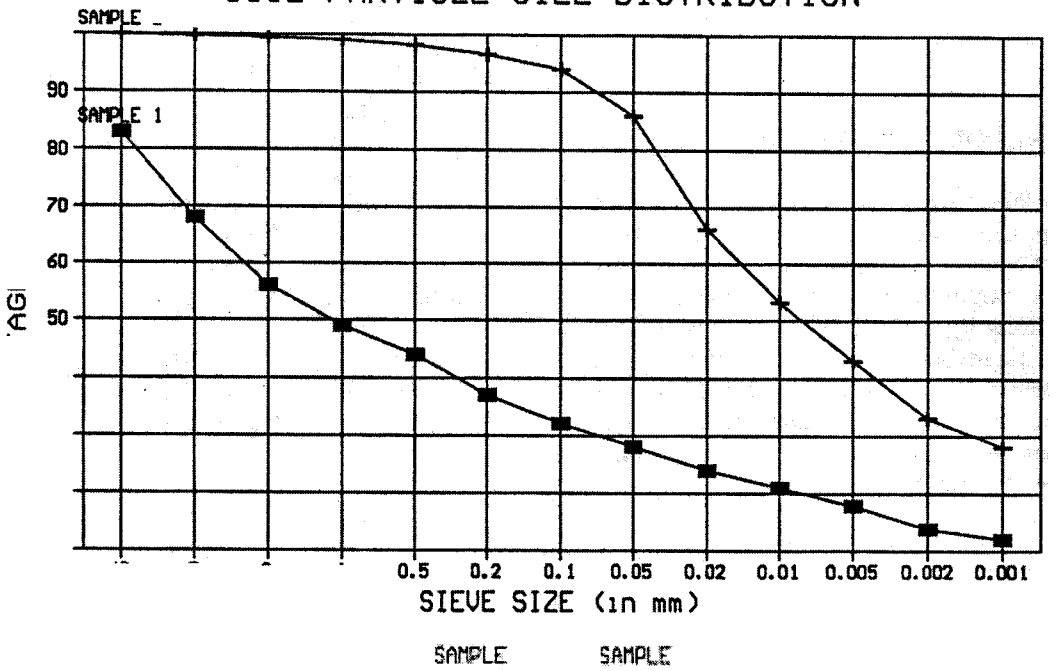
Moore, James F. 1982. Treatment of Remote Impoundment Ponds with Gel Flocculants, 1982 Symposium on Surface Mining, Hydrology, Sedimentology and Reclamation (University of Kentucky, Lexington, Kentucky, Dec 5-10, 1982).

Neutron Products Inc., Technical Bulletin 87102.

University of Kentucky,College of Agriculture, Design Manual for the SEDIMOT II Hydrology and Sedimentology Model.

TABLE

SOIL PARTICLE SIZE DISTRIBUTION



BIOSORPTION OF HEAVY METALS FROM URANIUM MILL TAILINGS EFFLUENT[1]

by

Joni M. Barnes, Arpad E. Torma,
Pete A. Pryfogle, and Don T. Maiers[2]

Abstract. The present study has investigated the applicability of alginate-based biosorbents in the remediation of uranium mill tailings (UMT) effluent. For this purpose, comparative biosorption studies have been carried out with synthetic metal solutions and effluents taken from the UMT site in Durango, CO. A kinetic model has been developed to describe the rate of metal uptake (V) as a function of biosorbent concentration (B), $V = V_m[B]/(K + [B])$. The kinetic values, V_m and K, were derived for Cd^{2+}, Ba^{2+}, UO_2^{2+}, and Zn^{2+} sorption by calcium alginate beads. From the effect of temperature, the activation energy (ΔE_a) and frequency factor (A) have been calculated to be 2.7 kcal (11.5 kJ) and 322.4 mg/l/min, respectively, for barium uptake on calcium alginate beads. Metal extractions greater than 97% were achieved. The importance of these findings relative to bioremediation of UMT is discussed.

Additional Key Words: alginate, biosorption, bioremediation, uranium mill tailings effluent.

Introduction

The introduction of biotechnological principles in the recovery of dissolved heavy metal and radionuclide contaminants from diverse industrial effluents has been gaining importance in recent years. This tendency is motivated by the fact that biosorbents (Volesky, 1986) are able to accumulate trace amounts of metal concentrations from large volumes of dilute solutions not only nonspecifically but also selectively. Therefore, biosorbents are considered for polishing effluents (Jeffers et al., 1989) which were treated first by conventional techniques such as chemical precipitation (using lime), solid and liquid ion-exchange, and reverse osmosis (Smith and Kalin, 1989).

Algae were found to remove uranium, molybdenum, and selenium ions from industrial effluents (Tsezos, 1987). The outline of the process can be given schematically as shown in Figure 1

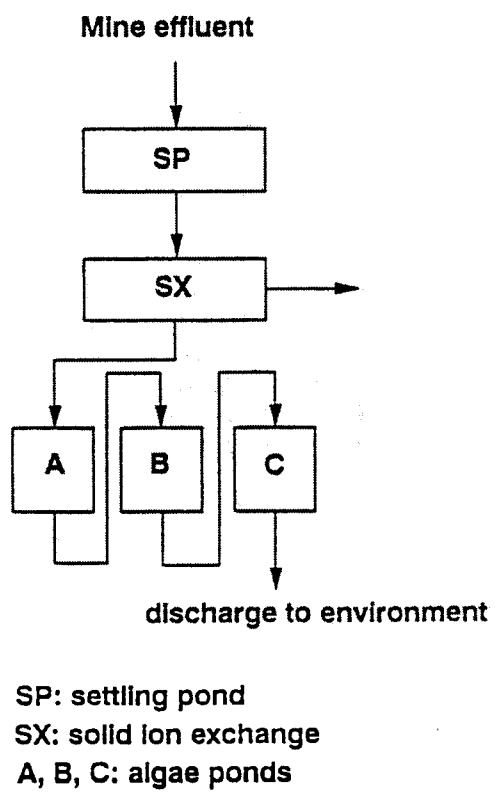


Figure 1. Schematic presentation of a chemical-biological method for the treatment of uranium mine drainage.

[1]Paper presented at the 1991 National Meeting of the American Society for Surface Mining and Reclamation, Durango, Colorado, May 14-17, 1991.

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The process is claimed to be applicable to many mining operations where the mine needs to be dewatered. For example, water is pumped from the mine to the surface to prevent flooding. Then the drainage water is introduced into settling ponds, where the suspended colloidal particles are deposited. The clear water is lead through solid ion exchange units where the major portion of uranium and heavy metals are removed. However, if the remaining trace metal concentration is too high in the effluent water, then further purification is needed before it can be released to the environment. This can be achieved by passing the water through algal ponds (Tsezos, 1987) as shown in Figure 1. The predominant algae found in pond (A) was Spirogyra. The (B) and (C) algal ponds contained, in addition to Spirogyra, an abundant growth of Chara, especially at the bottom of the ponds. Oscillatoria and other green algae species were also observed. In the settling ponds, the presence of sulfate-reducing bacteria was detected which contributed to the formation of metal sulfide precipitation. The reduction of uranium, molybdenum, and selenium concentrations can be demonstrated by the following comparison: mine water contained 5.8 ppm U, 2.3 ppm Mo, and 0.3 ppm Se, whereas the concentrations in effluent water at the discharge of pond (C) were 0.8 ppm U, 0.8 ppm Mo, and 0.01 ppm Se.

The ability of certain fungal, yeast, algal and actinomycete species in the adsorption of uranium has been investigated (Tsezos et al., 1989). On the basis of experimental results, a flowsheet has been developed for continuous operation for biomass loading and elution. The main features of the process are outlined in Figure 2. The authors (Tsezos et al., 1989) suggested that the method can be used in the underground leaching of low-grade uranium deposits at Denison Mines, which is located in the Elliot Lake area, Ontario, Canada. According to the authors (Tsezos et al., 1989), there is no particular problem associated with the scaling up of the process. The best sorption results were obtained with Penicillium species. However, the elution of uranium from the Penicillium cells was not fully resolved. Another biosorption process has been developed for the continuous recovery of uranium from industrial bioleach solutions (Tsezos, 1987). This process used immobilized inactive Rhizopus arrhizus biomass, which was found to be an excellent selective sorbent for uranium (Tsezos, 1984, Tsezos, 1985, Tsezos et al., 1988). The biosorbent exhibited a relatively high uranium uptake capacity of about 40 mg/g (Tsezos, 1987). The pilot plant testing

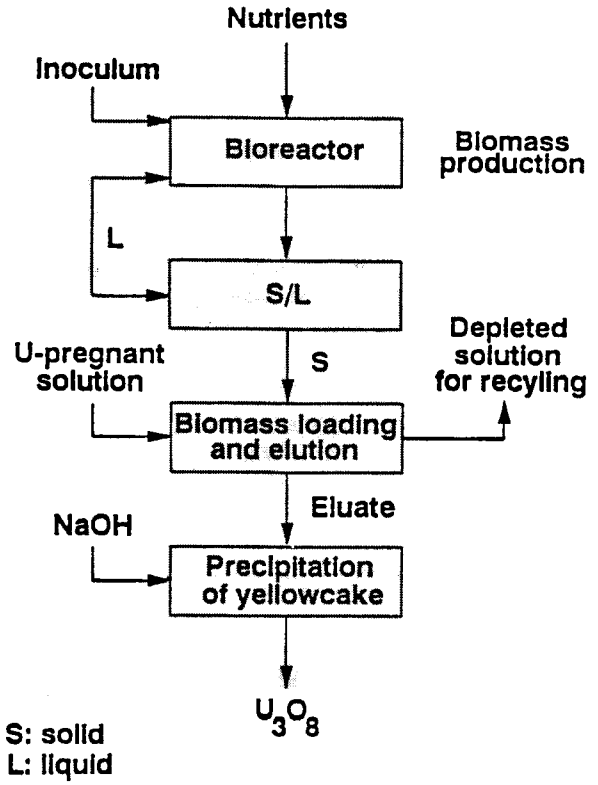


Figure 2. Simplified version of flowsheet for bioadsorption and recovery of uranium (Tsezos et al., 1989).

(loading and stripping) of the process was operating for over 100 days without any apparent reduction of the immobilized biomass uranium uptake capacity.

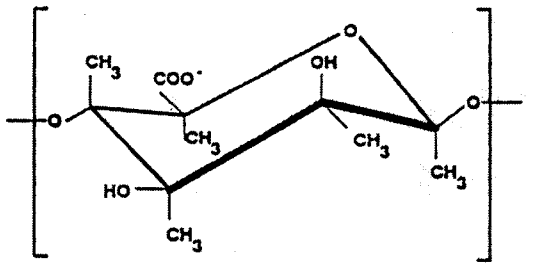
Radium-226, thorium-232 and uranium-238 uptake by twenty species of marine algae were studied (Edgington et al. 1970). It was found that the uptake of these radionuclides was controlled by two mechanisms: (a) ion-exchange or coprecipitation of the ions with calcium carbonate matrix, and (b) complex formation with either the protein nitrogen or some other component of the organic fraction. Radium and possibly thorium were concentrated by both of these mechanisms, while uranium only by the first mechanism. A review article (Van Der Borght et al., 1971) reported on the efficiency of sodium alginate in the removal of radium-226 from intestine of rats. Furthermore, it indicated that the formation of calcium alginate depended on the guluronic acid content of sodium alginate. The ion exchange efficiency of calcium alginate was found to increase from barium over strontium and calcium. Accumulation of radium-226 from uranium mill tailings effluent was studied (Havlik, 1971) using four

species of green algae: Ankistrodesmus falcatus var. acicularis, Chorella vulgaris, Coelastrum cambticum, and Chlamydomonas nidulans. It was found that radium-226 uptake was dependent on the species of algae, the concentration of radium-226 in solution, the growth rate of algae and their physiological condition, and the period of exposure. Radium-226 was adsorbed onto the gelatinous capsule and the cell wall of algae mainly during the logarithmic phase. Biosorption of radionuclides from varying aqueous solutions has been studied by a number of investigators (Tsezos and Volesky, 1981, Sakaguchi et al., 1978 and Heide et al., 1975). Others (Strandberg et al., 1981) reported on microbial accumulation of radium-226, cesium-137 and uranium by Saccharomyces cerevisiae and Pseudomonas aeruginosa. The optimum pH for biosorption of radium was found to be in the neutral or slightly alkaline range (Guiseley, 1989) for Penicillium chrysogenum. Bioaccumulation of radium-226 and other radionuclides by nanoplanktonic algal species and picoplanktonic blue-green algae was determined (Kuyucak and Volesky, 1989). The algal cultures used were the centric marine diatom Thalassiosira pseudonana (clon 3H), the chlorophyte Dunaliella tertiolecta (clon Dun), the coccolithophore Emiliania huxley (clon MCH No.1), the filamentous cyanophyte Oscillatoria woronichinii (clon Osc N4), and the picoplanctonic cyanophyte Synechoccus sp. (clon L1602). Generally, algal uptake followed the pattern Th-228 > Pb-210 > U-238 + Ra-226.

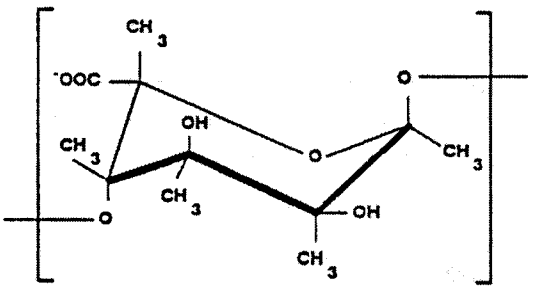
The present study will investigate the applicablility of alginate beads in the removal of metallic contamination from UMT.

Alginate

Algin is the general term used for structural polysaccharides that are extracted from some species of brown seaweed, i.e. from Macrocystis pyrifera (Guiseley, 1989). Chemically, the algin consist of linear polymers of 1,4-linked β-D-mannuronic acid and 1,4-linked α-L-guluronic acid (called alginic acid). Their structural features are shown in Figure 3 (Pictures a and b respectively). The structure of algin polymer can have three different types of arrangement: (a) blocks of alternating mannuronic (M) and guluronic (G) residues (...MGMGMG...), blocks of mannuronic acid (...MMMMMM...), and groups of guluronic acid (...GGGGGG...). The way these blocks are arranged controls the properties of the algin. In addition, polysaccharide chains can adopt ordered helical and ribbon like structures (Rees and Wels, 1977).



A. Conformation of mannuronic acid.



B. Conformation of guluronic acid.

Figure 3. Structure of alginic acids.

The alginate is defined as the alkali salt of the alginic acid (Kuyucak and Volesky, 1989). The alginates are non-toxic (McNeely and Kovacs, 1975), and are widely used in foods and in other industrial applications for thickening, gelling, stabilizing, and film-forming (Guiseley, 1989). The guluronic acid-rich algin is most suited for gelling, but all algins gell in the presence of calcium ion (Rees, 1969, Morris et al., 1973). Gels made with mannuronic acid-rich algin are more brittle. The dissociation constants of mannuronic and guluronic acids were determined to be pK = 3.38 and pK = 3.65, respectively (Haug, 1964).

Kinetics of Biosorption

The kinetic evaluation of biosorption phenomena is generally described by a variety of equations, which are variations of those originally developed for gas adsorption on solid surfaces by Freundlich and Langmuir (Gregg and Sing, 1982, Itoh et al., 1975, Selvakumar and Hsieh, 1988, Xue et al., 1988, Kuyucak and Volesky, 1989). The polysaccharide based biosorbents are known to have a complex sorption mechanism (Gadd, 1988). Metal uptake can occur simultaneously by adsorption, absorption,

chelation, and precipitation-coupled absorption. Therefore, the above kinetic approaches have a common shortcoming, since these are based on the adsorption phenomenon only. In order to avoid the above ambiguity of the kinetic interpretation and evaluation of biosorption data, a generalized rate equation has been derived that is based on the following assumptions: (a) all sites of the surface of biosorbent are identical, and (b) the biosorption process is an equilibrium phenomenon. If the sorption of X metal ionic species occurs on one of the surface sites of biosorbent (B), then it can be expressed as:

$$X + B = XB \tag{1}$$

where XB is the amount of metal uptake. For molar solutions, the equilibrium constant can be expressed as (Gadd, 1988, Leja, 1982):

$$K_{eq} = [XB]/([X][B]) \tag{2}$$

Let us suppose that from the original X concentration X_1 is sorbed so that the free metal ion concentration in solution is $X\text{-}X_1$. Therefore equation 2 can be rewritten as:

$$K_{eq} = [X_1]/([X\text{-}X_1][B]) \tag{3}$$

The fraction of metal adsorbed, θ, is given by:

$$\theta = X_1/X \tag{4}$$

or

$$X_1 = \theta X \tag{5}$$

Substituting equation 5 into equation 3, yields

$$K_{eq} = \theta X/([X\text{-}\theta X][B]) \tag{6}$$

from where

$$\theta = K_{eq}[B]/(1 + K_{eq}[B]) \tag{7}$$

Let V be the rate of metal uptake by the biosorbent and be proportional to the amount of metal sorbed as a function of time:

$$V = k\theta \quad \text{or} \quad \theta = V/k \tag{8}$$

where k is the reaction rate constant. The substitution of θ into equation 7 will yield:

$$V/k = K_{eq}[B]/(1 + K_{eq}[B]) \tag{9}$$

However, when all metallic species are sorbed, θ = 1 so that

$$k = V_m \tag{10}$$

where V_m is the maximum theoretically obtainable rate of metal uptake. Inserting equation 10 into 9 gives:

$$V = V_m K_{eq}[B]/(1 + K_{eq}[B])$$

$$= V_m[B]/(1/K_{eq} + [B]) \tag{11}$$

The $1/K_{eq}$ is redefined to be equal to a constant K, which is the concentration of biosorbent that results in the $V_m/2$. Therefore, it can be written:

$$V = V_m[B]/(K + [B]) \tag{12}$$

Equation 12 is similar to the Monod's empirical hyperbolic rate equation (Monod, 1949), and it has general applicability for the mathematical description of all biosorption rate phenomena. Equation 12 is used in the current study for the description of metal ion uptake phenomena.

Materials and Methods

Bead Precursor Material

Bead precursor material was prepared by adding 3.0 g dry sodium alginate powder (Keltone HV gelling grade, Kelco Co., Chicago, IL) to 97 g pure water (Barnstead, NANOpure II Water System, Boston, MA) in the mixing cup of a Waring blender and homogenizing it at a low speed setting for 5 to 6 minutes. The solution was transferred into a 250 ml beaker, autoclaved for 15 minutes at 120°C, and allowed to cool to room temperature.

Bead Formation

The bead precursor material was placed into a stainless steel dispenser, whose schematic outline is shown in Figure 4. The dispenser was pressurized by compressed air to force the precursor mass to leave the dispenser through the gauge holes as droplets which were collected in 500 ml of 0.1 M $CaCl_2$ solution and was stirred for 10 minutes. Then, 2.5 g polyethyleneimine (PEI) was added and the solution stirred for 5 minutes. This was followed by the addition of 500 ml of pure water, and shortly after the beads were filtered and washed with distilled water.

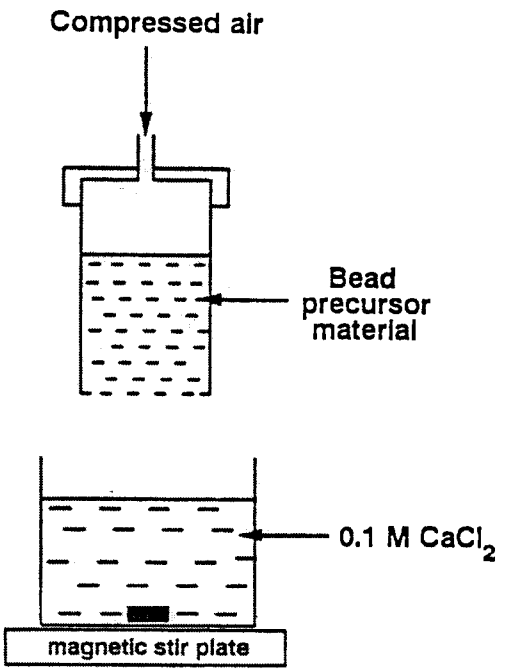


Figure 4. Schematic of dispenser used to form calcium alginate beads.

UMT Effluents

Uranium mill tailing effluents were taken from the UMT controlled containment site in Durango, CO. The solution samples were analyzed for their heavy metal and radionuclide contents and used in the column remediation experiments.

Biosorption

This series of experiments was performed in 500 ml reactors containing 400 ml synthetic solutions of varying concentrations of single metals at pH 5.0, 200 rpm, and 23°C temperature. The metal uptake by the beads was followed by periodically removing 1.0 ml samples from the experimental solutions for analysis.

Column Studies

This series of experiments was carried out at room temperature with 300 ml Ca-alginate beads (8.5 g dry weight of sodium alginate) and 1 liter UMT effluent. The Ca-alginate beads were introduced into a 500 ml glass column and charged with the mill tailings effluents at rates of 2 ml per minute. The throughflow was collected in 15 ml samples and analyzed for heavy metals and radionuclides. The schematic outline of the experimental setup is shown in Figure 5.

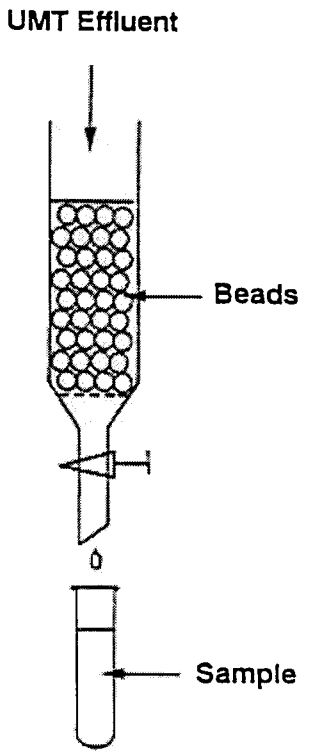


Figure 5. Schematic outline of the experimental setup used for calcium alginate column studies.

Analytical Methods

Heavy metal ion concentrations of different aqueous samples were assessed by Inductively Coupled Plasma Atomic Emission Spectrophotometry (ICP), (Applied Research Laboratories, Model 3520) and radionuclides by gamma ray spectroscopy (Princeton Gamma Tech and EG&G Ortec).

Results and Discussion

Effects of Alginate Bead Concentration

This series of experiments was carried out with synthetic single metal solutions containing 50 ppm barium, cadmium, uranyl or zinc concentration, and 150-200 mg/l calcium-loaded alginate beads at 23°C and 200 rpm. Figure 6 presents the zinc uptake data as a function of time. As it can be seen, the zinc uptake increases with the time of treatment and Ca-alginate bead concentration. The data points

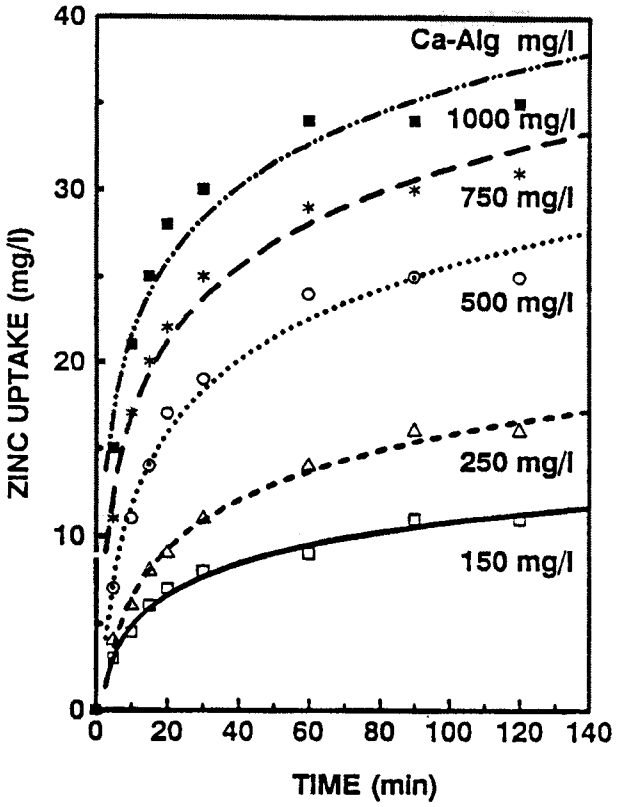


Figure 6. Zinc uptake by calcium loaded alginate beads.

were fit with a first-order logarithmic equation:

$$Y = a + b[\ln(t)] \qquad (13)$$

where Y is the zinc uptake in mg/l by the biosorbent, t is the time of treatment in minutes, and a and b are regression coefficients. The constant values (a and b) and the R^2 for the overall have been calculated for each experimental run by the logarithmic regression technique and the data reported in Table 1. The fitted lines calculated with the help of equation 13

Table 1. Regression analysis data of zinc uptake experiments.

Bead Concentration (B, mg/1)	a	b	R^2	V (mg/l/min)
150	-1.12494	2.59481	0.98489	0.61025
250	-2.95572	4.07770	0.99179	0.72142
500	-2.19992	6.04574	0.97650	1.50606
750	2.52565	6.24254	0.97621	2.51543
1000	7.26749	6.20714	0.94148	3.45150

using the regression coefficients from Table 1 are also indicated in Figure 6. The relative high R^2 values in Table 1 suggest a good fit for the experimental data for zinc uptake by the biosorbent.

The initial average rate of zinc (V, mg/l/min) uptake has been defined as the mass of zinc sorbed by the biosorbent in the initial 5 minutes of treatment. Thus, the V-values have been calculated for each series with the appropriate bead concentration (B) using the regression analysis data of Table 1 in equation 13. These results are indicated in the last column in Table 1. Figure 7 is the linearized graphical presentation of equation 12, achieved by plotting

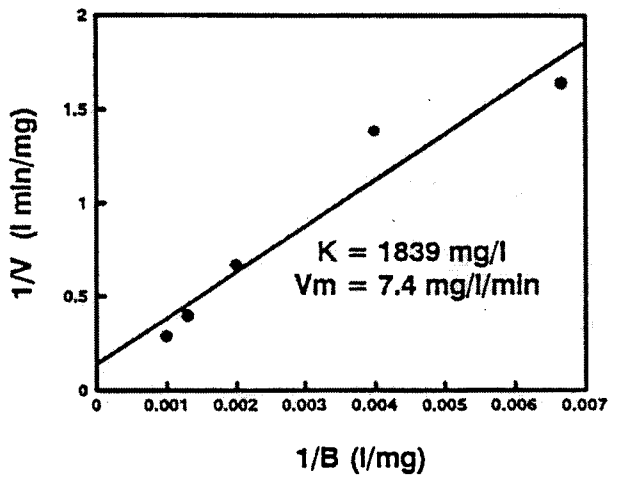


Figure 7. Determination of kinetic biosorption values V_m and K.

the inverse of zinc uptake rate (1/V) versus the inverse of calcium-alginate bead concentration (1/B). The intercept of the regression analysis line with the 1/V axis corresponds to $1/V_m$ and the slope of the straight line corresponds to K/V_m. From this presentation the V_m and K values have been determined to be 7.4 mg/l/min and 1839 mg/l, respectively.

Similarly to zinc biosorption experiments, the cadmium, barium, and uranyl ion uptakes were studied with calcium-alginate bead concentrations varying from 100 to 2000 mg/l, and this data is summarized in Table 2 in terms of V_m and K values. No data are available from the literature for comparison of the kinetic values derived in this investigation. However, the smaller K-values indicate a higher loading efficiency of the biosorbent material.

Table 2. Summary of metal uptake data by Ca-alginate biosorbent.

Metal ion	V_m (mg/l/min)	K (mg/l)
Cd^{2+}	17.4	2663
Ba^{2+}	24.7	4343
UO_2^{2+}	10.6	1303
Zn^{2+}	7.4	1839

Effect of temperature

The effect of temperature was studied for barium uptake by the calcium-alginate beads in the range of 20 to 65°C using 50 ppm Ba^{2+} ($BaCl_2$) solutions and 1500 mg/l bead concentration. The biosorption data were evaluated as it was shown for the zinc uptake experiments, and the rate of barium uptake related to the temperature by the Arrhenius equation (Laidler and Meiser, 1982):

$$V = Ae^{-\Delta Ea/RT} \quad (14)$$

where A is the frequency factor, ΔE_a is the activation energy, and T is the temperature in degree Kelvin. Equation 14 can be linearized by taking its logarithm:

$$\ln(V) = \ln(A) - \Delta E_a/RT \quad (15)$$

A plot of ln(V) versus 1/T yields a straight line whose intercept with the ln(V) axis corresponding to ln(A) and slope to $-\Delta E_a/R$, from which the frequency factor and activation energy can be approximated. Figure 8 shows the linearized Arrhenius plot for barium uptake by calcium-alginate beads.

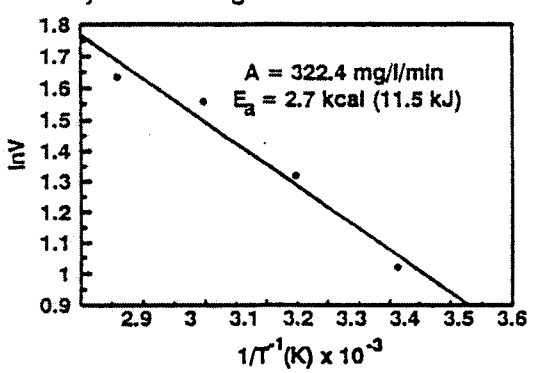


Figure 8. Arrhenius plot.

This presentation is typical for the temperature effect of chemical and biochemical reactions. The ΔE_a and A values derived for barium biosorption are 2.7 kcal (11.5 kJ) and 322.4 mg/l/min, respectively. The relatively low activation energy suggests that this biosorption process is diffusion controlled, and it involves the formation of an activated complex:

$$Ba^{2+} + B = \{BaB\} \rightarrow Ba\text{-}B \quad (16)$$

where the formation of the activated complex {BaB} is a slow equilibrium process that transforms fast to product, barium loaded alginate Ba-B, which is the barium alginate.

Remediation of Uranium Mill Tailing Effluent

The biosorption column was charged with 300 ml calcium-alginate beads (corresponding to 8.5 g alginate, dry weight) and contacted with one liter of uranium mill tailing effluent in 15 ml/min flow rate. The through-flow solution was continuously sampled and analyzed. It was found that approximately 200 ml of UMT effluent could be remediated with the beads in the column when the beginning of breakthrough occurred. Partial remediation was continued until about 400 ml of UMT effluent passed through when the complete breakthrough occurred. The difference in the metal ion concentration of inflow UMT effluent and initial breakthrough solution is compared in Table 3. Accordingly, the removal of various metal ions from the UMT effluent was 54 to 87%.

The biosorption approach for the remediation of UMT sites, where the underground water is contaminated, can be done by the pump and treat method. In this process, the contaminated ground water is pumped to the surface and treated by one of the conventional methods (Smith and Kalin, 1989), after which, the remaining trace concentrations could be removed by a biosorption process as suggested in this study.

The information generated in this investigation is preliminary in nature and does not represent the final capabilities of the process. Further studies are in progress using carrageenan, dextran, dextran sulfate, and xanthan gum based calcium and/or barium loaded beads for the remediation of uranium mill tailing effluents.

Table 3. Bioremediation of actual UMT effluent.

Metal ion	UMT effluent (ppm)	Remediated effluent (ppm)	Efficiency (%)
	17.3	3.7	78
	4.5	0.99	78
	>4.9	0.90	>82
	1.4	0.36	74
	1.18	0.16	86
	0.74	0.34	54
	0.25	0.10	60
	525.	132.	75
	578.	197.	66
	200.	30.	85
	76.	10.	87

Summary

The biosorbent (immobilized calcium-alginate beads) reported in this study has indicated a good potential for the remediation of uranium mill tailing effluents. It was found to be especially efficient for the removal of certain actinide and heavy metal ions from UMT effluent. The kinetic studies with synthetic single metal ion solutions contribute to a better understanding of the biosorption phenomena. Further studies are in progress.

Acknowledgments

The authors wish to express their appreciation for the excellent technical contributions by Ms. Karen M. Delezene-Briggs and Mr. Edward B. McNew, and to Ms. M. Lynn Apel for her help in kinetic evaluations of results.

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Literature Cited

Edgington, D. N., S. A. Gordon, M. M. Thommes, and L. R. Almodovar. 1970. The concentration of radium, thorium, and uranium by tropical marine algae. Immunology and Oceanography. 15:945-955.

Gadd, G. M. 1988. Accumulation of metals by microorganisms and algae. Biotechnology. Eds., H. J. Rehm and G. Reed. VCH Verlagsgesellschaftd, Weinheim, Germany, Vol. 6b:402-433.

Gregg S. J. and K. S. W. Sing. 1982. Adsorption, surface area and porosity. Academic Press, New York, NY, pp. 1-303.

Guiseley, K. B. 1989. Chemical and physical properties of algal polysaccharides used for cell immobilization. Enzyme Microbiol. Technol. 11:706-715.

Haug, A. 1964. Composition and properties of alginates. Norwegian Institute Seaweed Research, Trondheim, Norway, Report No. 30.

Havlik, B. 1971. Radium in aquatic food chains: radium uptake by fresh water algae. Radiation Research. 46:490-505.

Heide, E., M. Paschlke, K. Wagner, and M. Wald. 1975. Aus kultivierbaren Mutanten von einzelligen Grünalgen bestehende Matrix sowie Verfahren zur Urangewinnung dieser Matrix. German Patent, 2,345,430.

Itoh, M., M. Yuasa, and T. Kobayashi. 1975. Adsorption of metal ions on yeast cells at varied cell concentration. Plant and Cell Physiology. 16:1167-1169.

Jeffers, T. H., C. R. Ferguson and D.C. Seidel. 1989. Biosorption of metal contaminants using immobilized biomass. Biohydrometallurgy. Eds., J. Salley, R. G. L. McCready and P. L. Wichlacz. Canmet, Ottawa, Ontario, Canada. pp. 317-328.

Kuyucak, N. and B. Volesky. 1989. The mechanism of cobalt biosorption. Biotechnology and Bioengineering. 33:823-831.

Laidler, K. J. and J. H. Meiser. 1982. Physical Chemistry. Benjamin/Cumming Publishing Company, Inc., pp. 353-360.

Leja, J. 1982. Surface Chemistry of Froth Flotation. Plenum Press, New York, NY, pp. 356-432.

McNeely, W. H. and P. Kovacs. 1975. The physiological effects of alginates and xanthum gum. In Physiological Effects of Food Carbohydrates. Eds., A. Jeanes and J. Hodges, ACS Symposium Series 15, American Chemical Society, Washington, DC., pp.269-281.

Monod, J. 1949. The growth of bacterial cultures. Annual Review of Microbiology. 3:371-394.

Morris, E. R., D. A. Rees, and D. Thomas. 1973. Characterization of polysaccharide structure and interactions by circular dichroism. Order-disorder transition in the calcium alginate system. J. Chem. Soc., Chem. Communication, pp. 245-346.

Rees, D. A. 1969. Structure conformation and mechanism in the formation of polysaccharide gels and networks. Advances in Carbohydrate Chemistry and Biochemistry. 24:267-332.

Rees, D. A. and E. J. Wels. 1977. Secondary and tertiary structure of polysaccharides in solutions and gels. Angew. Chem. Int. Ed. Eng. 16:214-224.

Sakaguchi, T., T. Hirokoshi, and A. Nakajima. 1978. Uptake of uranium from seawater by microalgae. Journal of Fermentation Technology. 56:561-565.

Selvakumar, A. and H. N. Hsieh. 1988. Competitive adsorption of organic compounds by microbial biomass. Journal of Environmental Science and Health. A23(8):729-744.

Smith, M. P. and M. Kalin. 1989. Biological polishing of mining waste waters: bioaccumulation by the Characeae. Biohydrometallurgy. Eds., J. Salley, R. G. L. McCready and P. L.Wichlacz. Canmet, Ottawa, Ontario, Canada, pp. 659-665.

Strandberg, G. W., S. E. Shumate, II, J. R. Parrott, Jr., and S. E. North. 1981. In Environmental speciation and monitoring needs for trace metal containing substances from energy related processes: Proceedings of the DOE/NBS workshop held at the National Bureau of Standards (Washington, DC). Special publication 618, pp. 274-285.

Tsezos, M. 1984. Recovery of uranium from biological adsorbents-desorption equilibrium. Biotechnology and Bioengineering. 26:973-981.

Tsezos, M. 1985. The selective extraction of metals from solution by microorganisms. A brief overview. Canadian Metallurgical Quarterly. No. 2:141-144.

Tsezos, M. 1987. The performance of a new biological adsorbent for metal recovery. Modeling and experimental results. Biohydrometallurgy. Eds., P. R. Norris and D. P. Kelly. Science and Technology Letters, Kew Surrey, Great Britain, pp. 465-475.

Tsezos M. R., G. L. McCready, J. Salley and J. P. Cuif. 1989. The use of immobilised biomass for the continuous recovery of uranium from Elliot Lake Ore. First pilot plant results. Biohydrometallurgy. Eds., J. Salley, R. G. L. McCready and P. L. Wichacz. Canmet, Ottawa, Ontario, Canada, pp. 279-287.

Tsezos M., S. H. Noh, and M. H. I. Baird. 1988. A batch reactor mass transfer kinetic model for immobilized biomass biosorption. Biotechnology and Bioengineering. 32:545-553.

Tsezos, M. and B. Volesky. 1981. Biosorption of uranium and thorium. Biotechnology and Bioengineering. 23:583-604.

Van Der Borght, O., S., Van Puymbroeck, and J. Colard. 1971. Intestinal absorption and body retention of radium-226 and calcium-47 in mice: effect of sodium alginate, measured in

vivo with a Ge(Li) detector. Healths Physics. 21:181-196.

Volesky, B. 1986. Biosorbentmaterials. Biotechnology and Bioengineering Symposium, No. 16:121-126.

Xue, H. B., W. Stumm and L. Sigg. 1988. The binding of heavy metals to algal surfaces. Water Research. 22:917-926.

ACHIEVING COMPLIANCE WITH STAGED, AEROBIC, CONSTRUCTED WETLANDS TO TREAT ACID DRAINAGE[1]

by

Gregory A. Brodie[2]

Abstract. The Tennessee Valley Authority (TVA) operates 12 staged, aerobic, constructed wetlands to treat acid drainage at reclaimed coal mines, a coal preparation plant, and at coal-fired power plants. Nine systems produce consistent compliance quality discharges without chemical treatment. Four systems not achieving compliance have high Fe (e.g., > 100 mg/l) and zero alkalinity in the inflow that results in low pH due to Fe hydrolysis in the wetlands. These systems are being modified with anoxic limestone drain (ALD) pretreatment components to increase alkalinity of the inflow to buffer against pH decreases. One high-Fe, zero-alkalinity system has been in compliance since May 1990 when an ALD was added prior to the wetlands. TVA's wetlands rely on oxidative mechanisms in cattail (*Typha spp.*) marsh-pond type wetlands cells in addition to aeration structures and anoxic mechanisms in the ALDs. Systems are currently removing Fe at rates between 0.4 and 21.3 grams/day/m^2 of wetlands (GDM) and Mn at rates between 0.15 and 1.87 GDM. TVA's wetlands have been loaded at rates of 0.03 - 41.5 GDM for Fe and 0.17 - 2.0 GDM for Mn. All of the wetlands meet compliance for total suspended solids. Based on TVA's operational results, design recommendations have been developed.

Additional Key Words: Iron, manganese; buffering capacity; ash disposal; alkalinity

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Introduction

Constructed wetlands offer an inexpensive, natural, low-maintenance, and potentially long-term solution to treating acid drainage without chemical additives (Hedin 1989; Brodie 1990a,b). Since 1985, the Tennessee Valley Authority (TVA), the largest electric utility in the United States, has constructed 13 aerobic, staged, wetlands systems for treating acid drainage at coal mining and processing facilities and coal-fired power plants. Twelve of these sites, along with 2 separate research facilities, are now operational and have been evaluated in attempts to understand and refine the processes occurring in constructed wetlands.

Discussion

Guidelines for design, construction, and operation of aerobic, acid drainage treatment wetlands have been developed, although none should be considered comprehensive due to continued upgrading of the constructed wetlands technology (Kleinmann et al 1990; Reed et al 1988; Brodie 1990c). Wetlands require design for specific conditions because site characteristics restrict the use of standard engineering and construction methods.

Preliminary Considerations

Wastewater characterization and site hydrology were the two most important predesign data needs. Baseline water quality and flow were established for all source waters to be treated and for receiving streams to document existing conditions and evaluate the operational treatment system. Minimum analyses included pH, oxidation-reduction potential (ORP), total and dissolved Fe and Mn, total suspended solids, sulfate, dissolved oxygen (DO), alkalinity, acidity, and Al. Sampling should be performed on unaerated seepage to obtain representative values of DO and ORP, 2 parameters which are critical in determining the practicality for an anoxic limestone drain (Turner and McCoy 1990; Brodie et al 1990, 1991). Qualitative baseline surveys of aquatic biota in receiving streams were conducted at some sites to provide a means of documenting stream recovery. Flow patterns and depth to groundwater were characterized to identify inflows or outflows that could affect water quality or hydrologic balance.

Wetlands were often located off a permitted area or leased/owned surface. Thus, negotiations with landowners for initial access and long-term leases or easements were necessary. Topographic data were obtained in sufficient detail to plan the number and location of cells to minimize cut and fill requirements. Detailed topographic surveys were not usually warranted.

Geologic data were evaluated to determine if the site overlay shallow bedrock or lacked suitable growth media. If necessary, sources of borrow were identified for

construction materials. Wetlands substrates at all systems (except KIF6) consisted of local or in-situ materials and no additional substrate was imported.

Vegetation sources for transplantation into the constructed wetlands were identified. Sources included nearby wetlands and commercial nurseries. Cattail (Typha spp.), for deep water, (0.2 - 0.5 m) and rush (Eleocharis spp.); water sedge (Carex spp.); threesquare (Scirpus americanus); and wool grass (Scirpus cyperinus), for shallow water, (< 0.2 m) were the most tolerant, readily available species for transplantation. Another rush (Juncus effusus) was used with less success. Broadleaf cattail (Typha latifolia) and squarestem spikerush (Eleocharis quadrangulata) may provide higher radial oxygen loss than other common species, thereby enhancing substrate oxidizing conditions to bind insoluble forms of metal precipitates in the substrate (Copeland 1988).

Design and Construction

Figure 1 shows a typical schematic for an aerobic constructed wetlands. TVA's aerobic wetlands generally consist of a pretreatment stage (anoxic limestone drain and/or oxidation basin) followed by several cells of shallow to deep (0.1 - 2.0 m) cattail (Typha spp.) marsh-ponds. Most of have been constructed in streams created by the acid drainage, although a few sites required diversions to route drainage to the wetlands system (e.g., 950 NE). Some systems are followed by a final polishing pond (e.g., IMP4), which may improve long-term capacity and minimize storm event flushing of Fe and Mn precipitates from a constructed wetlands (Brodie and Taylor 1991).

Early constructed wetlands were sized based on hydraulic loading (Kleinmann et al 1986; Girts et al 1987). Recently, chemical loading has been suggested as the primary design criteria for wetlands sizing. Chemical loading can be expressed in grams/day/m^2 of wetlands (GDM) for specific chemical species (e.g., Fe, Mn, alkalinity, or acidity). Chemical loading rates have been suggested for sizing wetlands, but are difficult to develop and should be considered preliminary until further studies are completed (Stark et al 1990; Brodie 1990c; Kepler et al 1990; Hedin and Nairn 1990) TVA's wetlands are, on average, hydraulically loaded between 0.02 - 0.24 l/day/m^2 of wetlands (LDM). Maximum hydraulic loading ranges are 0.06 - 1.47 LDM and the average is 0.42 LDM. Chemical loading ranged from .03 - 41.5 GDM for Fe, and .17 - 2.0 GDM for Mn. Based on TVA's wetlands results only, aerobic wetlands systems should be designed for 2.0 - 11.0 GDM of Fe depending on pH, alkalinity, and Fe concentrations of the inflow (Brodie 1990c). TVA's early wetlands systems (i.e., those in use before 1988) were sized hydraulically and then increased if the site allowed. Cell areas were arbitrarily increased in size if very poor quality water was to be treated. The most

recent wetlands have been sized based on Brodie (1990c), but in most cases have been built larger than design size to increase the safety factor and lifespan of the systems.

To ensure long-term stability, dikes were sloped no steeper than 2 : 1 and riprapped or protected with erosion-control fabric on the slopes. Spillways were designed for handling a 100 yr, 6 hr event with a safety factor of 3 and protected with either large (> 30 cm) riprap or non-biodegradable erosion-control fabric planted with species such as wool grass (Scirpus cyperinus), sedge (Carex spp.), or threesquare (Scirpus americanus).

Wetlands shapes varied and were dictated by existing topography, geology, and land availability. Irregular shapes for wetlands cells enhanced their natural appearance and provided hydraulic discontinuity. Configurations were avoided that could increase flow velocities and cause channelization, scouring, or bank erosion.

The number of cells was determined by site topography, hydrology, and water quality. Level sites were amenable to large cells hydraulically chambered with rock or earthen finger dikes, large logs, or vegetated hummocks. Steeper gradients required more grading or a system of several cells terraced downgrade. Staged treatment using several cells may provide a more efficient system since chemical and hydraulic overloading of all cells would be minimized. It has been suggested that one cell should be constructed for each 50 mg/l Fe inflow due to the need for reaeration after oxidation of this amount of Fe (Kleinmann 1990).

Water depth and bottom slope were dependent on desired plant species, pollutant concentrations, freeze potential, and desired longevity of the system. Average water depth in TVA's wetlands ranged from 15-30 cm with some deeper and shallower areas to provide for species diversification. Isolated deep pockets of up to 2.0 m were included in many cells to provide for aquatic fauna refuge in drought events.

Wetlands construction began with site clearing and grading with dozers, followed by dike and spillway construction with backhoes or hydraulic excavators. The wetlands was then flooded and planted. Vegetation was hand dug to obtain complete root balls/rhizomes and planted on the same day as digging. Plants were not subjected to extreme temperatures, drying, or wind during transport. Cattail (Typha spp.) was set into the substrate and stems broken over at the water level to prevent windfall and to stimulate new growth from the rhizomes. Wool grass (Scirpus cyperinus), sedge (Carex spp.), and rush (Juncus effusus) clumps were simply placed in the desired location. Squarestem spikerush (Eleocharis quadrangulata) and scouring rush (Equisetum hyemale) were carefully set into the substrate. Complete wetlands installations were operating

in 6 to 10 weeks, depending on their complexity. Most wetlands were completed in early summer, although successful installations were completed as late as October. One system planted in November required replanting. Wetlands were fertilized with a phosphorous-potassium fertilizer such as 0-12-12 at 400 kg/ha. Fertilization beyond the first year was done only if the vegetation showed signs of nutrient depletion.

Mosquitos have not been a major problem at TVA wetlands except at the newest site, DLL. Several species of annoying biters (Anopheles punctipennis, A. quadriumaculatus, and Culex erraticus) have been identified in TVA wetlands. Additionally, Psorophora columbia and Aedes vexans, 2 aggressive biting species, have been identified in tire tracks and areas of pooled water left by inadequate grading. To aid mosquito control, mosquitofish (Gambusia affinis) were stocked in all wetlands and martin houses were constructed at some sites. Based on qualitative observations, it has been suggested that martins may not be very effective in mosquito control because of their affinity for dragonflies, which consume a greater number of mosquitos, including larvae (Tennessen 1990). The use of bats for mosquito control (Tuttle 1988) is also being investigated at the TVA wetlands with the installation of several bat houses.

Operation and Maintenance

Post-construction activities included water quality monitoring, fertilization, maintenance of dikes and spillways, and the addition of new ponds to further treat the wetlands discharge. Additional water, substrate, andvegetation sampling and biological monitoring was performed to quantify the wetlands development and treatment efficiencies.

Sampling and Analytical Techniques

The objective of sampling is to accurately represent the sampled material with a portion small enough to be conveniently handled and analyzed. Collection and handling of the sample must minimize changes in the sample prior to analysis. NPDES monitoring requirements included pH, total Fe and Mn, and total suspended solids (TSS). Effluent samples from the wetlands were obtained during daylight hours generally within the second and fourth weeks of the month. Sampling was always initiated within two weeks of system startup. All samples were analyzed according to standard methods (EPA, 1979).

Selection of Sampling Sites

Samples of acid seeps were collected from discrete boils or springs, if present. If there were no discrete points of groundwater discharge, then sample were obtained as follows. 1) For flat boggy areas, a site was located in the wet area high enough so surface water would not flow into an excavation large enough to obtain a sample. The hole was allowed to fill with seepage and, prior to sampling, the water

level lowered to just above the point where seepage appeared to be entering. The hole was then allowed to refill and the water clarify. The sample was then collectedwithout stirring up sediments. 2) For seeps with very low flows on dike faces, highwalls, etc., a site was located up-gradient of the seep area on the dike, a hole was excavated down to the seepage, and the sample obtained as above. (EPA, 1985). Effluent monitoring was performed several meters downstream of the final spillway so that any dike leakage was included in the sample.

Water Sample Collection and Analytical Techniques

The objective of sample collection techniques was to minimize aeration and carbon dioxide loss before analysis. Sample bottles were filled from a plastic tube that was been pushed up-gradient into the seep, or the bottle was gently tilted into the flow (USGS, 1977). For seeps with very low flows, the bottle was lowered into the collection pit described above or a peristaltic pump was used to draw the sample (EPA, 1985). For the analyses that required extra attention to gas exchange, a polyethylene syringe of appropriate volume was used for sample collection and for short transport. The syringe tip was placed directly in the seep flow to draw an unaerated sample. All undosed sampling containers were rinsed three times with sample prior to the actual sample (APHA, 1989).

Total metals samples were collected in 500 ml acid-rinsed polyethylene bottles, predosed with 5 ml of 1+1 HNO_3, usually by tilting the bottle gently into the seep (APHA, 1989). Care wastaken to not overfill the bottle. The sample was then placed on ice and transported to the Chattanooga Environmental Chemistry Laboratory for analyses. Total metals samples were taken from the field containers, digested with concentrated, redistilled HNO_3 and HCl, reduced to 20 ml, diluted back to volume, centrifuged or filtered depending on solids, and then analyzed by atomic emission or atomic adsorption.

Dissolved metals samples were collected in one-liter plastic containers (cubitainers) by the same method described for total metals, and either filtered immediately after collection, or by carefully expelling air from the cubitainer, storing on ice, and then transporting a short distance to a field lab for filtration. The sample was vacuum filtered through a 0.45 micron cellulose ester membrane filter and poured into a 125 ml acid-rinsed polyethylene bottle predosed with 0.5 ml of 1+1 HNO_3 (APHA, 1989). The sample was then transported on ice to the lab for analysis. Samples are analyzed as received in the lab with standards for acid matrix by atomic emission or atomic absorption.

Ferrous iron samples were collected in 250 ml acid-rinsed glass bottles that were predosed with 5 ml of concentrated HCl. The technique is the same as

described for total metals, with particular attention to preventing aeration (APHA, 1989). These samples were stored on ice and transportedto a lab for analysis by atomic emission or atomic absorption.

Total suspended solids (TSS) samples were collected in one-liter cubitainers. All air was expelled from the cubitainer and the sample was stored on ice for transport to the lab (APHA, 1989). Samples were filtered through glass fiber filter, dried at 102 to 105°C with the difference of weight retained on filter and reported as TSS.

Sulfate samples required a one-liter cubitainer and were handled the same as the TSS samples. Sulfate samples were determined by Automated Methyl Thymal Blue (MTB) Method. First samples were passed through a column to remove metal ions then reacted with an alcohol solution of barium chloride and methyl-thymal blue to form barium sulfate. The pH is then raised to 12.5-13.0 to react with MTB. The uncomplexed MTB is proportional to the sulfate concentration.

Acidity was field analyzed by two procedures, potentiometric titration curve and hot peroxide. Two samples were collected in 100 ml syringes, one being titrated electrometrically (Orion, Model 399A) with NaOH in 0.5 ml increments to check the equivalence point and determine normal acidity. The other sample was analyzed by the hot peroxide method to determine acidity after oxidation and hydrolysis of reduced metals (APHA, 1989). Comparison of these two acidity values gave a field check for appreciable amounts of acidity due to reducedmetals and/or levels of carbonic acid as carbon dioxide.

Alkalinity was field analyzed by collecting a sample with a 100 ml syringe and titrating electrometrically (Orion, Model 399A) with H_2SO_4 in 0.5 ml increments. This procedure was followed to check the equivalence point and determine the alkalinity (APHA, 1989).

Field analysis of the pH was performed by collecting the sample in a one-liter cubitainer, storing on ice, and transporting to a field lab for electrometric determination (Orion, Model 399A). In situ analyses were often made using a Hydrolab Model Surveyor II.

The Hydrolab was also used for in situ pH, DO, ORP, temperature, and conductivity analyses. These analyses were performed by lowering the instrument probes carefully into the seepage collection hole or a large sample container and recording the readings.

Results

A summary of characteristics and water quality parameters for TVA's 13 constructed wetlands is presented in Table 1. Significant water quality improvement has occurred at all of the wetlands. Nine systems have produced discharges that consistently meet NPDES discharge

limitations (pH=6 - 9 s.u.; Fe < 3.0 mg/l; Mn < 2.0 mg/l; TSS < 35.0 mg/l) with no chemical treatment. Where regulatorylimits were not entirely achieved, cost savings were realized as a reduction in chemicals needed for further metals precipitation or pH adjustment at IMP2, WCF6, and COF13.

Figures 2-4 show inflow/outflow data for Fe, Mn, and pH at the 12 operational wetlands. Data for WCF5 was not available. Ten of the 12 operating wetlands produce discharges in compliance with total Fe limitations (i.e., < 3.0 mg/l). Figure 2 shows Fe loading in the systems ranges from 0.03 GDM to 41.4 GDM. Fe removed ranges from 0.0 GDM to 21.3 GDM, corresponding to 0 to 99 % Fe removal. Note that the 0 % removal is associated with the very low Fe inflow (0.7 mg/l) at the COF wetlands; this data may be a result of sampling and analysis techniques whose standard error is greater than the concentrations being measured, or may be related to a lower limit of Fe removal possible at the COF wetlands.

Fe removal in the wetlands is very efficient for loadings up to 13 GDM, which occurs at the WCF6 wetlands. Fe removal is less efficient (51 %) at KIF, where Fe loading exceeds 41 GDM. More data for Fe loadings between 13 GDM and 41 GDM is needed to better assess the Fe loading limit for a constructed wetlands. There is no obvious relationship in TVA's wetlands between Fe removal and influent alkalinity (Brodie et al 1991), Fe removal and wetlands size, or Fe removal and hydraulic loading. However, preliminary results at a TVA wetlands research facility suggest a correlation between Fe and Mn removal and hydraulic loading (Tomljanovich et al 1991).

Figure 3 shows total Mn loading and removal in the 12 TVA wetlands. Data for WCF5 is not available. Nine of the 12 operating wetlands produce discharges in compliance with total Mn limitations (i.e., < 2.0 mg/l, if regulated). Mn loading ranges from 0.17 GDM to 2.00 GDM. Mn removed ranges from 0.15 GDM to 1.87 GDM, corresponding to 0 to 96% Mn removal. The low removal rates are all associated with low pH (2.9 - 3.9 s.u.) systems. Mn removal in the wetlands is very efficient for loadings as high as 2.0 GDM, which occurs at the 950NE wetlands. There is no obvious relationship in TVA's wetlands between Mn removal and wetlands size, or Mn removal and hydraulic loading. Figure 4 shows a relationship between Mn removal and influent alkalinity and acidity concentrations (Brodie et al 1991). Systems with zero alkalinity have removed 0 to 16.5% Mn, while systems with alkalinity greater than 62 mg/l and with excess acidity as high as 248 mg/l have removed 85-97% of the Mn load. Inflows with zero alkalinity have always resulted in low pH in the wetlands. Low Mn removal is associated with zero alkalinity and thus, low pH in the wetlands. This data may reflect Mn co-precipitation on Fe-oxides at circum-neutral pH as a likely mechanism of Mn removal (Faulkner and Richardson 1990).

Figure 5 shows influent/effluent pH for the 12 operating wetlands. Nine of the 12 systems increase or maintain inflow pH to produce discharges in compliance for pH (i.e., 6.0 - 9.0 s.u.). Three systems cause pH decreases due to Fe hydrolysis; these systems are being modified with anoxic limestone drains (Brodie et al 1991).

All of the wetlands produce discharges in compliance with total suspended solids (TSS) limitations (i.e., < 35 mg/l).

Impoundment 1

Impoundment 1 (IMP1), constructed in June 1985, was TVA's first acid mine drainage treatment wetlands. The system treats acid seepage emanating from an earth dike impounding 16 ha of coal slurry at TVA's reclaimed Fabius Coal Preparation Plant in Jackson County, Alabama.

Since construction, IMP1 has generally produced compliance-quality effluent. Figure 6 shows average water quality data during the period July 1985 to November 1990 for the wetlands inflow and the discharges from each of the 4 wetlands cells. Variations in flow from each cell were due, in part, to acid seeps encountered along a sandstone shelf underlying the site and in the leaky nature of the wetlands system. Effluent from the first cell alone has met discharge limitations 56 % of the time. Figure 7 shows total Fe and total Mn concentrations in the effluent for the same period. From June to August 1988 and again from June to September 1989, total Mn concentrations increased to several times the IMP 1 average discharge concentration of Mn. Similar, but less drastic, increases in Mn concentrations were noted in the summers of 1986 and 1987. When these anomalieswere compared to rainfall records and wetlands flow, no correlations were apparent. Other wetlands (e.g., 950NE and RT2) have exhibited similar patterns of Mn concentration variability. These increases are probably seasonally related and could be due to numerous factors, including temperature, degree of mixing, degree of electron acceptors, redox conditions, nutrient and/or carbon availability, or photosensitivity of Mn-oxidizing bacteria (Sunda and Huntsman 1988; Hem 1981).

Figures 7 and 8 show the amounts of Fe and Mn removed for one 13-month period at IMP1. These data show that the wetlands consistently removes about 1.25 GDM Fe year-round. Mn removal is seasonal averaging about 0.14 GDM.

IMP1 is one of 2 constructed wetlands receiving inflow total Fe concentrations exceeding 50 mg/l that has successfully produced compliance-quality discharges without chemical treatment. Other wetlands receiving greater than 50 mg/l total Fe (see Table 1) have been troubled with low pH, high proton acidity, and the resultant inability to remove Fe and/or Mn to meet discharge limitations. Investigations into differences among the wetlands revealed that IMP1 influent had an alkalinity often exceeding 200 mg/l and

may represent the oldest, working anoxic limestone drain (Brodie and Garvich 1991). The 3 other high-Fe wetlands had influent alkalinity ranging from 0 to 26 mg/l with high acidity. Further investigations into the IMP1 characteristics showed that the leaking coal slurry impoundment dike was constructed in 1974 over an existing limestone coal mine haul road. Historically, local limestone has been quarried from the Monteagle Formation, an oolitic, high-$CaCO_3$ limestone. Apparently, this road, and perhaps some carbonate riprap emplaced in the early 1980s on the dike outslope, is the source of the IMP1 influent alkalinity. Recent developments suggest that buried limestone-backfilled trenches, if maintained in an anaerobic state, can passively increase alkalinity in wetlands influents to sufficiently buffer the water and prevent drastic pH decreases due to Fe hydrolysis (Turner and McCoy 1990; Brodie et al, 1991). Relationships in TVA's wetlands among influent alkalinity, effluent pH, Fe, and Mn confirm that wetlands treatment is enhanced by higher influent alkalinity.

Stability problems at IMP1 resulted from inadequate spillway and dike designs. Each dike was repaired in late 1989 to increase the freeboard to over 30 cm. The spillways were reconstructed to provide long-term, erosion-resistant stability. Six species were originally planted in IMP1: broadleaf cattail (Typha latifolia), wool grass (Scirpus cyperinus), rush (Juncus effusus), scouring rush (Equisetum hyemale), and squarestem spikerush (Eleocharis quadrangulata). Over 60 vegetative species have been identified in IMP 1, dominated by Typha latifolia, Scirpus cyperinus, Juncus effusus, Eleocharis quadrangulata, and rice cutgrass (Leersia oryzoides).

Total cost of the IMP1 wetlands was $43,000 (1985 dollars). Annual costs have been about $13,000 due to repairs on the prototype design and extensive monitoring.

Impoundment 4

Impoundment 4 (IMP4), also at the Fabius plant site, was built in fall 1985 to treat acid seepage emanating from upstream plant process water recirculation ponds. These ponds were reclaimed in 1986 and the inflow to IMP4 essentially ceased due to the reclamation and drought conditions from June 1986 to December 1987.

IMP4 never produced compliance-quality effluent from November 1985 to May 1990 due to the low alkalinity and pH problems from high Fe hydrolysis. Therefore, the discharge has required chemical treatment with sodium hydroxide (NaOH) since initial operation. Chemical addition took place in the third wetlands cell. However, large rainfall events flushed low pH water from the upper 2 cells and lowered the discharge pH to below permit limitations. Chemical treatment of all cells was then implemented and a 0.1 ha retention pond was constructed in 1988 below the existing wetlands to facilitate chemical treatment.

In April 1990, an anoxic limestone drain was installed upstream from the wetlands to pretreat the inflow by increasing the alkalinity. Such buffering capacity in the inflow has prevented pH drop and neutralized acidity, thereby enhancing the overall treatment efficiency of IMP4 and allowing the cessation of chemical treatment since May 1990 (Brodie et al 1990, 1991). Total cost of the wetlands was $28,000 (1985 dollars) with $32,000 average annual costs through May 1990, primarily for chemical treatment. The anoxic drain cost $19,000; thus it paid for itself in about 8 months. Thirty-five vegetative species in IMP 4 are dominated by Eleocharis quadrangulata, Juncus effusus, Scirpus cyperinus, and Typha latifolia. The original planting of IMP4 took place in November 1986, but few plants survived through winter and the wetlands was replanted the following July.

950-1 and 2

The 950-1 and 950-2 wetlands was a 2-cell sedimentation basin treating acid mine drainage from the reclaimed TVA Fabius 950 coal mine in Jackson County, Alabama. The upstream cell naturally developed into a cattail (Typha spp.) marsh that has expanded into the lower cell. Treatment with NaOH was required from 1976 to 1984. The discharge was released from NPDES permit monitoring requirements in 1987.

Continued quarterly influent/effluent monitoring has shown that the 950 discharge has remained within regulatory limitations (see Table 1).

Impoundment 2

Impoundment 2 (IMP2) is a series of constructed wetlands intermediate in a 138 ha drainage basin. It receives high flows of acid drainage from non-TVA abandoned mine land, acid pumpage from the slurry lakes, and drainage from the coarse refuse (gob) disposal area at the Fabius plant site. Effluent from the wetlands is treated with NaOH and discharged into a 1.1 ha retention pond. The system receives the lowest pH inflow of all of the TVA wetlands (< 3.5 s.u.) and is still removing Fe from 40 mg/l to about 3 mg/l (4.9 GDM). Thirty-seven vegetative species are present in the IMP2 wetlands and are dominated by cattail (Typha spp.) and squarestem spikerush (Eleocharis quadrangulata). Future measures to improve this wetlands system include expansion of the wetlands and construction of an anoxic drain, in addition to reclamation of the gob pile and slurry lakes.

Widows Creek 005

Widows Creek 005 (WCF5) is located at TVA's Widows Creek Fossil Plant and treats acid drainage from an active ash pond dike and runoff from the limestone storage silo area. The ponds were built in 1987 and became devoid of vegetation due to extreme water depth and muskrats. The system was replanted in July 1990 and the water level reduced to less than 0.5 m. The inner slopes of the dikes

were lined in 1990 with metal fencing to discourage muskrat burrowing and habitation.

Widows Creek 006

Widows Creek 006 (WCF6, formerly known as WIF 018), located at TVA's Widows Creek Fossil Plant in Jackson County, Alabama, treats high flows of acid seepage from an abandoned coal ash disposal area. High-iron, zero-alkalinity inflows result in high-acid production and low-pH values in the wetlands (see Table 1). The wetlands has always required chemical treatment to achieve compliance discharges. An anoxic drain is being considered for this system.

Thirty-two vegetative species in the wetlands are dominated by *Eleocharis quadrangulata*, *Juncus effusus*, *Scirpus cyperinus*, and *Typha spp*. In August 1986, an infestation of cattail armyworms (*Simyra henrici*) significantly damaged 60 to 80 percent of the cattails in WIF6 (Snoddy et al 1989). The infestation was attributed to the rapid development and the monocultural nature of the cattails at WCF6 and was controlled with the insecticide Lorsban.

Widows Creek 019

Widows Creek 019 (WCF19, formerly known as WIF 019) treated acid seepage from abandoned and active coal ash disposal areas. Widows Creek Fossil Plant's operational needs at this site resulted in flooding the wetlands and installing a facility to pump water to an existing ash pond for treatment.

Impoundment 3

Impoundment 3 (IMP3) is located at the TVA 950 Coal Mine and treats acid mine drainage. It was constructed to replace a chemical treatment system which operated from 1976 to 1986 at a cost of $300,000. The wetlands was built at a cost of $40,000. When compared to previous annual operating costs of nearly $25,000 and the inability to maintain compliance even with chemical treatment, the cost and environmental benefits of this wetlands are obvious.

In August 1987, a muskrat burrowed into cell 2 dike of the wetlands which resulted in catastrophic failure of the dike. The dike was repaired and the inner slopes of all dikes were lined with chain link fence and coarse riprap to prevent muskrat burrowing.

IMP3 has always produced compliance-quality discharges. The ecological recovery of Kash Creek, the IMP3 receiving stream that was severely impacted by acid mine drainage and NaOH treatment, was documented in June 1986 and June 1987 macroinvertebrate surveys. Only 2 taxa were identified in the 1986 pre-wetlands survey. Nineteen taxa were identified in the 1987 survey in Kash Creek and 31 taxa were found in the constructed wetlands. Thirty species are present in the wetlands dominated by *Scirpus cyperinus*, and *Typha spp*.

IMP3 was released from NPDES monitoring requirements in August 1989. This action was the first release of a TVA constructed wetlands.

Rocky Top 2

Rocky Top 2 (RT2) is located at TVA's reclaimed Fabius Rocky Top coal mine in Jackson County, Alabama. Inflow is acid mine drainage. This wetlands consists of a .25 ha deep pond followed by 2 wetlands cells constructed to replace a chemical treatment system. Total Fe and total Mn effluent concentrations for the period October 1987 to July 1989 show seasonal variations, similar to IMP1, in metals removal efficiencies that have resulted in slightly elevated Fe and Mn concentrations during the late winter and spring months. The compliance record at this site allowed its release from NPDES monitoring in June 1990. Thirty-six vegetative species are present in the wetlands dominated by Scirpus cyperinus and Juncus effusus.

950NE

The 950NE is located adjacent to the TVA 950 coal mine and treats acid mine drainage from about 32 ha of reclaimed area. As found in data for IMP1 and RT2, there is seasonal variation in metals removal efficiencies at 950NE with elevated Fe and Mn concentrations in the winter months. This impoundment, however, has produced compliance-quality discharges since initial operation, and release from NPDES monitoring requirements was approved in March 1990.

Of special concern at 950NE were beavers. The spillways at 950NE consisted of wide, trapezoidal, coarse riprapped channels. In 1988, beavers began damming 2 of the spillways using mud and cattails. After unsuccessful attempts to eliminate them, the spillways were fitted with culverts with upstream 90° elbows to prevent water level increases in the cell due to beaver activity. This action has not been entirely successful and other control methods are being tested at this and other sites. Thirty-one vegetative species in the wetlands are dominated by Scirpus cyperinus and Typha spp.

Dead Lady Lake

The Dead Lady Lake Wetlands (DLL) is located at the TVA 950 Coal Mine and treats acid mine drainage. The wetlands was completed in May 1990. Preliminary results indicate that this system is producing compliance quality effluent.

Kingston 006

Kingston 006 (KIF) is located at TVA's Kingston Fossil Plant in Roane County, Tennessee. It was constructed to treat high flows of acid seepage from a coal ash disposal area. About 20 cm of high-calcium, minus-16 mesh limestone covered with about 30 cm of spent mushroom compost for vegetative substrate was included in the final cell of the wetlands

system in an attempt to elevate pH. No significant effects on the effluent were noted due to the limestone bed. KIF is another high-Fe, low alkalinity system that has resulted in extremely low pH (2.9 s.u.). Effluent from the third cell has been pumped to the active ash pond for treatment while the system is under development. Remedial plans are being implemented for the system which include the use of bactericides (Sanda 1989) and an anoxic drain and oxidation basin, in conjunction with partial reclamation of the ash disposal areas. Twenty-three vegetative species are dominated by a sedge (Cyperus erythrorhyzos) and Typha spp.

Colbert 013

Colbert 013 (COF) is located at TVA's Colbert Fossil Plant in Colbert County, Alabama. It treats acid drainage from an indefinite source near an active ash disposal area. The COF wetlands is unique in that the influent water quality is characterized by very low Fe and higher Mn (see Table 1). Total Mn to total Fe ratios in non-chemically treated TVA wetlands influents range from 0.03 to 0.81, with the exception of COF which has a Mn/Fe ratio of 7.60. TVA's wetlands have Mn removal efficiencies ranging from zero (in low-pH systems) to 96 %. COF has a Mn removal efficiency of 34 % but is a relatively high-pH system. TVA is currently investigating the Mn removal efficiency at COF which could be related to absence or inhibition of Mn-oxidizing bacteria in the system or lack of Fe-Mn coprecipitation due to the low influent Fe concentration (0.7 mg/l). Initially, only pH was beneficially affected within the wetlands. Because Mn levels exceeded permit limitations, NaOH treatment was required in the third and fourth cells since 1987. Removal of Mn limitations at this site in 1990 has allowed cessation of NaOH treatment. A pilot study is now underway aimed at improving Mn removal at the COF wetlands including evaluating the use of rock filters to biologically remove manganese (Gordon and Burr 1989). The wetlands is dominated by Typha spp. and Scirpus cyperinus.

Summary and Conclusions

TVA has constructed 13 and operates 12 aerobic, staged wetlands systems for treating acid drainage from coal mine spoil, coal slurry and gob, and coal ash. These systems offer a preferred alternative to conventional methods of treating acid drainage from various coal-related sources.

Nine wetlands systems now produce effluents meeting all discharge limitations without chemical treatment, 4 of which have been released from NPDES monitoring requirements.

These 9 systems are associated with moderate inflow water quality (i.e., total Fe = 0.7 - 69 mg/l, total Mn = 5 - 17 mg/l), relatively high total Mn to

total Fe ratios in the influent (average Mn/Fe = 0.44), significant inflow alkalinity (35 - 300 mg/l), and variable Fe loading (.03 - 6.13 GDM).

Five systems have experienced high proton-acidity production and low pH within the wetlands due to Fe hydrolysis. Four of these systems are associated with high influent Fe concentrations (40-170 mg/l), high Fe loads (5 - 41 GDM), and zero to very low influent alkalinity. Two of these wetlands discharges require NaOH treatment to achieve compliance quality. One system, IMP4, was modified with an anoxic limestone drain which has allowed cessation of chemical treatment and enabled the wetlands to produce compliance quality discharges. Another system, KIF, is currently being modified with an anoxic limestone drain.

One system (COF) that has experienced very little metals removal is associated with low Fe (0.7 mg/l) and higher Mn (5.3 mg/l). The performance of this wetlands may be related to absence or inhibition of Mn-oxidizing bacteria or lack of Fe-Mn coprecipitation.

Fe and Mn removal efficiencies and pH improvement in the TVA wetlands show no obvious relationship to calculated treatment areas for total Mn or flow. This, in part, is probably due to the effect of Fe hydrolysis and H^+ production overwhelming other wetlands system mechanisms.

Many factors affect the ability of wetlands to ameliorate acid drainage, including hydrology, Fe and alkalinity concentrations, and various wetlands characteristics such as depth, area, hydraulics, vegetative and microbial species and extent, and substrate. Because of the interrelationships among these many factors and their effects on wetlands treatment efficiencies, it is difficult to develop treatment area design guidelines. Additionally, with the relatively new concept of the anoxic limestone drain, required areas and designs of wetlands to achieve compliance may be greatly affected. However, TVA's data show that even in the absence of alkalinity, wetlands are removing up to 21.3 GDM of Fe. Mn is being removed up to 1.9 GDM in the presence of alkalinity. These numbers may represent crude upper limit sizing criteria.

TVA's encouraging results suggest that staged treatment wetlands systems are preferred designs, potentially capable of treating poor-quality acid drainage. Such staged treatment may consist of: 1) an initial anaerobic limestone trench at the source of the seepage to passively add alkalinity; 2) a large, deep settling basin to accumulate oxidized and precipitated Fe sludges; and 3) a 2 or 3 cell constructed wetlands for Mn and further Fe removal. Adjustment of pH, if necessary, may take place in a post-wetlands system incorporating an alkaline bed (Brodie et al 1991). TVA

plans to continue its research and evaluation of operational and experimental wetlands treatment systems, especially regarding methods to passively increase buffering capacity and pH in wetlands influents and effluents. As more information is made available by TVA and other operating systems and research activities, design guidelines for the components of staged-treatment wetlands systems should be improved.

Literature Cited

Brodie, G.A. 1990a. Treatment of acid drainage using constructed wetlands - experiences of the Tennessee Valley Authority. Pages 77-83 In Graves, D.H., ed. Proceedings 1990 National Symposium on Mining. University of Kentucky BU 153. Lexington, KY.

Brodie, G.A. 1990b. Constructed wetlands for treating acid drainage at Tennessee Valley Authority Coal facilities. Proceedings: 12th Annual Nat'l Assoc. of Abandoned Mined Lands Program Conference. Sept., 1990. Breckinridge, CO.

Brodie, G.A. 1990c. Workshop on design, construction, and operation of wetlands systems to treat acid drainage. Proceedings: 12th Annual Nat'l Assoc. of Abandoned Mined Lands Program Conference. Sept., 1990. Breckinridge, CO.

Brodie, G.A. 1991. Unpublished results of current research using alkaline beds for increasing constructed wetlands effluent pH. Project co-funded by the Pennsylvania Electric Company and the Tennessee Valley Authority.

Brodie, G.A.; C.R. Britt; H.N. Taylor; T.M. Tomaszewski and D. Turner 1990. Passive anoxic limestone drains to increase effectiveness of wetlands acid drainage treatment systems. Proceedings: 12th Annual Nat'l Assoc. Abandoned Mined Lands Program Conference. Sept 16-20, 1990. Breckinridge, CO.

Brodie, G.A.; C.R. Britt; H.N. Taylor 1991. Use of passive anoxic limestone drains to enhance performance of acid drainage treatment wetlands. Proceedings: 1991 ASSMR Reclamation 2000: Technologies for Success. Durango, CO. May 14-17, 1991.

Brodie, G.A. and C.M. Garvich 1991. Preliminary results of an investigation underway on the genesis of alkalinity at TVA's Impoundment 1 constructed wetlands. Tennessee Valley Authority. Chattanooga, TN.

Brodie, G.A. and H.N. Taylor 1991. Unpublished results of an ongoing study on storm effects on effluent water quality at TVA's IMP1, IMP4, and RT2 constructed wetlands. Tennessee Valley Authority. Chattanooga, TN.

Copeland, S.R. 1988. Relative Radial Oxygen Loss from five wetlands plants. School of Forestry and Environmental Studies, Duke University, Masters Degree Project, Durham, NC.

Cravotta, C.A.; K.B.C. Brady; M.W. Smith; and R.L. Beam 1990. Effectiveness of the addition of alkaline materials at surface coal mines in preventing or abating acid mine drainage: part 1: geochemical considerations. Pages 221-225 In J. Skousen et al, eds. Proceedings of the 1990 Mining and Reclamation Conference and Exhibition, Volume 1. W.V. Univ. Publication Services. Morgantown, WV.

Girts, M.A.; R.L.P. Kleinmann; and P.M. Erickson 1987. Performance data on Typha and Sphagnum wetlands constructed to treat coal mine drainage. In Proceedings of 8th Annual Surface Mine Drainage Task Force Symposium, Morgantown, WV.

Gordon, J.A. and J.L. Burr 1989. Treatment of manganese from mining seep using packed columns. Journal of Environmental Engineering, Vol 115, No 2.

Faulkner, S.P. and C.J. Richardson 1990. Biogeochemistry of iron and manganese in selected TVA constructed wetlands receiving acid mine drainage. Duke Wetland Center Publication 90-03. Durham, N.C.

Hedin, R.S. 1989. Treatment of coal mine drainage with constructed wetlands. Pages 349-362 In S.K. Majumbar et al, eds. Wetlands ecology and conservation: emphasis in Pennsylvania, The Pennsylvania Academy of Science, Easton, PA, p 349-362.

Hedin, R.S. and R.W. Nairn 1990. Sizing and performance of constructed wetlands: case studies. Pages 385-392 In J. Skousen et al, eds. Proceedings of the 1990 Mining and Reclamation Conference and Exhibitions, Vol 1. West Virginia University Publication Services. Morgantown, WV.

Hedin, R.S; R.L.P. Kleinmann; and G.A. Brodie 1990. Constructing wetlands to treat acid mine drainage. Course Manual. Virginia Tech University. Wise, VA.

Hem, J.D. 1981. Rates of manganese oxidation in aqueous systems. Geochimica et Cosmechimica Acta, 45:1369.

Kepler, D.A. 1990. Wetlands sizing, design, and treatment effectiveness for coal mine drainage. Pages 403-408 In J. Skousen et al, eds. Proceedings of the 1990 Mining and Reclamation Conference and Exhibition, Vol. 1. WV Univ. Publication Services. Morgantown, WV.

Kleinmann, R.L.P. 1990. Personal communication. U.S. Bureau of Mines. Pittsburg, PA.

Kleinmann, R.L.P.; R.S. Hedin; D. Hyman; and G.A. Brodie 1990. Constructing wetlands to treat acid mine drainage. Course Manual for workshop presented at the

1990 National Mining Symposium, Knoxville, TN.

Meehan, T. 1991. Personal communication regarding the Shade acid drainage treatment wetlands, Somerset County, PA. Wetland Resources, Inc. Somerset, PA.

Reed, S.C.; E.J. Middlebrooks; and R.W. Crites 1988. Natural systems for waste management and treatment, McGraw-Hill Book CO, New York, NY, 308 pp.

Snoddy, E.L.; G.A. Brodie; D.A. Hammer; and D.A. Tomljanovich 1989. Control of the Armyworm, Simyra henrici (Lepidoptera: Noctuidae), on cattail plantings in acid drainage treatment wetlands at Widows Creek Steam-Electric Plant. Pages 808-811 In D.A. Hammer, ed. Wetlands for wastewater treatment. Lewis Publishers, Inc., Chelsea, MI.

Stark, L.R.; S.E. Stevens Jr.; H.J. Webster; and W.R. Wenerick 1990. Iron loading, efficiency and sizing in a constructed wetland receiving mine drainage. Pages 393-401 In J. Skousen et al, eds. Proceedings of the 1990 Mining and Reclamation Conference and Exhibition, Vol 1 WV Univ. Publication Services. Morgantown, WV.

Sunda, W.G. and S.A. Huntsman 1988. Effect of sunlight on redox cycles of manganese in the southwestern Sargasso Sea. Deep Sea Research, Vol. 35, No.8, p. 127.

Tomljanovich, D.A.; G.A. Brodie; and H.N. Taylor 1991. Unpublished preliminary results of Phase II research on effects of hydraulic and chemical loading on Fe and Mn removal at the TVA Fabius Hard Rock Wetlands Research Facility. Tennessee Valley Authority. Knoxville, TN.

Turner, D. and D. McCoy 1990 Anoxic alkaline drain treatment system, a low cost acid mine drainage treatment alternative. Pages 73-75 In D.H. Graves, ed. Proceedings 1990 National Symposium on Mining. University of Kentucky BU 153, Lexington, KY.

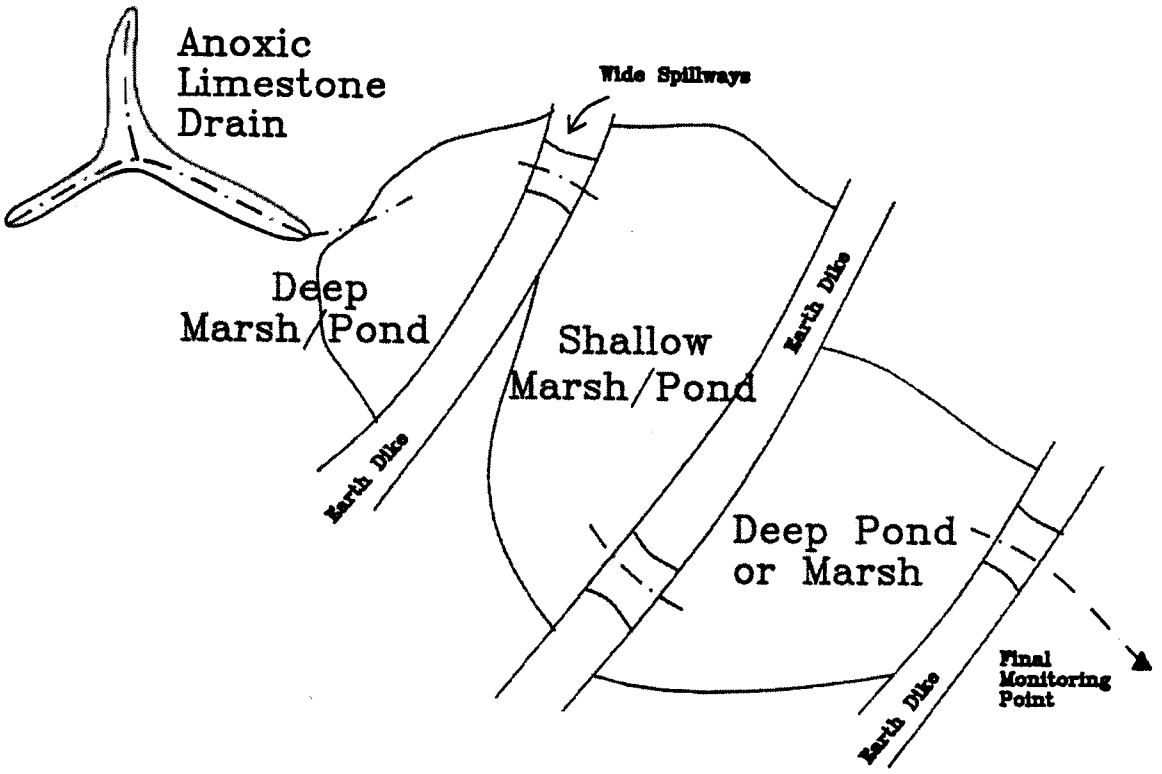
Tuttle, M.D. 1988. America's Neighborhood Bats. 96 pages. Univ. of Texas Press, Austin, TX.

TABLE 1

TVA ACID DRAINAGE WETLANDS TREATMENT SUMMARY

Wetlands System	Date Initiated Operation	Area m^2	Number Cells	Influent Water Parameters (mg/L) pH	Fe	Mn	TSS	Effluent Water Parameters (mg/L or L/min) pH	Fe	Mn	NFR	Flow Ave	Flow Max	Loading g/day/m^2 Fe	Loading g/day/m^2 Mn	l/day/m^2 Ave Flow
950	1-76	3400	3	5.7	12.0	8.0	20.0	6.5	1.1	1.6	5.4	83	341	.42	.28	.04
IMP1	7-85	5700	4	6.	69.0	9.3	9.5	6.7	0.9	.8	3.0	73	693	.27	.17	.02
IMP4	11-85	2000	3	6.3	65.0	16.8	21.0	6.3	0.4	0.6	6.0	131	693	6.13	.58	.09
WCF5	7-90	6600	4					8.4	2.2	0.7		973	2057			.21
WCF6	6-86	4800	3	5.6	150.0	6.8		3.9	6.4	6.2		289	1495	13.0	.59	.09
WCF19	6-86	25000	3	5.6	17.9	6.9		4.3	3.3	5.9		492	6360	.50	20	.03
IMP2	6-86	11000	5	3.5	40.0	13.0	9.0	3.1	3.4	13.0	0.8	1016*	1540*	5.32	.72	.13
IMP3	10-86	1200	3	6.3	15.8	4.9	21.4	7.0	0.5	0.7	9.0	58	250	.10	.34	.07
RT2	9-87	7300	3	5.7	45.2	13.4		6.8	0.6	1.8	3.2	277	1155	2.47	.73	05
950NE	9-87	2500	4	6.0	11.0	9.0	19.0	6.9	0.6	0.8	5.0	385	1386	2.44	2.00	.22
KIF6	10-87	9300	3	5.5	170.0	4.4	40.0	2.9	82.5	4.6		1574	2271	41.43	1.07	.24
COF	10-87	9200	5	5.7	0.7	5.3		6.7	0.7	3.5		288	408	03	.24	.05
DLL	5-90	7550	4	6.2	10.0	5.5	23.0	6.4	2.	2.2	10.0	385	7700	73	40	.07

*Also receives pumpage from slurry lake up to 4800 l/min.



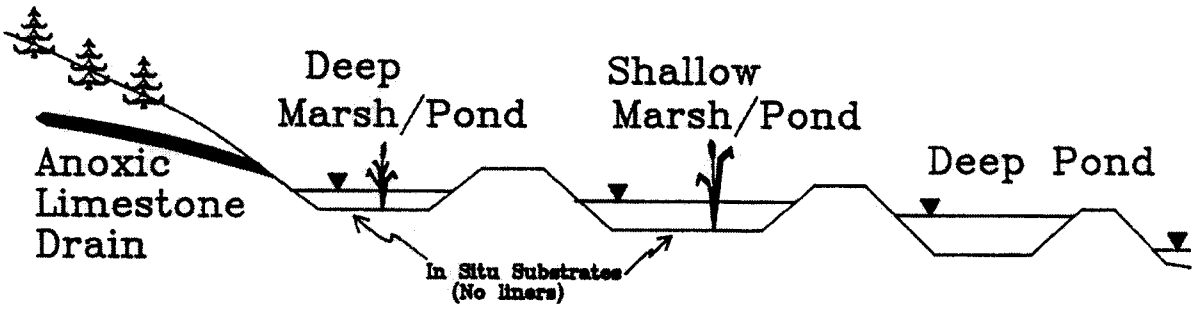


Figure 1. Schematic of Typical Staged, Aerobic Constructed Wetlands

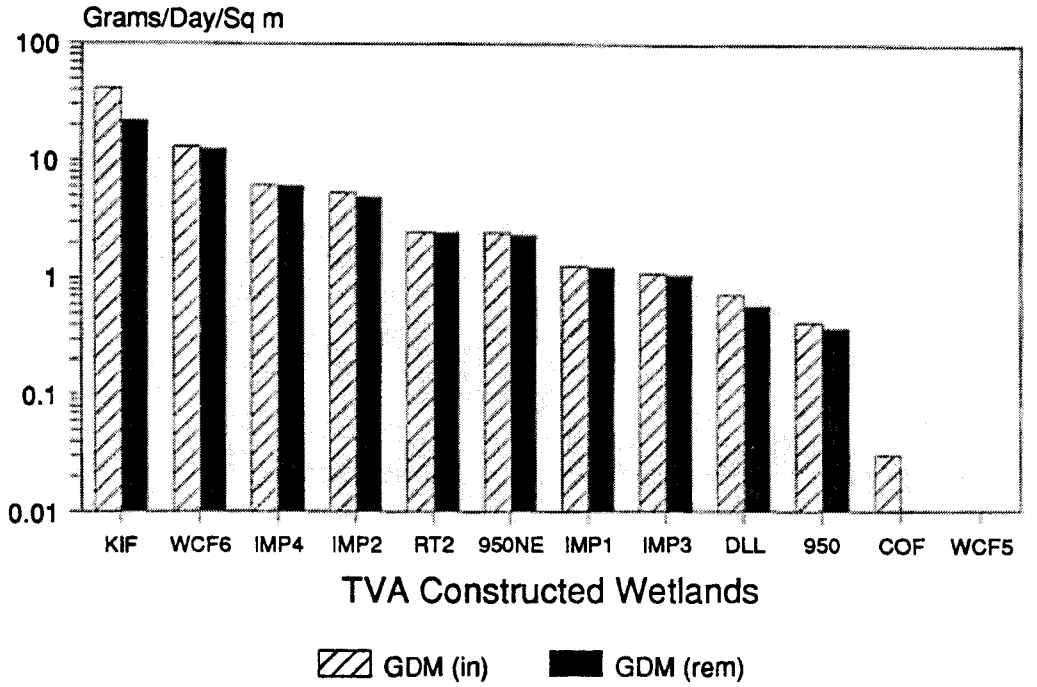


Figure 2. Fe Loading and Removal in TVA Wetlands

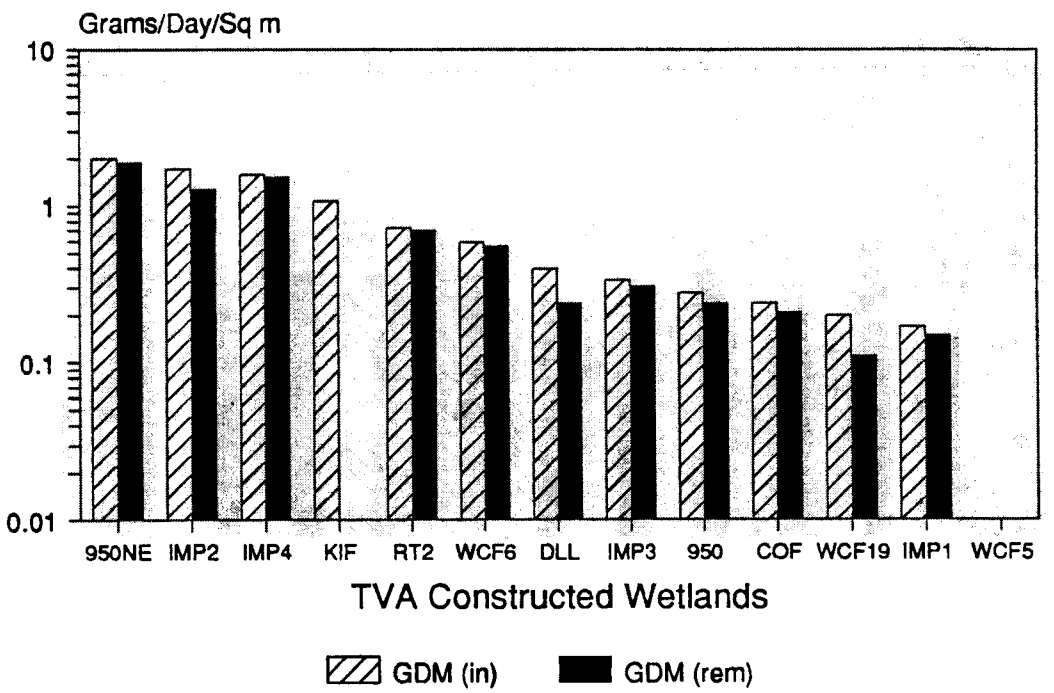


Figure 3. Mn Loading and Removal in TVA Wetlands

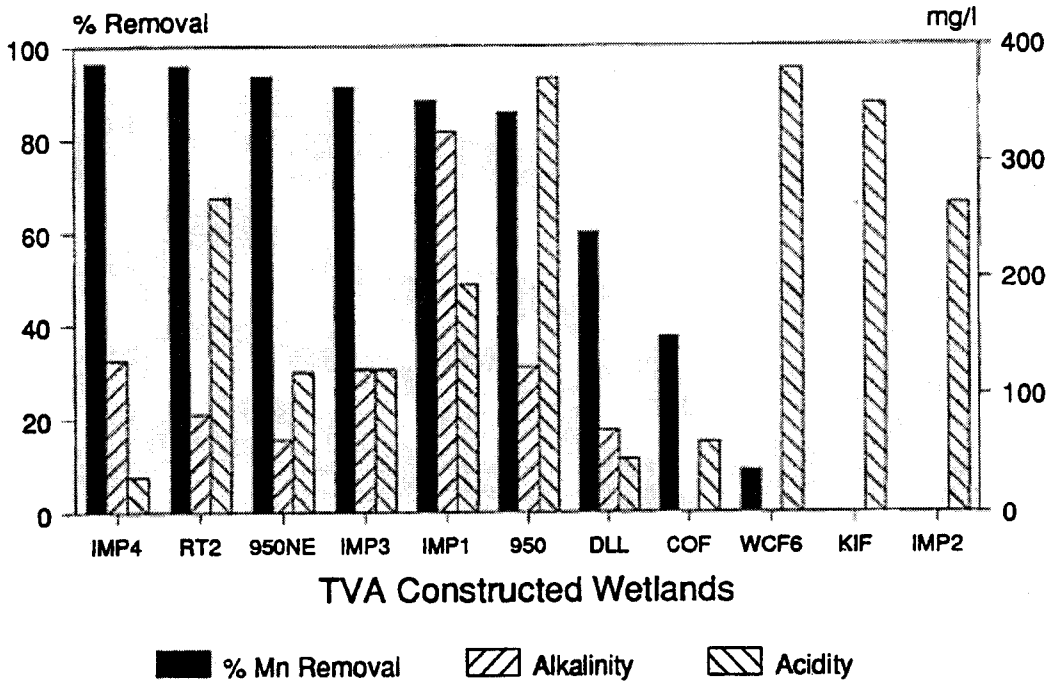


Figure 4. Mn Removal Related to Alkalinity and Acidity

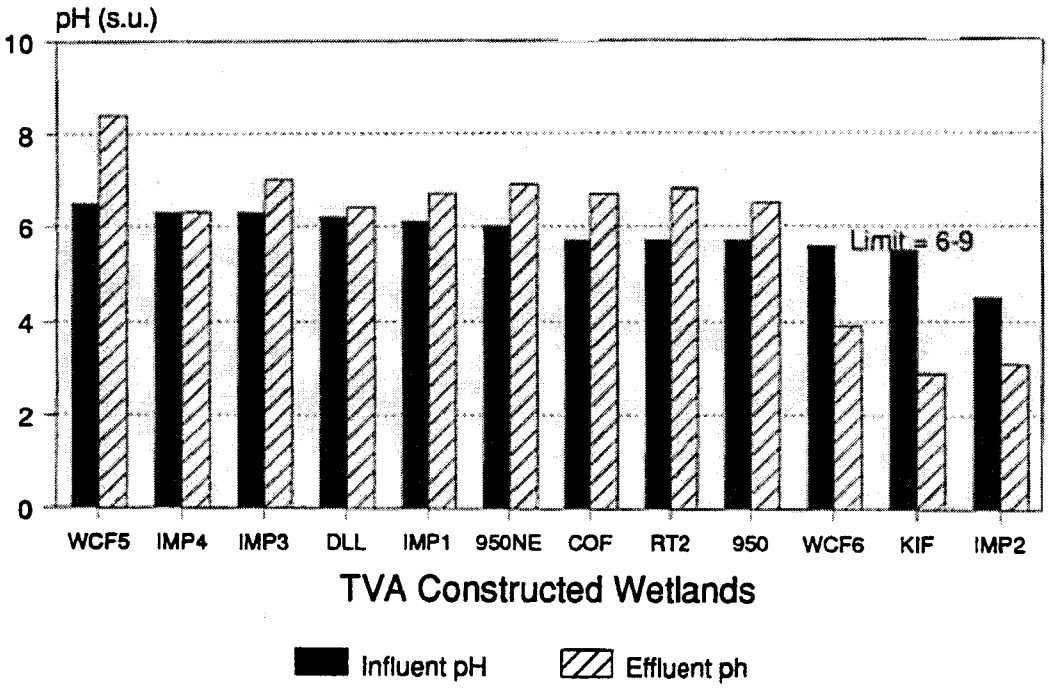


Figure 5. Influent and Effluent pH in TVA Wetlands

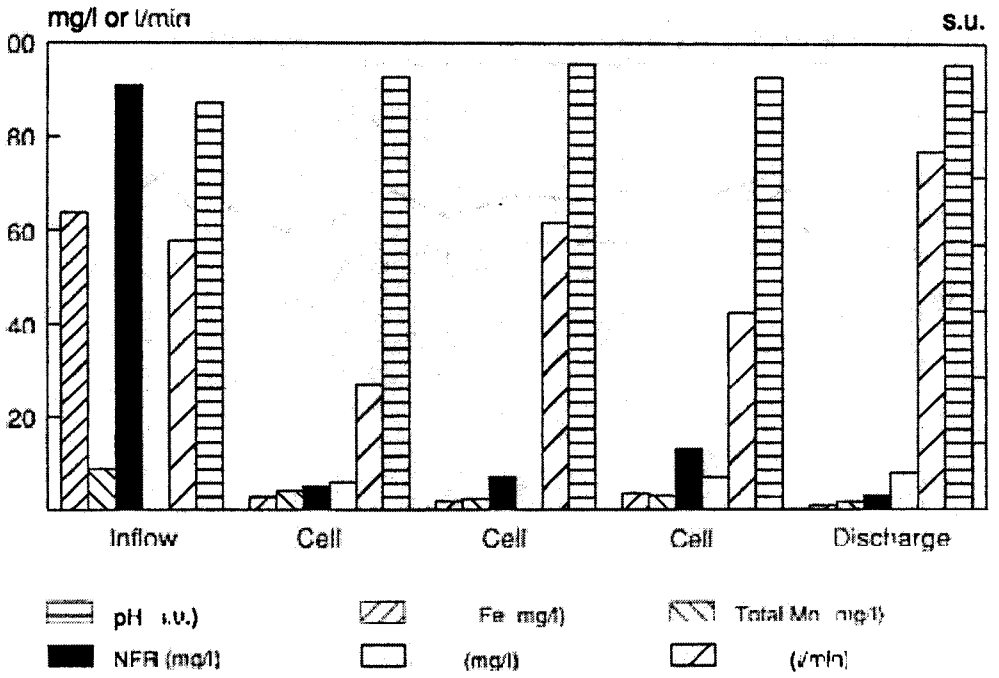


Figure Fabius IMP1 Wetlands Average Water Quality Data

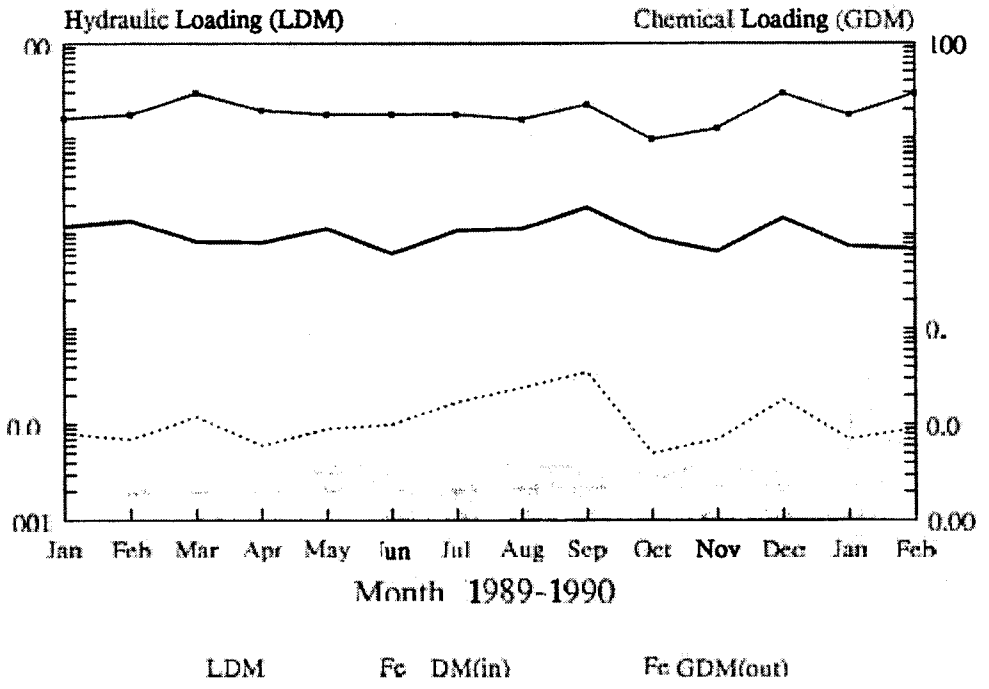


Figure Fabius IMP Wetlands Fe Loading and Removal

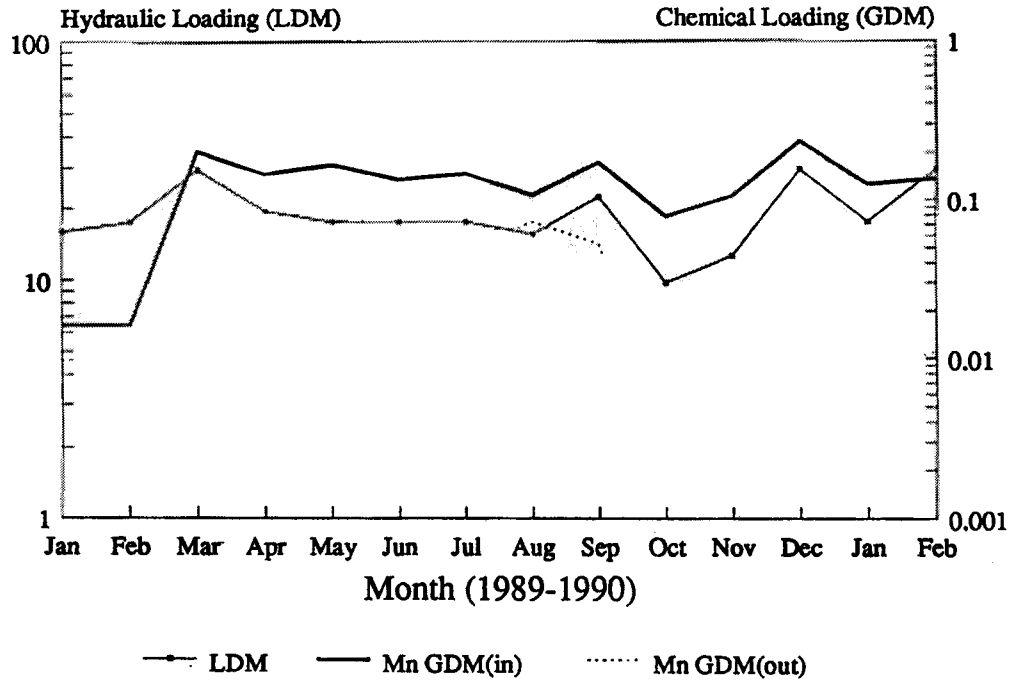


Figure 8. Fabius IMP1 Wetlands Mn Loading and Removal

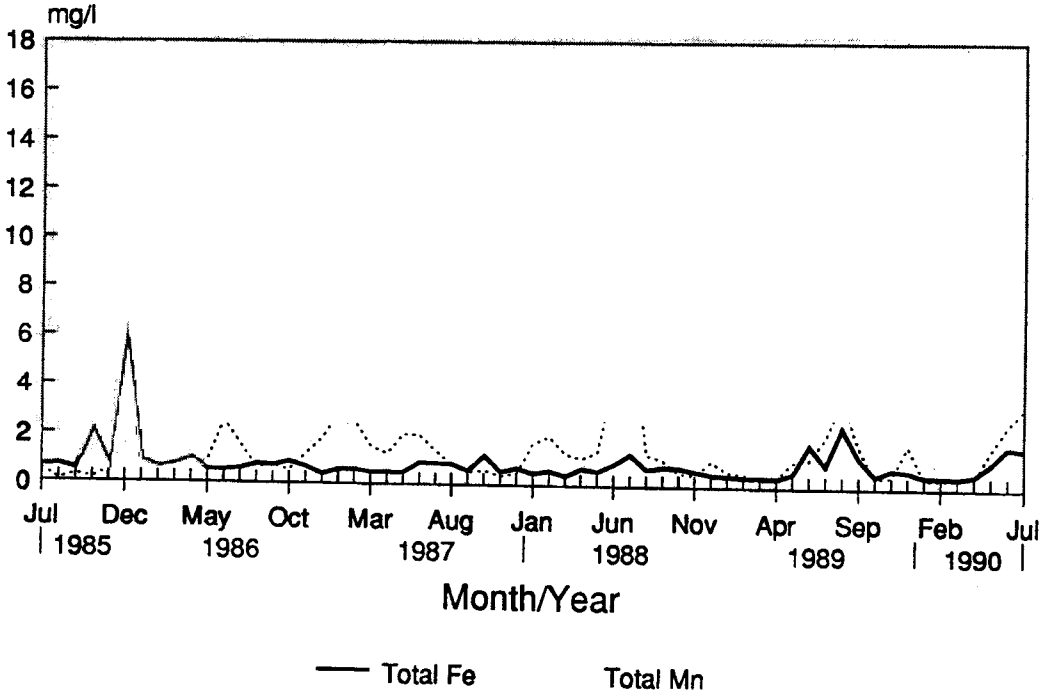


Figure 9. Fabius IMP1 Wetlands Effluent Fe & Mn Data

DETERMINATION OF THE RATE OF SULFIDE PRODUCTION IN A CONSTRUCTED WETLAND RECEIVING ACID MINE DRAINAGE[1]

by
Julia S. Reynolds, Steven D. Machemer, Thomas R. Wildeman,
David M. Updegraff, and Ronald R. Cohen[2]

Abstract. The Big Five wetland in Idaho Springs, Colorado was built to treat mine drainage with low pH and high concentrations of heavy metals. Field studies indicated that sulfate reduction and sulfide precipitation are important processes in removing metals from the mine drainage. The approximate summer in situ rate of sulfide production by sulfate-reducing bacteria at the wetland was determined to be 1.2 micromoles of sulfide per gram of dry substrate per day by a laboratory serum bottle experiment. Preliminary results indicated that the addition of sodium lactate or an extract of hay significantly increased the rate of sulfide production in the bottles. Sulfate and dissolved metal concentrations decreased, whereas acid volatile sulfide concentration and pH increased with time in the serum bottles. The conditions in the serum bottles were similar to conditions in the wetland output, indicating that the laboratory scale systems could be used to estimate the remediation potential of a constructed wetland for the treatment of mine drainage.

Additional key words: Sulfate-reducing bacteria, heavy metals remediation.

Introduction

Acid mine drainage from abandoned mining operations contributes significantly to water pollution in Colorado streams. Artificial wetlands are currently being considered as possible passive treatment systems for drainage from these sources, utilizing natural biological and geochemical processes to treat the water. The Big Five wetland in Idaho Springs, Colorado was constructed to determine the effectiveness of such a system in treating mine drainage with low pH and high concentrations of heavy metals and sulfate. The design, construction, and initial operating results of the Big Five wetland treatment system are given in Howard, et al. (1989a and 1989b).

Research projects over the past few years have studied several metal removal processes that could be occurring in the Big Five wetland, including adsorption of metals onto organic materials in the substrate, uptake of metals by the vegetation, and precipitation of metals as sulfides (Machemer et al., 1990, Laudon, 1989). Results of laboratory and field studies indicate that organic adsorption processes are important during the start-up phase of the constructed wetland. However, after several months of operation, organic adsorption sites are filled by the metals and sulfide precipitation becomes the dominant process of metal removal from the incoming mine drainage (Machemer and Wildeman, 1991).

Production of hydrogen sulfide from sulfate by dissimilatory sulfate-reducing bacteria has been shown to be an important process in the sulfur cycle of marine and fresh water environments (Smith and Klug, 1981). Sulfate-reducing bacteria mineralize organic matter in anoxic waters and sediments using sulfate as an electron acceptor according to the

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following reactions:

$$2CH_2O + SO_4^{-2} \rightarrow S^{-2} + 2CO_2 + 2H_2O \qquad (1)$$

$$S^{-2} + 2CO_2 + 2H_2O \rightarrow H_2S + 2HCO_3^- \qquad (2)$$

The products of sulfate reduction (i.e., hydrogen sulfide and bicarbonate ions) are desirable for the treatment of acid mine drainage as the increase in alkalinity will help raise the pH of the water and the hydrogen sulfide can react with the dissolved metals to form sulfide precipitates (Herlihy et al., 1987).

Results of microbiological studies of the Big Five wetland substrate indicate that sulfate-reducing bacteria are present in large numbers, with viable counts ranging from 1900 to 28,000,000 bacteria per gram of dry substrate (Batal, 1989). Analysis of outflow from the wetland shows a decrease in sulfate concentration of approximately 10-20%, significant decreases in concentrations of iron, zinc, and copper (i.e., consistently complete removal of copper and up to 100% removal of iron and zinc depending on flow rate), and an increase in pH as compared to the incoming mine drainage (Machemer and Wildeman, 1991). Significant increases in the sum of acid volatile sulfides (i.e., metal monosulfide precipitates such as FeS and ZnS) plus elemental sulfur over levels measured in the original substrate material have been demonstrated in areas of the Big Five wetland containing mushroom compost. Acid volatile sulfides (AVS) plus elemental sulfur represented 0.15% of the total sulfur in the original compost material. After ten months of operation of the wetland, the compost contained 1.1% of the total sulfur as AVS plus elemental sulfur. However, no significant increases in organic or pyritic forms of sulfur were detected in these areas after the same period of time (Laudon, 1989). All of these results indicate that bacterial sulfate reduction is an important process in the treatment of mine drainage at the Big Five wetland.

The objectives of this study included designing a laboratory scale system to determine an approximate in situ rate of sulfide production by sulfate-reducing bacteria by measuring the change in AVS in the substrate over time and to determine the effects of nutrient amendments on the rate of sulfide production. Another purpose of constructing these laboratory scale wetland substrate systems was to compare values of various parameters such as pH, concentrations of dissolved metals and sulfate, and temperature in the serum bottles to output waters at the Big Five wetland. From these comparisons, the usefulness of serum bottle systems in initial treatability studies could be evaluated.

Materials and Methods

Collection of Samples and Preparation of Serum Bottles

In June 1990, a 2-liter sample of substrate was collected from an area of the wetland containing mushroom compost. Twelve liters of mine drainage were collected from the adit of the Big Five Tunnel and deoxygenated in the field with nitrogen.

The substrate sample was homogenized on a paint shaker for five minutes. Subsamples of approximately 20 grams were then transferred to 120 ml serum bottles in a glove bag under a nitrogen atmosphere. The bottles were sealed in the glove bag. The following day, 70 ml of deoxygenated mine drainage was added by syringe to each bottle. The bottles were then incubated at 18° C. This temperature was chosen to simulate summer conditions at the wetland.

Determination of Dissolved Metals, Sulfate, and pH in Serum Bottles

Several parameters were determined to be important for comparing conditions in the serum bottles to output waters from the wetland, including pH and concentrations of dissolved metals and sulfate. At approximately five day intervals, an aliquot of the aqueous phase of the serum bottles was removed by syringe. Concentrations of dissolved metals (i.e., zinc, copper, iron, and manganese), sulfate concentration, and the pH of this subsample were determined. Concentrations of dissolved metals were measured by atomic absorption. The sulfate concentration was determined gravimetrically as $BaSO_4$.

Rate of Sulfide Production

Four bottles were analyzed on the first day after the mine drainage was added for acid volatile sulfides to provide a baseline level of AVS in the substrate sample. AVS was determined with a trapping train similar to the one described by Jorgensen and Fenchel (1974). The bottles were connected to the trapping train and approximately 25 ml of 6M HCl was added by syringe. The H_2S that was produced was flushed from the serum bottles with O_2-free nitrogen and

trapped in the first of two test tubes containing 1N NaOH connected in series. No sulfide was ever detected in the second test tube. Approximately 2 ml of 7.5 M NH_4OH was added to an aliquot of the first trap, and this solution was titrated with 0.01M $AgNO_3$ to determine the amount of sulfide trapped. The efficiency of the trapping train was determined to be 93% by acidifying a known quantity of ZnS in place of the substrate sample. AVS values determined by titration were corrected accordingly.

Subsequent determinations of AVS were made on triplicate samples at approximately 5-day intervals. The rate of sulfide production was determined by taking the difference in AVS per gram of dry substrate in the subsequent samples from the average AVS per gram of dry substrate in the baseline samples and dividing by the time interval.

Poisoned Controls

Poisoned controls were prepared by adding 11 ml of 5% sodium azide to each of three serum bottles for a final concentration of 0.5%. AVS in these bottles was determined at 15, 35, and 70 day intervals by the method described above.

Nutrient Amendments

Nutrient amendments of either sodium lactate (final concentration of 100 mg/l) or 30 ml of an extract of hay were added to a set of serum bottles. The sodium lactate was chosen because lactate has been found to be a substrate utilized by sulfate-reducing bacteria (Dicker and Smith, 1985). Hay has been used at the Big Five wetland as insulation for the substrate and has appeared to enhance the activity of the sulfate-reducing bacteria. The hay extract was prepared by soaking a sample of hay in distilled water for approximately one week and then removing the supernatant. The AVS produced in these bottles was measured by the method described above approximately two weeks after the addition of the amendments.

Results

Rate of Sulfide Production

Table 1 presents the AVS per gram of dry substrate produced in the serum bottles over 76 days at approximately 5-day intervals. The average rate of sulfide production in the bottles at each time interval is also presented. The initial rate was 1.7 umoles of sulfide per gram of dry substrate per day for the first 5-day interval. From 5 to 35 days the rate was relatively constant at approximately 1.2 umol/g/day. Beginning with the 40-day time period, the rate of sulfide production began to decrease and this trend continued for the rest of the experiment.

Figure 1 shows the rate of sulfide production in the serum bottles compared to the rate in the poisoned controls. The rate in the controls was minimal compared to the serum bottles, indicating that the production of sulfide in the wetland substrate is predominantly the result of microbial activity.

Effect of Nutrient Amendments

The rates of sulfide production measured in amended bottles were compared to rates measured in unamended serum bottles for corresponding time intervals. These rates in umoles of sulfide per gram of dry substrate per day were as follows:

Sodium lactate	2.4
Hay extract	4.3
No amendment	0.91

The addition of sodium lactate resulted in a rate approximately 2.5 times greater than the rate measured in the unamended bottles. The addition of hay extract resulted in a rate approximately five times greater than in the unamended bottles.

Comparison of Serum Bottles to Mine Drainage and Wetland Output Waters

Table 2 presents a comparison of pH, temperature, concentrations of dissolved metals, and sulfate concentration for serum bottles over a 35-day time period. Mine drainage and output waters from the Big Five wetland treatment system were measured at approximately the same time as the substrate sample was collected.

Table 2 shows that concentrations of dissolved metals in the baseline sample bottles (i.e., measured the day after adding the mine drainage) were lower than the concentrations in the mine drainage. Several processes could have contributed to this immediate removal of some of the metals, including precipitation due to the increase in pH, adsorption onto organic materials enhanced by the agitation of the substrate, and precipitation with residual sulfides in the substrate sample.

Over the course of the experiment, the pH of the serum bottle systems increased, the concentration of

TABLE 1. AVS Production and Rate of Sulfide Production in Serum Bottles.

TIME (days)	B*	5	10	15	20	25	30	35	40	48	55	66	76
AVS (umol/g)	43	52	55	59	68	73	77	84	81	85	89	99	100
RATE (umol/g/d)	**	1.7	1.2	1.1	1.2	1.2	1.1	1.2	0.95	0.86	0.84	0.84	0.74

* Baseline samples
** Not calculated
Note: Values for AVS and rate are the average of three replicates except for values on day 0 (Baseline), which are the average of four replicates and days 10 and 25, which are the average of duplicate samples.

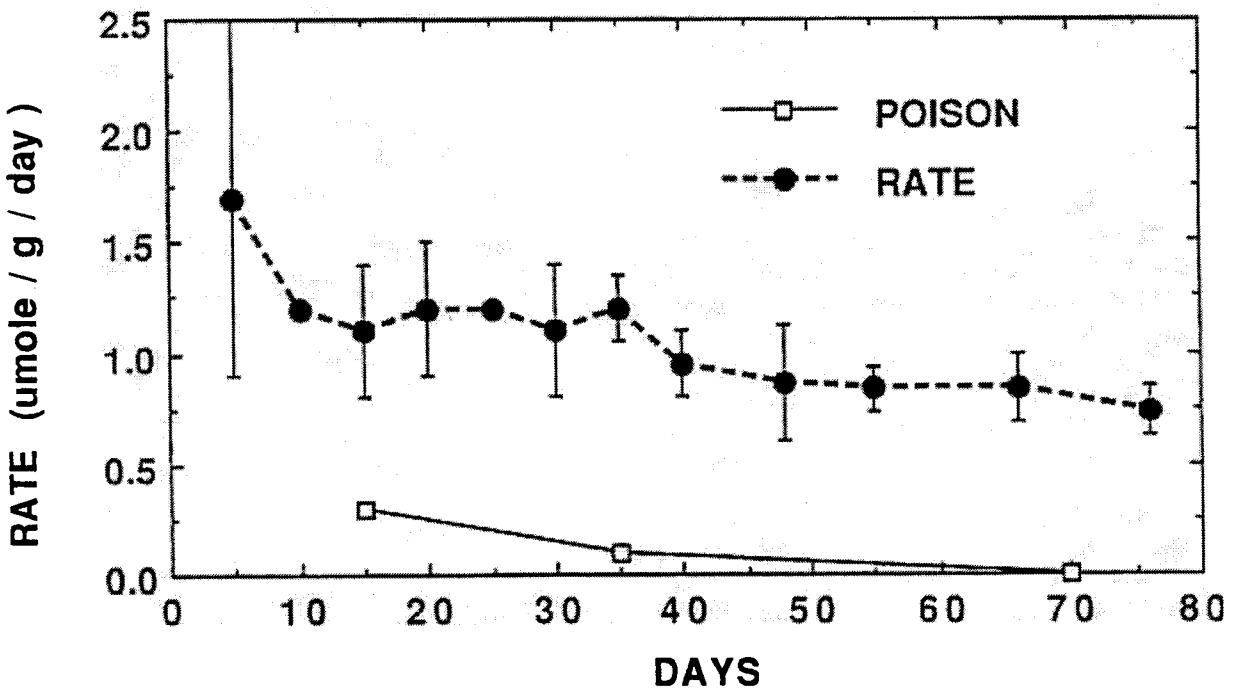

FIGURE 1. Rate of Sulfide Production in Serum Bottles and Poisoned Controls. Error bars represent one standard deviation. Data points without error bars are the average of two samples.

sulfate in the aqueous phase decreased, and the concentrations of dissolved metals decreased. These are the same trends observed when samples of output waters from the Big Five wetland are compared to samples of the incoming mine drainage.

Discussion

Results of these studies indicate the laboratory scale method developed for determining the rate of sulfide production in a wetland substrate could also be used as an inexpensive, initial treatability study of acid mine drainages. A relatively constant rate of sulfide production was measured over a 30-day period. For a treatability study, the serum bottles could be run for just two weeks to obtain a reasonable estimate of the rate of sulfide production in a given system. In addition, the serum bottles could be used to test the effectiveness of different substrates and combinations of nutrient amendments on treating a particular source of mine drainage.

The sulfide production rate measured in the laboratory could be used to estimate loading rates of metals that could be effectively removed by a constructed wetland. Several methods have been used to estimate loading rates. One method is based on the concept that the wetland operates most efficiently if a suitable microenvironment for the sulfate-reducing bacteria is consistently maintained (Reynolds, et al., 1991). The most important environmental factors are reducing conditions and a pH around 7. These conditions should exist when sulfide is being produced in excess of the amount required to precipitate all of the metals in the incoming mine drainage. In this case, metals are the limiting reagent in the precipitation of metal sulfides. The sulfide production rate measured in serum bottles could be used to estimate a loading rate for metals that would result in metals rather than sulfide being the limiting reagent.

Finally, measurements of other parameters in the serum bottles such as sulfate concentration, concentrations of dissolved metals, and pH could be used to qualitatively predict conditions in the output waters expected after the wetland treatment system is established.

Summary

The summer in situ rate of sulfide production by bacteria in the Big Five wetland substrate was estimated to be 1.2 umol/g/day. The rate of sulfide production measured in poisoned control bottles was minimal compared to the serum bottles, indicating that the process is predominantly microbiological. Preliminary results indicated that the addition of sodium lactate or an extract of hay significantly increased the rate of sulfide production in the serum bottles. Trends in sulfate concentrations, pH, and concentrations of dissolved metals were similar to conditions measured in output waters from the Big Five wetland, indicating that the serum bottle systems could be used in initial treatability studies for mine drainage.

Acknowledgments

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Literature Cited

Batal. W.H. 1989. Dynamics of the microbial populations in the substrate of the constructed wetland at the Big Five Tunnel, Idaho Springs, Colorado. Masters Thesis No. 3813. Colorado School of Mines, Golden, Colorado. 176 pp.

Dicker, H. J. and D. W. Smith. 1985. Effects of Organic Amendments on Sulfate Reduction Activity, H_2 Consumption, and H_2 Production inl Salt Marsh Sediments. Microbial Ecology 11: 299-315.

Herlihy, A.T., A.L. Mills, G.M. Hornberger, and A.E. Bruckner. 1987. The importance of sediment sulfate reduction to the sulfate budget of an impoundment receiving acid mine drainage. Water Resources Research 23 (2): 287-292.

Howard, E.A., J.E. Emerick, and T.R. Wildeman. 1989a. The design, construction and initial operation of a research site for passive mine drainage treatment in Idaho Springs, Colorado, p.761-764. In Constructed

Wetlands for Wastewater Treatment, D.A. Hammer, ed. Lewis Publishers, Ann Arbor, MI.

Howard, E.A., T.R. Wildeman, Laudon, L.S., and S.D. Machemer. 1989b. Design considerations for the passive treatment of acid mine drainage, p. 651-660. In Proceedings of the Conference "Reclamation, A Global Perspective." Alberta Land Conservation and Reclamation Council Report #RRTAC 89-2.

Jorgensen, B.B. and T. Fenchel. 1974. The sulfur cycle of a marine sediment model system. Marine Biol. 24: 189-201.

Laudon, L.S. 1989. Sulfur mineralization in a wetland constructed to treat acid mine drainage. Masters Thesis No. 3660 Colorado School of Mines, Golden, Colorado. 58 pp.

Machemer, S.D., P.R. Lemke, T.R. Wildeman, R.R. Cohen, R.W. Klusman, J.C. Emerick, and E.R. Bates. 1990. Passive treatment of metals mine drainage through use of a constructed wetland, pp. 104-114. In Proceedings of the 16th Annual Hazardous Waste Research Symposium, U.S. EPA, Cincinnati, OH. EPA/600/9-90-037.

Machemer, S.D. and T.R. Wildeman. 1991. Adsorption compared with sulfide precipitation as metal removal processes from acid mine drainage in a constructed wetland. Journal of Contaminant Hydrology. In press.

Reynolds, J.S., J.L. Bolis, S.D. Machemer, and T.R. Wildeman. 1991. Sulfate reduction in a constucted wetland. Preprints Div. Environ.. Chem. 31 (1).

Smith, R.L. and M.J. Klug. 1981. Reduction of sulfur compounds in the sediments of a eutrophic lake basin. Appl. Environ. Microbiol. 41 (5): 1230-1237.

TABLE 2. Comparison of pH, Temperature, Sulfate, and Metal Concentrations in Mine Drainage, Wetland Output, and Serum Bottles.

SAMPLE	pH	TEMP. (°C)	SO_4^{-2} (mg/L)	Cu (mg/L)	Fe (mg/L)	Mn (mg/L)	Zn (mg/L)
Mine Drainage	3.0	15.9	1720	0.573	38.6	30.6	8.58
Wetland Output	6.7	18.1	1460	<0.050	0.640	15.8	0.069
Serum Bottles Baseline*	6.1	18.0	1680	<0.050	10.5	15.5	0.036
Serum Bottles (5 days)*	6.2	18.0	1660	<0.050	7.28	10.8	0.534
Serum Bottles (10 days)**	6.3	18.0	1610	<0.050	4.70	9.78	0.272
Serum Bottles (15 days)**	6.3	18.0	1530	<0.050	8.80	15.3	0.129
Serum Bottles (20 days)**	6.4	18.0	1410	<0.050	8.06	12.0	0.368
Serum Bottles (25 days)**	6.4	18.0	1470	<0.050	6.90	11.3	0.221
Serum Bottles (30 days)**	6.4	18.0	1350	<0.050	4.93	9.72	0.213
Serum Bottles (35 days)**	6.7	18.0	1240	<0.050	4.51	10.6	0.162

* Values for these samples are the average of four replicates.

** Values for these samples are the average of three replicates.

Note: Mine drainage and wetland output values are the average of two samples collected in June, 1990.

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EFFECT OF ACID MINE DRAINAGE ON A RIPARIAN AREA: ELEMENT CONCENTRATIONS IN SOILS AND PLANTS[1]

by

Jeanne C. Chambers, Michael C. Amacher, and Ray W. Brown[2]

Abstract. The Stillwater River headwaters, located above Cooke City, Montana, have received acid mine drainage (AMD) from the McLaren gold mine since about 1935. To determine the cumulative effects of AMD on the riparian zone, we collected plant leaf material and soil from the upper 15 cm of the rooting zone of Carex paysonis plants along a gradient of decreasing river water pH. Sampling locations were above the source of AMD into the river, at the source of AMD, and below tha source of AMD. Soil metal concentrations (Al, Cu, Fe, Mn, Pb, and Zn) were generally related to pH or percentage OM. Plant metal concentrations were poorly correlated with soil metal cojcentrations. Plant available metals may have been lower in highly organic soils near the AMD source due to the formation of stable complexes, or high concentrations of some metals may have resulted in toxicity and reduced plant uptake. Concentrations of Cu in plant leaves were higher than suggested maximums for plants and livestock forages at and below the source of AMD.

Additional Key Words: Payson sedge, Cu, metals

Introduction

One of the consequences of unregulated heavy-metal mining during the early and mid-1900s in mountainous areas of the Western United States has been the generation of acid mine drainage (AMD). In many cases, AMD has flowed unchecked into high-elevation stream systems for decades. The AMD is often characterized by low pH and high concentrations of heavy metals. The cumulative effects of AMD on streams are potentially numerous and are dependent upon the environmental characteristics of the stream system and the type and amount of AMD. Aquatic organisms may be unable to survive for miles downstream of the AMD source. Also, the riparian zone adjacent to the stream may be negatively impacted through accumulation of heavy metals in the soils, uptake by vegetation, and bioaccumulation in food-chains.

The Cooke City Mining District, located above Cooke City, Montana, has been the site of mining activity and mineral exploration and, consequently, AMD since the 1880s. The Cooke City ore body is a highly mineralized hydrothermal pyritized-copper deposit that also contains gold and silver (Loverling 1929). Past mining consisted of both shallow open-pit and underground hard-rock operations with numerous small mines and exploration sites of varying age and extent throughout the area (Brown et al 1976). Two of the larger mines in the area, the McLaren and the Glengary, were actively mined from about 1935 until 1950 and 1967, respectively. Development of cyanide extraction technology for finely disseminated gold has resulted in renewed interest in the McLaren mine and adjacent areas. New plans are currently being developed by

[1]Paper presented at the 1991 National Meeting of the American Society for Surface Mining and Reclamation, Durango, Colorado, April 14-17, 1991.

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Noranda Exploration Inc., for mining this area, which has been designated the New World Project.

The New World Project is located at the headwaters of 3 major stream systems within the Greater Yellowstone Ecosystem. Miller Creek and Fisher Creek eventually flow into the Yellowstone River, and Daisy Creek is a tributary of the Stillwater River, which also flows into the Yellowstone River. Daisy Creek has been affected by AMD from the McLaren mine and Fisher Creek has been impacted by AMD from the Glengary mine for about 50 years. Information about the long-term effects of AMD on the riparian areas adjacent to these streams can provide baseline data for (1) establishing standards for new mining operations and (2) devising methodology for reclamation of degraded riparian areas. The purpose of this preliminary study was to investigate the effects of long-term AMD on riparian zone soils and vegetation of Daisy Creek.

Methods

This study examined the upper 2.5 km length of Daisy Creek, 1 of 3 tributaries that form the headwaters of the Stillwater River. Elevation over the study reach drops from 2,805 m at the stream's source (45°03′ N, 109°49′ N) to 2,609 m where it is joined by the other tributaries. Environmental characteristics of the area include 60-to 70-day growing seasons, low summer temperatures and relatively high solar radiation (Johnston et al 1975). Annual precipitation ranges between 110 and 150 cm and arrives primarily during the winter months (Johnston et al 1975). Riparian vegetation at the upper reach of the stream is characterized by wet meadow species, including elkslip marshmarigold (Caltha leptosepala), Holmes Rocky Mountain sedge (Carex scopulorum), water sedge (Carex aquatilis), Payson sedge (Carex paysonis), and several willow species. The lower reaches of the stream are more steeply downcut and riparian vegetation includes subalpine fir (Abies lasiocarpa), bluejoint reedgrass (Calamagrostis canadensis), Holmes Rocky Mountain sedge (Carex scopulorum), Payson sedge, and glaucous willow (Salix glauca).

AMD from the McLaren mine flows into Daisy Creek within 500 m of its source, a perennial spring. To determine the effects of AMD on the riparian zone, soil and vegetation samples were collected at the following locations: (1) above the source of AMD into Daisy Creek; (2) along the AMD tributary from the McLaren mine; (3) immediately below the source of AMD into Daisy Creek; and (4) at 500 m intervals along the remaining 2 km of Daisy Creek. Since Payson sedge occurred along the entire reach, it was selected for analyses. At each of the 7 sample sites, plant leaf material and soil from the upper 15 cm of 4 individual Payson sedge plants were collected. All samples were collected within 1 m of the active stream channel.

Plant leaf tissue was washed with distilled water and dried prior to analysis. Leaf samples were analyzed for P, K, Mg, Ca, S, total N (TN), Al, Cu, Fe, Mn, Zn, and Pb. For all elements except TN, plant tissue samples were digested using a nitric percloric acid digestion and analyzed by inductively coupled argon plasma spectrometry (ICAP). TN was analyzed using Kjeldahl digestion. Soil samples were analyzed for particle size distribution by the hydrometer method, organic matter (OM) (modified Walkely-Black), pH (saturated paste), cation exchange capacity (CEC) (1 N NH_4OAC at pH=7), P (Bray-1), SO_4-S (0.1 M CaH_2PO_4), KCl extractable Al, and HCl extractable Cu, Fe, Mn, Pb, and Zn. Analyses were conducted by the Utah State University Soil, Plant and Water Analysis Laboratory and methods are outlined in Benton (1989) (plants) or Page et al (1982) (soils).

One-way ANOVA was used to determine differences in plant and soil variables among sites. Mean separations were computed using Fisher's Protected LSDs (Steele and Torrie 1980). Relationships among soil element concentrations, pH, OM, CEC, and soil texture were evaluated with Pearson's product-moment correlation coefficients for sites at or below the source of AMD (Sokal and Rohlf 1981). These coefficients measure the degree of association between any two variables, and test if it is greater than expected by chance alone.

Results and Discussion

Soil Physical and Chemical Properties

Upstream sampling locations were characterized by wet meadow vegetation and soils. These sites had generally higher percentages of silt or clay and OM than downstream sites (see Figure 1). Soil pH reflected the proximity of the AMD source into Daisy Creek (see Figure 1). The highest pH values were found at sites above the AMD source and furthest downstream of the source. The lowest soil pH was at the source of AMD into Daisy Creek. These values were similar to those for stream pH (Brown and Amacher 1990). As

expected for wet meadow soils, CEC was highly related to percentage OM ($R^2 = 0.93$; $p < 0.001$) with high OM soils having high CEC (see Figure 1). Soil concentrations of inorganic P are frequently pH dependent, and in this study inorganic P was negatively related to pH (see Table 1), indicating that soil inorganic P was highest at low pH values.

Soil concentrations of Al, Cu, Fe, and SO_4-S were highest along the AMD tributary or at the AMD source into Daisy Creek (see Figure 2). Although highly variable among samples, these elements tended to decrease with increasing distance downstream. Concentrations of Mn, Pb, and Zn were high above the source of AMD (see Figure 2) because that particular

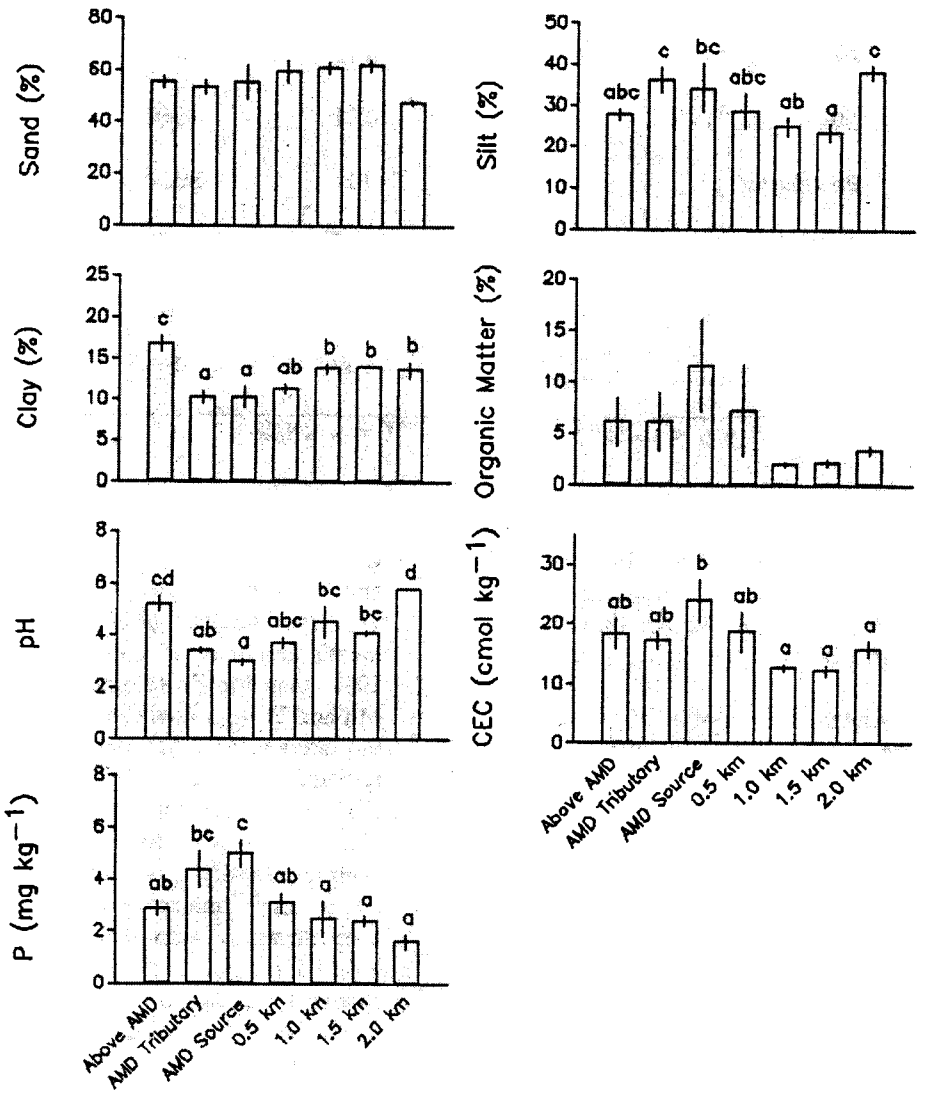

Figure 1. Selected physical and chemical properties of soils from the Daisy Creek riparian area above the AMD source, along the AMD tributary, at the AMD source and at 4 distances downstream of the source. Heights of histogram bars show means and error bars represent ± 1 SE; n = 4, except TN = 1. Unlike letters indicate significant differences among sites ($p < 0.05$) if shown.

Table 1. Product-moment correlation coefficients comparing soil elemental concentrations with pH, OM and CEC.

Element	pH	OM (%)	CEC (cmol kg^{-1})
Al (mg kg^{-1})	-0.69***	0.53**	0.45*
Cu (mg kg^{-1})	-0.18	0.36	0.21
Fe (mg kg^{-1})	-0.52*	0.72***	0.76***
Mn (mg kg^{-1})	0.20	0.01	-0.01
Pb (mg kg^{-1})	0.50*	-0.17	-0.35
Zn (mg kg^{-1})	-0.20	0.45*	0.29
SO_4-S (mg kg^{-1})	-0.49*	0.33	0.22
P (%)	-0.76*	0.47*	0.54*

* = $p < 0.05$; ** = $p < 0.01$; *** = $p < 0.001$.

area is part of a Mn deposit and has naturally high concentrations of these metals (Alan Kirk, Noranda Exploration Inc., personal communication). Concentrations of these metals did not differ among sites below the source of AMD.

Retention and movement of individual elements in soils depend on several factors, including soil pH, OM, and soil texture. In general, metal availability decreases with increases in pH, clay content, or OM. Soil pH has a major influence on solution concentrations of many metals and the solubility of metal compounds often increases with decreasing pH. With increasing pH, the number of sorption sites increases (Safaya et al 1987) and many metals are precipitated as insoluble compounds. Al has a very steep solubility curve and is largely unavailable above pH 5 (Donahue et al 1977). Concentrations of Al in the soil were highly negatively correlated with pH (see Table 1). The low concentrations of Al above the source of AMD and at the most distant site from the source may be attributable to high soil pH at these sites. Cu, Fe, Zn, and $S0_4$-S have less steep solubility curves than Al, but soil concentrations of these elements were also negatively correlated with pH (see Table 1).

Most metals can form stable complexes with OM. Concentrations of all of the metals, except Mn and Pb, were positively correlated with OM (see Table 1). The stability of these complexes varies among metals and may be greater for Cu and Pb (McBride 1981) than for Zn (Safaya et al 1987). The failure of Mn and Pb to follow the same patterns as observed for the other metals may be the result of several different factors. Low levels of Mn and Pb occurred in the AMD (Brown and Amacher 1990). Under natural conditions, Mn and Pb often form highly localized deposits and sample intensity may have been inadequate to explain either their distribution or chemistry. The low concentrations of Pb in high-OM soils (R^2 = -0.17) may have been due, in part, to the stability of the complexes that Pb forms with organic matter (McBride 1981). HCl may have been an inadequate extractant for these types of complexes. The redox status of the AMD and riparian soils (not measured specifically) will also influence the solubility of Mn. Metals can be adsorbed onto clay surfaces depending upon the exchangeable cation present on the clay surface and the metal species. The clay content at all study sites was low (see Figure 1). Consequently, metal concentrations were not positively correlated with clay content (data not presented). For this riparian system, pH and OM had

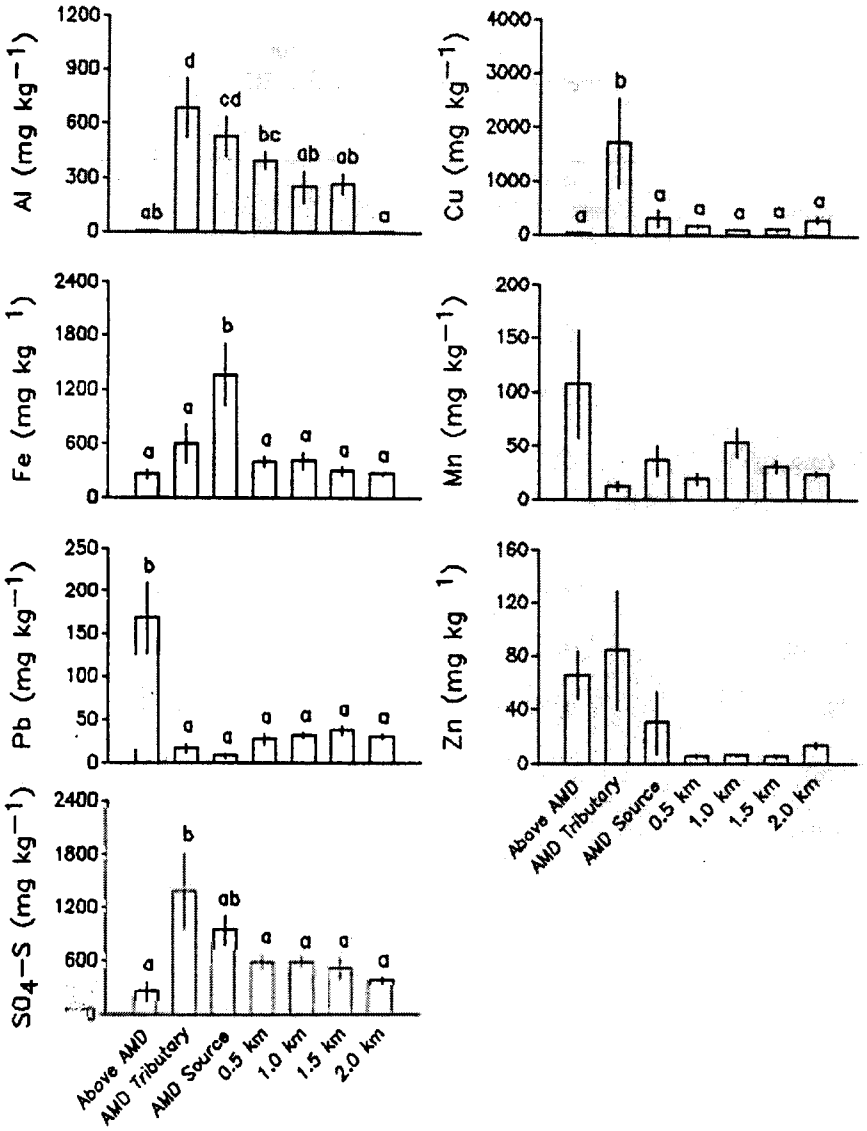

Figure 2. Metal and SO^4-S concentrations in soils of the Daisy Creek riparian area above the AMD source, along the AMD tributary, at the AMD source and at 4 distances downstream of the source. Heights of histogram bars show means and error bars represent ± 1 SE; n = 4, except TN = 1. Unlike letters indicate significant differences among sites if shown.

a greater effect on soil retention and plant availability of the metals than clay content.

Plant Elemental Concentrations

Concentrations of P, K, Mg, Ca, S, and TN in Payson sedge above the AMD source were generally similar to those at the site farthest from the AMD source (see Figure 3). Percentages of P, K, and S were highest along the tributary into Daisy Creek, at the AMD source or immediately below the source of AMD (see Figure 3). P and S were positively correlated to soil concentrations of these metals and P, K, and S were negatively correlated with soil pH (see Table 2). Concentrations of Mg and TN varied little among sites (see Figure 3). Percentage Ca was lowest along the

Table 2. Product-moment correlation coefficients comparing plant elemental concentrations with soil concentrations of the same element, pH, OM and CEC.

Element	Soil Concentration (mg kg^{-1})	pH	OM (%)	CEC (cmol kg^{-1})
Al (mg kg^{-1})	-0.02	-0.12	-0.16	-0.22
Cu (mg kg^{-1})	-0.06	0.00	-0.05	-0.15
Fe (mg kg^{-1})	0.30	-0.53**	0.13	0.11
Mn (mg kg^{-1})	0.24	0.37	-0.32	-0.38
Pb (mg kg^{-1})	0.23	0.23	-0.24	-0.27
Zn (mg kg^{-1})	-0.10	0.49	-0.39	-0.49*
S (%)	0.59*	-0.66*	0.00	0.05
P (%)	0.34	-0.53**	0.08	0.06
Ca (%)		0.82***	-0.32	-0.40
K (%)		-0.52	0.00	0.04
Mg (%)		0.15	-0.33	-0.41

* = $p < 0.05$; ** = $p < 0.01$; *** = $p < 0.001$.

tributary into Daisy Creek or at the AMD source and increased with distance downstream from the source (see Figure 3). Levels of plant Ca were highly positively correlated with soil pH (see Table 2). The relationships of the different elements with soil pH were consistent with their solubility curves (Donahue et al 1977).

Concentrations of Al, Mn, and Pb in Payson sedge did not differ significantly among sites (see Figure 4). Plant concentrations of Mn and Pb tended to reflect soil concentrations and were positively related to pH, but negatively related to OM (see Table 2). Concentrations of Fe in Payson sedge were highest along the AMD tributary, at the source of AMD, or immediately below the source of AMD (see Figure 4). Plant Fe concentrations were positively related to soil concentrations, but negatively related to soil pH (see Table 2) reflecting the solubility curve for Fe (Donahue et al 1977).

Concentrations of plant Cu were significantly lower above the AMD source than at any of the other sites (see Figure 4). There were no differences in Cu concentrations in Payson sedge among sites at or below the AMD source. Plant concentrations of Cu were unrelated to soil characteristics (see Table 2), despite high soil concentrations of Cu at some of the sites and large differences in soil Cu among sites. Many plant species exclude Cu from shoot tissue (Marschner 1986) and concentrations in roots are often several times higher than in shoots (Neuman et al 1987). Uptake curves for Cu in aboveground plant tissue frequently plateau above a certain level of soil availability. Concentrations of Cu in Payson sedge at or below the AMD source may have reflected the upper limit for this species.

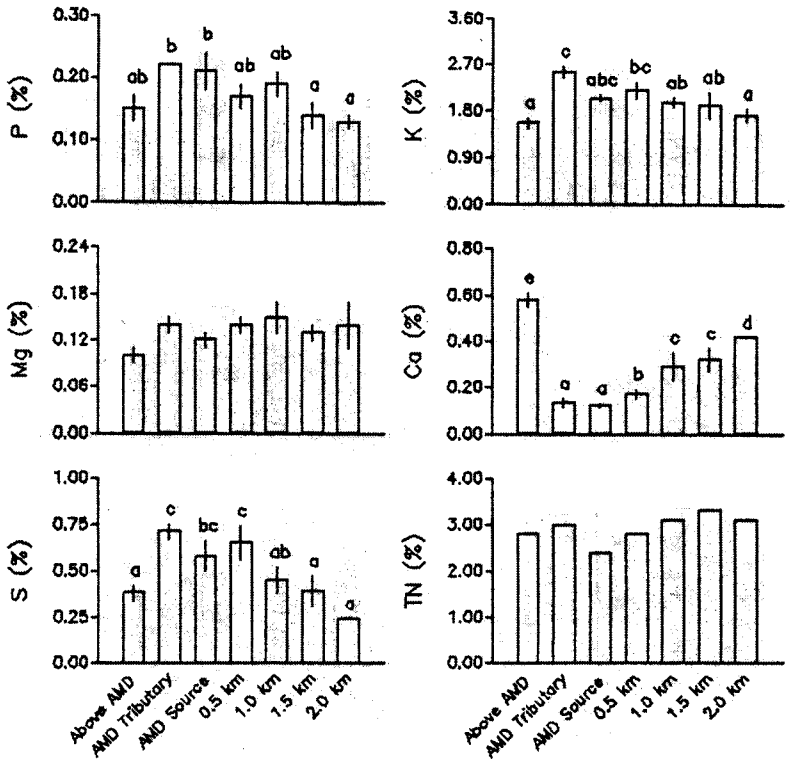

Figure 3. Foliar concentrations of selected elements in Payson sedge above the AMD source, along the AMD tributary, at the AMD source, and at 4 distances downstream of the source. Heights of histogram bars show means several times higher than in shoots and error bars represent ± 1 SE; n = 4. Unlike letters indicate significant differences among sites if shown.

Concentrations of Zn in Payson sedge were lowest above the AMD source, along the AMD tributary, or at the AMD source (see Figure 4). Plant Zn concentrations were positively correlated with pH, but negatively correlated with CEC (see Table 2). Plant Zn concentrations were lowest at sites with the highest soil Zn concentrations, indicating that other soil factors resulted in reduced plant uptake of Zn.

Conclusions

The Daisy Creek riparian area was affected by the AMD from the McLaren mine in several ways. The AMD lowered the pH of the riparian zone soils, which increased the solubility of many naturally occurring metal compounds and, consequently, increased the availability of these metals to plants and other living organisms. Also, the AMD contributed additional metals to the system in solution, including Mn, Fe, Al, Zn, and especially Cu (Brown and Amacher 1990). Soil pH was lowest along the AMD tributary and at the source of the AMD into Daisy Creek. As pH increased with distance downstream of the AMD source, soil concentrations of most of the metals that occurred in the AMD decreased (Fe, Al, Zn, and Cu). High levels of OM in wet meadow soils at or near the AMD source were positively correlated with CEC and soil concentrations of those metals in the AMD. The ability of OM to form stable complexes with metals is a well-known phenomenon that has led to the use of wetlands for AMD treatment.

Metal concentrations in Payson sedge were often poorly correlated with soil metal concentrations. High metal concentrations coupled with low pH may have resulted in toxicity and reduced plant uptake. Also,

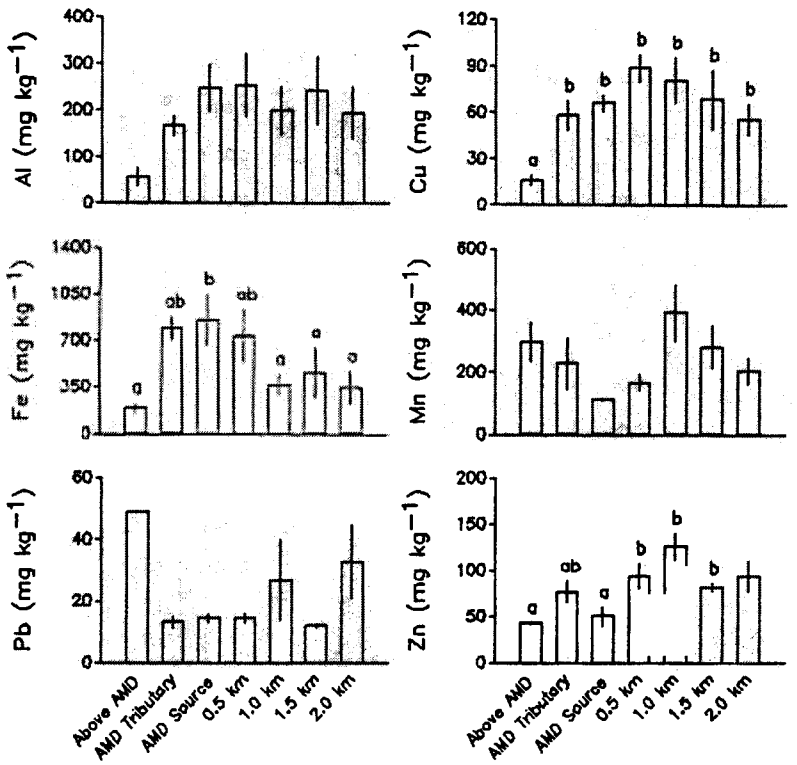

Figure 4. Foliar concentrations of metals in Payson sedge above the AMD source, along the AMD tributary, at the AMD source, and at 4 distances downstream of the source. Heights of histogram bars show means several times higher than in shoots and error bars represent ± 1 SE; n = 4. Unlike letters indicate significant differences among sites if shown.

plant availability of some metals may have been lower in highly organic soils near the AMD source due to the formation of stable complexes.

The riparian area is being negatively impacted by the AMD at distances greater than 2 km downstream. Leaf concentrations of Cu in Payson sedge exceeded suggested maximum concentrations for plants (Northeastern Coordinating Committee 1985) and livestock forages (National Research Council 1980) at all of the sample sites affected by the AMD. Payson sedge appears to exhibit relatively high-tolerance levels to AMD from the McLaren mine (Brown and Amacher 1990). Plant species more sensitive to the effects of the AMD may have already been excluded from the riparian area. Many animal species have low tolerance for Cu, and food-chain movement and bioaccumulation of metals within the area are of real concern.

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Literature Cited

Benton, J. J., Jr. 1989. Soil Testing and Plant Analysis Laboratory Manual. Benton, Laboratories, Inc., Athens, GA.

Brown, R. W. and M. A. Amacher 1990. Some effects of acid mine drainage on plant water relations. Agronomy Abstracts:34.

Brown, R. W.; R. S. Johnston; B. Z. Richardson; and E. E. Farmer 1976. Rehabilitation of alpine disturbances, Beartooth Plateau, Montana. p. 58-73. In R. H. Zuck and L. F. Brown (Eds.). High-Altitude Revegetation Workshop No. 2. Colorado State University, Fort Collins, CO.

Donahue, R. L.; R. W. Miller; and J. C. Shickluna 1977. Soils. 4th ed. Prentice-Hall, Inc., Englewood Cliffs, NJ.

Johnston, R. S.; R. W. Brown; and J. Cravens 1975. Acid mine rehabilitation problems at high elevations. p. 66-79. In Proc. Watershed Management Symp. American Society of Civil Engineers, New York, NY.

Loverling, T. S. 1929. The New World or Cooke City Mining District, Park County, Montana. U.S. Geological Survey Bulletin 811, 87 p.

Marschner, H. 1986. Mineral Nutrition in Higher Plants. Academic Press, New York, NY.

McBride, M. B. 1981. Forms and distribution of copper in solid and solution phases of soil. p. 25-35. J. F. Loneragan, A. D. Robson and R. D. Graham (Eds.). In Copper in soils and plants. Academic Press, Sydney, Australia.

National Research Council 1980. Mineral tolerance of domestic animals. National Academy of Science, Washington, D.C.

Neuman, D. R.; J. L. Schrack; and L. P. Gough 1987. Copper and molybdenum. p. 215-232. In R. D. Williams and G. E. Schuman (Eds.). Reclaiming Mine Soils and Overburden in the Western United States: Analytic Parameters and Procedures. Soil Conservation Society of America.

Northeastern Coordinating Committee. 1985. Criteria and recommendations for land applications of sludges in the Northeast. NEC-28. Bulletin 851. Pennsylvania Agricultural Experiment Station, Pennsylvannia State Univ., Uiversity Park, Pennsylvania.

Page, A. L.; R. H. Miller; and D. R. Keeney (Eds.) 1982. Methods of Soil Analysis. Part 2. Chemical and Microbiological Properties. 2nd ed. Agronomy Monograph No. 9. American Society of Agronomy, Madison, Wisconsin.

Safaya, N. M.; J. E. McLean; and G. A. Halvorson 1987. Cadmium and zinc. p. 283-312. In R. D. Williams and G. E. Schuman (Eds.). Reclaiming Mine Soils and Overburden in the Western United States: Analytic Parameters and Procedures. Soil Conservation Society of America.

Sokal, R. R. and F. J. Rohlf 1981. Biometry. 2nd ed. W. H. Freeman and Co. San Francisco, California.

Steel, R. G. D. and J. H. Torrie. 1980. Principles and Procedures of Statistics. 2nd ed. McGraw-Hill Book Co. New York, NY.

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THE EFFECT OF GROUT INJECTION ON MINE SPOIL GROUNDWATER HYDROLOGY[1]

by
Jay W. Hawkins
Terry E. Ackman
and
William W. Aljoe[2]

Abstract. A 3.2-hectare (8 acre) parcel of a reclaimed surface mine in Upshur County, West Virginia has been monitored to evaluate the effect of grout injection on the spoil groundwater hydrologic characteristics and geochemistry. In February and early March, 1990, the site was injected with a pozzolan grout in an attempt to ameliorate acid mine drainage production by encapsulating targeted zones of acid-producing spoil. The spoil aquifer was monitored for water-quality changes and tested to determine the effect of the grouting on the groundwater flow regime, water table and other aquifer properties. The grouting project has the potential to reduce porosity, eliminate large void space, or close connection between voids and consequently to reroute groundwater flow paths and produce changes in the water table configuration. Monitoring was initiated 14 months prior to grouting and continues to the present. Aquifer tests were performed 3 months before and 4 months after grouting to ascertain changes in hydraulic properties caused by the grouting efforts. Slug tests and constant-discharge aquifer (pumping) tests were performed to determine transmissivity, hydraulic conductivity, and other hydrologic parameters of the spoil directly adjacent to and between monitoring wells. The slug tests indicate that characteristics of the spoil aquifer directly adjacent to the monitoring wells were unaffected by the grout injection. The pumping tests indicate that hydraulic conductivity and transmissivity of the spoil between some wells were generally unaffected. Maps of the water table, under similar flow conditions, indicate no significant change in water level or flow direction has occurred due to the grouting. A high amount of sodium in the fly ash portion of the grout permitted the tracking of groundwater movement after grout

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[1]Paper presented at the 1991 National Meeting of the American Society for Surface Mining and Reclamation, Durango, Colorado, May 14-17, 1991.

[2]Jay W. Hawkins is a Hydrologist, Terry E. Ackman is a Mining Engineer, and William W. Aljoe is a Mining Engineer with the U.S. Bureau of Mines, Pittsburgh, PA 15236

introduction. Minor groundwater quality changes in two wells was attributed to elements added by the grout and possible groundwater flow path rerouting. Analysis of the sodium plume movement indicates a bimodal (porous media and pseudokarst) flow regime within the spoil, although in general the spoil behaves as a porous medium under steady state conditions.

Additional Key Words: pozzolan grout, porous media pseudokarst, slug test, constant-discharge test, plume

Introduction

Acid mine drainage (AMD) formation in surface coal mines occurs when iron disulfides contained in the spoil material are oxidized and subsequently hydrolyzed. AMD production and transport can be controlled by restricting the contact of oxygen and groundwater with the high sulfur spoil zones. An attempt was made to inject a pozzolanic grout, a mixture of fly ash, portland cement, and water, into selected zones in a surface mine backfill to reduce the effective permeability and restrict the contact of groundwater with potentially acid-producing spoil. Approximately 500 cubic yards of the grout was injected into 62 wells into the backfill. Well location was determined by electromagnetic terrain conductivity and magnetometry surveys. The focus of this study was to determine the effect of the grouting operation on the hydrologic characteristics. Because the work presented here is ancillary to the original intent of the project, detailed descriptions on the physical grouting will not be discussed here. Grouting of the spoil has the potential to fill up void space and cause changes in groundwater flow paths. To ascertain changes to hydraulic parameters before and after grout injection, aquifer testing (slug and pumping tests) was performed, water table maps were compared under average conditions and for synoptic records under similar flow conditions, and water quality at monitoring wells and the main discharge were analyzed. The effect of grouting on site hydrologic characteristics and water geochemistry will provide insight into the potential for hydrologic control of groundwater in mine spoil in the future.

Studies have shown that groundwater movement through surface mine spoil does not occur as it would in a pure porous medium. Large voids or conduits in spoil exist, permitting pseudokarst groundwater flow (Caruccio and Others, 1984; Hawkins and Aljoe, 1990). Piping of the fine grained material and differential compaction create or accentuate voids within the backfill (Groenewold and Bailey, 1979). These conduits influence the movement and storage of groundwater in spoil. When the aquifer is stressed during transient periods or from aquifer testing, the pseudokarst characteristics become even more prominent. Pseudokarst flow occurs within conduits, while porous media flow occurs between these conduits. Under steady state conditions, the aquifer generally exhibits porous media flow characteristics overall (Hawkins and Aljoe, 1991, In Press).

Site Background

A 3.2-hectare (8 acre) parcel of a reclaimed surface mine was monitored and tested to determine potential changes to the hydrologic characteristics, the groundwater flow regime, and water quality caused by the grouting operation. The site was mined in 1976 and reclamation was completed by the end of 1977. The mine was terrace backfilled creating a steep outslope. Figure 1 depicts the post mining site configuration.

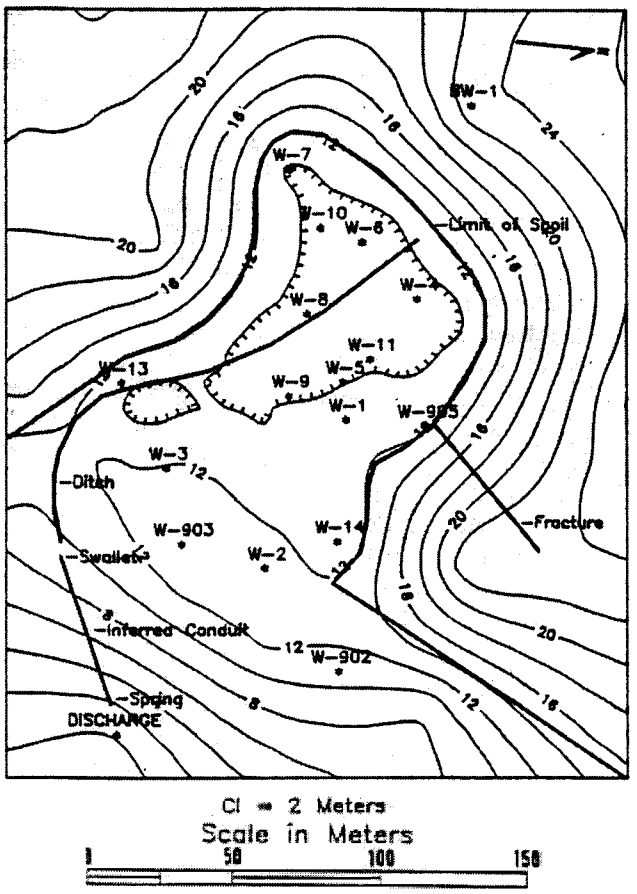

Figure 1. Map of study site exhibiting surface contours, monitoring wells, and other surface and subsurface features. The main discharge is datum.

The middle and lower Kittanning coal seams were mined on the site. The middle Kittanning was mined across the entire site. The lower seam, due to poor coal quality, was only mined in selected areas. A massive gray sandstone overlies the middle Kittanning (Figure 2). The sandstone becomes brown and highly friable upon weathering. The interburden between the two seams is primarily a dark gray to black carbonaceous shale. Acid base accounting (ABA) of the overburden indicates the black shale is a potentially acidic zone. ABA is a type of overburden analysis that determines the potential of rock units to produce alkaline or acidic mine drainage from total sulfur and calcium carbonate equivalent content. Total sulfur concentration in the shale ranges from 0.16 to 0.87 percent. In evaluating the ABA, total sulfur concentrations exceeding 0.5 percent are considered potentially acidic. The shale likewise contains the only significant neutralization potential (31.25 tons of calcium carbonate equivalent per 1000 tons of material). A neutralization potential value of over 30 is considered potentially alkaline. Although, the sulfur content of the sandstone is low (0.005 percent), the presence of effervescent salts (most likely sulfate salts) on subaerially exposed rock surfaces indicate it may also contribute significantly to AMD production.

The lithologic units of the premining overburden are such that the spoil consists of both large blocky fragments and fine grained material. This facilitates the formation of conduits and voids, which result in strong hydraulic conductivity heterogeneities in the spoil.

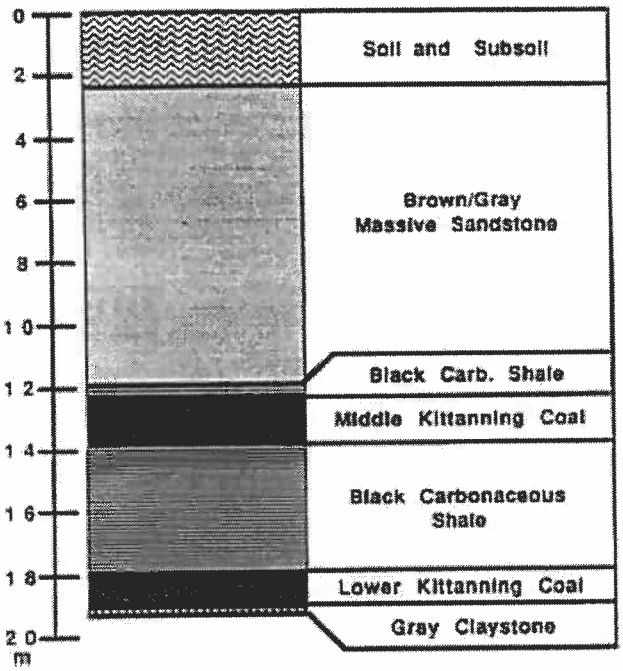

Figure 2. Stratigraphic section of the site overburden before mining.

Fifteen monitoring wells were constructed on the site. All but one of these wells (BW-1) are screened in spoil material. The wells were used to monitor groundwater level fluctuations, sample water quality, and conduct aquifer tests. The wells were constructed with 5.1 cm. (2 inch) PVC casing with the bottom 3 meters (10 ft) of slotted (0.01 inch) well screen. All holes were drilled to the pit floor, except well 12. The annulus between the casing and well bore was filled with drill cuttings and spoil material for all cased wells.

Slug Tests

Prior to grouting, slug withdrawal tests were performed on the spoil wells to determine aquifer characteristics. These tests along with post grouting slug injection tests were performed in an attempt to determine the effect of grouting spoil hydraulic conductivity and degree of grout propagation. For the slug withdrawal tests, a slug of water was removed with a bailer. The slug volume depended on the amount of water in the well. The recovery rate was recorded for each well with a pressure transducer placed into the well. The transducer had to be placed in the well after the removal of the bailer, because the bailer was too large to fit past the transducer cable. The testing revealed that some wells responded with a gradual recovery as in porous media groundwater flow. Other wells exhibited a dual recovery response (DRR), where a large part of the recovery was very rapid (almost instantaneous) and the remainder was more gradual. The first 20 seconds was usually lost with the slug withdrawal tests, because of the lag time required to set the pressure transducer. The early portion (first 20 seconds) of the recovery was too rapid (turbulent flow) to be testable by conventional means and is therefore not subject to Darcy's Law (Hawkins and Aljoe, 1991, In Press). The latter portion of the recovery did yield aquifer parameters, although these values may be somewhat questionable, because of the lack of the early test data. The testing suggests than the late data may be indicative of diffuse flow in the high recovery wells. Table 1 lists the hydraulic conductivity values obtained from the slug withdrawal tests. Hydraulic conductivity (K) values ranged from 2.1×10^{-7} to 5.7×10^{-5} meters per second prior to grouting. The Bouwer and Rice

	HYDRAULIC CONDUCTIVITY		TRANSMISSIVITY	
WELL	PREGROUTING	POST GROUTING	PREGROUTING	POST GROUTING
1	2.0686E-07	9.3679E-07	9.9086E-07	4.5434E-06
2	6.2580E-07	3.0357E-06	1.0513E-06	6.1625E-06
3	8.9360E-06	1.3427E-04	5.0935E-06	7.3580E-05
4	6.8995E-06	6.7560E-06	3.1669E-05	2.9186E-05
5	1.9254E-05	1.2434E-05	5.9302E-05	3.8545E-05
6	1.2974E-05	3.1400E-05	4.1776E-05	9.5456E-05
7	5.0955E-06	5.3352E-05	1.4369E-05	1.6112E-04
8	4.6605E-06	8.2299E-05	1.5519E-05	2.8475E-04
9	5.6940E-05	2.3191E-05	1.3609E-04	5.4963E-05
10	1.2617E-06	1.0066E-06	2.2837E-06	1.7314E-06
11	9.1445E-07	3.8857E-06	1.8929E-06	7.2663E-06
13	9.6128E-07	8.5636E-07	2.2109E-06	1.9439E-06
14	4.9261E-06	3.3362E-07	1.6897E-05	1.2077E-06
	m/sec	m/sec	m^2/sec	m^2/sec

Table 1. Hydraulic conductivity (K) and transmissivity (T) values obtained from the pregrouting slug withdrawal and postgrouting slug injection tests.

method was used to calculate these values from the data (Bouwer and Rice, 1976).

Four months after grouting was completed, the wells were retested using slug injection. In the slug injection tests a fixed amount of water was rapidly dumped down the casing. Slug injection permitted a larger amount water to be introduced to the aquifer than was withdrawn during the earlier slug withdrawal tests. The amount of water each well casing could accommodate without overflowing was selected as the slug volume. The pressure transducer remained in the well throughout the entire test, which permitted collection of water level data throughout the test. Hydraulic conductivity values for all slug tests are listed on Table 1. As with the slug withdrawal tests the Bouwer and Rice method was used to analyze the data (Bouwer and Rice, 1976). The same wells that strongly exhibited the DRR during the slug withdrawal tests likewise did so during the slug injection test; therefore, the later data points were used to determine hydraulic conductivity for the comparison.

No definite trends were observed that could be attributed to the grouting project. The majority of the wells exhibited a change of less than one order of magnitude from before to after grouting. Three wells (3, 7, and 8) showed a hydraulic conductivity increase of approximately one order of magnitude. The differences noted appear to be directly related to the rapid recovery of these wells and/or to the modification of the slug test procedure. The DRR effect was strongly exhibited in wells 3 and 8 and moderately exhibited in well 7. The non-Darcian type of recovery indicates that the applicability of this test to these wells may be questionable. Assuming the latter portion of the tests are valid and represent diffuse flow, the larger slug volume and

earlier data acquisition in the second set of tests (slug injection) increased the accuracy, which may account for the observed increase in hydraulic conductivity values.

Slug tests yield aquifer hydrologic data for the area in proximity of the well tested. However, no definite relationship was seen between proximity of grouting wells and hydraulic conductivity changes observed in the monitoring wells. Of the five monitoring wells located within 10 meters of grout wells (1, 3, 4, 10, and 14), three showed a decrease and two showed an increase in hydraulic conductivity (Figure 3 and Table 1). Well 14 was the only well within 5 meters of a grout well. This well exhibited virtually the same hydraulic conductivity (4.9261×10^{-6} to 3.3362×10^{-6}), this was within the expected variation of retesting based on experience.

Effect of grouting on the hydraulic conductivity of the monitoring wells will depend on the distance, direction, and/or degree of grout propagation. If grout propagation was under 5 to 10 meters no changes in response to the slugging would be expected in the monitoring wells beyond this distance from the grout wells. Grout propagation of at least 10 meters was observed by grout "break through" at the surface. This indicates that the degree of grouting may have been insufficient to significantly affect the hydraulic characteristics of these wells; however, it was more likely that the direction of grout propagation was anisotropic, and unlikely that it would flow directly toward the monitoring wells. The grout would tend to

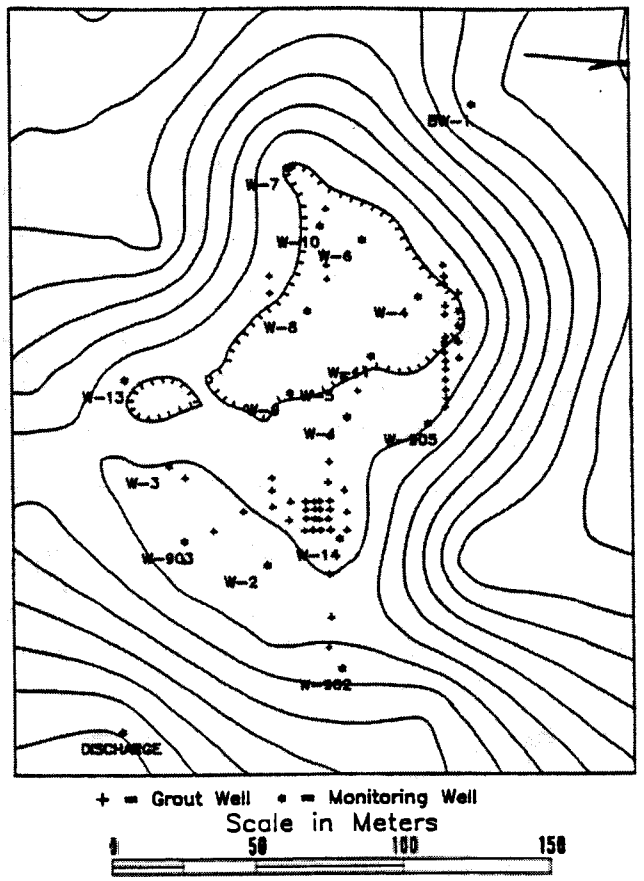

Figure 3. Map showing the location of the grout injection and monitoring wells.

follow the path of least resistance, therefore the direction of grout movement would be greatly influenced by the location and orientation of the conduits. Unless a conduit connected a grouting well and a monitoring well, little or no change would be expected.

Comparison of the hydraulic conductivity values determined from the slug tests before and after grouting indicates that, in general, no discernable change in hydraulic conductivity within 5 to 10 meters of the grout injection wells, thus attributed to grouting. The differences observed are easily attributable to minor testing errors and/or natural variation.

Constant-Discharge Tests

Two constant-discharge aquifer (pumping) tests were performed prior to grouting and were repeated afterward, utilizing the same wells and approximately the same pumping rate and duration. The pumping tests yield information over a larger area than the slug tests. The low transmissivity values yielded by the slug testing indicated the need for low pumping rates, therefore a bailer or a small hand pump was used to withdraw water during these tests. The first test consisted of pumping well 9 for 2 hours at a rate of 5 liters per minute, while wells 1 and 5 were monitored using pressure transducers linked to a data logger. During this test, air-rotary drilling was actively occurring approximately 50 meters to the east near well 14. When air was blown into the drill hole it would cause the water level in monitoring well 5 to rise above static water level, while the level in wells 1 and 9 declined. This suggested the presence of a conduit connection between wells 5 and 14. Because of the drilling interference, data collected from well 5 were not useable. The water level in well 1 was unaffected by the drilling however, and thus these data are useable. In the second pre-grouting pumping test, well 6 was pumped for two hours at a rate of 6 liters per minute, while the water levels wells 8 and 10 were monitored. The Theis method was used to calculate transmissivity, storativity, and other aquifer parameters on the time-drawdown curves of the three monitoring wells (Theis, 1935).

Table 2 lists the hydraulic conductivity and transmissivity calculated from the pre- and post grouting pumping tests. As with the slug tests, no appreciable changes in pumping test transmissivity values can be directly attributed to the grouting project. Transmissivity differences before and after grouting were slight. The differences in transmissivity determined from the pumping tests were less than one order of magnitude. These differences are all within the anticipated variation of retesting of a well and/or created by the subjectivity of curve matching using the Theis method (Theis, 1935). However, the transmissivities determined by pumping tests are over four orders of magnitude higher than those determined from the slug tests. These transmissivity differences may be caused by greater transmissivities in the spoil over greater distances than can be measured by slug testing or by the lack of early data during testing the DRR wells, which may not permit true determination of transmissivity.

There is a possibility that grouting did slightly effect the hydraulic characteristics of the spoil. Although the differences are small, the greatest net decrease/increase in transmissivity occurred in wells 8 and 10 by comparison to well 1. A substantial amount of grouting occurred in the near wells 8, 10, and the pumping well, while no grouting was performed between wells 9 and 1. The changes may be due to the physical action of the grouting breaching and/or connecting previously unconnected conduits. The possibility of this breaching action was indicated by the build up of back pressure during grouting, followed by a complete pressure

	HYDRAULIC CONDUCTIVITY		TRANSMISSIVITY	
WELL	PREGROUTING	POST GROUTING	PREGROUTING	POST GROUTING
1	8.6542E-03	1.4026E-02	3.2280E-02	4.7690E-02
8	1.3329E-02	5.0769E-03	4.8650E-02	1.6500E-02
10	9.3194E-03	2.7630E-02	2.6840E-02	6.5760E-02
	m/sec	m/sec	m^2/sec	m^2/sec

Table 2. Hydraulic conductivity (K) and transmissivity values (T) obtained from the constant-discharge tests conducted before and after grouting.

release during the injection of several wells. Additional data are needed to support that this action has occurred.

The lack of differences in the pre- and post grouting transmissivities may be caused by the small amount of grout in comparison to the spoil porosity. The spoil porosity may have been higher than originally anticipated (initial estimates were 20 to 30 percent). The total volume of grout injected during this project was 388 cubic meters. Depending on the size of the estimated area of grout influence (45,000 to 79,000 cubic meters), only 1.6 to 4.3 percent of the spoil pore volume was filled by the grout using the original porosity estimates. The porosity range for material similar to spoil (unconsolidated sand and gravel) is 25 to 70 percent (Freeze and Cherry, 1979). If this range were applied to the spoil, the grout would have filled 0.7 to 3.4 percent of the spoil pore volume. Even if the porosity of small discrete spoil areas around the injection wells were completely grouted, the overall site porosity was only very slightly affected. The consistency of the grout could also be a contributing factor to the lack of changes. The grout was approximately 47 percent water by volume. This high water content would permit greater propagation of the fluid and gravitational settling of the solid fraction of the grout than originally anticipated, thus causing only partial filling of the voids prior to, and especially after, solidification.

Water Table Variation

Grouting of the spoil has the potential to eliminate void space, open or close connection between voids, and consequently to reroute groundwater flow paths and produce changes in the water table configuration. Grouting-induced groundwater regime variations may be permanent or may be only seasonal or temporary. Flow path rerouting may be indicated by spatial variations in water quality and/or by directional or level changes in the groundwater hydraulic gradient.

Comparison of average static water table conditions before and after grouting indicates that no major changes occurred in groundwater flow directions or gradients (Figures 4 and 5), although the maps exhibit some variations. These maps were created by averaging static water levels for the pre- and post grouting period, respectively.

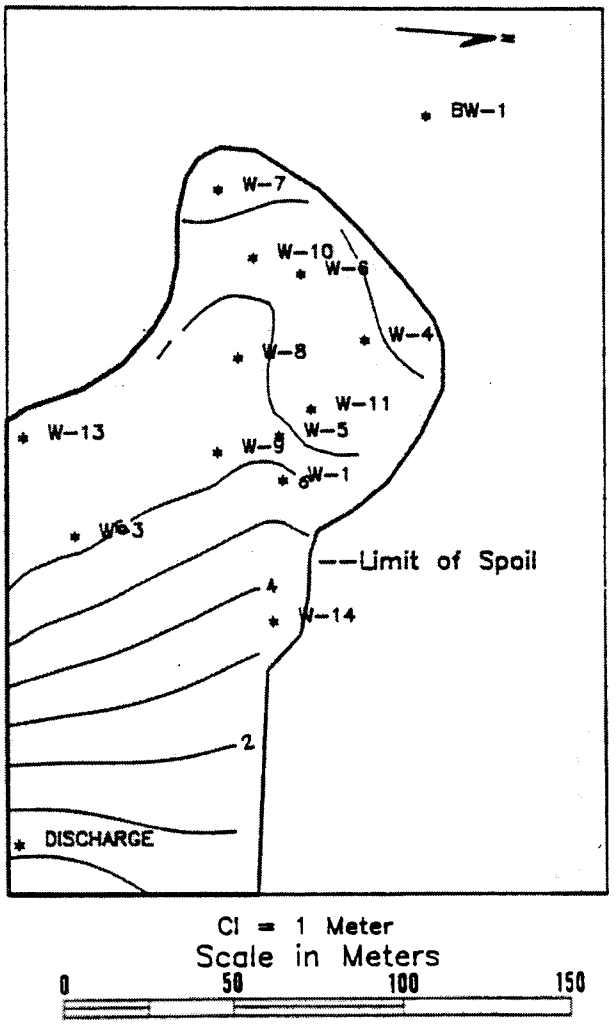

Figure 4. Average water table contour map prior to the grouting project. The main discharge is datum.

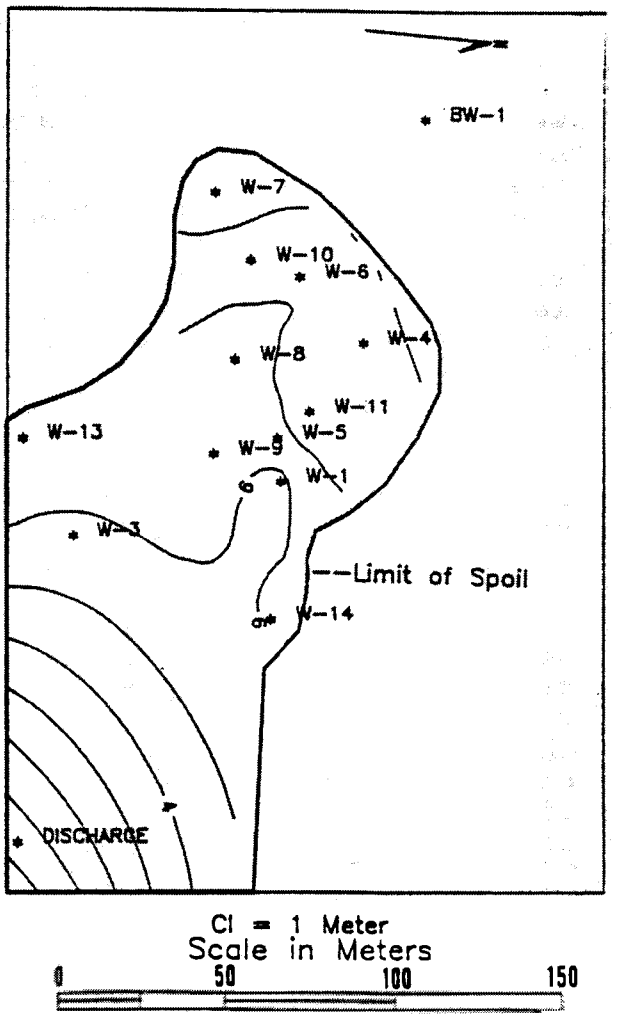

Figure 5. Average water table contour map after grouting was completed. The main discharge is datum.

The differences are likely due to temporal variations caused by differing precipitation amounts and subsequent recharge to the aquifer. The contour differences occurring between the wells and discharge point are caused by the contouring program extrapolating into an area with little control data, and does not reflect true changes there. Overall configuration and absolute water table levels are not

significantly different as a consequence of the grout injection, except for a small flexure in the contours in the area between wells 1 and 9 and well 14. This flexure appears to be directly related to the numerous grout wells (27) in that area. Additional data collection is needed to more accurately substantiate this change. The lack of major configuration changes is not surprising, because this was not the intent of the original project, which was to encapsulate selected isolated acidic spoil zones. The small amount of grout used compared to the potential void space is a possible explanation.

Two pregrouting monitoring periods were compared to two post grouting periods to determine if under similar flow conditions, changes to the water table configuration or levels are discernable. Comparison periods were chosen where precipitation type and amounts for the preceeding 30 days were approximately the same. Recharge rates were assumed to be approximately the same, because of similar seasonal conditions, no direct measurements were made. Groundwater recharge rate was assumed unchanged. Two pregrout periods were selected to compare to two post grout periods, March 30, 1989 to April 5, 1990 and September 28, 1989 to April 12, 1990. Figures 6 and 7 (March 30, 1989 and April 5, 1990 respectively) exhibit no major differences that can be attributed to the grouting operation. A comparison of the site on September 28, 1989 to April 12, 1990 likewise indicates no definite changes caused by grouting (Figures 8 and 9). Hawkins and Aljoe (1991, In Press) indicated that groundwater flow through the site generally follows porous media principles (except under transient conditions or periods of stress), therefore if the grout mainly filled conduits, it is not unexpected that no change was seen in the water levels. The contour line flexure noted for the average water table was not observed during this time. It is possible that the contour anomaly observed for the average conditions becomes evident under different flow conditions than those seen during the two comparison periods.

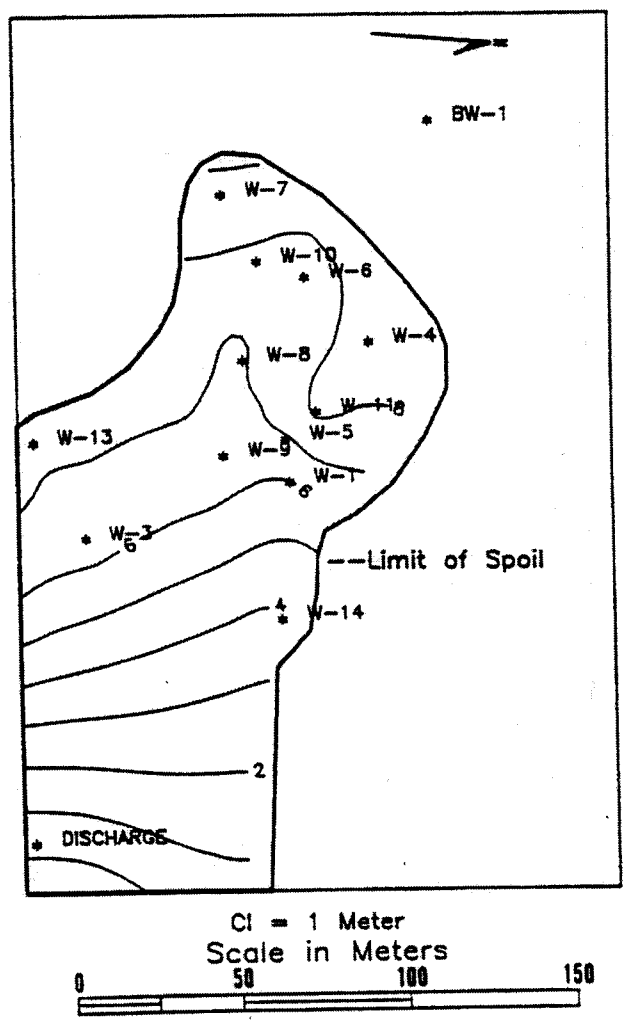

Figure 6. Water table contour map from March 30, 1989. The main discharge is datum.

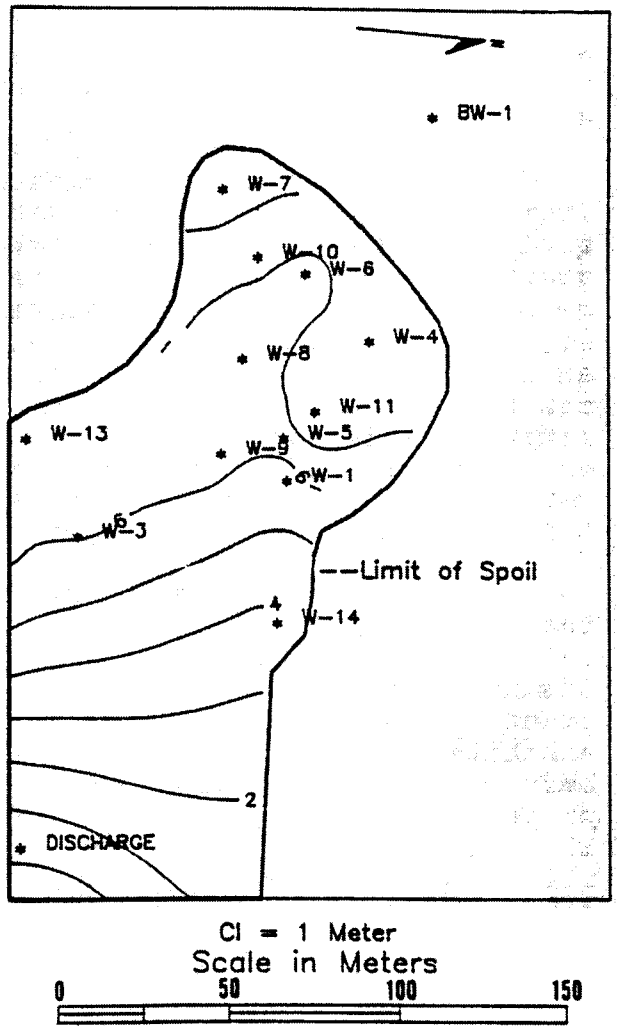

Figure 7. Water table contour map from April 5, 1991. The main discharge is datum.

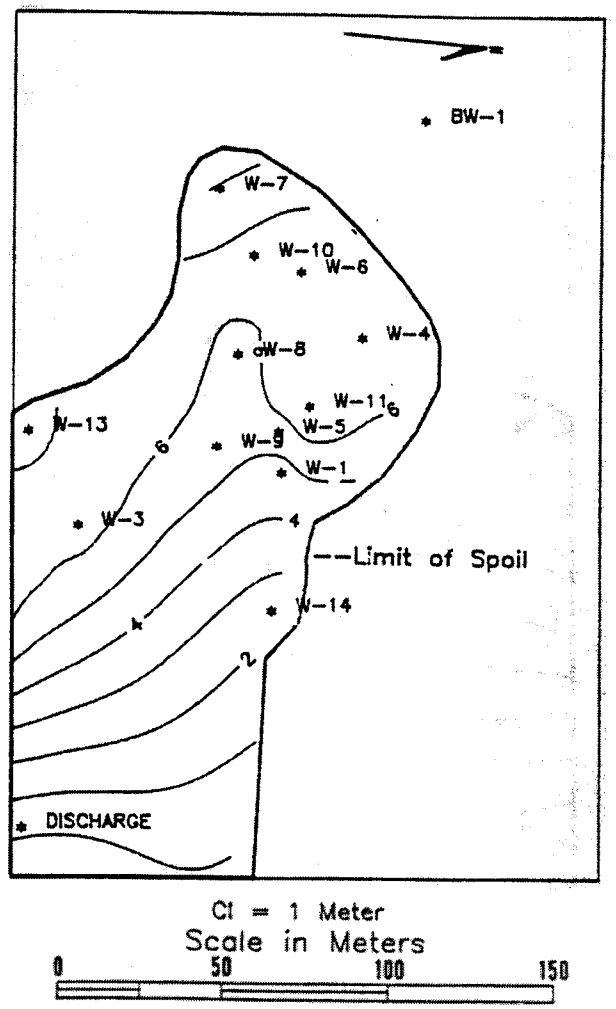

Figure 8. Water table contour map from September 28, 1989. The main discharge is datum.

Water Quality

Grouting is likely to induce water quality changes within the site in several ways. The grout material contained significant concentrations of both calcium and sodium. The fly ash was 2.4 percent calcium and 0.29 percent sodium, which means that nearly 6000 kg of calcium and 700 kg of sodium were injected. The main source of calcium was probably the portland cement portion of the grout. Calcium in the form of hydraulic calcium silicates, calcium oxides, and hydrated calcium sulfate are primary components of portland cement (ESSROC Materials). Chemical changes may be caused by the components of the grouting material reacting with groundwater. Chemical changes also may be caused by amelioration of the AMD production by the coating of potentially acidic spoil, thereby limiting physical contact of oxygen and/or groundwater with this spoil. Another possible consequence is the rerouting of vadose and phreatic groundwater flow paths within the spoil, thus possibly changing the spoil it comes in contact with, affecting

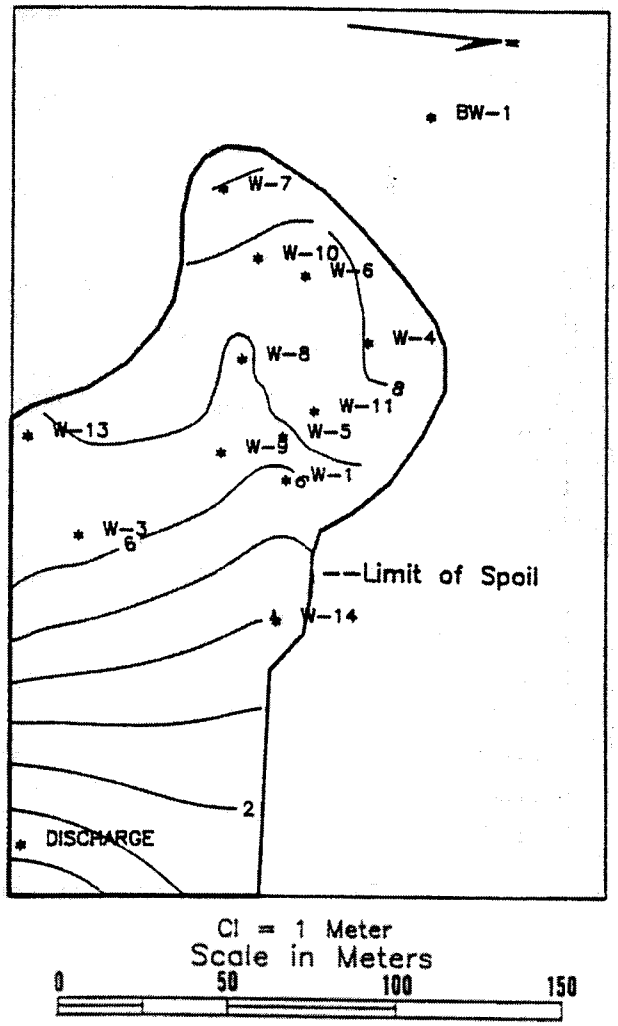

Figure 9. Water table contour map from April 12, 1990. The main discharge is datum.

the commingling of groundwaters of differing chemical quality, or changing lateral and vertical recharge rates.

In 1951, Stiff suggested a system where the cation and anion concentrations in milliequivalents per liter (meq/l) were plotted on opposite sides of a vertical axis. The points are connected by lines giving each plot a distinctive polygonal shape. This system was originally developed for analysis of natural waters, therefore care must be exercised that the high iron and sulfate levels usually associated with AMD do not mask trends of other cations and anions.

Stiff diagrams were created from the average spoil water quality data before and after grouting. These diagrams are a means of graphically displaying similarities in water sample analyses and showing differences caused by chemical reactions or mixing. Relative concentrations of cations and anions are converted to percent meq/l rather than milligrams per liter (mg/l).

The Stiff diagrams revealed that the main discharge and the majority of the wells showed no discernable change after grouting. Wells 2, 8, 11, and 13 exhibited minor changes from before to after the grouting project (Figures 10, 11, 12, and 13, respectively). As expected all sample points exhibited a strong sulfate type anion characteristic. The high sulfate concentrations associated with AMD strongly influence the data on the anion side of the diagram. Well 2 (Figure 10) exhibits an increase in calcium and sodium relative to the iron and magnesium. Changes in well 8 (Figure 11) are related to an increase in the sulfate and iron dominance after grouting. An increase in the relative concentrations of iron after grouting of wells 11 and 13 (Figures 12 and 13, respectively) is related to an increase in total iron concentration.

Well 2 exhibited a significant change in water quality in the period following grouting (Figure 10). The cation type changed from a mildly magnesium dominant type to a stronger calcium type with increasing sodium. This change

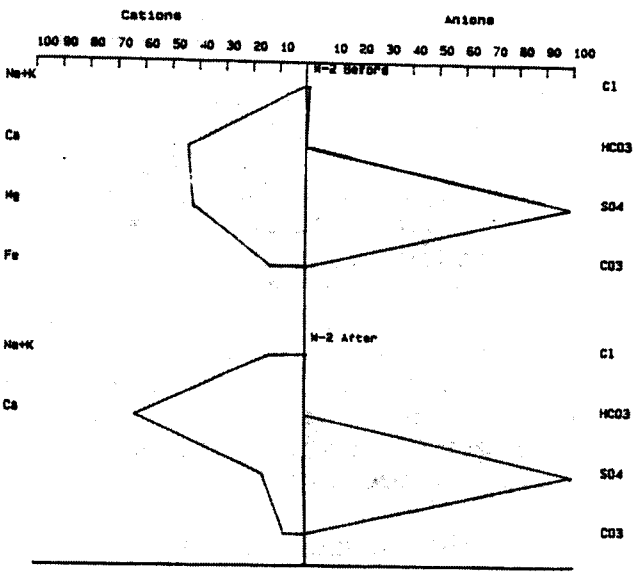

Figure 10. Stiff diagrams graphically illustrating cation changes in well 2. Cation and anion values are in percent milliequivalents per liter.

appears to be directly related to the grouting near the well. Numerous grout wells (26) are hydrologically directly up gradient of well 2.

Well 2 is located in a perched-water table zone within the spoil aquifer, which is underlain by a lower permeability material than the surrounding spoil (Hawkins and Aljoe, 1990). Groundwater accessed by this well is removed (above) from the water table reflected by the other spoil wells. Given lower permeability and being limited to direct recharge, flow through spoil in the vicinity of well 2 is slower than other portions of the site. Groundwater flushing through this area will take longer than through other parts of the site. Therefore, the water quality changes noted in well 2 are may only be temporary.

Well 8 became more strongly sulfate dominant after grouting (Figure 11). This trend is not due to an increase in sulfate, but is caused by a substantial decrease in the bicarbonate (HCO_3) concentration. It is possible that a rerouting of groundwater caused this change. The water quality has become more like that of wells 4, 6, and 7, which are hydrologically up gradient. Because of the limited amount of data, the apparent change must be verified by the collection of data over a longer time period. It is also possible that increased calcium content from the grout caused calcium carbonate ($CaCO_3$) to form and precipitate, thereby reducing the bicarbonate concentration.

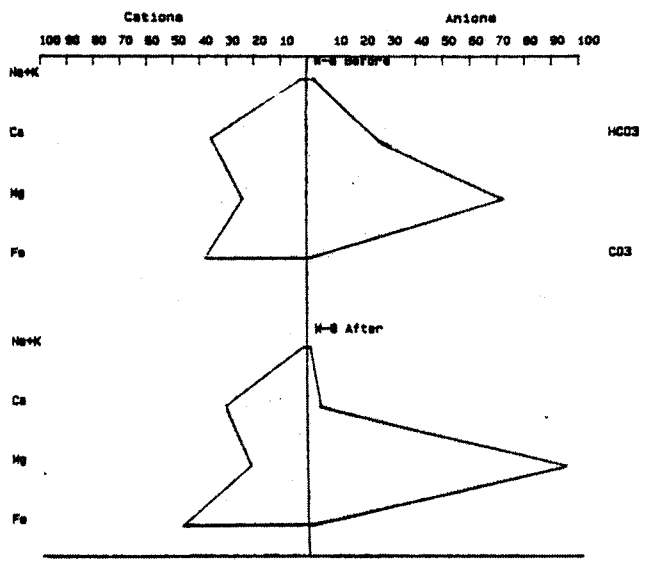

Figure 11. Stiff diagrams graphically illustrating anion changes in well 8 caused by grouting. Cation and anion values are in percent milliequivalents per liter.

The changes at well 11 are caused mainly by an increase in magnesium and iron (Figure 12). The differences found in well 13 resulted from an increase in iron, while calcium and magnesium decreased somewhat (Figure 13).

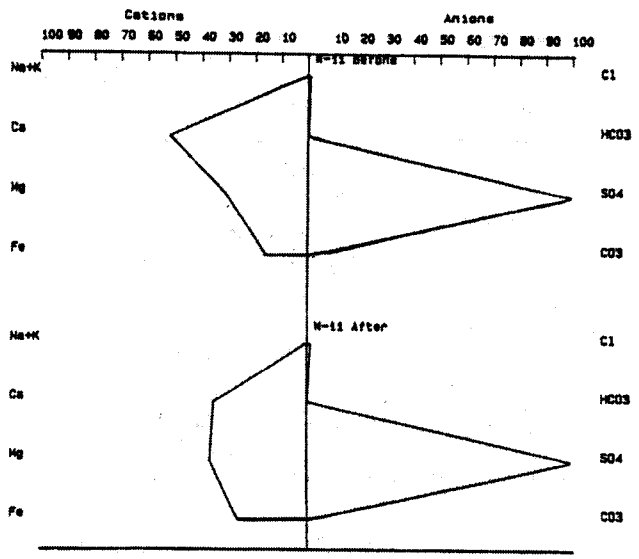

Figure 12. Stiff diagrams graphically illustrating cation changes in well 11 caused by grouting. Cation and anion values are in percenter milliequivalents per liter.

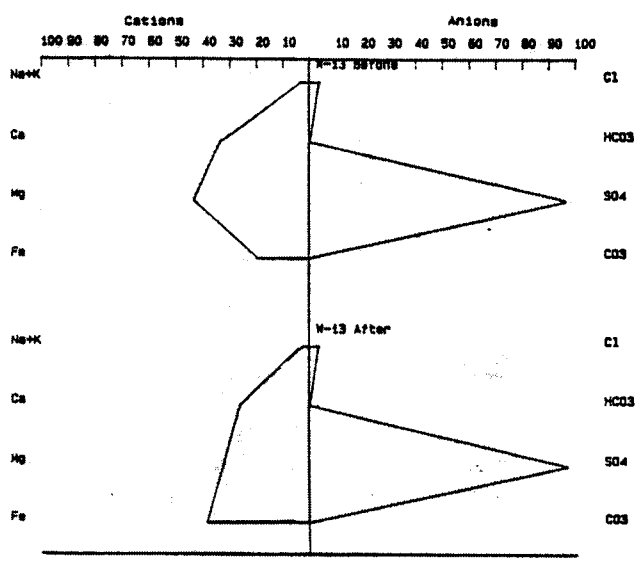

Figure 13. Stiff diagrams graphically illustrating cation changes in well 13 caused by grouting. Cation and anion values are in percent milliequivalents per liter.

There is no indication that these changes are related to the grouting. Only one grout well was within 25 meters of well 11 and none were hydrologically up gradient of this well. No grout wells were within 40 meters or hydrologically up gradient of well 13. The changes appear to be related to temporal differences which may be attributed to the small data set and the use of percent milliequivalents instead of actual concentration values.

Grout Plume Tracking

Background sodium concentrations in the groundwater were low prior to grouting, generally averaging below 2 mg/l. The substantial amount of sodium contained in the fly ash (700 kg) permitted its use as a groundwater tracer of the grout injection. The main discharge and wells 1, 2, 8, 10, and 11 all exhibited a significant sodium concentration spike following the grout injection. The remaining wells showed no definite sodium peak, although most exhibited apparent increases of sodium levels.

The main discharge, approximately 80 meters from the nearest grout injection well, exhibited a jump in sodium concentration (from about 1 to 5 mg/l) within about 20 days after the initiation, but before completion of grouting (see Figure 14). At this rate, average linear velocity is 4.6 x 10^{-5} meters per second. The average linear velocity is similar to values obtained from a earlier tracer test and is comparable to glacial sediments (Hawkins and Aljoe, 1991, In Press). The concentration began to decline exponentially after

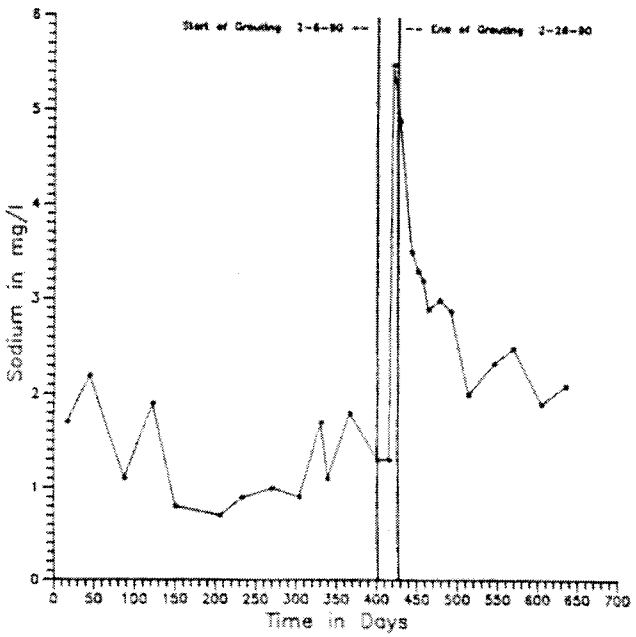

Figure 14. Sodium concentration at the main discharge.

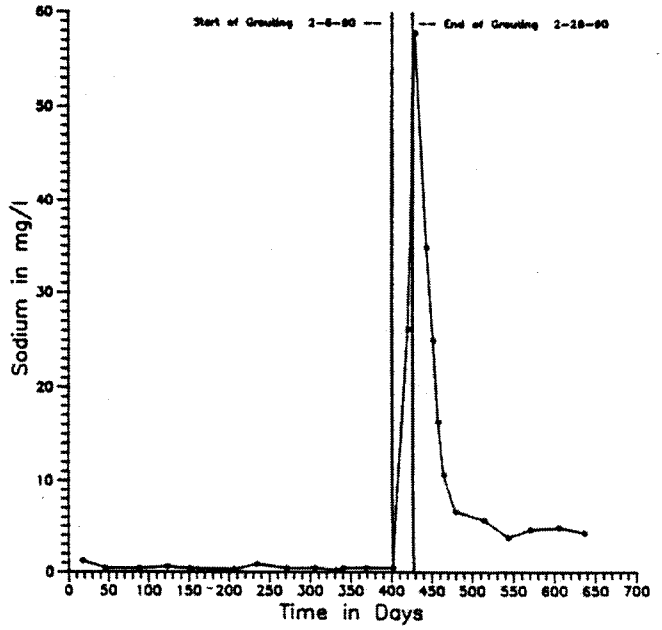

Figure 15. Sodium concentration at well 2.

completion of grouting. Given this rate of decline, the sodium concentration should return to the level of the pregrouting average approximately 280 days after completion of grouting. This indicates that groundwater flushing of the grouted portion of spoil should be virtually complete in under 10 months.

Wells 2, 8, and 10 also exhibited a very rapid sodium spike followed by a nearly as rapid decline (see Figures 15, 16, and 17). The sodium concentration of well 2 rose to almost 60 mg/l from a pregrouting background average of 0.5 mg/l. Sodium levels quickly dropped to about 5 mg/l and then more slowly decreased, although they have not yet returned to pregrouting background levels. The rapid rise in sodium levels appears to be caused by large amounts of sodium-rich grout forced into spoil by the numerous grout wells near well 2. The slow return to background levels can be explained by the limited recharge to, and the low transmissivity

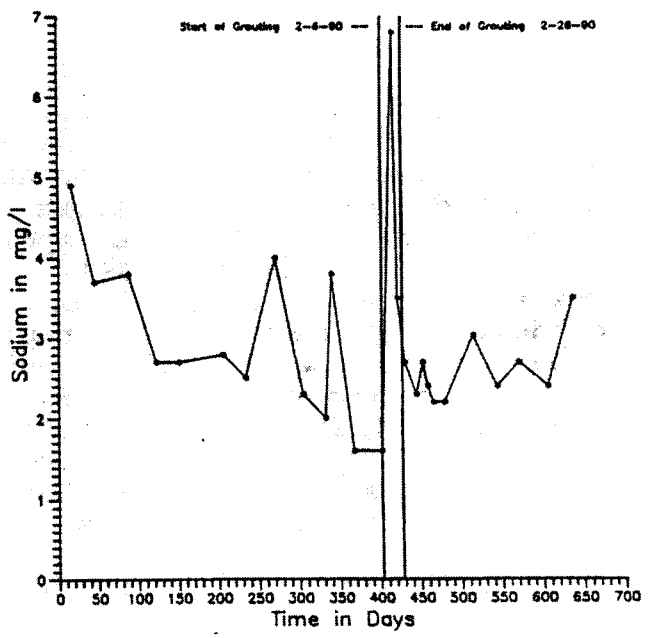

Figure 16. Sodium concentration at well 8.

of, the perched spoil zone intersected by well 2. The sodium concentrations in wells 8 and 10 returned to background levels nearly as fast as they rose. This indicates rapid

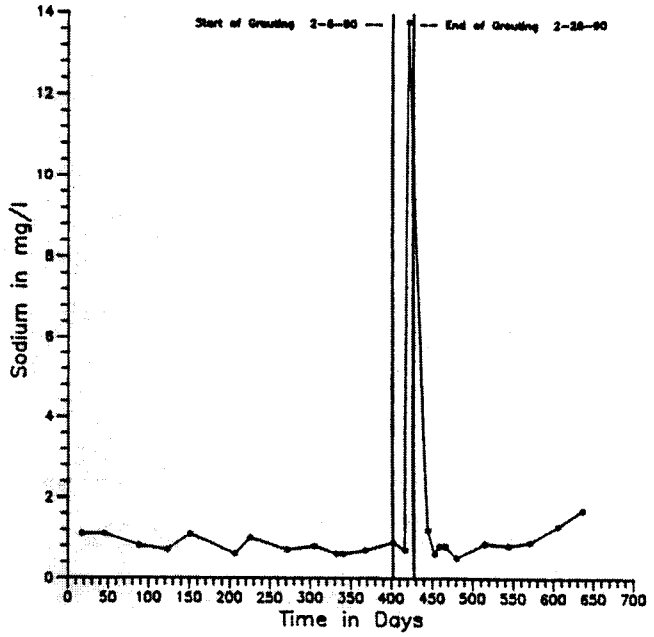

Figure 17. Sodium concentration at well 10.

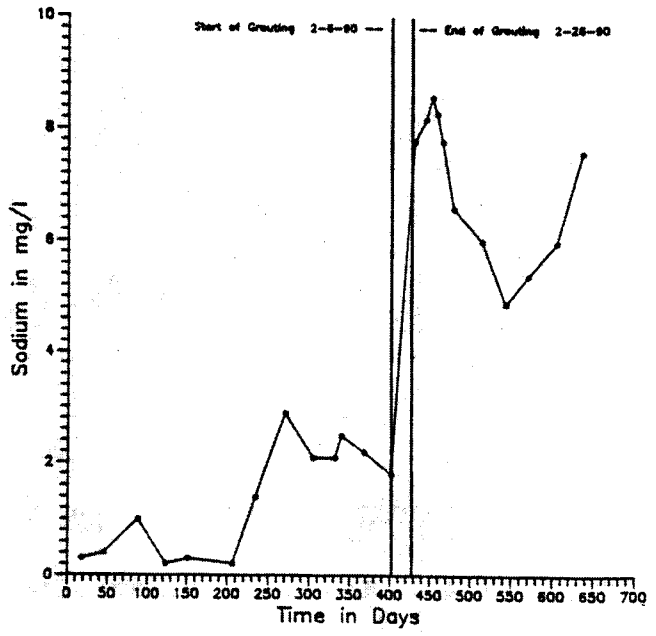

Figure 18. Sodium concentration at well 1.

groundwater movement quickly flushed much of the sodium out of the portion of the spoil around these wells. Previous work has indicated well 8 intersects a conduit or void in the spoil (Hawkins and Aljoe, 1991, In Press). The presence of a conduit will permit more rapid groundwater flow near and around well 8 and perhaps well 10 (data indicate that interconnected voids also exist in that area) than in portions of the spoil where primarily porous media flow occurs.

Wells 1 and 11 also exhibited a sodium spike that began a fluctuating decline after the effects of the grouting passed (Figures 18 and 19). Both wells show sodium concentration fluctuations after grouting that are below the peak, but well above background levels. These fluctuations appear to be directly related to recharge events. Both show a marked increase in the fall and early

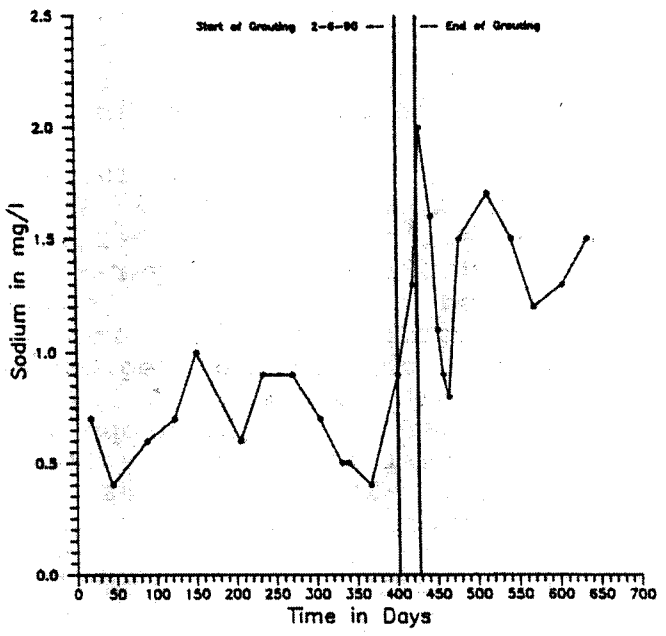

Figure 19. Sodium concentration at well 11.

winter months when recharge rates are lower. This indicates the

concentration at these wells is strongly controlled by the amount of dilution available from the recharging waters. The aquifer testing of these wells indicates groundwater flow in this area is porous media type, which will allow much slower movement than conduit flow. Sodium concentrations should continue to fluctuate with recharge and eventually return to background levels. Rate of return will depend mainly on the spoil recharge rate.

The differences in the sodium concentrations at various wells following grout injection indicate the spoil is highly heterogeneous and anisotropic. Zones of rapid groundwater movement appear to be related to conduits within the spoil. Areas of slower groundwater movement exist where porous media flow dominates. Sodium has proven to be an adequate groundwater tracer to determine the average linear velocity and direction of groundwater movement. Approximately 280 days are required for sodium at the main discharge to return to background levels. As stated earlier, overall the spoil aquifer behaves primarily as a porous medium under steady state conditions.

Conclusions

Slug tests and pumping tests give widely different results, possibly attributable to the subjectivity of the data reduction techniques employed. Nevertheless, aquifer tests before and after grout injection of the monitoring wells indicate the grouting caused no discernable widespread changes in the hydraulic properties of the spoil, although hydraulic conductivity in parts of the spoil may have changed. No major changes in groundwater flow direction or water table level were observed, although a localized flexure of the post-grouting water table appears to be caused by grouting. The original intent of the grouting project, to grout small isolated potentially acidic spoil zones to restrict contact with oxygen and groundwater, along with the small amount of grout injected relative to the total spoil pore volume and the watery consistency of the grout are the main reasons for the lack of significant hydrologic changes.

Two wells less than 20 meters hydrologically down gradient from grout injection wells exhibited slight water quality changes that could be attributed to the grouting operation. The changes were caused by compounds introduced by the grout and by groundwater flow rerouting. The remainder of the wells exhibited no water quality changes that can be attributed to grouting.

Sodium in the grout can be used to track the movement of groundwater through the spoil. Tracking of the plume and monitoring of the sodium concentrations will give insight into the groundwater flow regime and flushing rates. The movement of the plume as it passes monitoring wells indicates a bimodal flow regime of groundwater, as have previous studies. The sodium concentration at the site discharge indicates a porous media groundwater flow regime for the site as a whole.

Literature Cited

Bouwer, H. and Rice, R.C. 1976. A Slug Test for Determining Hydraulic Conductivity of Unconfined Aquifers with Completely or Partially Penetrating Wells, Water Resources Research, Vol. 12, No. 3 pp 423-428.

Caruccio, F.T., Geidel, G. and Williams, R., 1984. "Induced Alkaline Recharge Zones to Mitigate Acidic Seeps," 1984 Symposium of Surface Mining, Hydrology, Sedimentology, and Reclamation, University of Kentucky, Lexington, Kentucky, pp. 43-47.

ESSROC Materials, Inc, Undated, Material Safety Data Sheet for Portland Cement, Poland, OH.

Freeze, R.A. and Cherry, J.A. 1979. Groundwater, Prentice-Hall, Inc. Englewood Cliffs, N.J.

Groenewold, G.H. and Bailey, M.J. 1979. "Instability of Contoured Strip Mine Spoils--Western North Dakota." Ecology and Coal Resource Development, Wali, M.K. (ed), pp 685-692.

Hawkins, J.W. and Aljoe, W.W., 1990. Hydrologic Characterization and Modeling of a Heterogeneous Acid-Producing Surface Coal Mine Spoil, Upshur County, WV, Proceedings 1990 National Symposium on Mining, University of Kentucky, pp 43-52.

Hawkins, J.W. and Aljoe, W.W. 1991. "Hydrologic Characteristics of a Surface Mine Spoil Aquifer." Proceedings of the Second International Conference on the Abatement of Acidic Drainage. [In Press]

Stiff, H.A. 1951. "The Interpretation of Chemical Water Analysis by Means of Patterns." Journal of Petroleum Technology, Vol. 3, No. 10, pp 15-17.

Theis, C.V., 1935. "The Lowering of the Piezometric Surface and the Rate of Discharge of a Well Using Ground-Water Storage." Transactions, American Geophysical Union, Vol 16, pp. 519-524.

USE OF PASSIVE ANOXIC LIMESTONE DRAINS TO ENHANCE PERFORMANCE OF ACID DRAINAGE TREATMENT WETLANDS[1]

by

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Abstract. Constructed wetlands for treating acid drainage are preferred, low-cost, alternatives to conventional treatment. Drainage with high Fe (e.g., >50 mg/l) and zero alkalinity has not been amenable to treatment with wetlands alone, primarily due to Fe hydrolysis and resultant low pH which requires chemical treatment. Anoxic limestone drains (ALDs) increase the alkalinity of seepage that is then routed to a constructed wetlands. Increased alkalinity buffers the wetlands system from pH decreases, and enhances the effectiveness of wetlands treatment. The Tennessee Valley Authority has modified two low-pH constructed wetlands with ALDs. Results indicate retrofitted wetlands function at efficiencies meeting effluent limitations without chemical treatment. Designs of ALDs are site-specific, but generically consist of an excavated seepage-interception trench backfilled with crushed limestone covered with plastic and clay soil. Dissolution rates of limestone in operational and simulated ALDs were experimentally measured in attempts to estimate design parameters and longevity of an ALD. Potential problems with ALDs include structural and hydraulic stability, plugging due to reaction products within the ALD, and inadequate design and installation.

Additional Key Words: Tennessee Valley Authority, constructed wetlands, Alabama, Tennessee, alkalinity

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Introduction

Staged constructed wetlands are an effective alternative to conventional means of treating acid mine drainage (AMD) (Brodie 1990a,b,c; Hedin 1989). Wetlands efficiencies are related primarily to flow rates, pH, and concentrations of dissolved oxygen, iron, manganese, acidity, and alkalinity. Foremost are the relationships among influent dissolved oxygen, iron, and alkalinity concentrations, and influent/effluent pH.

Metals removal mechanisms in wetlands are variable and numerous, but it is probable that microbially-catalyzed Fe oxidation and hydrolysis are major reactions responsible for iron removal in acidic waters in aerobic wetlands systems (Faulkner and Richardson 1990). These reactions may dictate the ultimate success or failure of a wetlands system because of their acidity-producing natures, summarized below.

(1) $2FeS_2 + 2H_2O + 7O_2 = 2Fe^{+2} + 4H^+ + 4SO_4^{-2}$

(Pyrite oxidation)

(2) $4Fe^{+2} + O_2 + 4H^+ = 4Fe^{+3} + 2H_2O$

(Ferrous oxidation)

(3) $Fe^{+3} + 3H_2O = Fe(OH)_3 + 3H^+$

(Ferric hydrolysis)

Reactions 1-3 occur all in the backfill, but only reaction 3 acts to increase acidity in a wetlands. If sufficient buffering capacity is not present in the acid drainage, pH will decrease. Several aerobic wetlands systems, although removing substantial amounts of iron and manganese have had influent pH near 6.0 and effluent pHs of less than 3.0 (Brodie 1990a,c, 1991a,b; Kepler 1989). Table 1 shows typical pH decreases in TVA's 006 Kingston Fossil Plant constructed wetlands in Roane County, TN. This 2.3-acre system receives, on average, 379 gpm of acid seepage from an ash disposal area with an influent pH of 5.5 and total Fe of 170 mg/L. Effluent from the wetlands system has a pH of 2.9 and total Fe of 83 mg/L; thus the hydrolysis of about 87 mg/L of Fe is responsible for the decreased pH.

Numerous methods for treating acid drainage have been used to meet effluent standards; however these methods are expensive and require constant attention to maintain compliance with effluent limitations. Also, many chemical additives have an adverse impact on aquatic biota in receiving streams. Limestone treatment has many advantages over conventional chemical treatment including lower sludge production, lower cost, and less potential for overdosing. However, the use of limestone rock as a

buffering agent was abandoned because, in an oxidizing environment, iron hydroxides coat the limestone surface and inhibit or eliminate the dissolution of the limestone, thus preventing effective buffering.

In 1988, the Tennessee Division of Water Pollution Control (TWPC) constructed and evaluated prototype passive anoxic limestone drains (ALDs) at 2 mine sites in Tennessee (Turner and McCoy 1990). At the same time, Tennessee Valley Authority (TVA) recognized a correlation between alkalinity and dissolved oxygen of wetlands influent, and the relative success of 11 TVA constructed wetlands, and conducted several relevant bench-scale studies.

Results of a TVA study identified a correlation between wetlands influent alkalinity and effluent pH, Fe, and Mn. A possible "accidental" roadbed originated anoxic drain (AROAD) was identified at the TVA Impoundment 1 constructed wetlands, which treats high-Fe (100 mg/l) acid drainage emanating from a fine-coal refuse disposal area at the Fabius Coal Preparation Plant site in northeastern Alabama (Brodie 1990a,c). Air photo investigations showed that a 1400-ft long, 25-foot high earth dam was constructed in 1974 over an existing coal haul road built of crushed rock that was presumably obtained from the local Monteagle formation, a high $CaCO_3$, oolitic limestone (see Figure 1). Although this limestone roadbed was not intended for water quality enhancement, it is hypothesized that it is pretreating acid drainage seeping through the dike by adding alkalinity (300 mg/l) and buffering capacity so that the wetlands is producing compliance-quality discharges. TVA is currently drilling and sampling the dike, and conducting monitoring well sampling to determine the nature and condition of the AROAD (Brodie and Garvich 1991).

Several constructed wetlands in Tennessee and Alabama have now been enhanced by the addition of anoxic limestone drains (ALDs) as the initial component of a staged treatment system. The ALD, which consists of a shallow, limestone-filled trench excavated into the spoil and sealed from the atmosphere, passively introduces buffering capacity, as alkalinity, into the acid drainage. Changes in pH due to acid production from Fe hydrolysis in the wetlands are buffered due to the high alkalinity in the influent.

It is assumed that the following reactions are applicable within the ALD:

(4) $CaCO_3 + 2H^+ = Ca^{+2} + H_2CO_3$

(5) $CaCO_3 + H_2CO_3 = Ca^{+2} + 2HCO_3^-$

(6) $CaCO_3 + H^+ \; Ca^{+2} + HCO_3$

Equation 4 reacts limestone with acidity (at pH <6.4) present in the mine drainage to form free calcium and dissolved carbon dioxide (carbonic acid). The carbonic acid further reacts with

limestone in equation 5 to produce alkalinity. As reactions 4 and 5 act to increase pH above 6.4, equation 6 becomes the major reaction where bicarbonate is the dominant dissolved CO_2 species (Cravotta et al 1990).

Systems observed to date indicate that if the ALD is properly constructed, limestone in the ALD will not armour with Fe or Al precipitates and alkalinity can be significantly increased in the ALD effluent. This paper discusses the design, construction, and operational results of a few ALDs and some preliminary research on the utility and longevity of this potentially inexpensive component of a long-term acid drainage treatment system.

Discussion

Preliminary Considerations

The preliminary question is whether an ALD is necessary or beneficial to an existing or proposed wetlands treatment system. Hydrology and water-quality characteristics primarily determine the need for and feasibility of an ALD. Tables 2-5 show the relationships among influent/effluent pH, alkalinity, Fe, and Mn in TVA's 13 constructed wetlands. Table 2 shows that effluent pH of constructed wetlands is directly related to influent alkalinity. Only the 4 systems with zero alkalinity in the inflow fail to meet the NPDES permit limitation of 6.0 TVA's wetlands systems having influent alkalinity loading greater than 4 g/day/m^2 (GDM) (corresponding to 73-113 mg/L alkalinity, as $CaCO_3$) always produce complying pH (i.e., > 6.0) discharges, even with Fe contents as high as 110 mg/L. However, where influent Fe concentrations exceed 18 mg/L, low-pH effluent has been observed in cases of zero influent alkalinity (Brodie 1990a). Table 3 supports the idea that high-Fe concentrations are causative of low wetlands effluent pH. Table 4 suggests that Fe removal is not related to alkalinity concentrations. Table 5 shows a positive relationship between Mn removal and influent alkalinity. However, Fe removal occurs more rapidly at high pH (e.g., > 5.5) and is very slow at low pH (< 3.0).

Previously suggested guidelines have been revised to determine the utility for an ALD (Brodie et al 1990).

Case 1: Alkalinity > 80 mg/L, Fe > 20 mg/L; an ALD may be beneficial, but a wetlands system based on previously reported chemical loading rates (Brodie 1990b; Hedin et al 1990) is probably adequate.

Case 2: Alkalinity > 80 mg/L, Fe < 20 mg/L; an ALD is not necessary, only an adequately designed wetlands.

Case 3: Alkalinity < 80 mg/L, Fe > 20 mg/L; an ALD is recommended and probably necessary as the initial stage in a constructed wetlands system.

Case 4: Alkalinity < 80 mg/L, Fe < 20 mg/L; an ALD is recommended, but not necessary

Case 5: Alkalinity $\leq$ 0, Fe < 20; an ALD will likely be necessary as Fe approaches 20 mg/L.

Case 6: Dissolved oxygen > 2.0 mg/L or Fe oxidizing conditions exist (e.g., pH > 6.0, eH > 100 mv. An ALD should not be installed because of probable limestone armoring.

Case 7: Ferric iron present in appreciable concentrations in the unaerated seep sample; an ALD may not be appropriate due to potential limestone armoring.

Additionally, because the ALD is generally associated with a staged wetlands treatment system, preliminary considerations for constructed wetlands, such as available area, geology and topography, and the availability of soil and limestone must be regarded (Brodie 1988).

In order for an ALD to perform successfully, unaerated mine drainage must come into contact with the buried limestone. Discrete seeps or boils from embankments are generally good starting points for excavation of the ALD into the backfill. Non-point seep areas may require more innovative means of collection, such as specialized rock drains or the construction of an embankment to contain the ALD. Underground mine adits could be sealed and flooded, routing the drainage via a pipe to an ALD, or a mine adit could be backfilled with limestone and thereby delineate the boundaries of the ALD.

Maximum expected flow through the ALD should be determined to prevent hydraulic failures and disruption of the sealed nature of the ALD. Several methods exist for designing underdrains and French drains, which are similar in construction to ALDs; but ideally, maximum flow should be determined or estimated from actual flow measurements over an extended time period. Alternatively, flow can be predicted from various hydrologic methodologies, although this may be difficult and expensive due to the need for contributing area delineation and characterization of the geologic materials. Because of the relative low cost of an ALD compared to conventional treatment systems, an overdesigned ALD is recommended to ensure hydraulic stability and to maximize longevity. In fact, desired longevity of the ALD will likely dictate a design size far in excess of the hydraulic design requirements. A suggested crude, but conservative, method for hydraulically designing the ALD is to calculate infiltration from the contributing drainage basin at the point source of the seepage and assume an attenuation factor based on the mine fill characteristics. As an example, annual infiltration over a 100-acre watershed might be estimated at 12 inches, giving an average flow from groundwater of about 60 gpm. Assuming all flow is from the seep and high flow is 3 times the average flow, an

ALD might be designed to handle 180 gpm.

Another important preliminary consideration for ALD construction is water quality. The success of a wetlands system to meet effluent limitations is directly and primarily related to influent pH, acidity, alkalinity, Fe, and Mn concentrations. Alternatively, dissolved oxygen and oxidation-reduction potential (ORP) are critical for the proper operation of an ALD. All waters that would be routed through an ALD should be sampled and analyzed for the above mentioned parameters. Samples should be collected directly from the seep via methodologies precluding sample aeration (e.g., peristaltic pumps, large syringes, etc.). Dissolved oxygen (DO) and ORP must be field measurements. Fe^{+2} and Fe^{+3} are good indicators of ORP (and possible armouring). If samples are immediately acidified with HCl (or another non-oxidizing acid) Fe^{+2} can be determined accurately in the lab.

Design and Construction

The basic design of an ALD is shown in Figure 2. The ALD consists of an open, unlined trench or excavation backfilled with gravel-sized, crushed, high-$CaCO_3$ limestone. The limestone is covered with plastic to preclude oxygen infiltration and CO_2 exsolution. It is desirable to place geotechnical fabric over the plastic for protection of the plastic from puncture by equipment or manpower. A clay soil is then placed over the fabric.

As discussed above, adequate hydraulic design and subsequent oversizing is critical for the proper operation and long-term stability of an ALD. Maximum and average flow should be estimated and the dimensions of the ALD then determined in conjunction with consideration of other site restraints (e.g., steep topography, shallow bedrock, multiple seeps). Because of the infinite number of potential shapes and configurations of an ALD, it is beyond the scope of this paper to suggest guidelines for shapes and dimensional ratios of an ALD.

Side slopes of the excavation are not critical to the operation of the ALD and are best made near vertical to facilitate construction. High-calcium limestone (i.e., $\geq$ 90% available $CaCO_3$) should be used. TVA and TWPC have used 3/4 to 1-1/2 in crushed rock in existing ALDs because of its high hydraulic conductivity, large surface area, and ready availability; however, a different gradation, a well-graded mixture, or a layering of several grades of rock may be suitable. Larger rock size or more dolomitic (i.e., $CaMgCO_3$) stone is not recommended due to the loss of surface area in the ALD with the large rock and the lower reactivity of dolomite. The depth of limestone backfill should be determined by (1) the need to accommodate the maximum probable flow, (2) the desired longevity of the ALD,

and (3) a comfortable safety factor for both (1) and (2). Desired longevity is discussed below. TVA's and TWPC's ALDs have contained limestone depths of 2 to 5 ft. Because the very lowest portion of the backfill may be rendered ineffective due to its tendency to embed in the bottom of the excavation, about 6 inches additional depth of limestone should be included to account for this loss.

A minimum of 2 ft of soil cover should be placed and compacted over the plastic and fabric covered limestone backfill. Soil should be sufficiently impermeable to oxygen migration. If available and practicable, clay soil is recommended. Alternatively, a clay, clayey-silt, or silty-clay loam should be adequate. The final cover should be slightly crowned and protected with erosion control fabric or adequately waterbarred to prevent erosion. Crowning will allow for subsidence of the ALD over the years due to limestone dissolution. Ideally, the crowned ALD should be riprapped or revegetated with species such as sericea (Lespedeza cuneata) or crownvetch (Coronilla varia), which will discourage the establishment of trees whose roots could penetrate the ALD and render it ineffective.

Prototype installations of ALDs have used 5-mil plastic and/or filter fabric covered with clay soil to seal the limestone from the atmosphere (Turner and McCoy 1990). More recent ALDs have used 20-mil plastic or double layers of 10-mil plastic, which is significantly less expensive than 20-mil and is more readily available. Geotechnical fabric should be of quality sufficient to protect the integrity of the plastic from puncture under loads from equipment and workers.

An additional design recommendation is the use of an oxidation basin immediately after the seep discharges from the ALD and prior to routing that flow into a constructed wetlands. The purpose of an oxidation basin is aimed at high Fe influents (e.g., >50 mg/L). The basin allows the newly aerated and highly alkaline ALD discharge water to react and precipitate the majority of its Fe load, which can be achieved physiochemically and without the use of a constructed wetlands. The U.S. Bureau of Mines has suggested a general empirical guideline which states that about 50 mg/L Fe can be removed in a wetlands cell before reaeration is required (Kleinmann 1990). A basin will greatly enhance the efficiency and lifespan of a downstream constructed wetlands as the basin can be dredged, thus preventing excessive precipitate buildup in the wetlands. Such a pond needs simply to be designed according to existing guidelines with considerations of regulatory requirements, desired capacity, and maintenance. Alternatively, a modified marsh-pond cell with a major portion devoted to deep (3-6 ft) water might be more applicable to acid drainage with low to moderate Fe concentrations.

Results

To date 17 ALDs have been installed in Alabama and Tennessee with 3 more planned for 1991 installation (Brodie 1991a; Turner 1991). At least 1 ALD has been installed at a wetlands system in Pennsylvania (Meehan 1991). Tables 6-8 show typical pre-ALD and post-ALD water quality for TVA's Impoundment 4 constructed wetlands ALD system, which was installed in May 1990. As shown in Table 6, the ALD has successfully increased alkalinity and enabled the wetlands to decrease Fe and Mn concentrations to compliance levels; wetlands effluent pH rose from 3.1 to 6.3, and Fe decreased to <2.0 mg/l and Mn <2.0 mg/l. The Impoundment 4 wetlands influent (i.e., the ALD effluent) had an average pH of 6.3 and concentrations of 85 mg/L Fe and 17 mg/L Mn (see Table 7) before the ALD. After the ALD was installed, ALD effluent Fe and Mn concentrations have appeared to decrease. This phenomenon could indicate precipitation of Fe and Mn within the ALD, but is more likely a reflection of the general improvement of the seep-water quality over the past several years as a result of land reclamation.

ALD costs are associated with the design and engineering, manpower, equipment, materials and any operational or maintenance requirements. Table 9 shows the costs of an ALD installed at TVA's Fabius Coal Preparation Plant site in Jackson County, AL to treat up to 100 gpm of acid drainage flowing into the Impoundment 4 constructed wetlands (Brodie 1990a,c, 1991a).

The total installation cost of the ALD was about $19,000. This compares to annual costs of about $20,000 for NaOH and $10,000 for operation and maintenance associated with conventional treatment of the Impoundment 4 flow from October 1985 to May 1990. Thus, the payback period for the costs associated with the ALD was about 7 months. The TWPC reported total costs for two ALDs at mine sites in TN of $8000 and $6000 for limestone, labor, and heavy equipment (Turner and McCoy 1990). The significant differences between these costs and TVA's costs lie in the cost of rental equipment, which would generally be available at a mining operation. Thus, TWPC's reported costs may be more representative of what a coal operator might incur for an ALD.

Longevity of an ALD has been estimated by TVA and TWPC laboratory and field investigations into the dissolution rate of limestone. These studies include small-scale pilot studies and evaluations of existing ALDs. The TWPC suspended preweighed nylon bags of limestone in an access well within the ALD at the Prototype 2 site in Scott County, TN (Turner and McCoy 1990). After 6 months, the bags were retrieved and weighed. Average loss of the test limestone rocks was 0.24 g/kg/day. Average expected longevity of the ALD would be 23 years, at which time total dissolution will have occurred (Brodie et al 1991).

Table 9

Final Costs of TVA's IMP4 ALD

Design & Engineering	$3500
Labor & Supervision	3000
Equipment (dozer, hydraulic excavator, loader)	8000
Limestone (400T @ $7/T)	2800
Plastic	600
Geofabric	800
Seed, Mulch, Fertilizer	250
Total	$18,950

A study by TVA at its Kingston Fossil Plant in Roane County, Tennessee suggested that increased flow rates increased the rate of limestone dissolution and the amount of alkalinity in the effluent. Flow rates varied from 0 to 3.12 X 10^{-3} L/min/kg limestone. Anoxic seep water was routed through 4 55-gallon polypropylene barrels filled with high-$CaCO_3$ (about 92%), 3/4 in. crushed limestone. The anoxic seep water entered the bottom of the barrels and flowed upward, exiting at the top of the barrels; thus ensuring anoxic conditions prevailed in the limestone when seep flow was present. Flows were monitored and adjusted weekly, and effluent was sampled on a weekly basis. Table 10 shows the results of this sampling effort. Barrel 3 was removed from the experiment after 56 days because of difficulties in maintaining flow to it from the seep. A larger diameter inlet line was installed on barrell at the same time. The limestone dissolution rate for the first 56 days of the study, as calculated from weight lost by an approximately 20 kg sample in a PVC mesh bag in Barrel 3, was 4.19 g/kg or 0.0748 g/kg/day; implying a longevity of 37 years for a scaled-up equivalent system. Preliminary estimates for dissolution rates for barrels 1, 2, and 4 for the entire 90-day period range between 2.96 and 5.80 g/kg, implying daily rates of between 0.0329 and 0.0644 g/kg/day. At these daily rates, an ALD experiencing similar loading conditions would be expected to last between 42 and 83 years.

Another method of estimating longevity of an ALD is to compare pre-ALD and post-ALD data in the ALD effluent. For example, Ca^{+2} at TVA's Impoundment 4 seep increased from an initial 14 mg/L to about 56 mg/l after ALD construction. Thus, the ALD is adding 41 mg/l of Ca^{+2}, which corresponds to

Table 10

Preliminary Results TVA Limestone Dissolution Study at Kingston Fossil Plant

	Inflow	Bbl 1	Bbl 2	Bbl 3	Bbl 4
pH	5.9	6.8	6.5	6.5	6.3
Alkalinity (mg/l)	62.8	143.1	97.0	94.5	95.3
Acidity (mg/l)	20.2	-111.0	-68.2	-64.5	-49.7
Total Al (mg/l)	0.04	0.02	0.00	0.01	0.01
Total Fe (mg/l)	60.8	28.0	43.7	55.5	52.7
Total Mn (mg/l)	2.1	1.4	1.6	1.5	1.7
Total Cu (mg/l)	0.00	0.00	0.00	0.01	0.01
Total Ca (mg/l)	108.3	170.0	127.8	143.8	131.0
Total Mg (mg/l)	23.2	24.7	23.6	23.9	22.6
Total Zn (mg/l)	0.01	0.06	0.02	0.03	0.01
SO4 (mg/l)	413.3	403.3	427.8	368.5	381.8
Average Flow (l/min/kg)		2.0E-04	4.9E-04	8.6E-04	2.7E-03
Duration of Test (days)		90	90	56	90
Limestone Dissolved (g/kg)		5.3	3.0	4.2	5.8
Dissolution Rate(g/kg/day)		0.06	0.03	0.07	0.06
Expected Longevity (years)		46	83	37	42

105 mg/l $CaCO_3$. Average flow is 15 gpm and the ALD contains about 400 tons of 92% $CaCO_3$ limestone with 2% $MgCO_3$. Assuming that all the calcium carbonate is consumed and that the 2% Mg can bind with available Ca^{+2} rendering it nonreactive (i.e., only 90% of the tonnage should be assumed available for bicarbonate production), the lifespan of the ALD can be calculated at 102 years.

It is noted that longevity of an ALD will be affected by changes in the hydraulic characteristics of the ALD. Limestone dissolution and sediment clogging over several decades will reduce the hydraulic conductivity of an ALD and potentially result in hydraulic failure in the form of surface boils or blowouts. Overdesign of an ALD on the order of 2 to 3 times is the best insurance for a long-term, stable system. Thus, the effective lifespan of the above-referenced Impoundment 4 ALD is more likely about 50 years.

Conclusions

Passive anoxic limestone drains have been installed at sites in Tennessee and Alabama to increase buffering capacity and alkalinity in acid mine drainage and prevent pH decreases in effluent due to Fe hydrolysis. Results to date are optimistic and in most instances alkalinity has been significantly increased to levels sufficient to buffer the flow from pH decreases. Long-term results must be evaluated to establish the

stability of an ALD over the duration of acid drainage at a particular site.

Design, utility, and longevity of an ALD require further examination to develop guidelines and expectations. Particularly, stone gradation and composition, dissolution rates, reaction mechanisms and products, and the nature of ALD-enhanced Mn removal need to be researched. However, the relative simplicity and low cost of the ALD and preliminary studies indicating lifespans of several decades suggest that the system may be an effective means of renovating inefficient, existing aerobic wetlands and an important component of staged wetlands system designs, providing the capability of treating poorer quality waters with less area. Further evaluation is needed to identify the benefits of using an anoxic drain as a staged conponent of a sulfate reducing wetlands system.

LITERATURE CITED

Brodie, G.A. 1988. Selection and evaluation of sites for constructed wastewater treatment wetlands. Pages 307-317 In D.A. Hammer, ed. Constructed wetlands for wastewater treatment. Lewis Publishers, Inc. Chelsea, MI.

Brodie, G.A. 1990a. Treatment of acid drainage using constructed wetlands - experiences of the Tennessee Valley Authority. Pages 77-83 In Graves, D.H., ed. Proceedings 1990 National Symposium on Mining. University of Kentucky BU 153. Lexington, KY.

Brodie, G.A. 1990b. Workshop on design, construction, and operation of wetlands systems to treat acid drainage. Proceedings: 12th Annual National Association of Abandoned Mined Lands Program Conference. Sept. 16-20, 1990. Breckinridge, CO.

Brodie, G.A. 1990c. Constructed wetlands for treating acid drainage at Tennessee Valley Authority Coal facilities. Proceedings: 12th Annual National Association of Abandoned Mined Lands Program Conference. Sept. 16-20, 1990. Breckinridge, CO.

Brodie, G.A. 1991a. Achieving Compliance with Staged, Aerobic Constructed Wetlands to Treat Acid Drainage. In Proceedings: 1991 ASSMR Reclamation 2000: Technologies for Success. Durango, CO. May 14-17, 1991.

Brodie, G.A. 1991b. Unpublished data for the Kingston 006 Constructed Wetlands. Roane County, TN.

Brodie, G.A.; C.R. Britt; H.N. Taylor; T.M. Tomaszewski; and D. Turner 1990. Passive anoxic limestone drains to increase effectiveness of wetlands acid drainage treatment systems. In Proceedings: 12th Annual National Association Abandoned Mined Lands

Program Conference. Sept 16-20, 1990. Breckinridge, CO.

Brodie, G.A. and C.M. Garvich 1991. Preliminary results of an investigation underway on the genesis of alkalinity at TVA's Impoundment 1 constructed wetlands. Tennessee Valley Authority. Chattanooga, TN.

Cravotta, C.A.; K.B.C. Brady; M.W. Smith; and R.L. Beam 1990. Effectiveness of the addition of alkaline materials at surface coal mines in preventing or abating acid mine drainage: part 1: geochemical considerations. Pages 221-225 In J. Skousen et al, eds. Proceedings of the 1990 Mining and Reclamation Conference and Exhibition, Volume 1. West Virginia University Publication Services. Morgantown, WV.

Faulkner, S.P., and C.J. Richardson 1990. Biogeochemistry of iron and manganese in selected TVAconstructed wetlands receiving acid mine drainage. Duke Wetland Center Publication 90-03. Durham, NC

Hedin, R.S. 1989. Treatment of coal mine drainage with constructed wetlands. Pages 349-362 In S.K. Majumbar et al, eds. Wetlands ecology and conservation: emphasis in Pennsylvania, The Pennsylvania Academy of Science, Easton, PA, p. 349-362.

Hedin, R.S.; R.L.P. Kleinmann; and G.A. Brodie 1990. Constructing wetlands to treat acid mine drainage. Course Manual. Virginia Tech University. Wise, VA.

Kepler, D.A. 1990. Wetland sizing - design and treatment effectiveness. Pages 403-408 In J. Skousen, et al, eds. Proceedings of the 1990 mining and reclamation conference and exhibition. West Virginia University, Morgantown, WV.

Kleinmann, R.L.P. 1990. Personal communication. U.S. Bureau of Mines. Pittsburg, PA.

Meehan, T. 1991. Personal communication regarding the Shade acid drainage treatment wetlands, Somerset County, PA. Wetland Resources, Inc. Somerset, PA.

Turner, D. and D. McCoy 1990 Anoxic alkaline drain treatment system; a low cost acid mine drainage treatment alternative. Pages 73-75 In D. H. Graves, ed. In Proceedings 1990 national symposium on mining.University of Kentucky BU 153, Lexington, KY.

Turner, D. 1991. Personal communication. TN. Div. of Water Pollution Control. Knoxville, TN.

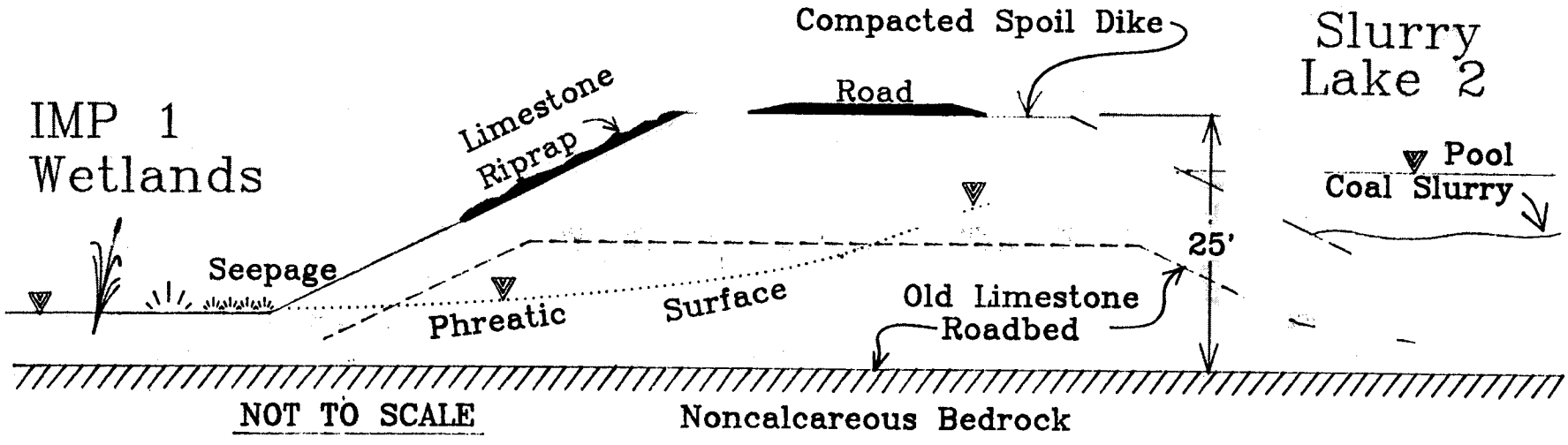


Figure 1. Schematic of Roadbed Originated Anoxic Drain at TVA's Fabius IMP1 Constructed Wetlands

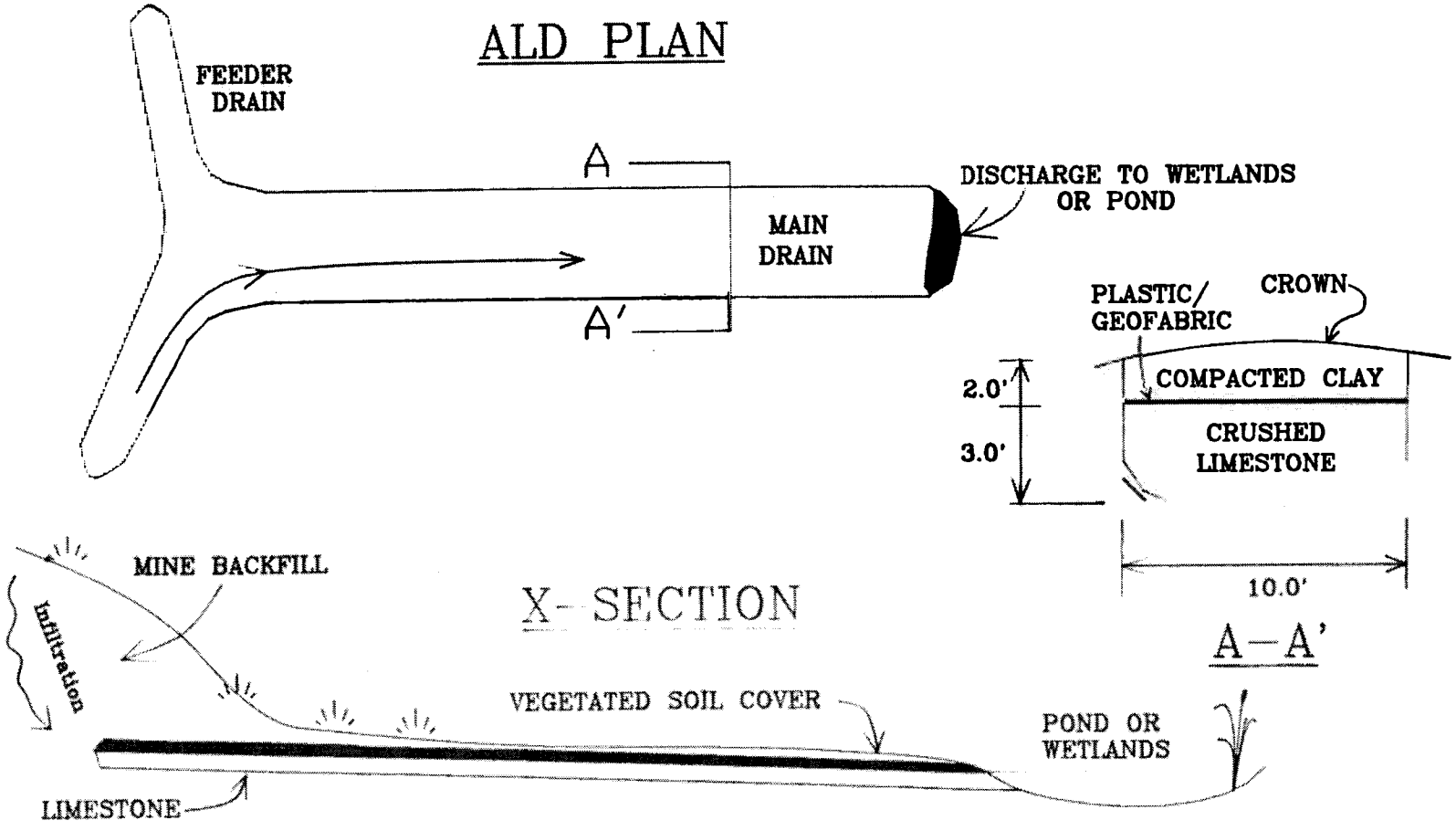


Figure 2. Generalized Schematic of Anoxic Limestone Drain

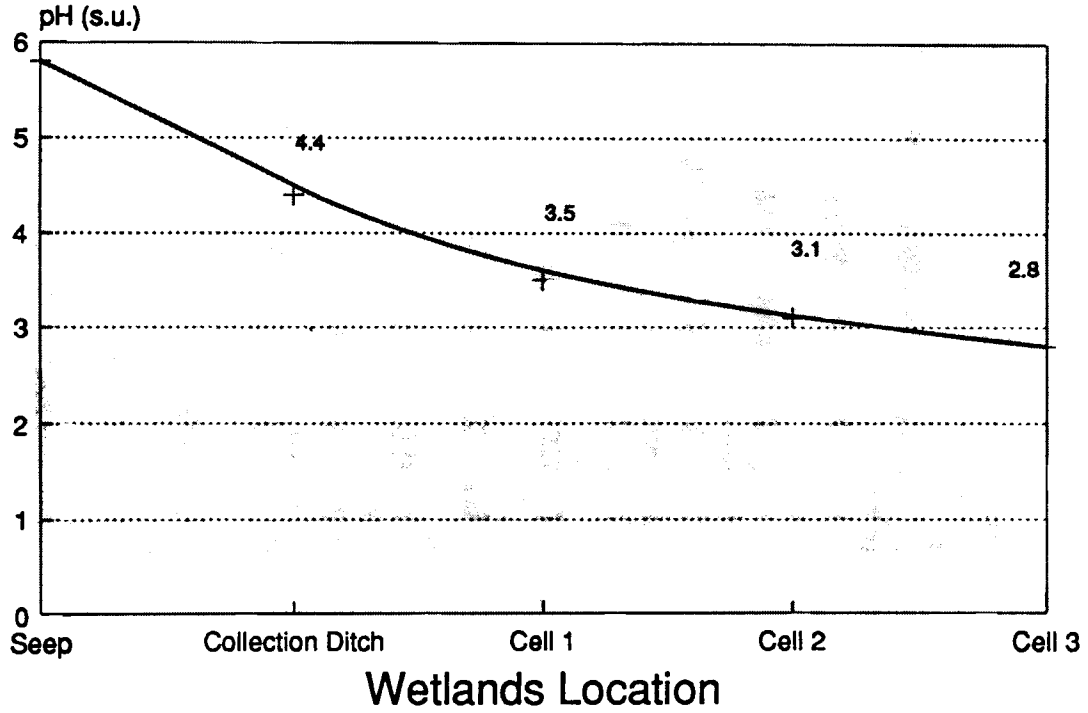


Table 1. pH Decrease at TVA Kingston Constructed Wetlands

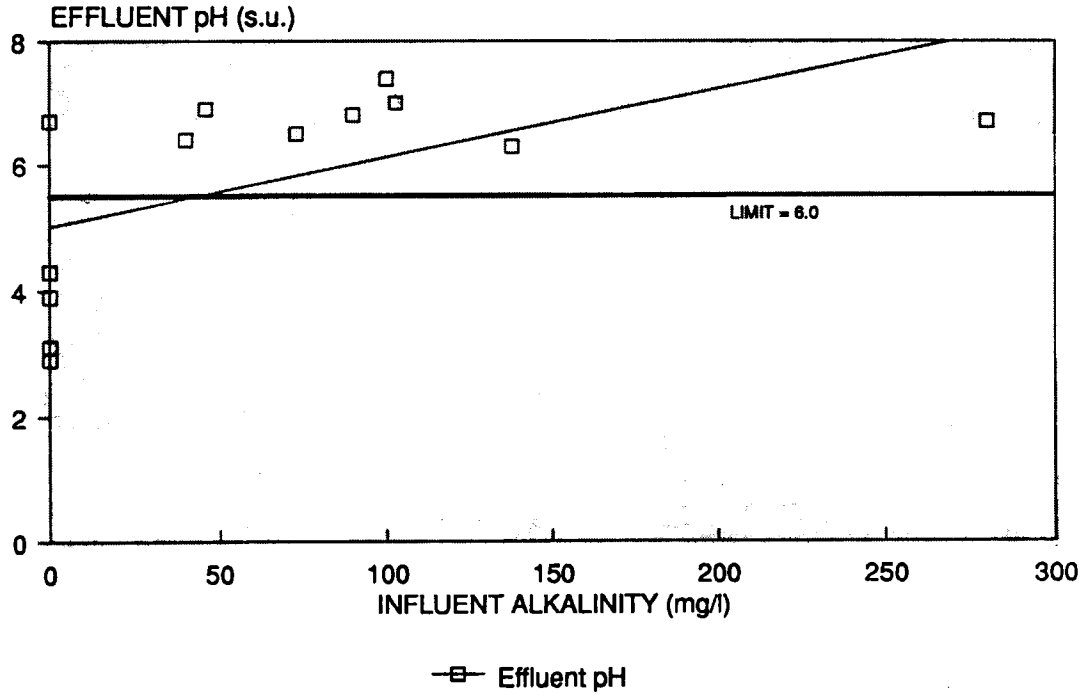
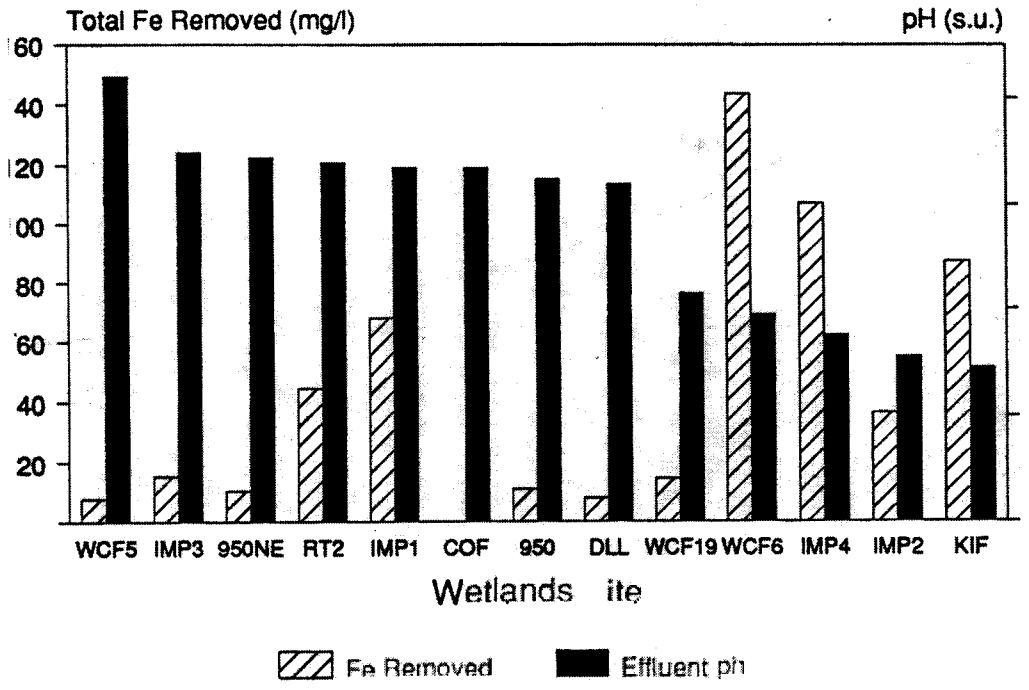
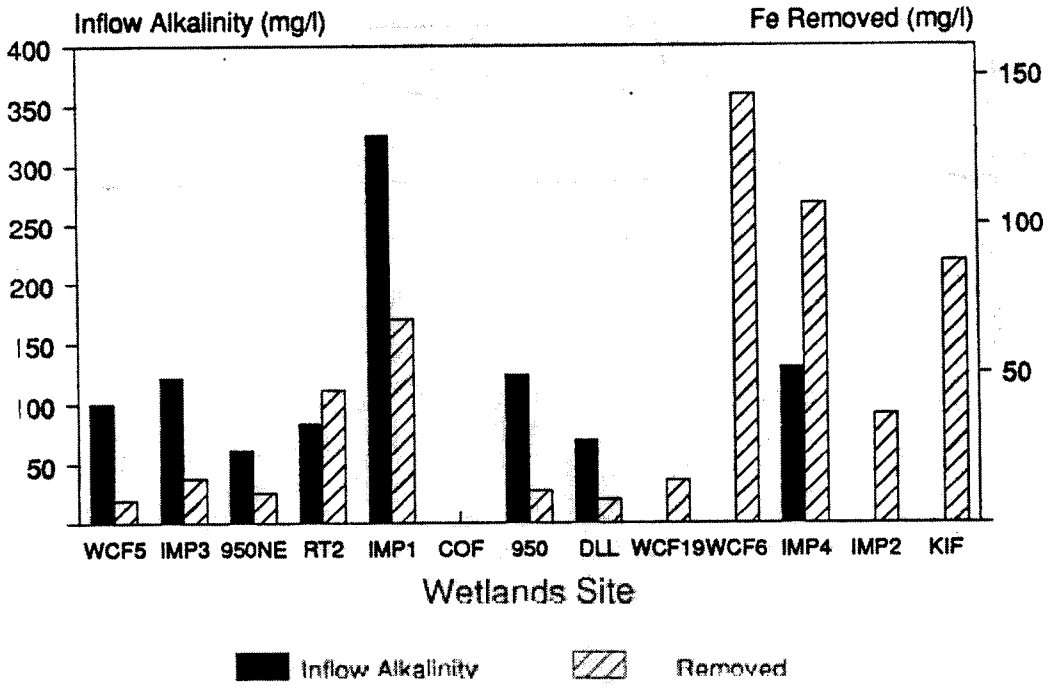


Table 2. Effluent pH vs. Influent Alkalinity (TVA Wetlands)



able Removed vs. Effluent pH (TVA Wetlands)



able Inflow Alkalinity Removed (TV. Wetlands

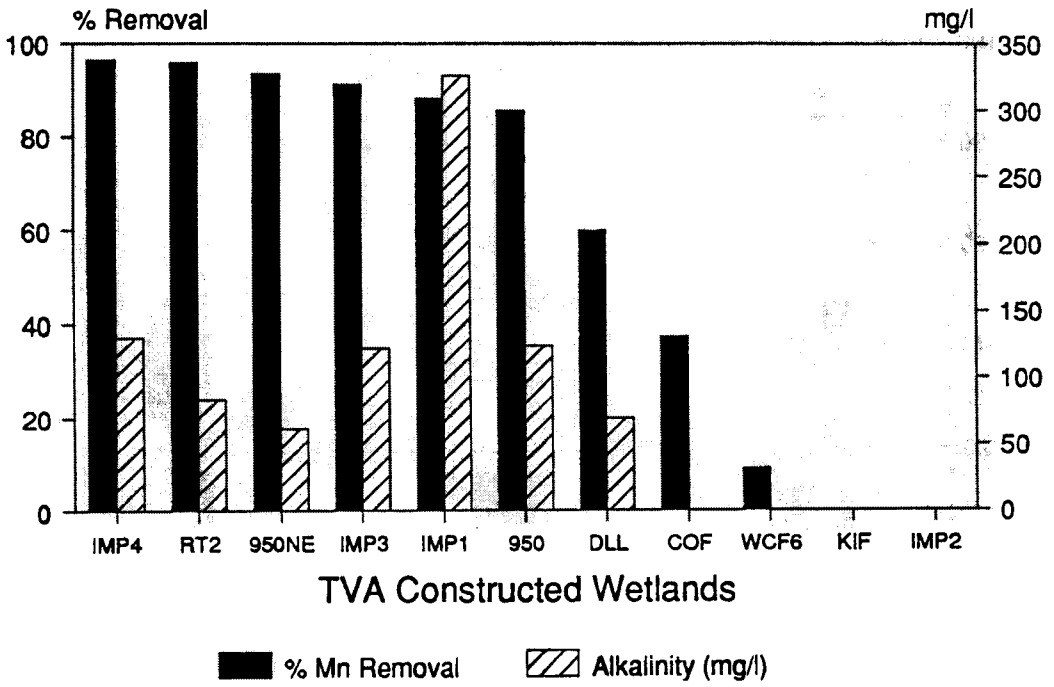


Table 5. Mn Removal Related to Alkalinity

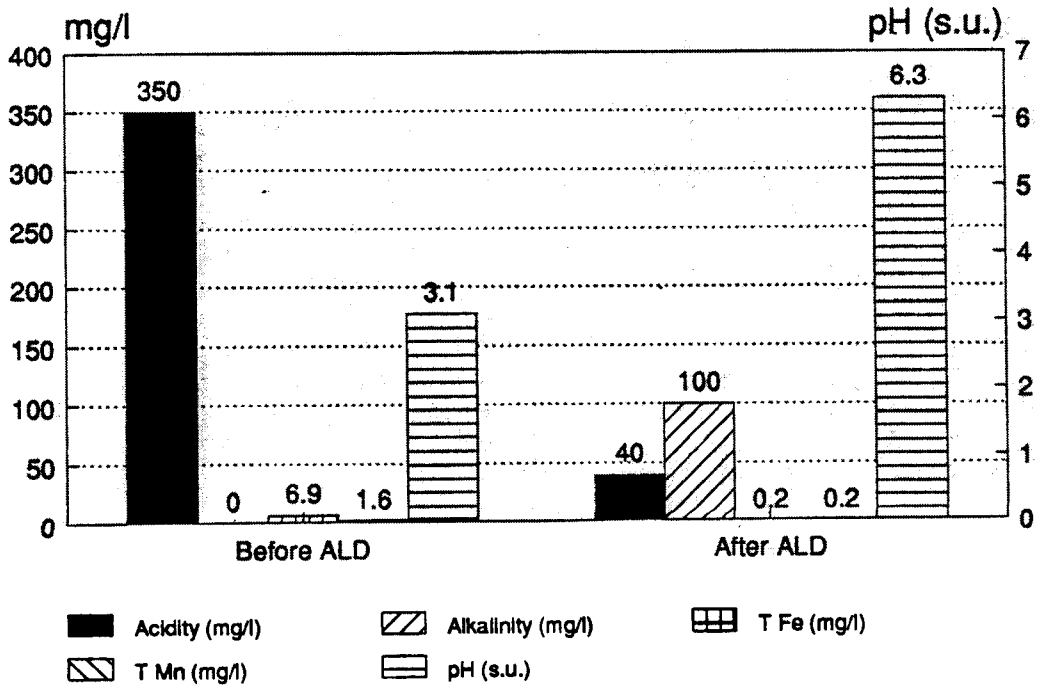


Table 6. IMP4 Wetlands Effluent Data Before and After ALD

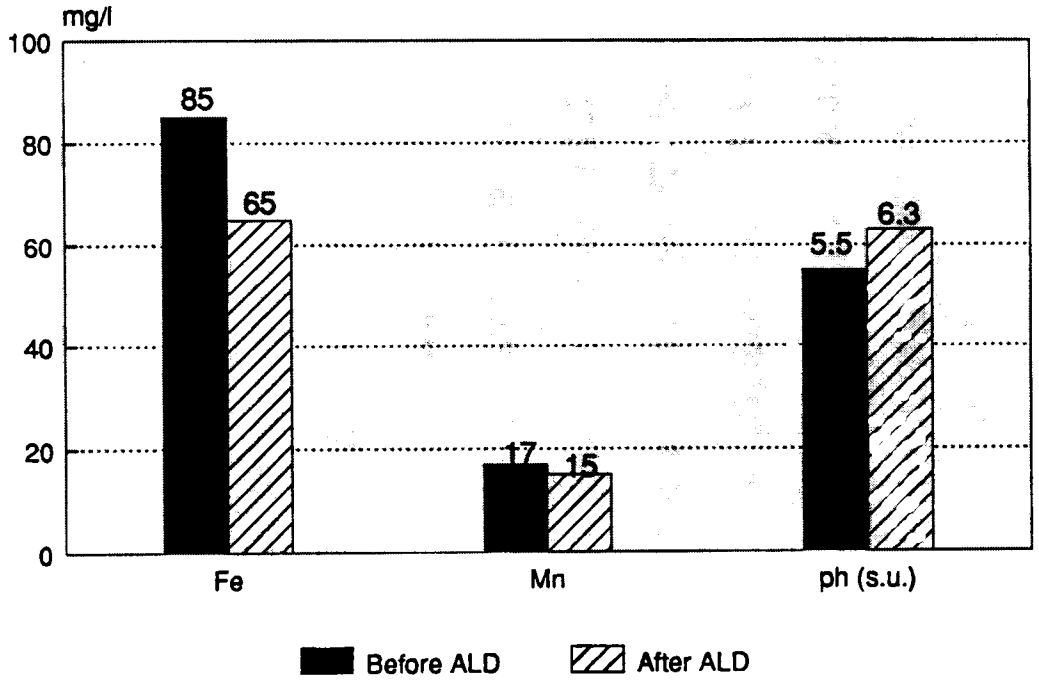


Table 7. IMP4 Seep Data Before and After ALD

A MODELING PROCEDURE FOR CONSERVING WETLANDS AND WATERFOWL HABITATS ON ABANDONED MINE LANDS AND OTHER RECLAMATION PROJECTS IN WYOMING RESULTS AFTER FIVE YEARS[1]

by

Larry D. Hayden-Wing[2]
Stephen A. Tessmann[3]
Timothy C. Richmond[4]

Abstract. Since 1986, a modeling procedure has been used in the Wyoming Abandoned Mine Land Program for conserving wetland values for waterfowl and other species. The model was initially applied to the reclamation of abandoned bentonite workings but was adapted for use on abandoned uranium pits and other reclamation projects. Use of the procedure produced repeatable output and provided an accounting system that facilitated the resolution of differences in program and agency goals, and quickly became a negotiating medium that provided a basis for agreement on reclamation design. The model was designed to conserve wetland habitat values for waterfowl, but experience showed that this process also conserved other functional values of wetlands. Model parameters reflect habitat needs of breeding and migrating Anatidae species. The process was applied to 976 wetlands on eight Abandoned Mine Land project sites and resulted in post-reclamation conditions that included: a 9.7% gain in wetland habitat values, a reduction in both numbers (65.3%) and acres (33.2) of wetlands, and a 90% increase in the average size of wetlands (1.00 to 1.90 A). Costs can be paid back within as little as three years, with recreational fishing providing most of the pay-back.

Additional Key Words: Mitigation banking, Anatidae

Introduction

A modeling procedure has been used in the Wyoming Abandoned Mine Land (AML) Program since 1986 for evaluating and conserving wetland functional values for waterfowl and other wildlife species. The model was initially applied to the reclamation of abandoned bentonite workings in northeastern and northcentral Wyoming, but was subsequently adapted and used on abandoned uranium pits and other reclamation projects throughout the state. Use of the procedure produced repeatable output and provided an accounting system that greatly facilitated the resolution of major differences in program and agency goals, and quickly became a negotiating medium that provided a basis for agreement on reclamation design. The model was designed specifically to conserve wetland habitat values for waterfowl, but experience showed that the application of this process also resulted in the conservation of other associated functional values of wetlands.

Rationale for the development, mathematical derivation, and structure of the model have been described in detail by Hayden-Wing et al. (1987), and

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earlier assessments of results were reported by Hayden-Wing et al. (1989) and Hayden-Wing et al. (1990). The purpose of this paper is to summarize and evaluate the results of the program after five years of application to the reclamation planning process. This evaluation involves the analysis and integration of previous assessments with recent, previously unreported data, into an overall review of the program. Relevant portions of the previous papers (Hayden-Wing et al. 1987, 1989, and 1990) on this subject have been incorporated into this paper for the sake of collecting all of the information into a single document to facilitate comprehensive review and analysis.

Background

A wetland habitat evaluation model was developed in 1986 for the purpose of comparing existing and post-reclamation conditions on bentonite reclamation sites in the Wyoming AML Program (Hayden-Wing et al. 1987). The fact that many of the sites scheduled for reclamation contained water impoundments of various sizes which had developed wetland characteristics that provided substantial habitat value to migratory waterfowl created a need for such a model since the AML Program was justifiably charged with filling many of these ponds and pits in order to reduce hazards to livestock, wildlife, and humans, to retard soil erosion, and restore land productivity. The accomplishment of the objectives of the AML Program, while simultaneously preserving wetland habitat values, presented challenges of major proportions, in that, in order to accomplish AML goals it was necessary to eliminate or drastically alter large numbers of existing waterbodies. Other regulations, such as Section 404 of the Clean Water Act, the Fish and Wildlife Coordination Act, various Executive Orders, and consultation with the Wyoming Game and Fish Department (WGFD), collectively made it necessary to protect the wetland habitats and ensure that reclamation activities did not reduce the value of such habitats below preexisting levels. Also contributing to the challenge were economic considerations, engineering limitations, and the wishes of land and mineral rights owners.

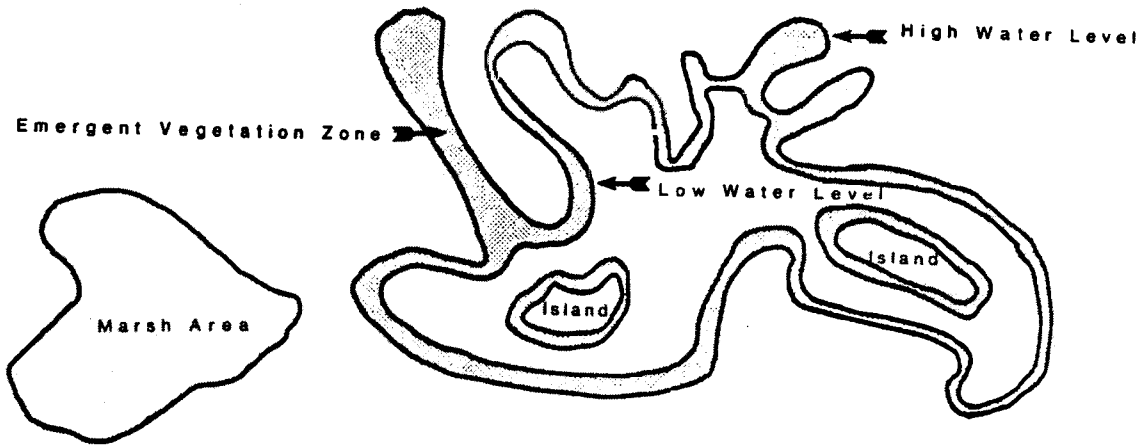
Basic decisions and agreements had to be made concerning the mechanism by which wetland values would be measured before solutions could be addressed. Such a process needed to measure "before" and "after" wetland values on reclamation sites in a quantified, repeatable manner. In response, an ecological book-keeping system or model was developed that measured relative changes in several key wetland parameters that reflect the general habitat needs of breeding and migrating waterfowl species. The model reflects relative habitat improvement or degradation, and provides a repeatable output upon which management decisions can be based. In general, the key parameters used deal with wetland size, quality, and longevity. Values of wetlands are quantitated into points or habitat units and represent the cumulative value of all input parameters.

The wetland evaluation program was developed specifically for the abandoned mine land program but has, after some trial and error and appropriate adjustments and revisions, been applied to other programs and circumstances.

The Model

The model is sufficiently specific to be useful in guiding the development of reclamation designs that will achieve desired mitigation goals. Model parameters are based upon general habitat needs of breeding and migrating Anatidae species and include: wetland size, proportion of emergent vegetation, fraction drawdown exposure, water quality (including ph), permanence of water supply, sedimentation rate, sinuosity of shoreline, associated marsh zones, numbers of islands, bays, and peninsulas, status of adjacent terrestrial vegetation, and relationship to other wetlands. For a detailed description of model derivation, parameters, applications, and assumptions see Hayden-Wing et al. (1987).

In general, relatively more habitat points were assigned as: (1) wetland size increased, (2) proportion of wetland covered with emergent vegetation approached the optimum of 40%, (3) fraction of drawdown exposure approached the optimum percentage for wetland size, (4) water quality and permanence increased, (5) sedimentation rate decreased, (6) sinuosity of shoreline increased, (7) acreage and proximity of associated march zones increased, (8) numbers of islands, bays, and peninsulas increased, (9) quality of associated adjacent terrestrial vegetation increased, and (10) the number of wetlands less than 2 acres in size, that are within 1/2-mile of wetlands larger than 2 acres in size, increased. Optimum drawdown percentage is relatively higher (approximately 60%) for smaller wetlands (1-acre) and decreases as wetland size increases, until it levels out and remains nearly constant (20%) for wetlands 10 acres in size and larger. The pond design illustrated in Figure 1 exemplifies a hypothetical, idealistic



Emergent vegetation occupies 40% of surface area.

Water visibility exceeds 2 ft. with fair to good water quality.

Low sedimentation rate with pond longevity expected to exceed 50 years.

Presence of associated marsh area.

40% of surface area is drawn down or exposed during a median precipitation year.

Permanent water supply with annual drawdown not normally exceeding 50% of surface area.

Highly sinuous shoreline.

2 Islands, 5 Bays, 3 Peninsulas.

Value added for pond less than 2 acres in size occurring within 1/2 mile of a pond 2 acres or larger in size.

Proximal 2 acres pond is not shown.

Figure 1. Top view of an idealistic pond configuration designed to maximize wetland values of a 1.9 acre waterbody.

configuration which would maximize wetland values relative to the size shown.

The model was originally developed specifically for the Hewlett-Packard Model 11 hand calculator, but most programmable calculators can be used. A GW BASIC program was subsequently developed by Tessmann (1986) and can be run on any personal computer.

Applications

The application of this book-keeping process allowed reclamation planning that compensated or more than compensated for the wetland habitat values lost from the elimination of numerous ponds that was necessary in order to achieve other important AML Program goals. The issue of avoiding substantial reductions in post-reclamation values of wetland habitats on the sites while simultaneously eliminating large numbers of ponds was resolved by: (1) saving or enhancing existing ponds which had high values and presented little or no hazard, and (2) designing and building new ponds that met all the AML safety and environmental requirements while providing higher wetland habitat values than ponds which were eliminated.

In order to retain or increase wetland habitat values on reclamation sites it was necessary to make more efficient use of annual precipitation. Since other requirements of the AML Program reduced the total amount of water available for impoundments, it was essential to utilize the reduced water supply in the most efficient way possible. Factors which reduced water availability included: (1) loss of water used to periodically flush or turnover impoundments in order to eliminate stagnation and maintain water quality standards, (2) the decreased runoff and increased retention of precipitation as ground water due to the pitted surfaces and increased vegetation cover produced during reclamation and (3) a substantial increase in evapo-transpiration losses due to the revegetation of extensive disturbed areas.

Methods

Wetland Values

Project summary data on pre and post-reclamation wetland numbers, acreages, and habitat values were obtained from 404 Permit Applications and the files of the Wyoming Department of Environmental Quality - Land Quality Division in Cheyenne. These data were then synthesized and

analyzed to produce summary figures for the eight completed projects evaluated in this paper.

Comparative Design and Construction Costs

Construction cost data were summarized for the 349 ponds that were processed on one of the largest single AML projects to date. Estimates of what the project would have cost if wetland values were not considered were developed for comparison with what the project actually did cost. This project site was selected for construction cost comparisons because wetland considerations were brought into the design from the onset of the project and because of the large number of ponds involved.

Project construction costs were analyzed to establish average excavation and reclamation unit prices. Bid prices and measured quantities were used for completed tasks and for tasks under construction. Engineers' estimates were used for tasks that were not bid yet.

Site-specific Geomorphology and Reports of Investigation (ROI) that were prepared prior to the required application of wetland conservation measures were compared with design summary reports. These studies included topsoil and overburden analysis; hydrology; sedimentology; geomorphology; water quality; vegetation analysis; and landowner, mineral owner, and lessee contacts. Through comparisons it was possible to recognize the design changes that were attributable to the wetland considerations. Such comparisons were possible because the wetland conservation requirements were implemented during the early stages of the project design phase. Typical pond characteristics and weighted mean construction unit prices were used to determine the project costs and savings resulting from the design changes. Average wetland sizes and staking point densities were assumed for newly constructed wetlands to estimate additional surveying costs.

Design and permitting considerations were analyzed to estimate additional costs in the pre-construction phases of the project. The preparation costs for three U.S. Army Corps of Engineers (ACE) 404 Permit Applications and thirty-five Wyoming State Engineer Reservoir Permit Applications were totalled. The additional engineering design costs attributable to the wetland considerations were estimated and factored to include computer and clerical charges.

Governmental agency costs related to the additional review and administration of the wetland policies were not considered in this study.

Values of Associated Benefits

Since a variety of recreational uses occur on and in the proximity of wetlands on AML project sites it is reasonable to assume that expenditures generated by such activities would increase if the value of wetland habitats in the area were increased. Increasing the useful life span of wetlands, raising the water quality level, and increasing the volume of use by waterfowl and other water-loving organisms should also increase the amount of use they receive by wetland-oriented recreational users. Increased use and monetary expenditures would be expected from such recreational activities as waterfowl hunting, sport fishing, swimming, picnicking, trapping of furbearers, nature hikes, outdoor education, etc.

Since no statistics on such recreational activities are available for the AML project sites we do not know to what extent an increase in wetland values will increase associated recreational activities and it is not possible to accurately project increases in expenditures likely to be generated. In order to derive at least a gross quantitative estimate of the potential value of these associated benefits, a series of calculations was made. These calculations were applied only to one of the single largest AML projects completed to date and made the following three basic assumptions:

1. The County's share of annual expenditures made by hunters, trappers, and sport fishermen in the state of Wyoming is directly proportional to the fraction of the total state population which lives in the county (1.5%).

2. The proportion of County hunter, trapper and fisherman expenditures which comes from the AML project area is directly proportional to the fraction of the County occupied by the project (15%).

3. Increases in hunter, trapper, and fisherman spending on the project area are directly proportional to increases in wetland habitat values there (14.6%).

These assumptions were not made because we think they are true, but because they provide a basis for making relative comparisons of potential increases

in expenditures among the various recreational activities.

Results

AML Wetland Statistics

Between December 1986 and December 1990 the model was used in determining wetland habitat values on a total of 976 ponds of varying size on 8 AML reclamation projects. These projects were concentrated in the Northeastern quarter of the state, but extended westward into the Big Horn Basin and the Gas Hills region of central Wyoming (Figure 2).

The 976 ponds present before reclamation activities commenced collectively occupied 963.6 acres and represented 2,212.31 wetland habitat value points (Table 1). Upon completion of reclamation activities 339 ponds, representing 643.4 acres and 2,426.34 wetland habitat value points, remained. The reclamation activity on the eight sites resulted in a 65.3% reduction in total number of ponds, a 33.2% reduction in the total wetland acreage, and a 9.7% increase in total wetland habitat values (Table 1). These numbers reflect the filling of relatively large numbers and acreages of small, low-quality and/or hazardous ponds and saving, enhancing, or rebuilding relatively smaller numbers of the higher-quality larger ponds. In the process, the average size of wetland increased 90.0% from 1.00 acres to 1.90 acres (Table 1).

The percent change in "before" and "after" wetland habitat values varied considerably between the eight sites. Part of this variation is due to inherent differences among site environments, amounts of water available, and corresponding differences in potential for retaining and increasing point values. Part is also due to the timing of application of the point evaluation process to individual projects. For example, reclamation work was already well underway and many ponds had been filled when several of the projects were subjected to the evaluation process. Projects which showed the greatest increase in point values, were subjected to the process at or near the beginning of the work and had relatively much more total water and many more ponds available to work with. One project area was extremely dry and had very little water and few ponds to work with. It produced only a modest gain in absolute habitat points (27.18), but showed the greatest single percentage gain in points (64.7%) of all the projects.

The different point-saving and-gaining potentials among sites exemplifies one of the

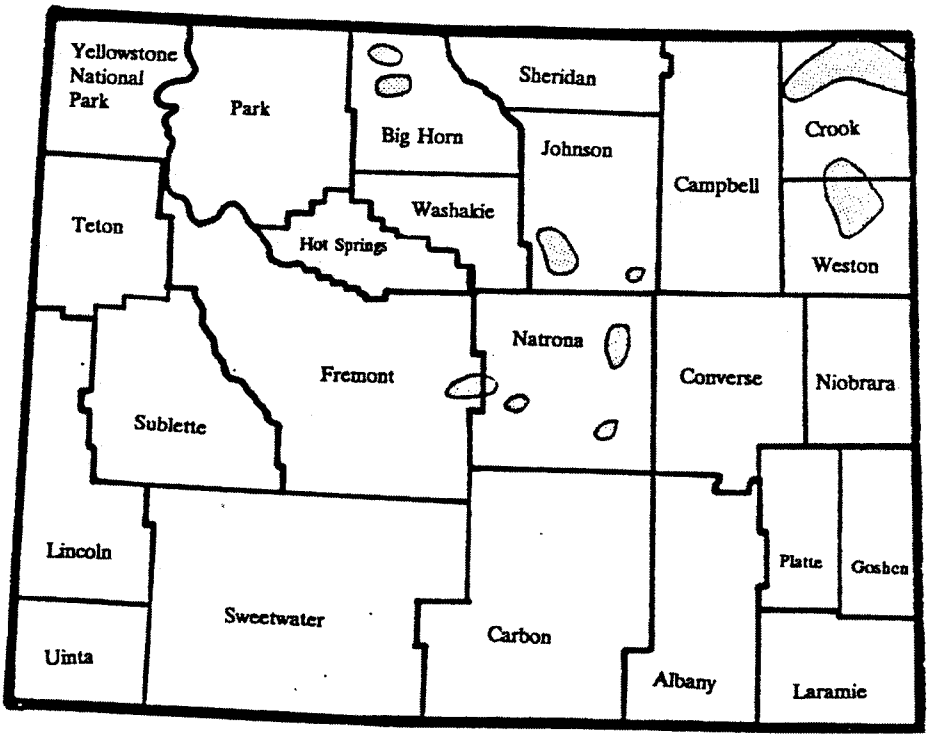


Figure 2. AML Project Locations in Wyoming, by County.

Table 1. Comparison of wetland parameters before and after reclamation on eight project areas.

Wetland Parameter	Before Reclamation	After Reclamation	Difference
Numbers	976	339	-637.0 (65.3%)
Acres	963.6	643.4	-320.0 (33.2%)
Habitat Value*	2,212.31	2,426.34	+214.0 (9.7%)
Mean Size	1.00 A	1.90 A	+0.9 (90.0%)

advantages in maintaining a running total of wetland habitat values gained or lost between projects as it facilitates the transfer of points among projects to balance deficits with surpluses. Although not extensively applied, the transference of points between projects is a manifestation of the increasingly common practice of "mitigation banking". Such an approach is often used in resolving wildlife impacts that occur over large areas and extended time periods.

Project Costs and Savings

Additional project costs associated with the implementation of wetland considerations are discussed below and illustrated in Table 2. Actual construction costs for completed tasks and estimated construction costs for tasks not completed were analyzed to determine the weighted mean construction costs for two phases of construction: 1) unclassified excavation, and 2) revegetation with soil amendment applications. The unclassified excavation prices on tasks varied from $0.36 per cubic yard (c.y.) to $0.75 per c.y., with quantities ranging from 30,500 c.y. to 1.2 million c.y. The wetland features were not considered significant to the unclassified excavation unit prices because of the relatively small amount of additional work (when compared to the total task required to incorporate them). The weighted mean price for unclassified excavation was $0.544 per c.y. for an estimated total quantity of 7.7 million c.y.

The revegetation phase of construction consisted of spreading and incorporating lime, gypsum, wood residue, nitrogen and phosphorous into the soil prior to drill seeding or pitting and seeding. The costs for the revegetation phase were totalled for each construction task and then analyzed for the total project to determine a weighted mean cost per acre. The costs varied from $1,155.75 per acre to $2,678.12 per acre. The weighted mean cost for the revegetation and soil amendment phase of construction was $1,797.26 per acre for 1,871 acres of revegetated area.

In implementing the design changes necessary to comply with the wetland preservation restrictions, the following points became evident:

1. The addition of islands, bays, peninsulas, and shallow areas increases the wetland value of ponds. The proximity of wetlands to each other is also a key factor in their value. In some cases, it was more feasible to fill an existing wetland and build a new one in a more advantageous location in order to gain proximity to other wetlands, to gain wetland value by incorporating the above mentioned features, and to make more efficient use of the available water supply. For these reasons, five less ponds were saved than planned in the ROIs.

2. The review of the 404 Permit Applications by the ACE, U.S. Fish and Wildlife Service

TABLE 2. Additional costs associated with the implementation of wetland considerations on a Wyoming AML project involving 339 wetlands.

Item	Cost Per Additional Acre of Wetland* (Dollars)	Total Cost (Dollars)
1. Construction Costs*		
a. Increased Excavation	$1,982.22	$158,875
b. Decreased Revegetation	-1,797.26	-144,050
c. Increased Surveying	129.76	10,400
Subtotal	$ 314.72	$ 25,225
2. Pre-Construction Costs*		
a. Develop Wetland Model, COE 404 Permits	$ 986.28	$ 79,050
b. Wyoming S.E. Permits	118.53	9,500
c. Increased Design Cost	305.68	24,500
Subtotal	$1,410.48	$113,050
Total For Additional Wetlands	$1,725.20	$138,275
Total For AML Project ***	$ 64.92	$138,275

* There were 80.15 additional acres of wetland habitat built.
** Governmental Agency costs were not included.
*** There were 2,130 total acres of reclamation on this AML Project.

(FWS), U.S. Forest Service, and the WGFD, as well as construction feasibility reviews, resulted in two less ponds being filled than planned in the ROIs.

3. The reclamation designs were influenced by the need to maintain existing wetland habitat and to also mitigate wetland habitat lost by dewatering and filling numerous small wetlands of little individual value, but of significant value when considered collectively. As previously mentioned, in some cases it was more efficient to fill an existing pond and rebuild it in a more suitable location to better utilize the available water supply, to incorporate valuable wetland features, and to change its proximity to other wetlands. For these reasons, thirty-eight more new ponds were built than planned in the ROIs.

The mean sizes of wetlands on the project before reclamation and after reclamation are 1.15 acres and 2.20 acres, respectively. Assuming that the average maximum depth of a pond initially planned for saving was eight feet, the average maximum dept of a pond planned for filling was two feet, and the average maximum depth of a new pond was six feet, results in an increase of 292.050 c.y. of unclassified excavation and a decrease of 80.15 acres of revegetation (because of the increased wetland water surface areas). Applying the unit costs previously derived indicates that the application of the wetlands model cost roughly $158,875 because of increased excavation, but saved roughly $144,050 because of decreased revegetation acreages. These and other costs are further summarized in Table 2.

Surveying costs for grade staking prior to commencement of construction and for quantity calculations after construction grading were increased by an estimated $10,400 as a result of the wetland program. The additional design and permitting considerations necessary to comply with the wetland requirements were significant. Three ACE 404 Permit Applications were prepared for the project, and the Wetland Evaluation Model was developed and revised on this project through the application and review process. The existing wetlands were evaluated and the Wetland Evaluation Model was used to establish additional design criteria. The site-specific ROIs were scrutinized to determine the natural wetland development limitations and to also establish the maximum feasible wetland development. The reclamation plans were then revised and evaluated with the Wetland Evaluation Model. The revised reclamation plans were then used to prepare the 404 Permit Applications. The cost of the model development and preparation of three 404 Permit Applications was $79,050. The one-time developmental cost of the model is estimated to be $34,311 and is included in the $79,050.

As previously discussed, the reclamation plan revisions resulted in five less ponds saved, two less ponds filled, and thirty-eight more ponds built, which necessitated the preparation and filing of thirty-five additional Wyoming State Engineer Reservoir Permit Applications. The preparation and filing costs were $9,500.

The additional engineering design costs attributable to the wetland habitat preservation and mitigation responsibilities were considered. The reclamation plan changes related to the wetland protection efforts were evaluated and the manhours of design time required to incorporate those changes were estimated. The estimated time was then factored to reflect computer and clerical charges. The estimated additional design charges were $24,500. These and other charges are summarized in Table 2.

The costs of applying the model and the "no-net-loss" policy to 349 waterbodies on this project resulted in a net increase in one-time construction and pre-construction costs of $103,964.

Values of Associated Benefits

Projected estimates of expenditures of wetland bird hunters, fur trappers, and sport fishermen for Weston County are presented in Table 3 along with calculated estimates of increases in these expenditures that might result from increasing wetland habitat values in the area. Since these projections are based on untested assumptions, little credence can be assigned to the absolute values. At the very least, however, these calculations offer a relative comparison of potential increases in expenditures among the various recreational activities. Although the 14.6% increase in wetland habitat values would probably result in moderate increases in spending by bird hunters and fur trappers in the area, by far the greatest potential for increasing revenues lies in the improvement of recreational fishing opportunities.

Although there will very likely be an increase in the quantity of local waterfowl production that is exported each year to other states and countries

Table 3. Projected expenditures of wetland bird hunters, fur trappers, and sport fishermen in Weston County, Wyoming during 1988.

	State of Wyoming - 1988 (1)			Estimated Total Expenditures		Total Increase(4) in Expenditures in the AML Project Area
	Non-License Expenditures	License Revenue	Total Expenditure	Weston(2) County	AML(3) Project Area	
Duck Hunting	1,475,376	57,700	1,533,076	22,996	3,449	504
Goose Hunting	1,051,992	41,177	1,093,169	16,398	2,460	359
M.Dove Hunting	407,089	15,736	422,825	6,342	951	139
Rail/ Coot/Snipe Hunting	33,579	1,337	34,916	524	79	11
Furbearer Trapping	1,706,838	29,656	1,736,494	26,047	3,907	570
Sport Fishing	99,450,047	2,521,991	101,972,038	1,529,581	229,437	33,498
					Hunting/Trapping	1,283
					Sport Fishing	33,498
					TOTAL:	34,781

(1) Wyoming Game and Fish Department 1988.
(2) Calculated by taking 1.5% of total state expenditure. 1.5% of Wyoming's population lives in Weston County (Furtney 1988).
(3) Calculated by multiplying Weston County expenditure by 15%. The AML Project occupies approximately 15% of Weston County.
(4) Calculated by multiplying AML Project expenditures by 14.6%. Wetland Habitat Values on the AML Project were increased by 14.6%.

during the fall months when the birds migrate south, no estimates of this cost benefit were made. Other activities which undoubtedly benefit from the increase in wetland values include swimming, picnicking, nature hikes, outdoor education, the incidental sightings of wildlife associated with the wetlands, and the aesthetic pleasure that many humans derive from the mere awareness that such enhanced habitats exist. Increases in values associated with these activities could not be assessed.

The cost and recreational expenditure estimates in this analysis represent a set of site-specific conditions and the degree to which they can be applied to other sites and circumstances will vary considerably.

Model Adjustments

When the evaluation procedure was applied to waterbodies in abandoned uranium pits in the Gas Hills in central Wyoming the model was found lacking in parameters to adjust for the highly acidified waters that exhibited no signs of biological productivity. Although the specific relationship between ph and biological productivity varies between sites and geographic regions, the general relationship is very consistent. Acidified waterbodies show marked decreases in their biological communities of decomposer, primary producer, invertebrate, and fish populations.

Based on available information, a curvilinear adjustment to the calculated wetland value, consisting of a multiplier of 0.0 to 1.0, was derived. The curve assumes a sigmoid configuration asymptotic to 0 and 1, with the greatest change occurring between 5.0 and

6.0 (Hayden-Wing et al. 1990). The application of this adjustment formula reduced the uncorrected wetland values for the acidic waters in the Gas Hills to levels that were more reflective of true values to waterfowl.

Wetland Banking System

In 1988, the WGFD, Wyoming Highway Department (WHD), and several other state agencies, along with the Federal Highway Administration (FHwA), FWS, Environmental Protection Agency (EPA), and the ACE began discussions regarding wetland banking for highway construction projects. The WHD felt there were opportunities to create wetlands during project construction which could be considered "credits" when circumstances precluded avoidance or on site mitigation at certain locations.

In conjunction with formulation of a wetland banking Memorandum of Understanding (MOU), WGFD Environmental Biologist Steve Tessmann, who was instrumental in developing the wetland habitat evaluation model SUPERBOG, devised a banking program named BOG BANK. BOG BANK is a mitigation accounting system integrated with the wetland habitat evaluation model which chronologically tracks impacts and credits within 4 broad wetland categories, 9 major drainage basins, and 3 biotic regions.

Conditions set by the involved parties for the banking system include:

the bank will operate with no deficits.

mitigation credits will apply to the same drainage basin, biotic region, and wetland type.

credits or deficits will be calculated using acreage, however habitat unit values will be used to assure habitat values of mitigation wetlands area at least equivalent to those lost from wetland impacts.

The last condition listed above addresses the concern that SUPERBOG only evaluates habitat values and does not account for other wetland functions. It is assumed that by maintaining an account by wetland type some of the functions other that habitat values will be replaced by virtue of the fact that there will be no overall loss of each of the various types. In addition, by maintaining a bank that requires no deficits within biotic regions and major drainages, wetland losses within those categories will be minimized.

The wetland banking MOU is in it's final revision, and all involved parties with the exception of ACE and EPA are willing to sign. These two agencies have supported development of the system, but feel they should remain outside this process for several reasons, including the fact that they are regulatory agencies.

Interest has been expressed in using this wetland banking system as the foundation for a similar system for all Wyoming state agencies that may impact wetlands. The governor has recently signed a state wetland policy, which has set the stage for creation of a state wetland banking system.

Discussion

The application of the wetland evaluation system resulted in post-reclamation conditions that included: greater habitat values, lower total numbers and acres of wetlands, and a larger average size wetland. The increase in average wetland size reflects the tendency to build larger wetlands to replace smaller ones in order to maximize habitat point values while minimizing construction costs. Care must be taken not to over-respond to this tendency in that it can quickly imbalance the wetland size class distribution by disproportionate reduction of smaller wetlands (0-1 acre). The ground rule of not allowing the transference of wetland values among size classes prevents undue modification of original size class distribution of wetlands but, allows agency regulators to modify original distributions when such changes result in a better wetland complex. e.g. Creating smaller ponds in areas which originally had none.

On the basis of cost/benefit information analyzed, it appears that the $103,964 net cost for wetland considerations on a large AML project involving 349 ponds could potentially be paid back to society within three years if the benefits ($34,781/year) described in the study are realized. It is not likely that the full extent of these cost benefits will be realized since most wetlands were not specifically designed for sport fishing, the principle source of cash returns. Because of the great potential sport fishing has for returning revenue to the state of Wyoming, priority consideration should be given on future AML projects to designing as many wetlands as possible to support sport fisheries.

The wetland model, its applications, and results are still in a developmental stage and continue to be improved and changed in response to new circumstances and the knowledge provided by a growing experience base. Because the system was developed for application to an environment which supported small and shallow wetlands with neutral to basic ph values and non toxic water it is not equally applicable to other dissimilar environments. Although the ph modifications previously described have expanded the range of circumstances to which the system can be applied, we continue to encounter new circumstances in which the model tends to produce apparently distorted values. One such case involves large, deeply excavated pits fed by groundwater which is non toxic with normal ph values, but apparently biologically very sterile. The model as it currently is configured assigns much higher values to such waterbodies than they appear to be worth.

Political and administrative issues raised by the suggested potential application of the model as a mitigation banking medium for use by other agencies and application to private lands within the state include: (1) the consideration of whether or not man-made wetlands on private lands should be subjected to the same evaluation process as naturally occurring ones or whether preexisting credits should be assigned to wetlands created by human activities, (2) the issue of how much flexibility is allowable in mitigating a wetland loss in an environment physically distant from the site of wetland impact, and (3) inter-agency territoriality created largely by differences in goals, policy, and programs.

In Wyoming, the ACE, WGFD, and FWS all have immediate and direct input to determining which wetlands qualify for replacement in a mine reclamation, highway construction or private development activity. The EPA, although deferring to the above listed agencies, has final regulatory authority over the findings and determinations. On occasion, conflicts - differences - have arisen between the agencies in their determination of jurisdictional wetlands, with on-site coordination and communications ultimately leading to resolution.

The fact that the current model generates habitat values that are based entirely on parameters which rank values of wetlands to waterfowl has produced criticism that other water uses and values are not adequately represented. Water that is suitable for waterfowl habitat may not meet standards for other uses because of acidity, alkalinity or chemical constituents such as heavy metals (selenium, for instance) or radioactivity. Other critics feel that issues involving private land owner preferences, economics, and goals of public land management agencies are overshadowed by the objective of no-net-loss of waterfowl habitat.

The wetland model, its applications, and results are still in a developmental stage and continue to be improved and changed in response to new circumstances and the knowledge provided by a growing experience base. The results presented in this paper are meaningful and significant, but should still be regarded as preliminary. As follow-up evaluations are made over time of the effectiveness of reclamation and man-constructed wetlands an even more accurate assessment will be possible. Furthermore, the adaptive extension of the process to new environments and types of wetlands will lend additional perspectives.

This wetland evaluation process exemplifies or embodies several of the key issues under consideration across the country at this time. Specifically, it: (1) employs an indexing system based on wetlands value to waterfowl for achieving a no net loss goal, (2) exemplifies one effective method for creating and restoring wetlands, (3) constitutes one way in which wetland impacts can be mitigated, and (4) illustrates the application of a wetlands accounting system at both ecological as well as state-wide levels.

By applying this system we have been able to resolve major differences in program and agency goals and have achieved a total net gain in waterfowl habitat values over the past five years. Key ingredients in the success of this program and in effectively dealing with the complex issue of no net loss of wetlands proved to be: an interdisciplinary approach, and a high degree of interagency cooperation.

Acknowledgments

A number of individuals and organizations contributed in a variety of ways to the development of the wetland model and this paper. In particular we would like to thank Mr. Gary Beach and his colleagues in the Wyoming Abandoned Mine Lands Program for financial support and Dr. Harry Harju and Reg Rothwell of the Wyoming Game and Fish Department for the provision of technical support. We are grateful to Mr. Ron Schreibeis who, early in the development of the model, provided valuable

inputs that affected design and applications. Mr. Bruce Yates and Mr. Roger Sanders of HKM Associates developed construction cost estimates used here and in an earlier paper. Dr. Archie F. Reeve of HWA was instrumental in the development of the ph parameter currently used in the model. Other organizations associated with the development of the model include: U.S Fish and Wildlife Service, U.S. Army Corps of Engineers, HKM Associates, and Chen Associates.

Literature Cited

Furtney, Steve. 1988. Wyoming population and employment forecast report. Div.of Res. and Stat., Dept Admin. & Fiscal Control, State of Wyoming, Cheyenne. Typewritten. 43 pp.

Hayden-Wing, Larry D., Stephen A. Tessmann, and Ronald G. Schreibeis. 1987. A wetland evaluation model for quantifying changes in habitat values on reclaimed abandoned mine lands in Wyoming. Pp. 8-21 IN J. Emerick, S. Q. Foster, L. Hayden-Wing, J Hodgson, J. W. Monarch, A. Smith, O. Thorne, II, and J. Todd (eds), Proceedings of a national symposium on issues and technology in the management of impacted western wildlife. Thorne Ecological Institute, Boulder, Colorado.

Hayden-Wing, Larry D., Stephen A. Tessmann, Bruce R. Yates, and Roger L. Sanders. 1989. Changes in wetland values on reclaimed abandoned mine lands in Wyoming. Pp. 445-463 IN Proceedings of a symposium on the evolution of abandoned mine land technologies. Wyoming Department of Environmental Quality, Cheyenne.

Hayden-Wing, Larry D., Stephen A. Tessmann, Reg Rothwell, and Archie F. Reeve. 1990. A wetland evaluation process for quantifying changes in waterfowl habitat values in Wyoming. IN Proceedings of the 12th Annual Conference of the National Association of Abandoned Mine Land Programs, Breckenridge, Colorado. In Press.

Tessmann, Stephen A. 1986. SUPERBOG and BOG II instructional documentation. Typewritten: Wyoming Game and Fish Department; Cheyenne, Wyoming. 15 pp.

Wyoming Game and Fish Department. 1988. Annual Report Wyoming Game and Fish Department. Cheyenne, Wyoming. 72 pp.

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INVESTIGATION AND CHARACTERIZATION OF GROUNDWATER FLOW SYSTEMS IN ABANDONED UNDERGROUND COAL MINES[1]

by

William W. Aljoe
and
Jay W. Hawkins[2]

Abstract. Surface coal mines often face operational or environmental problems when located in close proximity to flooded, abandoned underground mines. A basic understanding of the groundwater flow systems within abandoned mine pools may help surface mine operators assess the probable hydrologic consequences of their operations or evaluate in-situ water quality improvement techniques. Substantially different mine pool flow systems were found at two acid-producing, abandoned underground mines in western Pennsylvania. Mine maps, surface observations, discharge rates, precipitation records, water levels in monitoring wells, and water quality analyses were used to characterize the systems. At one site, the mine pool piezometric surface was horizontal, and most of the mine pool flow occurred through open entries at the base of the system. Water quality analyses and tracer tests indicated that flow was probably not uniform through all mine entries, and that flow through monitored entries was relatively slow. At the second site, water levels in monitoring wells showed a distinct water table gradient. This indicated the presence of diffuse flow through caved entries. However, the water flowing from the monitored section of the mine pool may have represented only a small portion of the total flow at the two monitored discharge points. A tracer test revealed a strong hydrologic connection between the tracer injection well and one downgradient well, but the tracer was not detected at the main discharge 6 months after injection. A more detailed assessment of the mine pool hydrology at the second site was not made because of the suspected large size of the pool and the effect of multiple discharges on pool behavior.

Additional key words: mine hydrology, mine pools, acid mine drainage

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Introduction

Surface coal mine operations are frequently performed on properties that contain abandoned underground mines. Special problems occur when abandoned mines discharge water at the surface or contain pooled water. Obviously, operational problems can occur if the surface mine intercepts or comes close to a flooded portion of the deep mine. More importantly, under the

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Surface Mine Control and Reclamation Act, surface mine operators are held completely liable for all deep mine discharges that are affected by their operations, as determined by the state or Federal regulatory authority. If the deep mine discharge is of poor quality (e. g., acidic), as is often the case in the eastern U.S., the cost of controlling and treating the discharge can be so expensive that the economic viability of the entire surface-mining operation may be jeopardized. Indeed, a surface mine permit may not be granted if the regulatory authority determines that unacceptable post-mining water quality of the deep mine discharge will occur.

A thorough understanding of mine pool hydrology, including knowledge of flow paths and pool turnover rate, is critical to the success of any water-quality improvement technique, such as addition of alkalinity to the overburden or the mine pool itself. Toward this end, the U. S. Bureau of Mines performed hydrologic studies of two "typical" acid mine pools in western Pennsylvania. The study sites were located at Keystone State Park, near Latrobe, Pennsylvania, and Friendship Hill National Historic Site, near Uniontown, Pennsylvania (Figure 1).

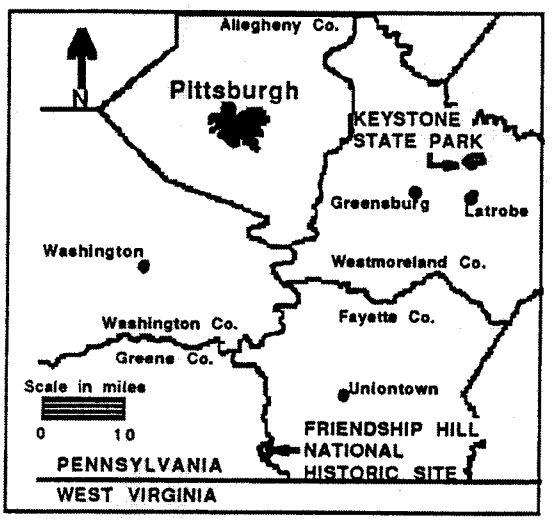

Figure 1. Locations of mine pool hydrologic study sites.

The near-term purpose of these studies was to gather the hydrologic data needed to assess the feasibility of abating acidic discharges from the mines by injection of alkaline solutions into the mine pools. During the studies, it became evident that the hydrologic characterization of abandoned underground mine pools could be of use in a more general context. Therefore, this paper focuses on the hydrology of the mine pools; of special interest is the vast difference between the fundamental hydrologic characteristics of the two pools. A more complete discussion of the experimental alkaline injection treatment is provided elsewhere (Aljoe and Hawkins 1991). The hydrologic investigations at the Keystone and Friendship Hill sites consisted of: (1) monitoring of mine discharge flow rates and quality; (2) drilling and installation of mine pool monitoring wells; (3) monitoring and interpretation of water levels and water quality in the wells; (4) examination of the response of the mine pools to precipitation; and (5) tracer tests to determine mine pool flow rates, flow paths, and pool volume turnover time. The subsequent application of alkaline injection at the Keystone State Park site also provided useful information about the hydrology of this mine pool.

Hydrologic Study - Keystone State Park

One of the greatest advantages of the Keystone site was that its history was relatively well-documented compared to most abandoned mine sites. The primary sources of information were a report on an attempt to seal one of the mine portals (Chung 1973) and a 1941 mine map that contained mine floor elevations. Documentation of subsequent mine reclamation projects was obtained from the Pennsylvania Department of Environmental Resources, Bureau of Abandoned Mine Reclamation, and Keystone Park personnel.

Site Background

The mine at Keystone State Park, which was originally known as the Salem No. 2 mine of the Atlantic Crushed Coke Co., was developed in the Upper Freeport coal seam using room-and-pillar methods. The total undermined area was approximately 300 acres. The mine maps and the absence of surface subsidence indicated that pillars were not removed in the vicinity of the mine portals, although pillars may have been removed elsewhere in the mine. Figure 2 illustrates the general geologic structure in the vicinity of the Keystone site (strike N 76^0 E, dip approx. 2^0 NW). Most of the mine workings are situated on the northwest limb of the Fayette Anticline, although southeast portions of the mine cross the anticlinal axis.

As shown in Figure 3, the main portals of the mine were located at the lowest structural point of the coal seam. When the abandoned mine portals were sealed in the early 1970s, water began to build up in the mine behind the seals. Eventually, the hydraulic pressure of the mine pool became sufficient to force the water to the surface approximately 150 ft behind the portal seals. A borehole was installed to relieve the pressure and route the water through a pipe network to a surface stream about 250 ft away. This free-drain condition allows relative

equilibrium between recharge and discharge, so the mine pool level fluctuates only slightly over time.

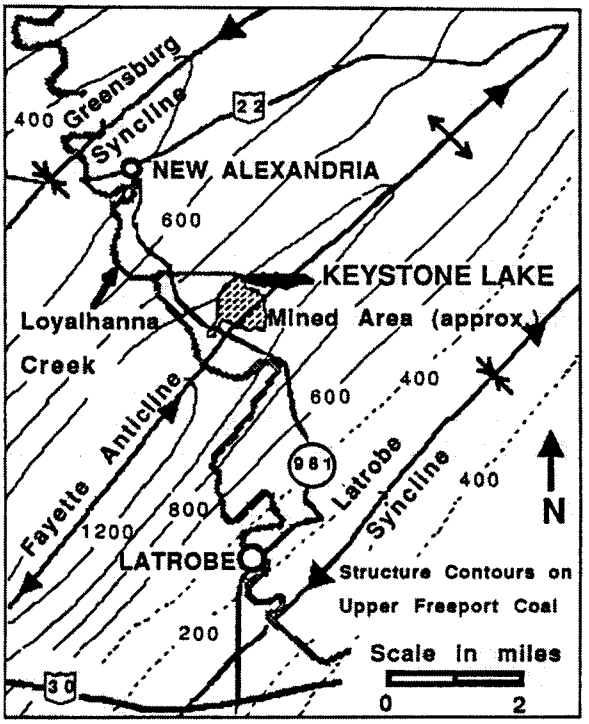

Figure 2. Geologic structure in the vicinity of the Keystone site.

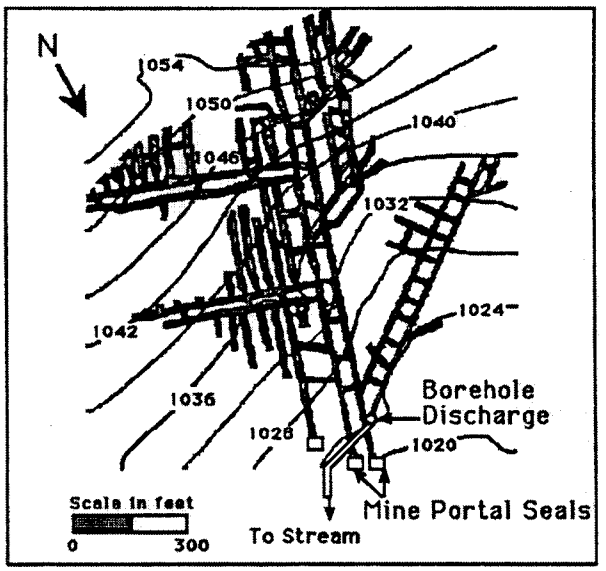

Figure 3. Mine floor structure contours near Keystone mine portal area.

Mine Pool Size Estimate. During the mine sealing effort, a steel-cased vent hole was installed approximately 250 ft behind the portal area. The vent hole apparently did not penetrate a mine entry, but was hydrologically connected to the mine pool. The elevation of the mine pool as measured in the vent hole was approximately 29 to 33 ft above the mine floor elevation at the portal seals, or 1,047 to 1,050 ft above sea level (see Figure 4). At these elevations, the flooded area was approximately 10 acres; assuming an extraction ratio of 50 %, the pool volume was estimated to be 23 to 26 million gallons.

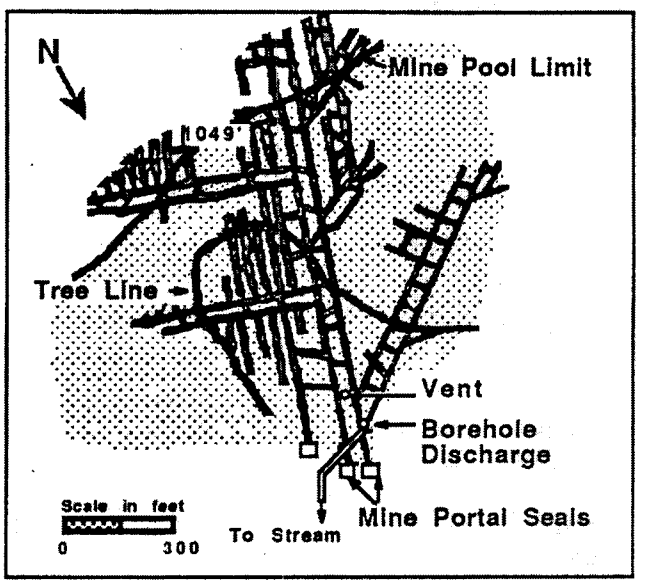

Figure 4. Limits of mine pool at Keystone site.

Monitoring Wells. To prevent damage to Keystone Park property, well drilling was limited to the north side of the tree line shown in Figure 4. Efforts were made to place most of the wells in main entries of the mine, since these were most likely to have been well-supported and thus remain open to serve as preferred flow paths for the mine pool. Lack of precise correlation between the mine map and existing surface features limited the accuracy of these efforts. As shown in Figure 5, five of the monitoring wells encountered open mine voids; three were located in a main entry (wells 1, 2, and 6), one was in a submain (well 3) and one was in a room entry (well 8). Four wells penetrated solid coal (wells 4, 5, 7, and 9). All holes were 6-1/4 in diameter and cased with 4 in diameter PVC pipe. In void wells, the annulus between the casing and hole was grouted from the top of the mine void to the land surface. In wells penetrating coal, 10-ft screens with sand packs were installed through the coal and isolated from the grout by a 2-ft layer of bentonite.

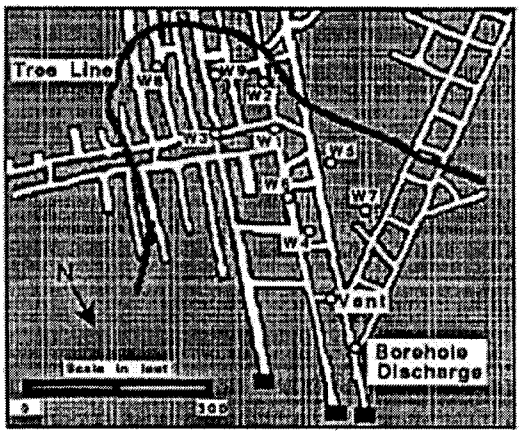

Figure 5. Locations of mine pool monitoring wells at Keystone site.

Mine Pool Hydrology

Unlike most groundwater systems, which have regular, lateral hydraulic potential gradients that govern the rate and direction of flow, the Keystone mine pool had a horizontal piezometric surface, (i.e., water levels in all void wells were the same). Figure 6 is a cross-section of the Keystone site showing the conceptual pool flow system. This system is analogous to a surface water reservoir with an underdrain discharge; flow occurs because the drains (mine voids) are open to the atmosphere (discharge borehole) at an elevation that is somewhat lower than that of the pool surface.

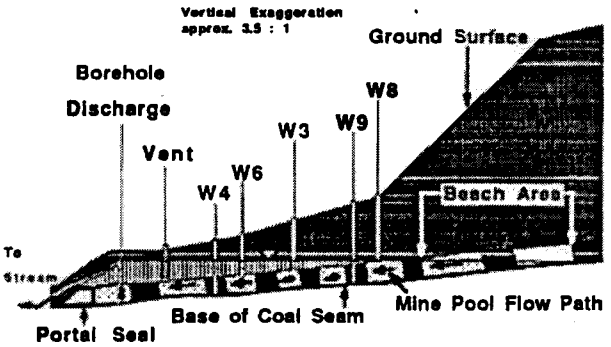

Figure 6. Cross-section through wellfield, Keystone site.

Lateral flow occurs primarily through the open mine entries at the base of the system, in a direction generally perpendicular to the geologic structure contours due to the location of the discharge borehole. Flow through the saturated overburden is downward toward the voids. The absence of surface subsidence and the fact that no caved conditions were encountered during drilling suggested that all voids remained completely open and were equally likely to serve as conduits for mine pool flow.

Mine Discharge Flow Rates and Pool Levels. Mine discharge flow rates were measured at least twice weekly for a period of more than one year. The measured flow rates varied widely (from 7 to 156 gal/min) with a mean of 54, standard deviation of 29, and median of 47 gal/min. Mine pool elevations were measured at least weekly throughout the study period. The average mine pool elevation showed little variation, fluctuating over a range of only 1.66 ft; however, a strong linear correlation was found between pool elevation and discharge flow rate. Figure 7 shows that the pool elevation and discharge flow rate rose and fell together throughout the study period, while Figure 8 clearly illustrates the strong linear correlation (R_{xy}= 0.947). This functional relationship is to be expected, and is determined by both the head in the mine pool and the conditions at the discharge borehole.

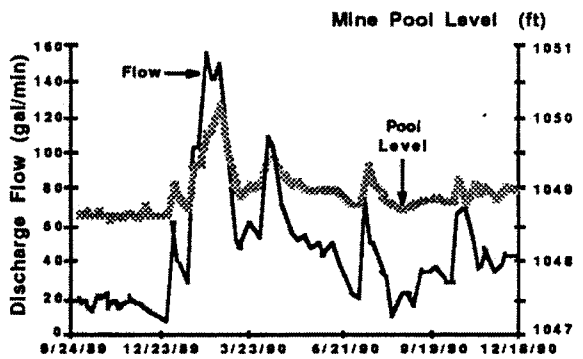

Figure 7. Mine pool levels and discharge flows at Keystone site.

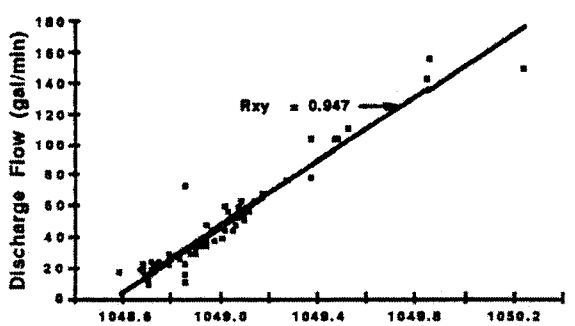

Figure 8. Linear regression - mine pool level vs. discharge flow rate, Keystone Site.

Response to Precipitation. Rainfall data were obtained from a permanent weather station approximately 5 miles from the Keystone site. Figure 9 shows how the discharge flow rate responded to rainfall during the first 11 months of the study period (October 1989 through August 1990). Because of the linear relationship between the mine pool level and discharge flow (Figure 8), response of the mine pool level to rainfall exhibited a similar pattern. However, discharge flows were chosen to represent the overall pool response in Figure 9 and in the following discussion because of the higher magnitude of flow response and greater density of flow data.

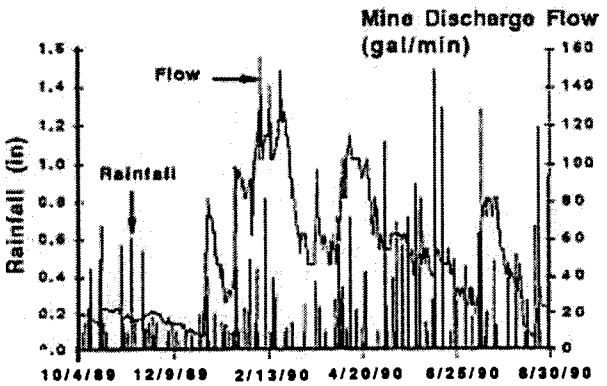

Figure 9. Response of Keystone mine pool to rainfall, October 1989 to August 1990.

In general, response of the mine pool to applied rainfall was much greater during winter and spring than in summer and fall. Note in Figure 9 that the pool did not respond significantly to five very large precipitation events that occurred between October 4 and November 19, 1989. At this time of year, two factors may have served to limit deep infiltration and mine pool recharge. First, the moisture-retaining capacity of the surface soils, subsoils, and fractures in the unsaturated overburden would have been relatively high because of low rainfall and high rates of evapotranspiration during the summer and early fall. Most of the precipitation that infiltrated the surface would serve to resaturate the soil and overburden. Conversely, a large, rapid pool response coincided with a rainfall/snowmelt period from December 26, 1989 through January 2, 1990, despite the fact that this event was no larger than those that had occurred during the fall. It is believed that a series of small rainfall and snowfall events during late November and December, 1989, along with lower evapotranspiration rates during this period, may have allowed the moisture the soil and the walls of overburden fractures to reach field capacity. The onset of additional precipitation and infiltration would then cause rapid recharge to the mine pool and subsequent pool response.

Between January 2, and January 17, 1990, the pool flows and levels declined steadily despite the occurrence of several small precipitation events. Although the overburden probably remained saturated during this period, the low precipitation rates and frozen ground conditions may not have permitted significant amounts of infiltration. However, the next significant precipitation event (January 18-22) was accompanied by another large, rapid pool response. From January 22 through February 21, a fairly steady series of precipitation events was accompanied by a consistent increase in flow and pool level, with localized flow peaks occurring shortly after each precipitation event. This behavior suggests that the overburden was completely saturated and pool recharge rates were at a maximum; note that the maximum flow values for the study period were recorded at this time.

Pool levels and flow rates declined steadily from February 21 through the end of March 1990, although flow again showed several localized peaks that coincided with small rainfall events. Longer days and new plant activity during this time may have resulted in increased evapotranspiration and decreased moisture content of the soil and overburden. Note in Figure 9 that the frequency, duration, and intensity of rainfall events from March 30 to May 11 were similar to those of January 18 to February 21, but the pool response was not as great. This general decline in flow rate, pool level, and magnitude of pool response continued throughout May and June 1990. The more subdued response suggested that significant amounts of overburden had to become resaturated before pool recharge could occur. Only large, consistent rainfall periods such as the one of July 10 to 16 were capable of achieving the resaturation necessary to permit substantial pool recharge during the summer months.

Water Quality Considerations

Mine Discharge. Water quality was monitored weekly at the mine discharge throughout the study period, and water quality in the voids and pillars was monitored periodically. In general, the concentrations of contaminants at the discharge showed only minor variations over time. The concentration of acidity at the discharge is plotted along with the discharge flow in Figure 10; all other contaminant concentrations, such as iron, sulfate, and manganese, behaved in a similar manner. From April through June 1990, acidity concentrations were somewhat lower than at other times of the year. However, Figure 11 shows a very strong linear relationship between acidity loading (flow times concentration) and discharge flow.

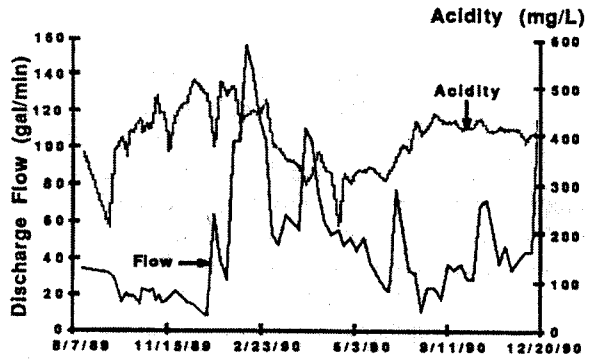

Figure 10. Acidity concentrations and discharge flows, Keystone site.

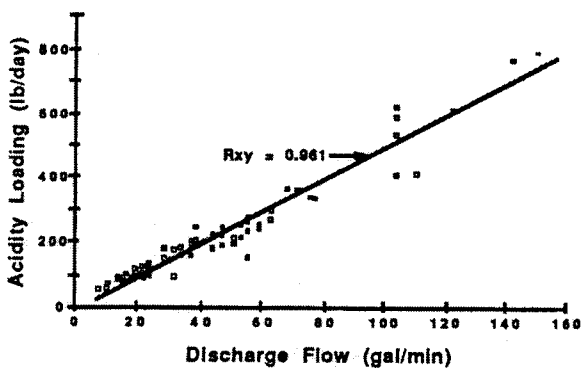

Figure 11. Linear regression - acidity loading vs. discharge flow rate, Keystone site.

This suggests contaminant loading rates were governed by flow variations, with concentration differences playing only a minor role; this is the case for most deep mine discharges. The slightly reduced concentrations during April through June may reflect the delayed release of water that had been diluted by infiltration and stored in upper reaches of the mine pool during the high-recharge period between January and March. The consistency of acidity concentrations throughout the observation period suggested that the overall rate of acid production and/or salt dissolution in the pool system was relatively constant.

<u>Voids vs. Pillars.</u> Figure 12 compares the average values of six major acid mine drainage parameters (pH, acidity, total iron, sulfate, aluminum, and manganese) for the mine void wells, the pillar wells, the vent hole, and the mine discharge. The differences in contaminant concentrations among the five void wells were minor, so they were averaged for comparison in Figure 12; the same was true for three of the four pillar wells (5, 7, and 9).

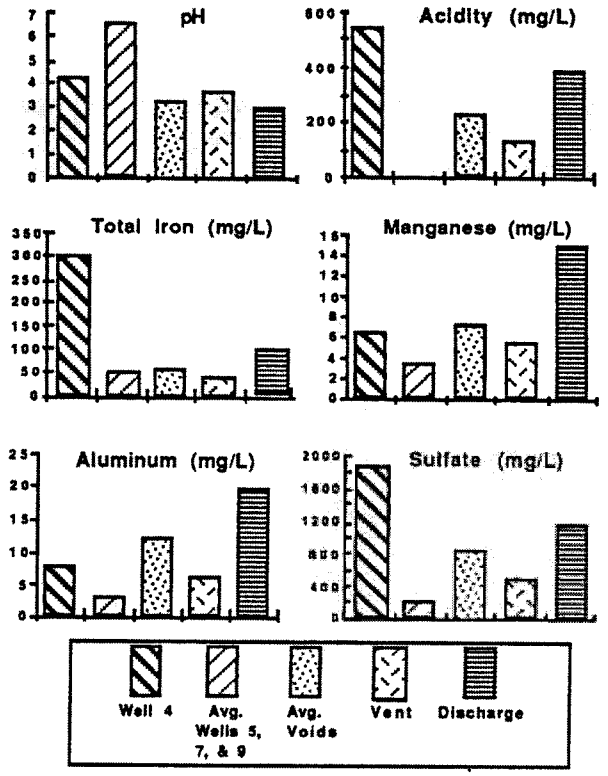

Figure 12. Comparison of water quality in mine voids, pillars and discharge, Keystone site.

The significant differences in water quality between the pillars and voids supported the assumptions that lateral flow occurred mainly through the voids, and that the pillars were recharged from above rather than from the side. For example, the water quality in wells 5, 7, and 9 was generally better than in the voids; conversely, the water quality in well 4 was substantially worse. If large amounts of lateral flow were occurring through the pillars, greater overall similarity in water quality would be expected. Note in Figure 12 that the water quality in the vent hole, which is open only to the overburden, was generally better than in the voids but poorer than in wells 5, 7, and 9. This was not inconsistent with the assumption of pillar recharge by vertical flow; the water quality differences could indicate either inherent spatial variations in acid production within the overburden or changes in water quality after downward flow into the voids or pillars.

In this regard, the extremely poor water quality of well 4 was quite anomalous. Acidity, total iron and sulfate concentrations in well 4 were consistently higher than either the voids or the discharge, while pH was higher and aluminum and manganese concentrations were lower.

Clearly, acid mine drainage existed at well 4, but the source of the acidity cannot be accurately identified. For reasons described above, lateral flow from an adjacent contaminated entry was considered to be unlikely. One possibility is that a localized zone of pyritic overburden or coal exists at well 4. Further research to investigate the cause of the poor water quality at well 4 was beyond the scope of this study.

Voids vs. Discharge. Figure 12 also shows that water quality in the voids, while indicative of acid mine drainage, was generally better than water quality at the discharge. One possible explanation for these differences is that a zone of acid-producing material, either within the mine or the overburden, may be located between the wells and the discharge. The former possibility was considered because, at the time when the mine was operating, it was not uncommon for mine operators to dispose of acid-producing refuse material in unused entries near the portal area. Overall contaminant concentrations would increase as water from the wellfield flowed past this area. It was also noted that the mean percentage of ferrous iron in the voids was somewhat higher than at the discharge (86 vs. 75 %). Under the scenario above, this difference may have occurred due to conditions within the discharge borehole and the 135 ft length of PVC pipe that connected the borehole to the discharge sampling point. Here, the turbulent flow conditions and exposure to the atmosphere would allow oxidation of some of the iron from the ferrous to the ferric state.

A second, more likely reason for the differences in water quality between the voids and the discharge was that flow from other, unmonitored entries contributed greatly to the total discharge flow. Examination of the mine maps (see Figures 3, 4, and 5) showed that the discharge borehole was located at the intersection of one of the main mine entries and an apparently isolated set of entries that had been driven to the southwest. If the latter were indeed isolated from the rest of the mine openings, flow through them would be insignificant compared to flow through the monitored main entries. However, if an open connection between these entries and the rest of the mine were present, and the monitored entries were partially blocked in some manner (e.g., by dumped refuse or buildup of iron hydroxide precipitates) a large percentage of the total pool flow could bypass the wellfield. The discharge water quality would thus reflect, to a significant extent, the quality of the water flowing through the unmonitored entries.

Water Quality Stratification. If the second flow scenario described above were true, flow through all entries would not be uniform as previously assumed, and the flow velocity through the monitored mine entries would be close to zero. Under such near-stagnant conditions, a marked worsening of mine water quality with depth has been noted (Ladwig et al 1984). In order to check for such water-quality stratification, an interval sampler was used to collect water samples from the top, center, and bottom of the voids, which were each approximately 6 ft in total height. Samples from all voids were grouped by level and statistically analyzed to check for water quality differences between levels. As shown in Figure 13, the water quality at the top of the voids was significantly better than at the center or bottom. Although the water quality at the center appeared to be somewhat better than at the bottom, the overlap of the confidence intervals prevented a definitive conclusion. These data suggested that some degree of stratification was occurring within the monitored voids, and that the flow velocity was relatively slow. It was decided that further experimentation would be necessary to define the flow rate through these entries, which would ultimately determine their suitability for alkaline injection.

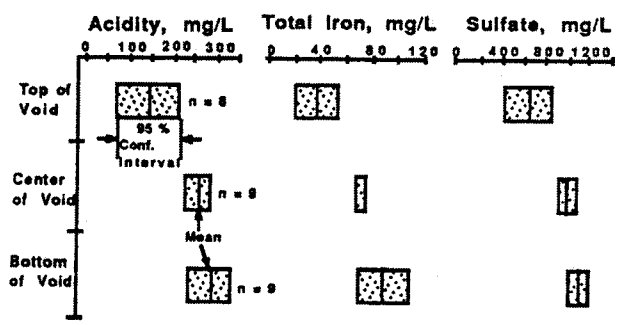

Figure 13. Stratification of water quality in mine voids, Keystone site.

Tracer Test

The approximate flow velocity within the mine pool can be estimated by introducing a chemical tracer into a monitoring well, noting the time of peak tracer concentration at the discharge, and dividing this mean travel time into the travel distance as measured on the mine map. Well 3 was chosen for the tracer test because it was located in an entry that was directly connected to the vast majority of upgradient voids, and was closer to the beach area than any other well of this type. Figure 14 shows the anticipated flow path from well 3 to the borehole discharge.

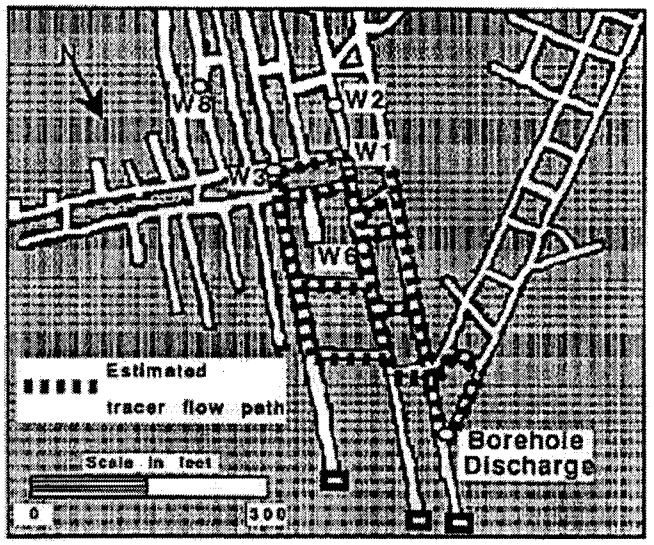

Figure 14. Estimated flow path of bromide tracer, Keystone site.

Bromide, in the form of a sodium bromide solution, was used as the tracer chemical. Bromide appeared to be an appropriate tracer choice because it is conservative, stable, and inexpensive (Davis et al 1985). Bromide concentrations as low as 0.1 mg/L could be detected by Bureau of Mines' analytical laboratory, and background concentrations of bromide were negligible. The quantity of tracer to be introduced was chosen such that if it were dispersed uniformly throughout all the entries in the assumed flow path, the bromide concentration at the discharge would be 15 mg/L, more than two orders of magnitude above the laboratory detection limit. The tracer test was initiated on February 14, 1990; 6.0 kg of granular sodium bromide were dissolved in water on the surface and introduced into well 3. An additional 30 gallons of fresh water were then added in order to flush the bromide from the well casing. Mine discharge samples were collected at 6-hr intervals by an automatic sequential sampler for a period of six weeks. Since no bromide was detected during this time, the sampling frequency was gradually reduced to once per day for the next eight months. Samples from wells 1, 3, and 6 were collected weekly to monitor tracer movement through the mine pool.

Early results of the tracer test suggested that flow was not uniform through all open entries. After 92 days of sampling, no trace of bromide was detected at the discharge or at wells 1 or 6, which were on the assumed flow path from well 3 to the discharge. During this time, the mean discharge flow rate was 76 gal/min, or 14,644 ft^3/day; under the uniform flow assumption, the flow velocity in the vicinity of well 3 would have been approximately 25 ft/day. Under these circumstances, traces of bromide would be expected in well 1 after 4 days, well 6 after 10 days, and at the discharge after 22 days. Obviously, flow was not occurring uniformly through all open entries as first assumed. However, bromide was apparently migrating of away from well 3, indicating that water in that entry was not completely stationary. Immediately after tracer introduction and flushing, a sample taken at the center of the void at well 3 contained 468 mg/L of bromide; after 92 days, the concentration had declined to less than 1.0 mg/L (see Figure 15). This decline could not be attributed to molecular diffusion because the initial bromide concentration was too dilute to produce significant solute movement via diffusion (Lide, 1990). Therefore, it was concluded that some flow, albeit slow, was occurring in the entry penetrated by well 3.

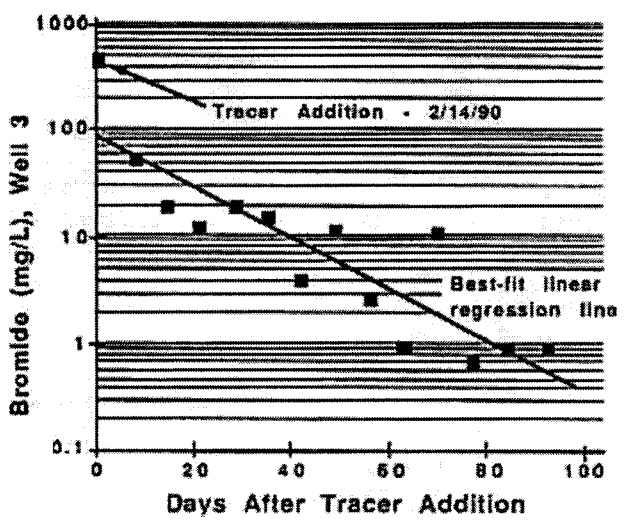

Figure 15. Dilution of bromide tracer in well 3, Keystone site.

In order to obtain a rough estimate of the velocity in the well 3 entry from the tracer data, a borehole dilution equation (Drost, et al, 1968; Grisak, et al 1977) was employed:

$$v_a = -(V/At) * \ln(C/C_o) \qquad (1)$$

where: v_a = apparent velocity
V = dilution volume
A = cross-sectional area of flow
t = time since tracer introduction
C = tracer concentration at time t
C_o = tracer concentration at t = 0

Support for using equation 1 to describe tracer movement is provided by noting that the plot of tracer concentration versus time on a semilogarithmic scale (Figure 15) approximates a straight line, as would be expected by rearranging the equation:

$$\ln(C) = -(v_a A/V) * t + \ln(C_0) \qquad (1a)$$

It was recognized that the use of equation 1 involved some error, partly from the underlying assumptions that flow is steady and that the tracer is homogeneously distributed throughout the dilution volume, and partly from the uncertainty associated with estimating the parameters, especially the dilution volume. In this case, the area was estimated at 108 ft^2, and the dilution volume was estimated by dividing the total tracer mass (6.0 kg) by the average tracer concentration at the center of the void over the time period being considered. Since the tracer was in an open conduit, the apparent velocity did not have to be corrected for wellbore and screen effects.

Velocities calculated from equation 1 during the first 3 months after tracer addition ranged from 1.9 to 4.5 ft/day, depending on the time frame being considered. Correlation was not found between the calculated velocity and measured mine pool elevation at a given time. At the mean calculated flow velocity, 2.8 ft/day, the tracer would have been expected at well 1 after 42 days and at well 6 after 70 days. The lack of tracer detection at these wells after 92 days suggested that the entries connecting well 3 to wells 1 and 6 did not constitute a primary flow path. Also, note that at a velocity of 2.8 ft/day, the tracer would be expected to arrive at the mine discharge after approximately 200 days. However, at this velocity and a cross-sectional flow area of 108 ft^2 at well 3, the mean discharge rate through that entry during the observation period would have been only 300 ft^3/day. This was only about 2 % of the mean mine discharge rate (14,644 ft^3/day) during the observation period. Since the remaining 98 % of the discharge flow would come from other sources in the mine, it was suspected that the bromide concentration would be diluted below detection limits by the time the tracer reached the discharge borehole. Therefore, no reliable quantitative estimates of travel time or flow velocity through the mine pool were obtained from the tracer test.

Alkaline Injection

Although a distinct flow path and travel time through the mine pool could not be identified, it was determined that a one-time attempt at alkaline injection would still be worthwhile. Even if no improvement in discharge water quality were achieved, monitoring of the water quality in the wells after alkaline injection would provide additional information about the mine pool hydrology. Based on an average discharge acidity of 402 mg/L, a minimum of 1570 kg of sodium hydroxide (NaOH) would be required to neutralize the estimated 4.6 million liters of water contained in all entries downgradient of well 3. On May 23, 1990, this quantity of NaOH (2000 gallons of 25 % sodium hydroxide solution) was injected into the mine pool. About half the solution was placed in well 3 to maximize the treated pool volume, and the other half was placed in well 6 with the intent of achieving a quicker response at the discharge. As with the bromide tracer, the wells were flushed with fresh water after injection to minimize the amount of alkaline reagent remaining in the well casings.

Results. A thorough discussion of the results of the alkaline injection treatment is provided elsewhere (Aljoe and Hawkins, 1991). Not unexpectedly, the treatment had no apparent effect on the water quality of the mine discharge. However, the water quality data obtained from wells 3 and 6 (Figure 16) provided further information about flow through the monitored entries.

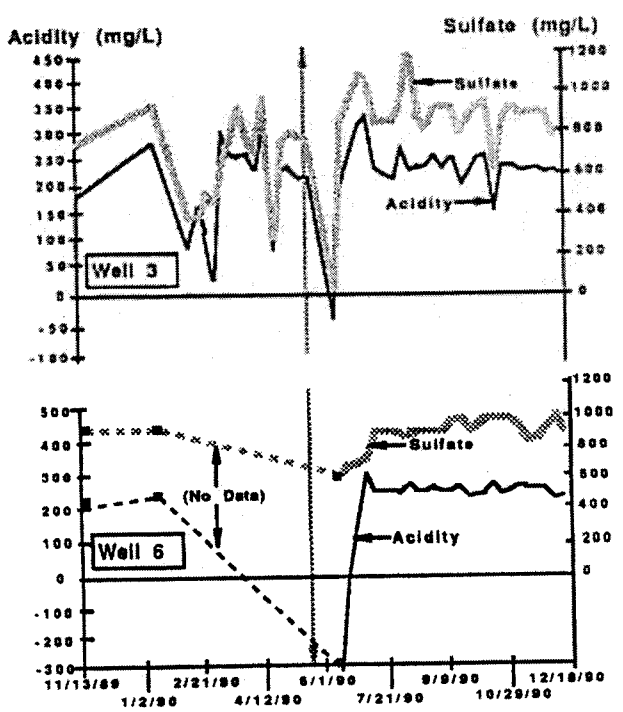

Figure 16. Acidity and sulfate changes in alkaline injection wells, Keystone site.

As expected, alkaline conditions (shown as negative acidity) were present in both wells immediately after injection; however, a concurrent decrease in sulfate concentration was also noted. Since sulfate concentrations typically remain constant during acid neutralization with sodium hydroxide, it is likely that displacement or dilution rather than neutralization was largely responsible for the decreased acidity. The return of the acidity and sulfate concentrations to their pre-injection levels after six weeks was interpreted as a movement of the displacing/diluting media (alkaline solution and flushing water) away from the injection wells. As with the tracer test, this result suggested that flow was occurring through the entries at wells 3 and 6, although not rapidly enough to comprise a substantial percentage of the total pool flow. Thus, the alkaline solution may have become mixed with such large volumes of untreated water that any neutralization effects have gone undetected. Also, much of the alkaline solution may have become trapped and stratified in a stagnant portion of the mine pool, and will remain unreacted unless flow velocities increase enough to promote more rapid mixing and downgradient movement. These possibilities could be examined by continuously injecting larger quantities of alkaline solution, but such an effort was beyond the scope of the current study.

Future Work

One of the primary efforts in the future will be to install up to four additional monitoring wells in the area shown in Figure 17. If open connections exist between this area and the remainder of the upgradient mine workings, wells in open entries could intercept a primary flow path. After these wells are installed and baseline water quality is established, tracer tests will be performed to determine pool flow velocity and travel time.

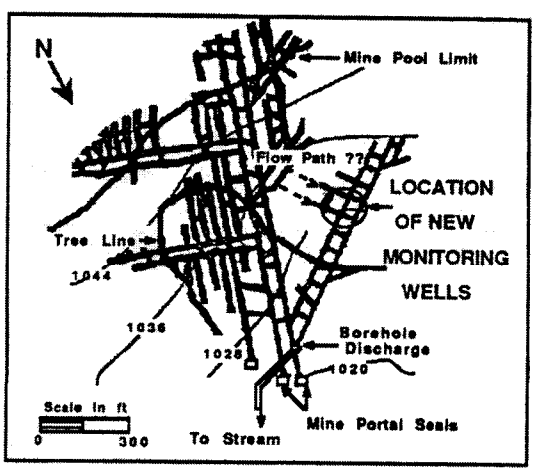

Figure 17. Proposed location of new wells, Keystone site.

Hydrologic Investigation - Friendship Hill National Historic Site

For several reasons, the hydrologic investigation at the Friendship Hill site (see Figures 1 and 18) was not as extensive as for the Keystone site. The mine map was not as complete or as detailed (e. g., no mine floor elevations), and the history of the mine and the circumstances under which the mine pool developed were more complex and not as well-documented. Early field reconnaissance revealed that the mine pool had at least two significant discharge points, which would have made a detailed investigation much more complex, costly, and time-consuming. Finally, several of the Friendship Hill mine pool monitoring wells were vandalized about six months into the investigation, thereby discouraging the use of this site for alkaline injection and reducing the near-term need to perform more rigorous studies. Nevertheless, the results of the preliminary investigation suggested that the nature and behavior of the mine pool were substantially different than those of the Keystone site.

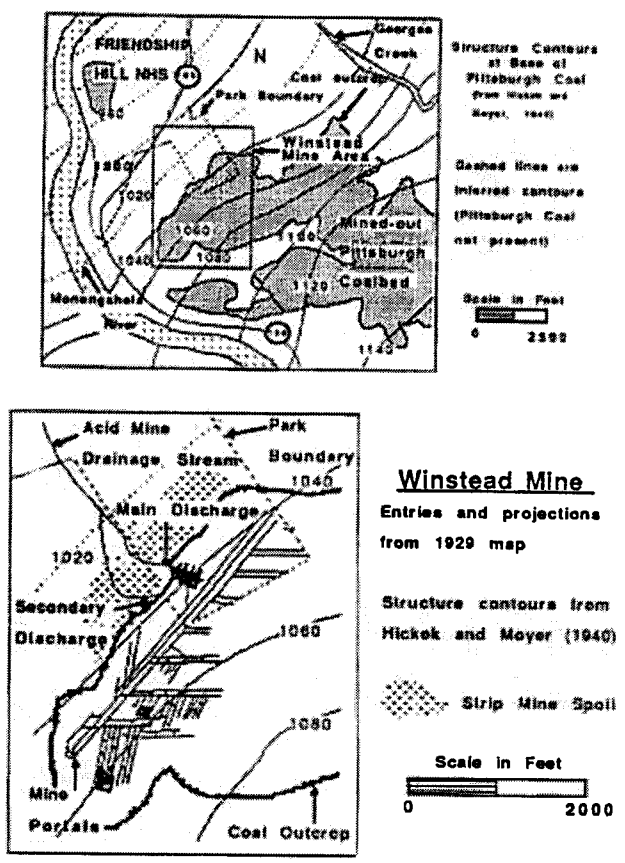

Figure 18. Geologic structure and mining activity in vicinity of Friendship Hill site.

Site Background

Figure 18 (from Hickok and Moyer, 1940) illustrates the general geologic structure in the vicinity of the Friendship Hill site (strike N 55^0 E, dip approx. 1.3^0 NW). Ground water flow in the study area is controlled by both topography and geologic structure; however, widespread mining in the area has made a significant impact on the ground water flow regime. A map prepared by Shaulis (1985) showed that all of the Pittsburgh coal seam areas shown in Figure 18 had been mined by underground methods, and strip mining had been performed on most of the Pittsburgh seam outcrop. The underground mines act as ground water sinks, and the associated low-permeability underclays result in numerous mine discharges along the Pittsburgh seam outcrop line. Because of the geologic structure, these effects are most prominent on northwest facing outcrops.

The abandoned mine at the Friendship Hill site was located in the Pittsburgh coal seam, and was operated by the Winstead Coal Co. in the 1920s and perhaps the 1930s. A mine map, dated 1929, showed the location of existing and projected mine entries with respect to coal outcrops, property lines, and an access road, but did not contain information on mine floor elevations or other topographic features. Property line boundaries and coal outcrop lines were correlated as closely as possible with current information to establish the position of the Winstead mine with respect to National Park Service property (Figure 18). There are actually two mapped mines at the site; the main mine discharge appears to originate from a partially-collapsed opening of a very small, unnamed mine that is surrounded by the larger Winstead mine. Mine maps suggested that as the main entries of the Winstead mine approached the small mine from the southwest, a single entry was driven almost due north, connecting the Winstead mine to the smaller mine. The location of this entry suggests that it served to drain water away from the Winstead mine and out through the smaller mine. Although the mapped portion of the Winstead mine stopped just to the east of the small mine, mine projections indicated that the Winstead mine continued its development to the north and east. Considering the relative locations of the mines and geologic structure, it is likely that the small mine continues to serve as a drain for much of the Winstead mine, as well as other mines to the southeast (upgradient) that may be interconnected with the Winstead mine.

Field observations were the only means of locating mine discharge points. Only one other discharge was found within 1000 ft of the main discharge; this secondary discharge, shown in Figure 18, actually represents the discharges from two mine openings located about 350 ft southwest of the main discharge and 100 ft from each other. One of these openings was relatively intact and contained an air-water interface that provided a visual indicator of the mine pool level. Access for water sampling and flow measurement was precluded by pooled water in front of this opening. The second mine opening was completely collapsed, but its discharge contained a freely-flowing section from which representative water samples were taken. The two discharges combined on the surface within 10 ft of the second opening, and flow was measured with a portable flume at this point.

Much of the barrier coal between the Winstead mine and the northwest coal outcrop, and perhaps some of the pillars within the Winstead mine and the unnamed mine, were subsequently removed by strip mining. Field observations confirmed the presence of strip mine spoil piles to the northwest of the existing coal outcrop. However, the extent of strip mining with respect to the underground mines could not be determined with enough accuracy to permit mapping. Field observations also revealed the existence of several large sinkholes above the mine that were obviously the result of mine subsidence. However, the sinkholes could not be related to specific mine areas, and the general extent of caved conditions in the mine could not be determined prior to drilling of monitoring wells.

Monitoring Wells. If the pool surface were horizontal as at the Keystone site, the difference between the elevations of the pool and the seat clay (pool depth) would decrease to the southeast. The drilling plan was to first complete several holes within 200 ft southeast of the main discharge, where a mine pool was almost certain to be present. These holes would ensure that hydrologic monitoring and tracer tests could be conducted if subsequent holes farther away from the discharge failed to intercept the pool. Drilling would then proceed to the southeast until a beach area was reached or until ten holes were drilled. Well construction was to be the same as at the Keystone site.

Figure 19 shows the locations of all monitoring wells with respect to surface topography, the mine discharges, and the site access road. The first three wells all penetrated a highly rubblized zone or zones, consisting of numerous small (1 to 3-in) voids near the mine level. Cuttings from the air rotary drill were lost after the first small void was encountered, thereby eliminating the use of cuttings to identify the location of the seat clay. The driller's "feel" for resistance to penetration provided only a rough estimate of the depth to clay. Therefore, the rest of the drilling was not conducted as planned because the

pool height could not be determined accurately. The fourth through ninth wells were drilled to the east and southeast, in locations that provided relatively easy access for the drilling rig and at least 75 ft spacing between wells. Wells 4 through 8 encountered caved conditions similar to the first three; this result, coupled with the observations of surface subsidence (Figure 19), indicated that the mine entries were mostly caved in the area accessible to drilling. Well 9, located only 50 ft from the southeast park boundary, penetrated solid coal. The pool depth at well 9 was found to be more than 7 ft; this suggested that the mine pool actually extended beyond park boundaries to the southeast.

Well 10 was drilled toward the southwest corner of park property, and encountered a 9 ft high void. However, rapid hole collapse prevented the installation of casing to the full hole depth; the bottom of the casing was approximately 3 ft above the seat clay. Extrapolation of water levels in the other wells indicated that the pool elevation at well 10 would have been slightly below this. Indeed, no water was detected in well 10, so the mine pool, if present, was no more than 3 ft above the seat clay at this point. Experience of mine operators in this area has shown that the Pittsburgh coal seam contains numerous localized "rolls" that oppose the general structural trend. Well 10 may have been drilled into an entry located on a high spot in the local structure; this would account for the shallow (less than 3 ft) pool depth.

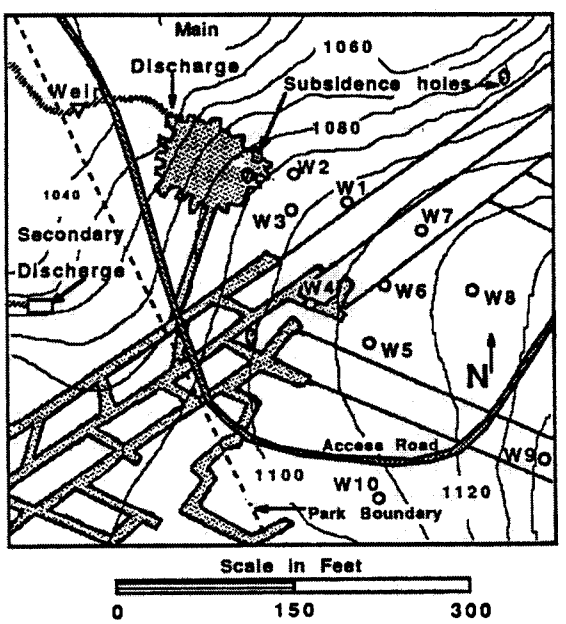

Figure 19. Surface features and topgraphic contours, Friendship Hill site.

Mine Pool Hydrology

As with the Keystone site, the first task after completion of well drilling at Friendship Hill was to characterize the nature of the subsurface flow system. Unlike Keystone, however, the piezometric surface at Friendship Hill was not horizontal, but had a distinct, regular hydraulic gradient (Figure 20); Figure 21 is a cross-section through the wellfield at the Friendship Hill site.

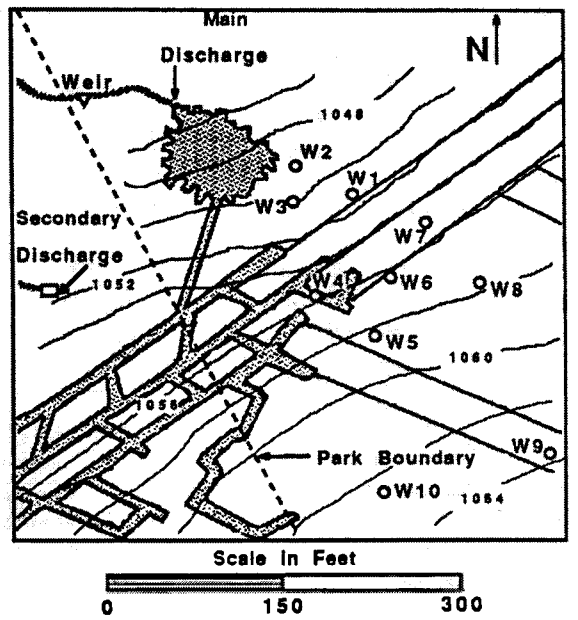

Figure 20. Mine pool level contours, Friendship Hill site.

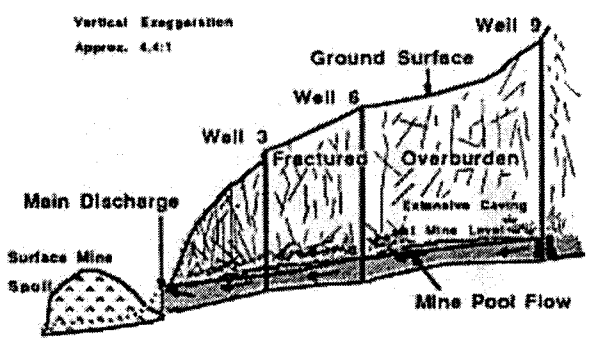

Figure 21. Cross-section through wellfield at Friendship Hill site.

Because of the water surface gradient, the flow system in the wellfield at Friendship Hill was more like that of a water table aquifer than that of a reservoir with an underdrain. However, this water table is quite different than it would have been had mining not occurred. In unmined conditions, the water table would have roughly

paralleled the surface topography and existed in a series of perched aquifers. After mining, the increase in vertical ground water flow resulting from widened overburden fractures and mine pumpage probably desaturated the overburden. Even after mine pumpage ceased and the deep strata collapsed into the mine openings, the overall porosity and permeability of the caved zone would still have been much greater than that of the fractured overburden. Although the caved material appears to have provided enough resistance to flow to allow the development of a water table gradient, its capability to store water and transmit it to the free drain (mine opening) at the low point of the flow system appears to have been great enough to suppress the redevelopment of the pre-mining water table. Thus, the current flow system may represent an equilibrium condition between high recharge to an aquifer of high transmissivity and storativity (the caved material) and discharge from a free drain at its base.

One factor complicating the flow system through the wellfield is the inherent heterogeneity of the aquifer formed by the caved material. The caving process does not occur uniformly, and some entries or portions of entries that were better supported than others would remain partially open to serve as preferred flow paths. This was evident in preliminary aquifer tests (slug withdrawal) that were conducted in four of the wells. In wells 6 and 7, water level recoveries occurred so rapidly that conventional analytical methods were not appropriate. In wells 4 and 8, recovery occurred as expected; hydraulic conductivities calculated by the Bouwer and Rice (1976) method were 3.9×10^{-5} ft/min and 2.6×10^{-3} ft/min, respectively, which was not unexpected for this material. The vast differences in well responses were similar to those observed by Hawkins and Aljoe (1991) in heterogeneous surface mine spoil, and supported the notion that preferred flow paths through the caved material could exist despite the presence of a regular steady-state water table.

Perhaps the most important aspect of the mine pool flow system is the likelihood that not all of the flow at the main and secondary discharges comes from the monitored area. The drainage entry connecting the Winstead mine to the smaller mine (see Figure 18) probably continues to contribute a substantial but unquantifiable percentage of the main discharge flow. A similar uncertainty exists for the secondary discharge. Given the location of these openings with respect to the rest of the mine and geologic structure (see figs. 18-20), the hydrologic connection, if any, between the wellfield and the secondary discharge is even less clear. Therefore, interpretations of hydrologic and water quality data collected at the site must reflect this uncertainty.

Mine Discharge Flow Rates. Flow rates of the main mine discharge were measured at least once per week from late October 1989 through early November 1990. During the study period, the measured flow rates ranged from 24.5 to 193 gal/min, with a mean and median of 65 and a standard deviation of 31 gal/min. Unlike the Keystone site, extremely low flows (less than 20 gal/min) were not measured at the Friendship Hill site. One possible reason is that the Friendship Hill pool area is much larger, allowing higher flows to be sustained for longer periods with a minimal drop in pool level.

A key factor governing the discharge flow rates of the mine pool at Friendship Hill was the existence of the known secondary discharge, and perhaps other discharge points that were not found during field reconnaissance. Figure 22 shows the flow rates of the two measured discharges over the five-month period when secondary discharge flow rates were measured. The strong positive correlation between the flow rates at the main and secondary discharges (Figure 23) supported the assumption that the two were connected to the same mine pool.

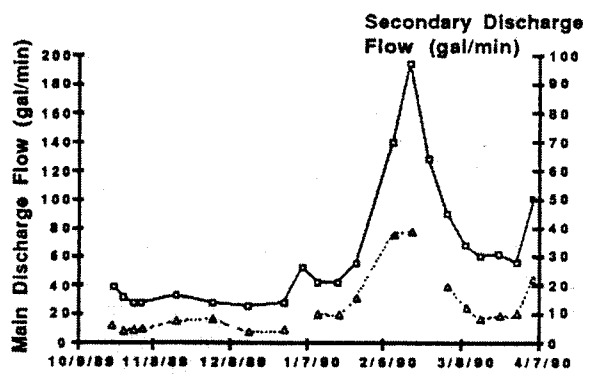

Figure 22. Flow rates of main and secondary discharges, Friendship Hill site.

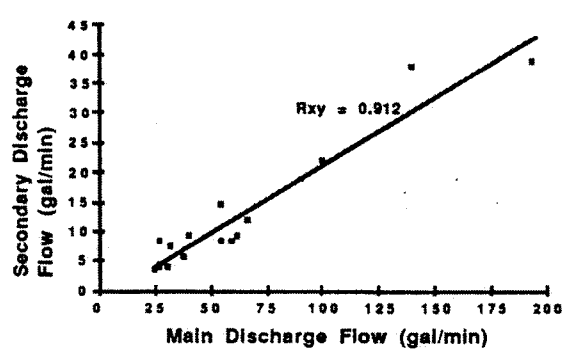

Figure 23. Linear regression - flow rates at main vs. secondary discharge, Friendship Hill site.

Note in Figures 19 and 20 that the topographic and water surface elevations of the secondary discharge are higher than those of the main discharge. Therefore, it is possible that the secondary discharge functions as a type of relief valve for the mine pool, especially since one of the mine openings at this discharge appeared to be unrestricted. The effect of the secondary discharge, along with other unmonitored discharges, would be to reduce the flow rate of the main discharge, especially during high-flow periods.

If the secondary discharge were a preferred outlet for the mine pool during high recharge periods, it would be expected that the percentage contribution of the secondary discharge to the total discharge (secondary plus main) would increase with total discharge. A slight positive correlation between these two variables was found (R_{xy}= 0.295), but the greatest percentage contribution of the secondary discharge did not occur when the measured flows were highest. The lack of a strong correlation may be related to the small size of the data set (19 samples) and the inaccuracy of flow measurements made with the portable flume at the secondary discharge. However, it is possible that other upgradient mine openings limit the maximum flow of the secondary discharge and reduce its contribution to the total pool flow.

Mine Pool Levels. Water levels in all nine water-bearing monitoring wells were measured weekly from November 1989 through March 1990. After three of the wells were vandalized beyond repair in early April 1990, monitoring frequency was gradually decreased to twice monthly, but continued until early November 1990. The most notable finding was that the water levels in all wells remained almost the same throughout the study period despite the wide variations in discharge flow (Figure 24).

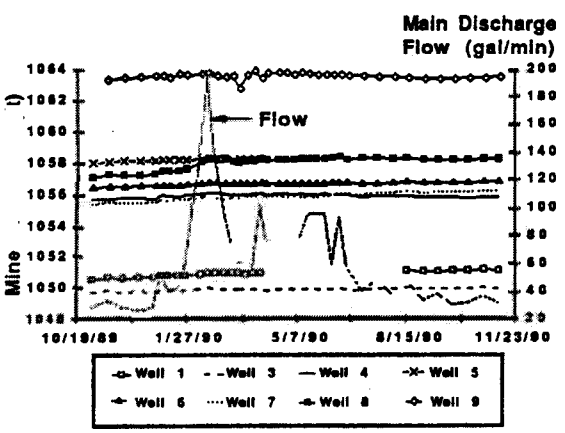

Figure 24. Water levels in monitoring wells, Friendship Hill site.

This contrasted markedly from the Keystone site, where pool level fluctuations were small but easily detected. Of course, in order for flow changes to occur, the mine pool level at Friendship Hill would have had to change, but the large size and storage capacity of the pool and the presence of multiple discharge points may have rendered the changes undetectable. For example, preliminary estimates of total pool storage capacity indicated that net pool discharge (total discharge minus recharge over the same time period) would have to be about 1.5 million gallons in order for the pool level to drop 0.25 inches, the functional accuracy of the electric water level measurement tool. Noting that the two Friendship Hill discharges release about 30 gal/min at low flow, and assuming that they represent about 20 % of the total flow from all discharges, approximately 7 days of zero recharge would be required for a detectable drop in pool level to occur. Considering the ease of pool recharge through the fractured overburden and the lack of long dry spells during the study period, actual pool drops would have been difficult to detect. Similarly, even the highest pool recharge rates would not result in detectable pool rises because such recharge could be dissipated almost instantaneously by high flows at multiple discharges, at least some of which have no restrictions to flow.

Response to Precipitation. Daily rainfall data at Friendship Hill were collected and recorded by National Park Service personnel. Figure 25 shows that the flow rate of main mine discharge responded to precipitation in a manner similar to the mine discharge at the Keystone site (Figure 9), for reasons previously discussed. During the late summer and fall, large precipitation inputs produced minimal changes in discharge flow rates. Conversely, following the first major snowmelt of the season and continuing through spring, even minor precipitation

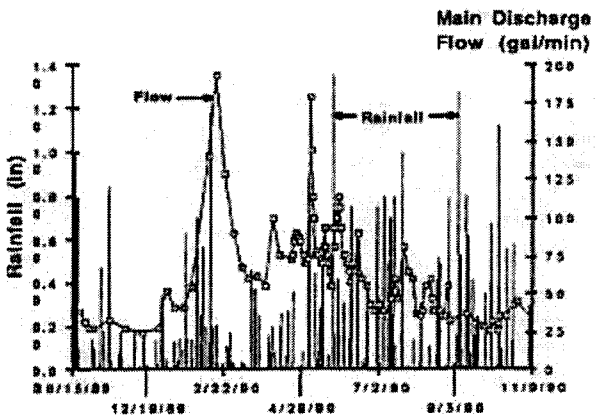

Figure 25. Response of Friendship Hill mine pool to rainfall, October 1989 to November 1990.

events produced very rapid increases in flow. Allowing for these seasonal effects, the magnitude of the flow response generally reflected the intensity and duration of the antecedent precipitation. At Friendship Hill, as at Keystone, it is likely that the relationship between main discharge flow and precipitation is controlled by greater pool recharge rates during the winter and spring months. However, for reasons discussed above, this could not be confirmed by examining the mine pool water levels.

Water Quality Considerations

Mine Discharge Water Quality. Water quality samples were collected from the main and secondary discharges each time a flow measurement was made. As with most deep mine discharges, contaminant loading rates in both locations were dominated by flow. Plots of contaminant loadings versus flow at Friendship Hill were similar in appearance to those at Keystone (see Figure 12), indicating that variations in contaminant concentrations were small compared to variations in flow. However, contaminant concentrations appeared to change slightly with flow variations. Figure 26 shows that from October 1989 through June 1990, contaminant concentrations at the main discharge (represented by acidity and sulfate) dropped noticeably during periods of increasing flow, and rose as the flow rate declined. This pattern suggested that some dilution of the mine drainage was occurring during periods of increased flow. The source of this dilution could not be confirmed; it may have resulted from general recharge throughout the mine pool, locally enhanced infiltration through the heavily-fractured overburden just behind the main discharge (see Figure 21), and perhaps small amounts of surface runoff into the weir where water samples were collected.

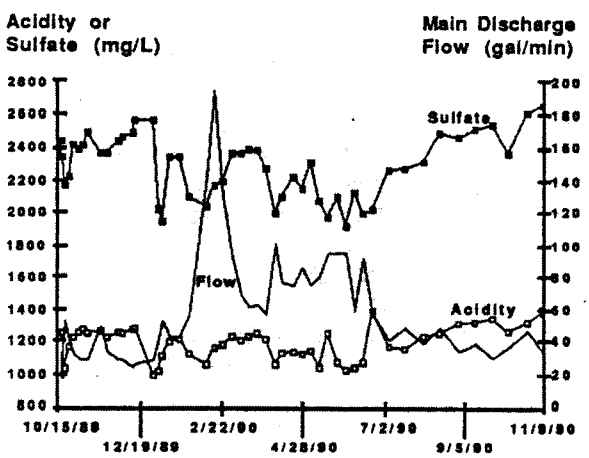

Figure 26. Acidity and sulfate concentrations, main discharge, Friendship Hill site.

Note also in Figure 26 that contaminant concentrations increased steadily during July through November 1990, and that the correspondence between contaminant concentration decreases and flow increases was less pronounced. Despite reduced infiltration during this period, the unsaturated caved zone and fractures immediately above the mine pool would still contain enough moisture to sustain pyrite oxidation and acid salt formation. When pool recharge became sufficient to produce a flow increase, the effects of dilution may have been offset by increased salt dissolution by infiltrating waters. Due to the lower frequency of such flushing events during the summer, fresh pyritic surfaces exposed as the result of salt dissolution would have more time to react before the next event. The increasing contaminant concentrations and decreasing flows shown in Figure 26 may represent the net result of the lower frequency and magnitude of flushing events.

Figure 27 shows that the percentage of ferrous iron in the main discharge was never greater than 30 %, and was consistently below 5 % during the high-flow period from January through June 1990. This differs markedly from the Keystone site, where the iron in the discharge was consistently greater than 75 % ferrous. The lower ferrous percentages at Friendship hill probably occurred because the mine pool had much greater access to oxygen than the pool at Keystone, thereby enhancing oxidation of iron from the ferrous to ferric state by direct aeration and the action of aerobic bacteria. The numerous subsidence sinkholes and associated overburden fractures at Friendship Hill, which were absent at Keystone, allowed easier diffusion of atmospheric oxygen. Also, the pool surface at Friendship Hill was located below the top of the mine void (or caved zone) throughout the site, whereas the Keystone pool surface was well above the void except

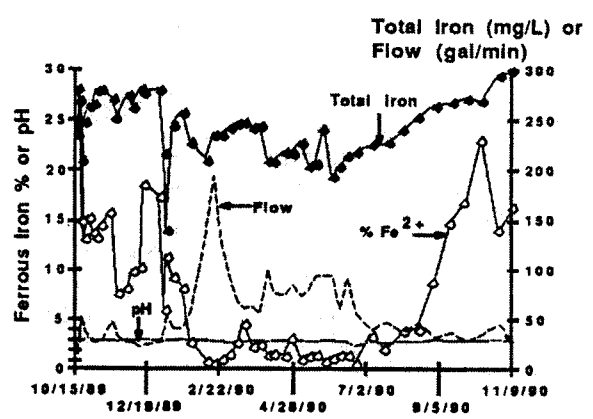

Figure 27. Concentrations of total iron, ferrous iron, and pH, main discharge, Friendship Hill site.

in the beach area (compare Figures 6 and 23). Thus, the pool surface area open to oxygen and subsequent ferrous to ferric conversion was much greater at Friendship Hill. The pH of the main discharge remained nearly constant (between 2.5 and 3.0) throughout the study period, suggesting that bacterially-mediated iron oxidation was dominant. Also note in Figure 27 that the ferrous percentage appeared to be inversely related to flow. This behavior may be related to the greater flushing of ferric salts from pyritic surfaces near the air-water interface during high-flow periods. The concentrations of all acid mine drainage contaminants were consistently higher at the secondary discharge than at the main discharge. However, the same relationships between concentration, flow, ferrous percentage, and pH discussed above (Figures 27 and 28) were also found at the secondary discharge. This supported the assumption that both discharges drained the same large pool, but suggested that significant water quality differences may have been present in different areas of the pool.

Monitoring Well Water Quality. A regular, comprehensive well sampling program was not conducted at Friendship Hill, primarily because it became clear that the Keystone site was more suitable for alkaline injection. As shown in Figure 28, the water quality in the eight wells that were completed in caved material varied widely; note the wide confidence intervals (95 % level) around the mean. This suggested that although all areas of the pool produced acid mine drainage, some locations were more active than others. For example, the worst individual sample (well 5, March 15, 1990) contained an acidity concentration of 7393 mg/L, total iron of 2032 mg/L, and sulfate of 8775 mg/L. This variability, if indicative of conditions in the entire pool, could be responsible for the observed water quality differences between the main and secondary discharges. In general, the water quality in the wells was much poorer than at the discharge. However, contaminant concentrations in well 6 were closer to those of the main and secondary discharges than most of the other wells (Figure 28), and showed the same behavior over time as the main discharge (see Figure 26). Ferrous iron percentages in well 6 were relatively low (1 to 40 %), but were consistently higher than at the main discharge and showed the same steady increase from July through October 1990 (see Figure 27). This was consistent with the previous evidence of less pool dilution and less ferric salt flushing during the low-recharge periods of late summer and early fall.

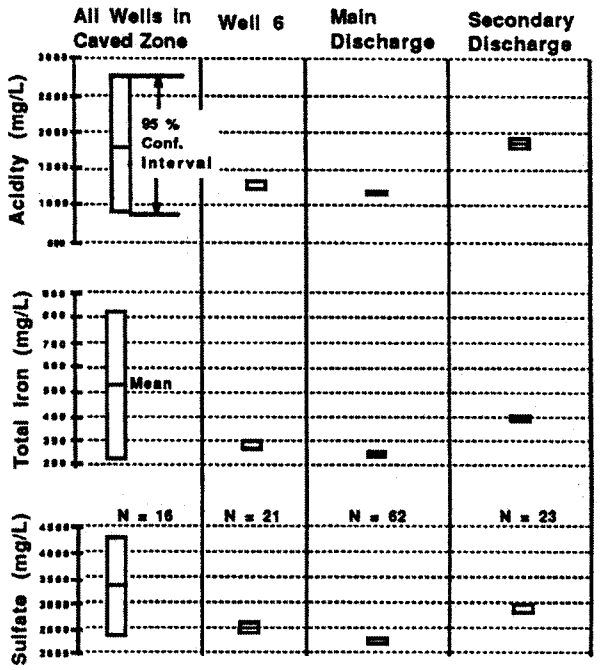

Figure 28. Comparison of water quality in monitoring wells and discharges, Friendship Hill site.

Tracer Test

It was determined that a bromide tracer test similar to the one at Keystone could be conducted at Friendship Hill despite the vandalism and reduced sampling schedule. Well 6 was chosen for tracer introduction because it was hydrologically upgradient and within 100 ft of two of the remaining accessible monitoring wells 4 and 7). Also, its water level had recovered almost instantaneously after slug withdrawal, suggesting that it may have intercepted a preferred flow path in the caved zone, and its water quality was similar to that of the main discharge. Because of the large size of the overall pool and porous-medium characteristics of the pool flow system in the wellfield, flow velocities were expected to be relatively slow. For example, if it were assumed that: (1) flow occurred entirely by porous-media methods; (2) the hydraulic conductivity of the medium equaled the average of the measured conductivities in wells 4 and 8 (3.02×10^{-4} ft/min); and (3) the porosity of the medium were 60 %, then application of Darcy's law would yield a travel time of 42 years between well 6 and the main discharge. Tracer detection at the main discharge therefore depended on the existence of a preferred flow path from well 6.

The tracer test began on April 20, 1990, with the introduction of approximately 6 kg of sodium bromide in solution form, followed by approximately 30 gallons of flushing water. If this quantity of sodium bromide were uniformly dispersed throughout the pool volume downgradient of well 6 (estimated at approximately 4 million gallons), the concentration at the main discharge would have been only 0.4 mg/L, barely above the detection limit of the laboratory equipment. However, if a preferred flow path did exist, as required for detection within a reasonable time period, uniform dispersion would not occur and the concentrations reaching the discharge would be higher. Weekly sampling of the downgradient wells and daily sampling of the main discharge was believed to be sufficient to detect tracer arrival and subsequent movement. The secondary discharge was not monitored for tracer because it was farther from well 6 and its potential hydrologic connection with the wellfield was not demonstrated.

Six months after the start of the tracer test, no evidence of bromide had been detected at the main discharge. Given the large pool size and the amount of tracer added, this was not unexpected. However, Figure 29 summarizes the somewhat surprising results of the well sampling conducted during the tracer test. Within one week after tracer addition in well 6, the bromide concentration in well 4 had increased to 21.5 mg/L; it then decreased steadily to below the detection limit (0.1 mg/L) six weeks after tracer injection. This suggested the peak tracer concentration in well 4 had occurred before the first sample was taken, and that the mean travel time between wells 6 and 4 was less than one week. Although the decline in bromide concentration over time in well 6 was much more erratic than in well 4, the rate of decline was similar in both wells. The straight lines on the semilogarithmic plot of Figure 29 suggest that flow-related dilution was occurring. Since the distance from well 6 to well 4 was approximately 100 ft, the flow velocity would have been more than 14 ft/day, considerably higher than expected. Although the projected locations of wells 6 and 4 on the mine map (see figs. 19 and 20) suggested that an open mine entry may have connected the two, well 4 was one of the wells that responded in a steady, predictable manner in the slug withdrawal tests, with a relatively low hydraulic conductivity of 3.9×10^{-4} ft/min. Thus, the rapid flow velocity suggested by the tracer test could not be directly attributed to the presence of an open conduit between wells 6 and 4. However, since a slug test influences only a very small aquifer volume, there may have been a conduit in the vicinity of wells 6 and 4 that was not detected in the slug tests.

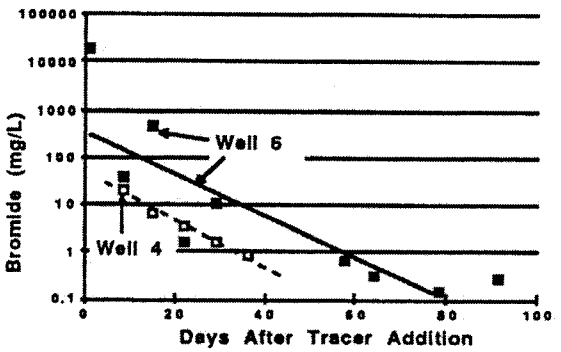

Figure 29. Results of bromide tracer tests, Friendship Hill site.

Future Work

A complete understanding of the mine pool hydrology at the Friendship Hill site can be obtained only by broadening the study to include all mine discharges that occur along the section of Pittsburgh coal outcrop shown in Figure 18. Monitoring wells should be installed in the mined areas near several of the discharges, and the hydrologic and water quality data should be collected over a period of several water years. In this manner, the observed hydrologic conditions at Friendship Hill (e.g., stable pool levels, regular water table gradient in caved zone) can be placed in the proper regional perspective and related to behavior at sites which may drain the same large mine pool.

Summary and Discussion

The hydrologic studies conducted at the Keystone and Friendship Hill sites in western Pennsylvania showed that abandoned underground mine pools can have substantially different flow systems. At the Keystone site, the flow system was relatively simple, primarily because a single mine with a single major discharge point was involved. The mine pool formed behind portal seals that were deliberately placed to cause the mine to flood. The mine entries appeared to be mostly intact, with minimal pillar removal, thereby providing a set of highly transmissive flow paths at the base of the mine pool. The net result was a horizontal piezometric surface that was above the top of the mine void in all locations except for a "beach area" at the upgradient extremity of the pool. Flow within the pool was assumed to consist of downward flow through the saturated overburden to the mine voids, and lateral flow through the voids to the discharge. Flow direction within the voids was assumed to be parallel to the structural gradient of the mine. Fluctuations in pool level, although small, were easily

observed and could be directly related to precipitation events and changes in discharge flow. This implied a relatively small pool area available for storage. A tracer test and subsequent injection of an alkaline solution into mine pool monitoring wells revealed that flow rates through the monitored entries, although detectable, were relatively slow. This indicated that the monitored entries may not be carrying the major portion of the pool flow. Mine maps were used to identify other entries that were capable of carrying significant pool flow to the discharge point, consistent with the conceptual flow system.

The Friendship Hill site was significantly more complex than the Keystone site, both in mining history and current hydrologic behavior. Numerous mines, both large and small, penetrated the coal seam at different elevations along a sinuous outcrop line. Some or all of these mines were probably interconnected, allowing flow to occur freely over a large mined area. The resulting pool or pools contains many discharge points, each at a different elevation. Subsequent strip mining of the outcrop probably exposed additional mine openings and created new discharge points. Portal seals were not emplaced at the monitored discharges; although collapse of strata at the discharge openings and strip mine spoils that were pushed into these openings have provided a damming effect, a significant zone of saturated overburden behind the discharges did not develop. Water levels in monitoring wells revealed a regular water table gradient in an area of predominantly collapsed entries behind a major discharge point. However, not enough data were available to determine either the proportion of the total discharge flow coming from the caved zone or the proportion of the mine that may be governed by the implied porous-media flow system. In marked contrast to the Keystone site, wide variations in flow were not accompanied by detectable changes in pool level; in fact, water levels in all wells remained almost constant throughout the one-year study. A reasonable explanation for this behavior is that the pool storage area is so large that extremely long periods of zero pool recharge would be required to cause detectable decreases in pool elevation. Conversely, increases in pool elevation during periods of high recharge are prevented by the existence of multiple pool discharge points, some of which provide minimal resistance to flow. A tracer test revealed a strong hydrologic connection between the tracer injection well and one downgradient well in the caved material, but the tracer was not detected at the main discharge six months after injection. This result, along with preliminary aquifer testing, suggests that the caved material is highly heterogeneous. This "aquifer" may behave as a porous medium in terms of steady-state water levels, but flow may occur primarily through discrete channels under transient recharge conditions, as observed in surface mine spoils (Hawkins and Aljoe, 1990)

The implications of the studies described in this paper are somewhat problematic in terms of the future of in-situ neutralization of pooled water in abandoned underground mines. The unsuccessful initial alkaline injection at the Keystone site, where comparatively good information was available prior to the hydrologic study, exemplifies the difficulty in obtaining the precise information needed to make the treatment work. A much larger expenditure in well drilling, monitoring, and hydrologic testing will be needed before any similar treatment efforts are conducted at this site. At Friendship Hill, the pre-treatment investigation would be even more extensive and costly because of the larger mine pool size, multiple discharges, and poorer water quality. Furthermore, such expenditures would be needed merely to assess the technical feasibility of the technique; the economic feasibility can be determined only after the treatment is successfully applied, when total costs can be quantified and compared to costs of conventional treatment. In-situ neutralization may yet prove to be cost-effective in mitigating acid drainage from abandoned underground mines, but only if the responsible party is willing to risk the initial investment needed to implement and optimize the process.

Literature Cited

Aljoe, W. W. and J. W. Hawkins 1991. Hydrologic Characterization and In-Situ Neutralization of Acidic Mine Pools in Abandoned Underground Coal Mines. Accepted for publication in Proceedings, Second International Conference on the Abatement of Acidic Drainage, September 16-18, 1991, Montreal, Canada.

Chung, N. K. 1973. Investigation of Use of Gel Material for Mine Sealing. U. S. EPA Report No. R2-73-135, Jan. 1973, 67 p.

Davis, S. N.; D. J. Campbell; H. W. Bentley; and T. J. Flynn 1985. Ground Water Tracers. (National Water Well Association, Columbus, OH), 200 p.

Drost, W.; D. Klotz; A. Koch; H. Moser; F. Neumaier; and W. Rauert 1968. Point Dilution Methods of Investigating Ground Water Flow by Means of Radioisotopes. Water Resources Research, Volume 4 Number 1, p. 125.

Grisak, G. E.; W. F. Merritt; and D. W. Williams 1977. A Fluoride Borehole Dilution Apparatus for Groundwater Velocity Measurements. Canadian Geotechnical Journal, Volume 14, pp. 554-557.

Hawkins, J. W. and W. W. Aljoe 1990. Hydrologic Characterization and Modeling of a Heterogeneous, Acid-Producing Surface Coal Mine Spoil, Upshur County, WV. In Proceedings, 1990 National Symposium on Mining, May 14-18, 1990, Knoxville, TN.

Hawkins, J. W. and W. W. Aljoe 1991. Hydrologic Characteristics of a Surface Mine Spoil Aquifer. Accepted for publication in Proceedings, Second International Conference on the Abatement of Acidic Drainage, September 16-18, 1991, Montreal, Canada.

Hickok, W. O. IV and F. T. Moyer 1940. Geology and Mineral Resources of Fayette County, Pennsylvania. Pennsylvania Geologic Survey, County Report 26.

Ladwig, K. J.; P. M. Erickson; R. L. P. Kleinmann; and E. T. Posluszny 1984. Stratification in Water Quality in Inundated Anthracite Mines, Eastern Pennsylvania, U.S. Bureau of Mines RI 8837.

Lide, D. R. (ed.) 1990. Handbook of Chemistry and Physics. 71st Edition,1990-1991. (CRC Press, Inc.) p. 6-151.

Shaulis, J. R. (ed.) 1985. Coal Resources of Fayette County, Pennsylvania. Pennsylvania Geologic Survey, Mineral Resource Report 91, Part 1.

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