

GEOCHEMISTRY

GENERAL CONCLUSIONS

As part of the watershed study, a geochemical survey was conducted to determine the condition of the streams, with respect to coal mine drainage. The geochemical characteristics of coal mine drainage as well as the chemical reactions taking place between mine discharges and receiving streams were investigated with applications of the geochemistry to abatement procedures. Analysis performed on water samples included pH, acidity, alkalinity, Ca, Mg, Na, K, Al, Ni, Si, Total Fe, Fe^{2+} , and SO_4^{2-} .

Water pollution caused by coal mine drainage has destroyed or severely affected large parts of Pennsylvania. Over 3,000 miles of streams and 302,400 acres of wildlife habitat have been adversely affected by strip and surface mining as a result of coal production in the Commonwealth (5). In the Mahanoy Creek watershed alone over 84 MGD of mine drainage enters the streams resulting in deterioration of water quality throughout the watershed.

BRIEF REVIEW OF COAL MINE DRAINAGE

The general nature of acid mine drainage, although complex, has been well reported to date (6) (8) (9). During mining, ground-water movement as well as aquifers are disrupted, bringing subsurface waters in contact with pyritic materials in the coal and in the associated rock strata. In many cases the flow directions are so drastically changed that the mine workings are inundated forming underground mine pools and causing water to drain through numerous mine openings. By exposing the sulfuritic materials, primarily pyrite and marcasite, to air and moisture, oxidation of these minerals occurs, resulting in products such as ferric hydroxide, ferrous sulfate and sulfuric acid. The ferric hydroxide and ferrous sulfate are commonly referred to as yellow boy.

The result of these oxidation reactions is a complex water system containing ferric and ferrous iron, aluminum and iron oxyhydroxides, various sulfur complexes including sulfate ions and other soluble salts. Precipitation of iron hydroxides will also remove other cations such as Ni by adsorption processes and coprecipitation. Changing equilibrium conditions as well as oxidation of iron sulfides by bacteria are other significant factors in the production of coal mine drainage.

SUMMARY OF GEOCHEMICAL CONCLUSIONS

The result of the geochemical study of the Mahanoy Creek watershed is summarized as follows:

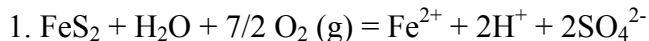
1. The analysis of the mine discharges in the watershed indicates that the chemical composition of the drainage from any given coal mine has been found to be characteristic of that particular mine.
2. There is a tendency for concentrations of pollutants within the study area, especially sulfate and pH in mine waters, to increase as the season changes from high to low flow periods.
3. There are two distinct types of mine drainage occurring in the watershed, alkaline - pH >6.1 with net alkalinity and acidic discharges - pH < 4.5 with net acidity.
4. Acidic discharges are characterized by lower total Fe, Na, SO₄, K, Mn, Mg, Ca, and higher Al concentrations.
5. Ni and Si content did not show any significant differences between the two types of mine discharges.
6. Silicate minerals may be breaking down aiding, in some cases, in the neutralization of acid mine waters.
7. Silt and culm banks become important contributors to acid mine drainage on a local basis.
8. The Little Mahanoy Creek Subwatershed is the only basin not affected in coal mine drainage.
9. Mouse and Schwaben Creeks in the polluted Lower Subwatershed are not affected by coal mine drainage.
10. North Mahanoy Creek, the entire length of Mahanoy Creek, Shenandoah Creek, Big Run, and Zerbe Run all are polluted by coal mine drainage. Streams severely polluted by mine waters include: Zerbe Run, Shenandoah Creek, Big Run, and the Eastern section of Mahanoy Creek (from the head waters east of Mahanoy City westward to Gordon, PA).

CHEMICAL ENVIRONMENT

The formation of coal mine drainage is dependent on several factors. Of primary concern is the amount and availability of the reactants. The amount of iron sulfides

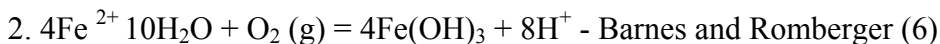
present as well as the form of the sulfide minerals is also of importance. It is generally assumed that as the amount of iron sulfides increases acidity increases. However, this is not always the case. In fact, the particle size of the iron sulfides has been shown by Caruccio (7) to be the controlling factor in many cases where the small particles of pyrite (2-15 microns) rapidly decompose when exposed to the atmosphere, and where coarse grains of pyrite (greater than 50 microns) remain stable. In addition, marcasite usually will produce more acidity than pyrite as a result of its crystal structure.

A distribution of the sulfur content of anthracite is shown in Figure 12. The sulfur usually exists as sulfides, sulfates and organic free sulfur. Since most of the sulfur is held by the sulfide minerals, the sulfur content may be an indirect indicator of the amount of iron sulfides and hence may indicate general trends in potential acid production. In the presence of sufficient oxygen (air) and moisture the iron sulfides will readily decompose. The rate of oxidation (and hence generation of acid) is also dependent on the high porosity of the sulfides. As oxygen content of the chemical environment increases so does the oxidation of the sulfides (10). The effect of water and oxygen can be seen in the following reaction:



Barnes and Romberger (6) have indicated that pH's of 3 or less can result from oxidation at partial pressures of oxygen at 10^{-60} atmospheres or more. This indicates that air sealing of mines above the water table will be largely ineffective and impractical. For this reason as well as the numerous mine openings in the Mahanoy Creek watershed, mine sealing in most cases was rejected as an abatement technique.

The presence of bacteria also greatly increases the rate of oxidation of pyrite and its associated products as in reaction 1 and the following reaction:



The two parameters which most effectively describe the equilibrium conditions encountered in coal mine drainage are oxidation potential (Eh) and pH. Additional parameters important in influencing the solubility of iron are dissolved carbon dioxide and sulfur species. The Eh-pH diagram shown in Figure 14, p. 44 indicates the limiting conditions and the chemical behavior, which also determines the stability fields of the various elements involved in coal mine drainage. Three assumptions which are made with the diagram in applying it to real systems are:

- a. That the system is at equilibrium
- b. that complexes not considered in the calculation of the diagram are absent or exist in negligible amounts.

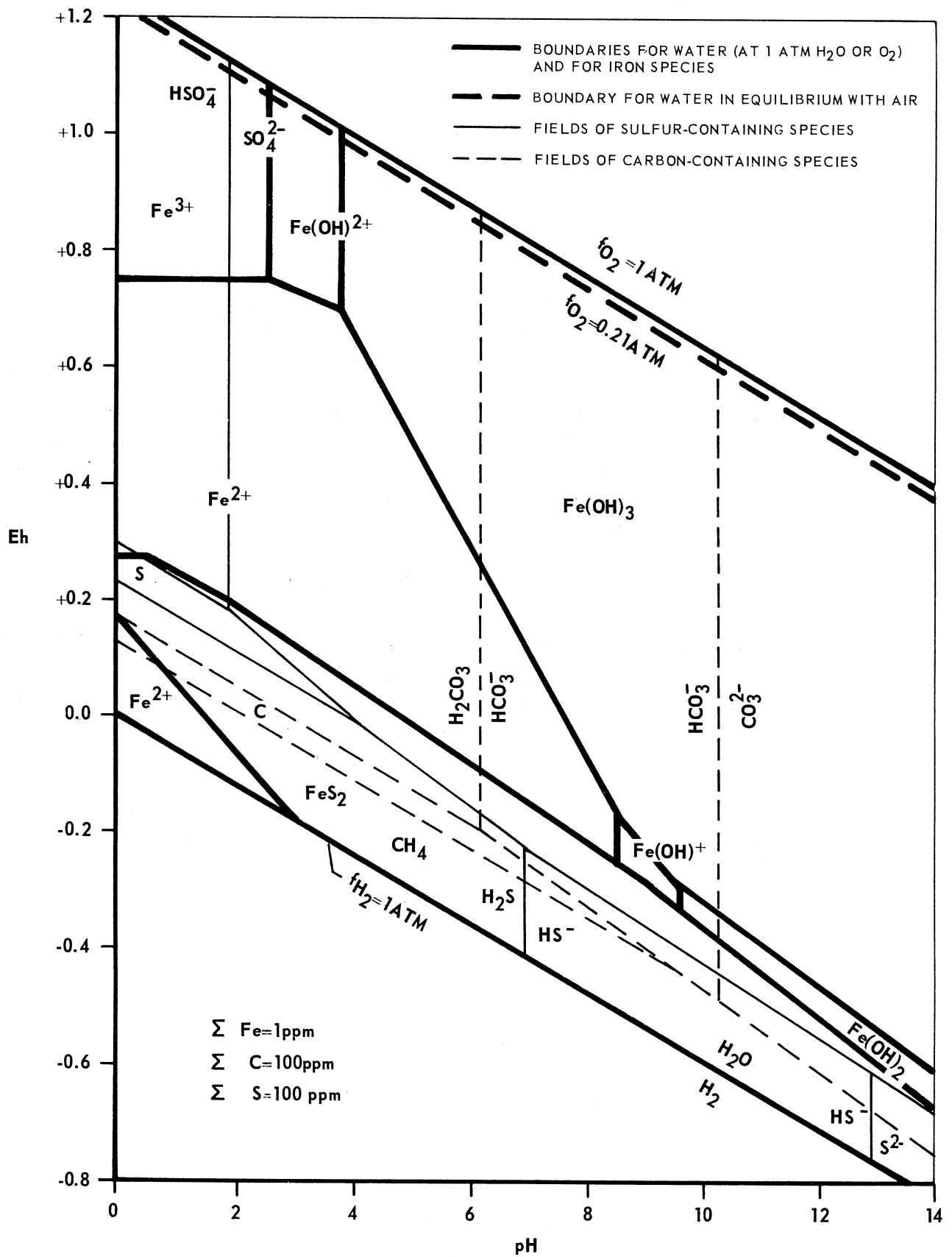


Figure 14. Stability fields of various elements involved in coal mine drainage
(After Barnes and Romberger, 1968)

- c. that solid phases shown in the system are relatively pure.

Oxidizing environments are indicated by a positive oxidation potential and reducing environments by a negative potential. Normal surface waters in contact with the atmosphere have a pH range between 6 and 8 and potentials between .35 and .6 volts. Both pyrite and marcasite with a composition near FeS_2 are out of equilibrium under these conditions (see Figure 14).

The formation of acid due to the oxidation of iron sulfides (the principal source of acid) usually occurs by at least two steps as in reactions 1 and 2. Both reactions 1 and 2 result in large amounts of acid produced through the decomposition of each mole of pyrite or marcasite oxidized. Ferrous and ferric sulfates are additional sources of acid (see Tables 4 and 5). The Eh-pH diagram shows the conditions under which the principal reactions occur. Usually iron sulfides are not found to decompose directly to ferric hydroxide. This is shown in the Eh-pH diagram where ferrous iron is formed in all cases before the hydroxide is formed. This indicates that the decomposition of iron sulfides can occur at relatively low Eh conditions found in some mine waters. It also explains the relatively high ferrous iron found under alkaline and neutral pH values in the streams of the watershed.

The iron now mobilized in the ferrous state will oxidize in the mine pools as oxygen is replenished by circulating waters or as the iron approaches the surface environment through mine discharges and enters streams. Indeed, relatively high amounts of ferrous iron are found in most discharges and streams in the Mahanoy Creek Watershed. The stability field of Fe^{2+} indicates it is stable over a wide pH range if Eh values are only slightly oxidizing. Lower dissolved oxygen values in the streams of the watershed due to higher BOD values from the sewage present in the streams may result in lower than expected Eh values, thereby increasing the mobility of iron. The presence of the ferrous iron, an acid precursor, inhibits higher net alkalinities of the streams.

Under the conditions indicated in the Eh-pH diagram there are insufficient amounts of dissolved carbon dioxide or other carbonate species to form a stable iron carbonate as siderite. Only in waters containing much greater amounts of total carbon will an iron carbonate be stable in the conditions shown in Figure 14.

NEUTRALIZATION

Dilution effects, geology, and the role of silicate hydrolysis reactions in the neutralization of acid mine waters of the watershed were studied. The interdependence of these factors should be noted. Dilution includes water originating from surface runoff such as streams directly entering deep mines, water percolating through soil, and water

TABLE 4
INORGANIC CONSTITUENTS OF COAL

ELEMENT	
Si	Silicates and Sand
Al	Alumina in Combination with Silica
Fe	Pyrite and Marcasite Ferrous Oxide (in small quantities) Ferrous Sulfate Ferric Oxide Ferric Sulfate Iron Silicates "Organic" Iron
Ca	Carbonates, Sulfate, Silicates
Mg	Carbonates, Silicates
Na, K	Silicates, Carbonates, Chlorides (in small quantities)
Mn	Carbonates, Silicates
S (Inorganic)	Pyrite, Marcasite Ferrous Sulfate (in small quantities) Ferric Sulfate Calcium Sulfate
P	Phosphates

(After Pennsylvania State University Special Research Report SR-83)

TABLE 5

COMMON ELEMENTS FOUND IN THE ASHES OF COAL

CONSTITUENT	PERCENT
Silica (SiO ₂)	30-60
Aluminum Oxide (Al ₂ O ₃)	10-35
Ferric Oxide (Fe ₂ O ₃)	5-35
Calcium Oxide (CaO)	1-20
Magnesium Oxide (MgO)	.3-4
Titanium Oxide (TiO ₂)	.5-2.5
Alkalies (Na ₂ O + K ₂ O)	1-4
Sulfur Trioxide (SO ₃)	.1-12

(After Pennsylvania State University Special Research Report SR-83)

originating from disturbed aquifers. pH can be increased in the acid mine pools by simple dilution and by buffering when water in the mine pool is mixed with water containing various concentrations of HCO₃⁻. The effects of dilution on pH of acid mine waters can be shown using the following equation from Barnes and Romberger (2):

$$pH_2 = pH_1 + \text{Log } X$$

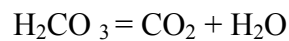
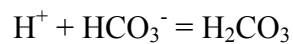
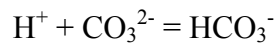
Where pH₂ = Final pH, pH₁ = initial pH, x = ratio of final to initial volume. pH of the diluent is assumed to be 7. For example, if 100 volumes of water having a pH = 3.5 are diluted to a final volume of 10,000 volumes, x = 100 and the final pH would be 5.5.

A concentration of 10 ppm HCO₃⁻ in water results in much less diluent being used for neutralization due to the efficiency of bicarbonate neutralization. For example, acid water with a pH = 3.5 and containing 10 ppm HCO₃⁻ would need a dilution factor of 1:4 thus 100 volumes of water would be diluted to a final volume of 400 volumes, with a final pH = 7.0 (6).

The types of rock present, amounts of chemical constituents in the rocks, mineralogy, and structural geology all affect the quality of water in the mine pools. The role of iron sulfide has been previously mentioned. The porosity of the unsaturated zone in

the subsurface environment as well as amount and type of fractures, joints, and faults control the rate of water infiltration and the travel path in the subsurface environment. The amount of carbonates in the rock strata, although variable, could aid in the neutralization of acid waters. Due to the lack of carbonate rocks in the watershed the streams do not contain sufficient bicarbonate concentrations which could neutralize acid mine water.

Although the existence of carbonates in coals (see Table 4) is known, only small amounts are present resulting in insignificant amounts of bicarbonate produced. However, calcareous shales are found throughout the eastern portion of our watershed. In the vicinity of Mahanoy City, boreholes have indicated the presence of calcite and calcite and quartz veins which if exposed in the mine pool, could contribute to neutralization (12). Rocks containing calcite veins are also found in several of the refuse banks in the watershed which may influence the quality of leachate produced from some of these refuse piles. The carbonates decompose through a series of chemical reactions which result in neutralizing the acid waters thereby raising pH, and then precipitating the iron contained in these waters. The reactions are as follows:

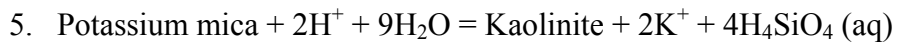
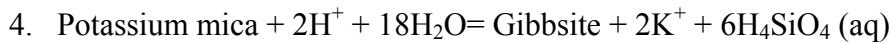
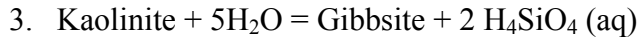


A comprehensive trace element analysis of the mine waters and streams of the watershed (data appears in Table 6, p. 51) indicates that the role of silicate reactions may be important, at least on a local basis, in the neutralization of acid mine waters. Silicates present in the coal or in the associated rock types decompose under acid conditions and in the process of breaking down release alkali metals and silica. The inorganic constituents of coal which are, in part, a source of these silicates and a list of elements found in coal are shown in Tables 4 and 5.

Alkalinities of several samples coupled with high sulfate indicate that the sulfate was derived from acid mine drainage which was neutralized. The Packer 5A Discharge having a net alkalinity of 115 ppm and a sulfate concentration of 1,037 ppm is an example. Equilibrium reactions indicate that a sulfate content of 740 ppm is usually associated with an acidity of 75 ppm (as CaCO_3). This suggests that neutralization has occurred and has resulted in an alkaline discharge.

Silica concentrations in certain mine discharges ranging between 20 and 45 ppm (i.e. samples 25, 29, 31, and 38) as well as high magnesium, sodium and alkalinity

concentrations suggest that silicates are breaking down through hydrolysis reactions. In the process of hydrolysis these elements as well as aluminum and potassium are released. The numerous shales and claystones of the region are the sources of these silicates. Typical shales in the region contain 2-31 percent kaolinite, 0-1 percent feldspar, 34-51 percent mica (illite), 35-36 percent quartz and 0-2 percent chlorite-vermiculitemontmorillonite (13). Examples of chemical reactions which may occur follow:



Both potassium and aluminum (Gibbsite) are released as shown in the above reactions. However, the potassium has a strong tendency to be adsorbed by clays and iron hydroxides and will not stay in solution. Low potassium values result. When sufficient silica is present as is the case with certain discharges aluminum appears to rapidly precipitate, forming a poorly crystallized aluminum hydroxide such as gibbsite. Kaolinite can also breakdown as follows:



The aluminum hydroxide eventually precipitates, forming aluminum compounds.

In reactions 4, <5 and 6,> pH will be increased as the hydrogen ions are used. This results in neutralizing the acid mine water in the mine pools. Carbonates may account for calcium, some magnesium, and the neutralization of mine waters as well. Neutralization is probably a result of carbonate and silicate reactions with carbonate reactions predominating. However, magnesium concentrations which are higher than calcium concentrations as well as a lack of dolomite present (which could contribute magnesium) indicate that silicate reactions may predominate in certain instances. Supporting this are the high silica and alkali concentrations.

Two basic types of coal mine drainage have been identified in the watershed: 1) alkaline (net alkalinity, pH >6.0), and 2) acid (net acidity, pH <4.5). Acid discharges are generally characterized by lower total iron, ferrous iron, sodium, potassium, manganese, magnesium, calcium, and sulfate concentrations, and higher aluminum concentrations when compared to the alkaline discharges. Nickel and silica did not show any significant differences between the two types of mine discharges. General concentration values for the major pollution factors other than acid content of the two types of discharges are:

	ACID	ALKALINE
Total Iron	16 ppm	27 ppm
Ferrous Iron	9 ppm	20 ppm
Sulfate	500 ppm	720 ppm
Aluminum	10 ppm	1 ppm

On a local basis leachates from silt and culm banks can be a significant source of coal mine drainage. Between sample sites #2 and #3 silt banks containing pyritic material contribute significant concentrations of iron and acid as well as large amounts of silt to the North Mahanoy Creek. Substantial amounts of pyrite are found throughout several silt and culm deposits along Mahanoy Creek between samples #43 and #47 and samples 5 and 8.1 which significantly affect water quality as shown in Figure 17, p. 94. In addition, oxidation of ferrous iron to ferric iron also occurs between samples #43 and #47 resulting in additional amounts of acid produced. Evidence for this reaction is the abrupt decrease in ferrous iron between these two sample sites.

The geochemical analysis was also applied to other pollution source problems in the watershed. Acidity, total iron, ferrous iron, aluminum, sodium and silica indicate that Ashland Nos. 1 and 2 Discharges (samples 40 and 41 in Table 6) are two separate mine discharges draining different sections of the tunnel mine or possible separate mines and not, as previously reported before this watershed study, a single discharge which had two different overflow locations. This is important in determining the abatement measure to be used for these discharges.

The contribution of three silt banks in the production of coal mine drainage was evaluated using the geochemistry data. The silt banks were located between sample sites 52 and 55, 5 and 8a, and 2 and 3. Higher acid and total iron values were found downstream of the silt bank located west of site 52. However, other analytical data were inconclusive. Between sites 5 and 8a silt banks are probably contributing acid but the water analyses other than acid did not indicate a major influence on water quality of the Mahanoy Creek. The analyses for pH, aluminum, total iron, and sulfate did indicate a major influence of siltbanks on water quality in the North Mahanoy Creek between sites 2 and 3. To substantiate these results a field visit was conducted in the area which found several refuse pile leachate sources.

In Girardville two large water-filled strip pits located just above several discharge points were thought to be directly contributing mine drainage to mine discharges 10 and 11 as well as several seepages originating from the refuse piles which appear to separate the pits and mine discharges. Water analyses were taken of the two water-filled pits and

compared to water analyses of the mine discharges. The mine discharges had significantly lower pH values and much greater acidity, total iron, ferrous iron, manganese, silica, potassium and sulfate. Total and ferrous iron, manganese and silica values indicate that water from the pits is picking up substantial amounts of pollutants. Considering the short distance separating the pits and discharges, the concentrations are not the result of direct flow through pyritic materials in the refuse pile, since a longer residence time is required to pick up these constituents. The analyses therefore indicate that the water from the strip pits enters the Girard mine workings first and then discharges at several mine openings located along Mahanoy Creek. This conclusion has been supported by mine map data of the area.

Mine pool stratification has been indicated by several chemical analyses of the mine discharges in the watershed. An example is the Bast Mine Pool. Chemical analyses at three different elevations in the mine pool (samples 31, 34, 38) indicate that layers of differing water quality exist. The top layer (Site 31) at 1020 feet elevation is alkaline and contains very high concentrations of iron, manganese, and silica. The middle layer (Site 34) at an elevation of 930 feet is highly acid and contains higher sulfate and aluminum concentrations with other chemical constituents at approximately the same levels. At an elevation of 874 feet the lower layer (Site 38) becomes alkaline with lower iron, manganese, and silica and no aluminum. These results indicate that in certain mine pools, where stratification exists, the elimination or reduction in water entering the mine pools may cause the layers to change in water quality. This may result in changing certain alkaline mine discharges to acidic discharges. Acid mine drainage may also become alkaline. To determine the changes in water quality more precisely a further study is recommended.

TABLE 6

CHEMICAL CHARACTERISTICS OF VARIOUS WATERS OF THE MAHANOY CREEK WATERSHED

Sample	pH	Acid	Alk	TotFe	Fe ²⁺	Al	Ca	Mg	Mn	K	Na	Ni	SO ₄	Si
1*	3.3	80	-	1.7	-	22.6	.4	14.1	1.0	.8	4.9	.2	235	13.9
2	4.8	10	-	-	-	.4	.6	3.9	.1	.2	1.0	-	8	-
3	4.5	12	-	.4	-	.8	.6	5.9	.1	.3	1.0	-	40	-
4*	4.5	82	-	16.0	9.0	6.1	8.4	31.7	1.7	1.0	20.3	-	185	7.8
5	5.0	56	-	5.1	2.2	3.8	5.8	24.9	.9	1.8	15.5	.1	170	15.7
6	5.9	6	2	-	-	-	.7	3.9	.1	.2	-	.1	8	-
7*	6.2	190	64	59.0	56.0	.4	35.5	58.7	16.1	1.5	12.7	.4	850	6.3

TABLE 6 (Continued)

Sample	pH	Acid	Alk	TotFe	Fe ²⁺	Al	Ca	Mg	Mn	K	Na	Ni	SO ₄	Si
8.1	4.6	74	—	6.0	5.6	4.7	9.2	29.4	1.1	1.0	14.6	.2	165	5.7
8.2	6.2	194	64	49.1	46.0	2.1	50.0	58.7	12.7	1.6	12.0	.4	800	6.9
9	6.8	66	—	46.1	40.3	3.8	41.1	61.3	14.4	1.6	14.0	.4	800	8.1
10*	5.9	120	60	24.8	22.4	—	38.9	58.7	14.4	1.6	17.5	.2	700	4.7
11*	6.0	80	48	30.6	16.8	—	36.9	58.7	12.1	1.9	16.5	—	375	4.2
12*	5.6	48	4	19.4	14.6	—	32.1	58.7	5.8	1.7	13.6	—	90	4.9
13*	3.5	80	—	11.5	10.1	.8	33.9	61.3	7.4	1.8	16.5	—	425	6.5
14	6.8	74	2	40.2	39.2	3.4	40.2	64.8	12.7	1.6	13.6	.6	950	7.9
15*	6.3	100	256	27.2	26.9	—	54.0	66.6	26.3	1.7	14.8	.6	1050	7.0
16*	6.2	130	242	29.6	26.9	—	51.1	66.6	24.8	1.3	14.0	.3	1150	6.4
17	6.3	100	—	46.1	40.3	11.6	42.2	64.8	15.5	3.1	20.2	.9	775	14.0
18	6.2	100	34	24.8	1.1	10.5	42.3	64.8	12.1	2.8	20.2	.6	675	14.9
19	4.3	340	—	46.1	—	24.1	36.5	64.8	47.1	7.3	18.1	1.2	650	18.3
20	4.3	340	—	510.7	46.0	33.0	52.9	64.8	36.9	8.0	29.1	.3	950	27.5
21*	4.0	28	—	.3	—	2.0	2.3	15.0	.6	1.0	26.8	.3	60	.9
22	5.9	6	10	.1	—	—	1.8	7.2	.1	.4	4.0	—	30	.6
23*	—	—	—	—	—	—	—	—	—	—	—	—	—	—
24	4.1	320	—	66.2	60.5	44.8	42.3	63.0	36.9	10.0	20.5	.9	675	66.8
25	6.1	216	240	46.1	—	—	39.1	63.0	14.9	2.0	51.2	.6	1125	45.4
26*	3.6	380	—	22.5	—	10.0	47.2	64.8	18.0	3.56	60.8	.2	1375	17.9
27	4.9	200	—	50.7	43.7	33.2	34.6	70.5	27.1	7.0	25.9	.5	950	64.9
28*	6.4	—	288	1.2	—	—	43.4	63.0	8.8	2.4	51.3	.2	725	5.4
29*	6.6	80	244	31.8	20.2	—	47.4	64.8	19.9	1.3	18.1	—	900	24.3

TABLE 6 (Continued)

Sample	pH	Acid	Alk	TotFe	Fe ²⁺	Al	Ca	Mg	Mn	K	Na	Ni	SO ₄	Si
30	5.2	14	0	57.1	35.8	31.4	45.9	64.8	25.4	5.9	25.7	.3	675	65.9
31*	6.1	6	34	45.8	43.7	—	47.0	64.8	13.4	2.3	48.4	.2	800	44.8
32*	6.4	8	98	24.0	20.2	—	26.0	57.8	3.0	.8	8.3	—	275	19.9
33	6.2	6	88	30.5	30.2	3.2	54.1	64.8	21.7	1.9	21.5	.2	925	40.2
34*	3.4	360	—	41.4	22.4	15.3	57.1	68.5	13.4	.7	4.4	.4	975	41.1
35	6.4	16	56	39.9	39.2	5.3	42.3	64.8	20.3	2.7	19.2	—	800	56.0
36*	3.4	480	—	19.4	10.5	61.6	24.7	51.3	12.2	.8	6.2	.5	800	14.2
37	6.3	140	30	34.4	23.5	7.1	42.3	64.8	19.6	2.4	17.0	.3	875	48.4
38	6.5	80	146	27.9	24.6	1.6	37.0	64.8	5.4	1.1	15.0	.2	900	37.3
39	6.6	80	24	35.8	34.7	4.9	53.4	66.6	2.0	1.8	15.0	.3	825	49.7
40*	5.6	100	4	33.1	30.2	.7	39.0	66.6	7.5	1.4	18.5	.2	800	35.5
41*	7.1	—	406	7.6	—	—	47.2	66.6	2.9	2.1	51.3	—	825	9.0
42*	6.7	8	8	1.5	—	1.1	35.4	43.8	.7	.3	8.1	—	135	5.5
43	6.8	80	60	20.7	20.2	5.5	67.2	64.8	16.9	1.7	19.2	—	800	8.4
44	6.8	8	34	.3	—	—	6.8	17.0	.1	.5	5.7	—	45	1.9
45	6.7	8	8	—	—	—	1.6	7.2	—	.2	5.7	.3	9.0	.5
46	6.8	8	24	.3	—	—	5.1	15.0	—	.5	5.7	—	11	1.5
47	6.7	80	54	18.5	17.9	5.5	39.6	66.6	13.7	1.5	14.6	.2	825	8.0
48*	6.3	240	550	37.8	37.0	—	51.2	64.8	8.6	4.0	152.7	.2	1100	5.7
49*	6.4	140	414	16.4	15.7	—	44.6	66.6	4.1	1.4	18.8	—	775	4.9
50	7.3	60	334	24.0	11.2	—	41.1	64.8	3.9	1.4	41.6	—	725	5.2
51	7.6	—	228	1.8	—	—	39.1	64.8	2.0	1.2	34.4	—	550	3.7
52	6.5	20	50	14.2	6.7	6.1	40.2	64.8	13.2	2.5	21.3	.5	600	27.8

TABLE 6 (Continued)

Sample	pH	Acid	Alk	TotFe	Fe ²⁺	Al	Ca	Mg	Mn	K	Na	Ni	SO ₄	Si
53*	3.3	76	—	2.7	—	3.0	2.1	18.1	1.8	.6	7.2	.5	175	12.5
54*	6.5	40	68	26.4	13.4	1.5	34.6	64.8	5.0	1.0	6.2	—	525	7.1
55	6.2	40	36	20.6	7.8	4.2	43.4	64.8	12.2	1.9	16.0	.2	600	7.2
56*	3.9	260	—	27.2	24.6	12.0	38.0	66.6	11.8	1.2	6.2	.6	800	7.8
57	6.1	40	22	26.4	10.1	4.2	43.4	63.0	13.7	1.1	17.0	.3	825	7.2
58	6.5	60	26	18.9	15.7	3.4	42.3	64.8	13.7	1.5	15.0	.3	525	6.4
59	5.8	60	6	16.1	—	5.1	42.2	64.8	9.1	1.7	12.9	—	400	8.7
60	6.2	40	16	21.0	—	7.2	39.1	64.8	10.3	1.2	14.0	.3	475	8.9
61	5.9	10	8	.3	—	—	2.2	11.0	—	.1	3.5	—	5.0	3.1
62*	3.9	180	—	41.6	37.0	3.0	32.9	66.6	7.9	1.0	3.5	.7	550	6.5
63*	3.3	120	—	9.4	—	4.7	1.5	20.2	1.7	.5	1.7	.5	200	8.8
64	3.8	180	—	13.3	12.3	4.7	33.0	59.5	3.7	1.1	4.4	.5	375	21.4
65*	3.2	180	—	2.5	—	3.4	1.6	19.2	2.1	.4	.9	.2	175	3.2
66	3.2	220	—	30.6	13.4	12.1	22.6	49.8	3.7	.6	3.5	.5	325	20.0
67	5.5	140	10	22.0	—	9.0	35.3	63.0	9.4	1.4	14.0	.2	600	39.6
68	6.5	14	48	.4	—	—	8.0	21.3	.1	1.1	4.4	—	425	2.0
69	6.3	10	48	.2	—	.8	13.1	24.7	.1	1.1	6.2	—	6	1.1
70	7.2	10	68	.2	—	—	19.5	29.4	—	.8	4.4	—	18	.7
71	5.7	80	6	30.5	—	10.5	42.3	63.0	9.4	1.3	12.0	.3	650	43.8

This analysis was completed in November, 1973 and does not represent average values.

* =Mine Discharge.

No discharge appeared at sample site 23 during November.