

THE ROLE OF SULFATE AND IONIC STRENGTH ON THE SHIFT FROM ACID TO ALKALINE MINE DRAINAGE IN SOUTHWEST PENNSYLVANIA¹

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Abstract: Four Mile Run, Latrobe, PA, receives discharges from abandoned deep mines. In 1971, the effluent was characterized as having low pH, high acidity, and high concentrations of iron, manganese, and sulfate. After 22 yr of neglect, the water flow rate, pH, and alkalinity all increased, while the acidity, iron, manganese, and sulfate concentrations decreased. The overall loading of iron and sulfate to the stream has not changed significantly. This change from acid to alkaline drainage is fairly typical for mine effluent in the surrounding area. However, the mechanism for change is not well understood. Laboratory studies have shown that the neutralization rate of marble chips (CaCO_3) is depressed by high ionic strength or elevated levels of sulfate. The decrease in the rate of neutralization can be explained in terms of a static water film model. The decline in sulfate levels may be an important factor contributing to the change in water quality discharged into Four Mile Run. A similar kinetic phenomenon may occur with mine spoils and anoxic drains.

Introduction

Four Mile Run is located adjacent to the Saint Vincent College Campus in the town of Latrobe about 40 miles east-south-east of Pittsburgh, PA. The stream receives mine drainage from a series of abandoned deep mines that were used to remove coal from the Pittsburgh Seam. The run has been studied because it is the first major input of mine drainage in the Loyalhanna, a prominent area trout stream.

A comprehensive postmining study of water quality and mine drainage in the Loyalhanna Watershed was conducted in 1971 as part of Operation Scarlift (Schutz 1972). Four Mile Run received acid mine drainage (AMD) from six sources. The effluent from these sources contained elevated levels of iron, sulfate, acidity, and manganese and had a low pH. The water quality of the stream had degenerated to a point where the following parameters were reported: pH, 3.7; sulfate, 760 mg/L; acidity level, 210 mg/L.

After 22 yr, Four Mile Run still receives mine drainage with elevated levels of sulfate, iron, and manganese. However, the alkalinity and pH of the water have drastically increased to a point where the mine drainage possess a net alkalinity. The shift from acid to alkaline mine drainage is not uncommon in this region (Hedin 1993), although the factors that contribute to this change are not well understood.

Laboratory studies have shown that the rate of acid neutralization by marble chips is depressed by high ionic strength and the presence of anions such as sulfate and oxalate. These anions form relatively insoluble calcium salts. The decrease in the rate of acid neutralization is explained in terms of a static water film model.

This model has important implications beyond alkaline mine drainage. Limestone is used to neutralize effluent from mine spoils (Brady 1990) and AMD in anoxic drains (US Bureau of Mines 1992). Both of these processes are expected to have slower neutralization rates for waters with high ionic strength and elevated sulfate levels.

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Experimental Work

Quadruplet water samples were taken from each of the nine sampling sites on a biweekly basis during June through August 1993. Two samples from each site were acidified with HCl (pH ≤ 2) and refrigerated. The other two replicates were immediately analyzed for pH, conductivity, acidity, and alkalinity. Weirs were installed at sites 2-8 to determine the flow rates. The weir flow rates at sites 3-5 and 7 were checked by measuring the flows with a bucket and stopwatch. The two methods were found to differ by no more than 10%.

The pH was determined with a pH meter equipped with a combination electrode and calibrated using buffers of pH 4.00 and 7.00. Conductivities were recorded at 25°C with a conductivity meter calibrated with a 0.0100M KCl solution. Acidity and alkalinity measurements were performed as outlined in Standard Methods (Clesceri 1989).

Sulfate concentrations were determined by a turbidimetric method (Schutz 1972). Five milliliters each of sample and a conditioning reagent were added to a 100 mL volumetric flask and diluted with de-ionized water. A few crystals of BaCl₂ were added to the solution, and the contents were mixed for 1 min. The absorbance of the solution was measured at 420 nm and compared against known standards. The conditioning reagent was composed of 50 mL glycerol, 30 mL concentrated HCl, 100 mL ethanol, 75 g NaCl, and 300 mL of de-ionized water.

The concentrations of iron, manganese, calcium, magnesium, and sodium were determined with a flame atomic absorption spectrophotometer using the conditions shown in table 1. The metal concentrations of samples were determined from the calibration curves.

Table 1. Wavelengths and oxidant gases used in metals analysis.

Metal	Oxidant gas	Wavelength, nm
Iron	Air	386.0
Manganese	Air	403.1
Calcium	Nitrous oxide	239.9
Magnesium	Air	202.6
Sodium	Air	330.2

Neutralization studies were performed in a 1-L beaker. To the beaker were added 700 mL of de-ionized water, the appropriate quantity of salt, and a magnetic stirbar. The pH of the solution was adjusted to approximately 3 with 1/10 molar HCl. Sixty grams of marble chips were added to the stirring solution, and the pH was recorded as a function of time.

Results and Discussions

In the past 22 yr the location and flow rates of the mine drainage sites have changed. None of the drainage sites identified in the Scarlift study are known to be active along Four Mile Run (fig 1 sampling sites 52, 59, 60, 61), although the current sampling locations are in the same general area. Sampling sites 1 and 9 are the run itself, downstream and upstream, respectively, of the drainage area. Site 2 is a bore-hole drilled in 1973 as part of an exploratory study. Site 3 is the output of a wetland which is passively treating the mine drainage. Sites 4, 5, 6, and 7 are outputs from wetlands along the stream. Site 6 is fed by a number of artesian discharges 20 to 75 yd from the sampling location. Site 8 is a large artesian discharge.

The Scarlift study reported that the flow of AMD entering the stream from the original six sources averaged 213 gpm. During the summer of 1993, an average of 821 gpm of mine drainage entered the run. Recent mine subsidence upstream of the sampling area may be contributing to the higher influx of surface and ground water into the mines.

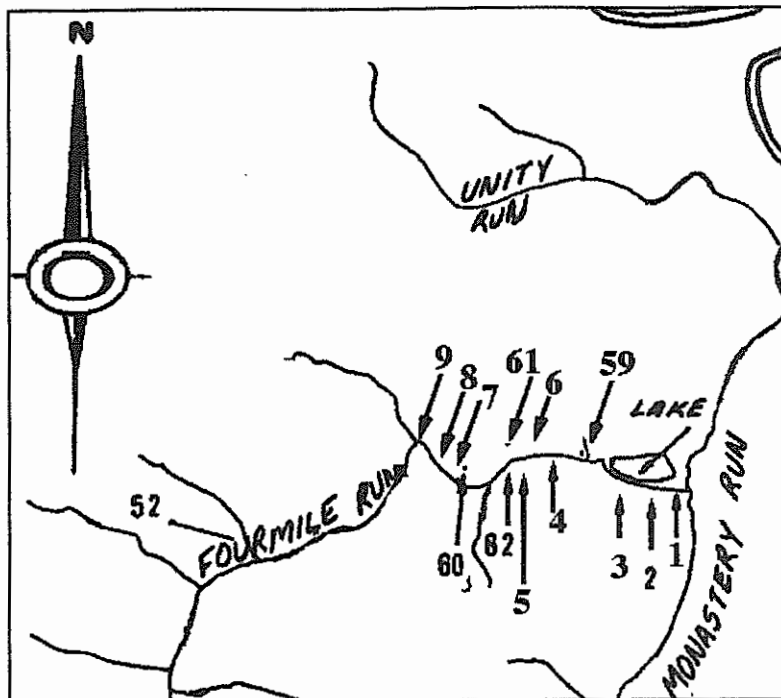


Figure 1. Map of the past and present discharge sites along Four Mile Run.

Operation Scarlift's 1971 water quality data for mine discharge sites along Four Mile Run are displayed in table 2. Except for site 53, not shown on the map, a small pond, all the effluent is quite acidic. It is plausible that the water in the pond was either neutralized by the sediments in the bottom or contained a significant quantity of uncontaminated surface water. The chemistries of the other sites are typical of AMD. The artesian like flows of these sites suggest that the mine was flooded. From the limited amount of data in the Scarlift study, it is difficult to draw many conclusions concerning the water chemistry.

Table 2. 1970 mine drainage discharges into Four Mile Run (Schutz 1972). All concentrations are expressed in mg/L.

Site	pH		Acidity		Sulfate		Iron		Manganese	
	High	Low	High	Low	High	Low	High	Low	High	Low
52	2.7	2.5	6350	1410	13600	10600	980	752	600	432
53	7.9	7.5	25	5	500	110	10	1	1	0
59	6.5	2.7	2010	825	5000	2700	574	30	60	28
60	3.1	2.5	1150	685	4400	2500	450	296	75	27
61	3.3	2.6	1225	770	6000	3750	514	164	76	44
62	3.2	2.7	1070	520	5400	3225	325	108	100	44

An overview of the current water chemistry is give in table 3. The concentrations of iron, manganese, sulfate, and acidity have declined significantly, while the pH and alkalinity have risen dramatically with respect to the Scarlift data. The mine drainage inputs from all the sources are quite hard (high concentration of Ca and Mg) and possess a large net alkalinity. The mean sulfate concentrations are 2 to 10 times larger than that predicted from the oxidation of iron pyrite, FeS_2 , suggesting that the overburden is composed of sulfate containing minerals such as gypsum. The concentrations of magnesium, manganese, and sodium are fairly homogeneous from source to source, implying that they have a common origin.

Table 3. Water quality data and flow rates for mine drainage effluent entering Four Mile Run during the summer of 1993. (The data expressed as the mean \pm 95% confidence limit.) All concentrations are expressed in mg/L, and flow rates are in GPM.

Site	1	2	3	4	5	6	7	8	9
pH	6.3 ± 1.1	6.03 ± 0.19	6.58 ± 0.13	6.35 ± 0.20	6.18 ± 0.19	5.51 ± 1.7	6.06 ± 0.21	5.69 ± 0.49	7.45 ± 0.37
acidity	3.90 ± 4.6	8.42 ± 0.89	0.38 ± 0.69	3.64 ± 2.3	7.84 ± 1.1	21.6 ± 23	45.2 ± 12	37.3 ± 7.7	ND ¹
Alk.	206 ± 102	381 ± 112	305 ± 68	262 ± 79	368 ± 111	247 ± 247	191 ± 83	286 ± 94	245 ± 104
SO ₄	540 ± 76	915 ± 65	770 ± 47	680 ± 82	722 ± 82	679 ± 90	520 ± 111	613 ± 124	37.7 ± 13
Fe	35.0 ± 3.5	70.8 ± 2.6	7.6 ± 1.7	47.6 ± 6.3	71.5 ± 3.7	55.6 ± 21	52.5 ± 7.2	59.4 ± 3.6	0.14 ± 0.06
Ca	184 ± 13	282 ± 10	263 ± 7.5	262 ± 8.0	258 ± 8.2	234 ± 23	168 ± 11	188 ± 12	79.5 ± 6.6
Mg	64.0 ± 4.3	73.0 ± 3.1	77.0 ± 4.8	83.7 ± 2.8	83.4 ± 3.4	79.4 ± 5.4	67.1 ± 1.3	73.6 ± 3.2	27.4 ± 1.7
Mn	2.93 ± 0.30	4.43 ± 0.15	2.56 ± 0.26	4.46 ± 0.15	4.08 ± 0.10	4.06 ± 0.16	3.84 ± 0.12	3.98 ± 0.11	0.10 ± 0.00
Na	63.1 ± 4.9	95.4 ± 6.5	89.0 ± 6.0	88.6 ± 4.7	88.7 ± 4.8	82.6 ± 7.3	60.2 ± 1.8	71.2 ± 3.3	21.6 ± 1.2
Flow	ND	350 ± 43	26.5 ± 17	25.5 ± 8.4	25.5 ± 8.4	140 ± 57	6.5 ± 5.4	235 ± 256	ND

¹ND indicates not determined.

Much of the water that currently enters the mine is most likely surface runoff entering through a large area of mine subsidence just upstream from site 8. At one spot, a culvert from the road discharges runoff directly into a subsidence pit. This would explain the large variability in discharge flow rates measured at site 8 and the lower concentration metals and sulfate in the current mine drainage.

Operation Scarlift reported that loadings of contaminants to Four Mile Run in 1970 were as follows: Mn, 38 to 77 kg/d; Fe, 120 to 400 kg/d; and sulfate 3,000 to 5,100 kg/d. The current average loadings of Mn (18.3 kg/d), Fe (273 kg/d), and sulfate (6280 kg/d) are remarkably similar. Twenty years of mineral dissolution in the mine appears to have had little impact on the current loadings. The larger volume of water currently flowing through the mine appears to be diluting the contaminants and is the main factor contributing to the lower concentrations of iron, manganese, and sulfate. The higher flow rate may also be a factor contributing to the shift from acid to alkaline mine drainage.

The capacity to neutralize the acid may have always existed, but the rate of neutralization may have been slow. To test this hypothesis, the rate of acid neutralization was studied in the laboratory. The change in pH of de-ionized water acidified with HCl and stirred over a bed of marble chips was followed with respect to time. Neutralization plots of $\ln[H^+]$ versus time were found to be linear over a pH range of 3.10 to 5.29 (fig 2). From the slope of the lines, an apparent first-order rate constant was calculated according to the following equation:

$$d[H^+]/dt = R_n [H^+], \quad (1)$$

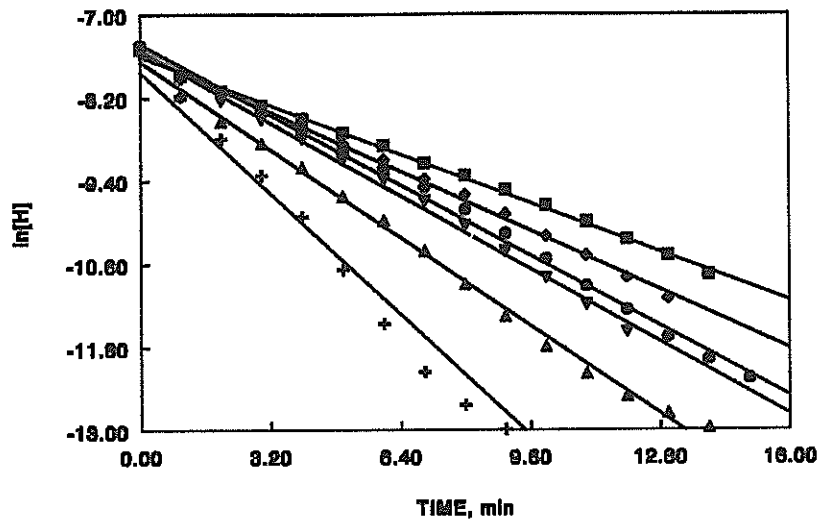


Figure 3. Plot of $\ln[H^+]$ versus time for solutions containing sulfate concentrations of (+) 0, (Δ) 1600, (\odot) 2600 (∇) 3600, (\diamond) 4600, and (\blacksquare) 5600 ppm.

where $[H^+]$ is the hydrogen ion concentration, t is the time, and R_n is the rate constant. pR_n , $-\log$ of R_n was found to increase linearly with increasing ionic strength (fig. 3).

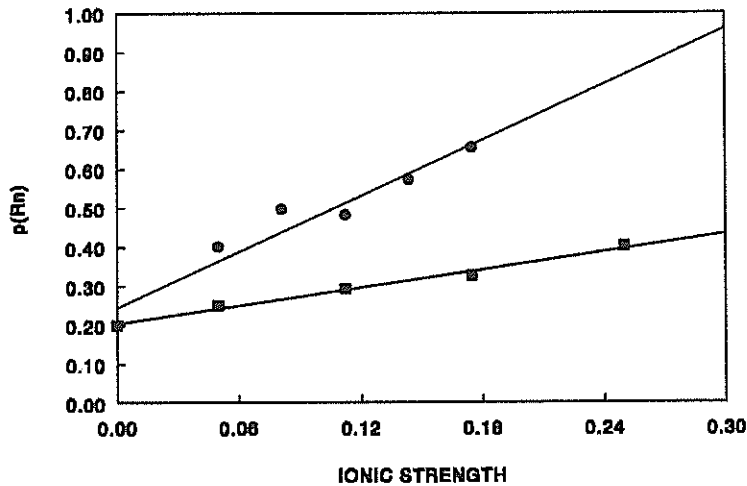


Figure 4. Plot of pR_n versus ionic strength of (\odot) sodium sulfate and (\blacksquare) sodium chloride.

Addition of sodium sulfate depresses R_n to a greater extent than sodium chloride. In addition, pR_n was found to be a linear function of sulfate concentration with a correlation coefficient of 0.967 (fig. 4), and can be described by the following empirical equation:

$$pR_n = K C + pR_{n0}, \quad (2)$$

where the constant K equals 7.46×10^{-5} , C is the sulfate concentration in ppm, and pR_{n0} is $-\log$ of R_n for pure water. Addition of 6,000 ppm sulfate (Na_2SO_4) reduces R_n by about 65%. The rate of neutralization can be further depressed by elevated levels of other ions, which increase the ionic strength.

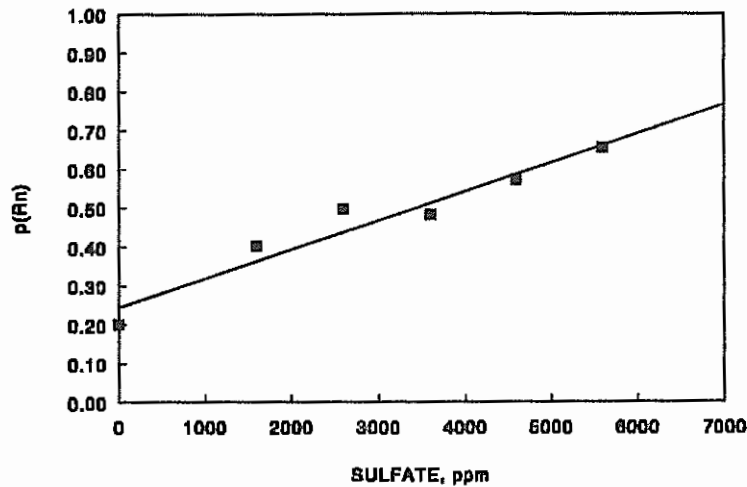


Figure 3. Plot of pR_n versus sulfate concentration for solutions of sodium sulfate.

The above changes in R_n can be explained in terms of a stationary film model. Water films are known to form at the interface between a liquid and a surface (Perry 1973). Neutralization is accomplished by the diffusion of ions through the film, and their motion can be described by the following equation (Castellan 1971):

$$l = Z e / 6 \Pi \eta r \quad (300), \quad (3)$$

where l is the mobility, Z is the charge of the ion, η is the viscosity of the solution, and r is the ionic radius. Increasing the ionic strength of the solution increases the viscosity of the medium (Weast 1978), which reduces the ions mobility and slows the rate of diffusion. Additionally, ion pairs and larger aggregates of ions may form at higher ionic strengths (Fuoss 1959), which increases the radius of the diffusing particle and reduces its mobility.

The effect of the oxalate anion on the rate of calcium carbonate neutralization was studied to further clarify the role the sulfate ion plays in depressing the neutralization rate. Calcium oxalate is nearly insoluble in water. Addition of low levels of sodium oxalate resulted in the formation of a white precipitate on the surface of the marble chips, which completely stopped the reaction.

Sulfate and oxalate anions further depress R_n because their calcium salts are relatively insoluble. For solutions containing elevated levels of sulfate, the concentration in water film is nearly equal to that in the bulk water. However, the concentration of calcium ions in the water film should be much higher than that in the bulk water. Their concentration is governed by the K_{sp} of calcium sulfate, $K_{sp} = 2.45 \times 10^{-5}$ (Weast 1978), and the concentration of sulfate ions. With elevated levels of sulfate, the solubility of calcium ions in solution is depressed, as is the rate solubilization of limestone and R_n . Addition of oxalate anions to solution completely stops the neutralization process. The much lower $K_{sp} = 2.57 \times 10^{-9}$ (Weast 1978) of calcium oxalate severely limits the equilibrium solubility of calcium ions. The ions that dissolve quickly reprecipitate onto the chips' surface as calcium oxalate. This process is similar to armoring, which occurs when mine drainage containing elevated levels of Fe^{2+} and Al^{3+} contacts limestone (Hedin 1992). Fortunately, mine drainage does not contain significant levels of oxalate.

The depression in the neutralization rate has broader implication beyond Four Mile Run. A similar process occurs in waters flowing through anoxic drains (Brodie 1990) and mine spoils containing limestone (Brady 1990). Although elevated levels of sulfate may not severely reduce the rate of neutralization, the results of this paper suggest that the neutralization capacity of systems should be overdesigned whenever possible.

Conclusion

Four Mile Run has received mine drainage from deep mines for over two decades. In that time the flow rate, pH, and alkalinity have increased, while the acidity, iron, manganese, and sulfate concentrations have decreased. The overall loadings of iron, manganese, and sulfate to the stream have not changed significantly.

The change from acid to alkaline drainage is fairly typical for mine effluent in the surrounding area and probably involves a number of complex processes. One factor contributing to the switch from acid to alkaline mine drainage is the lower ionic strength and sulfate concentrations. These two factors have been shown to depress the rate of acid neutralization. Addition of 6,000 ppm sulfate reduces the rate of neutralization by 65%. A similar reduction in the rate of neutralization may occur in other abatement processes containing elevated levels of sulfate or ionic strength.

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