

## CONCLUSIONS

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A. GEOLOGIC SETTING OF AREA

The particular watershed is located on the Allegheny Plateau and drains to the Ohio River System. Local ridges and hills rise 300 to 400 feet above valley floors and slopes vary from gentle to very steep. The area lies on the axis of the Shawmut Syncline with the exposed surface rocks being those of the Allegheny Series. Higher ridges are probably capped with rock of the Conemaugh Series.

Mining in the area under consideration was begun at the turn of the century with the opening of drift mines into the Lower Kittanning coal seam which averages approximately 30 inches in thickness. The original headings were driven in the valley to the east of Brandy Camp and gravity drainage of mine water was possible. (See Appendix A3)

As local dips and folds were encountered, additional headings were driven, probably to avoid pumping and for ventilation, since only a few of the headings were used as haulways. Twenty-eight separate openings are known leading to the two seams which were mined.

The mine in the Lower Kittanning Seam, (The Elbon Mine) had been worked out by the 1930's and a second mine, called the Shawmut Mine, was opened in the Middle Kittanning Seam, lying approximately 50 feet higher than the lower mine. This mine lasted until 1950, with a small force (5 men) working the mine as late as 1959. (Appendix A4)

Mine maps show that the room and pillar method of mining was employed with headings spaced approximately 500 feet apart. One large area in the lower mine was apparently mined out completely, with pillars removed, although it is not known whether this was done before or after the upper mine was worked.

In the post-war period, the advent of larger surface mining machinery led to the removal of much of the barrier which had been left by the deep mine operation. Absence of backfill regulations permitted removal of the coal without subsequent land restoration. The situation at that point in time, is generally what still exists today. (Appendix A2) Some surface mining is taking place on the Curry Run watershed with the result that old spoil piles are being leveled and regraded by the coal operators.



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As outlined in the preceding paragraphs, the situation does not seem unduly alarming, except that the lower mine is discharging approximately 0.75 MGD of acid drainage. In actuality, the deep mining created the underground conduits for a giant filter, and the strip mining ensured that most of the runoff from the overlying hills, would enter the underground mine by way of the strip mine ponds and come in contact with acid producing materials. (FeS<sub>2</sub> minerals, pyrite and marcasite).

It is the result of the two mining methods in the above geologic setting which is considered the major factor contributing to the formation of acid drainage.

Overlying strata above the mines include several layers of sandstone, slate, and shale. The Freeport Group, immediately overlying the Kittanning Group, probably contains sandstone and shale, and possibly the Freeport clays and limestone.

A review of a report to the Coal Research Board by Caruccio and Parizek, considered the low vertical permeability of this type of formation and suggested that the prevalent flow pattern for ground water in such strata is horizontal, rather than vertical. If we neglect the effects of the "retreating" of the mine, it is not unreasonable to theorize that a deep mine would not receive much seepage through the mine roof if the room and pillar method were used with full roof support. The critical factor, of course, is the condition of the mine roof.

In the case of the mines in question, some areas were worked out completely and the pillars were removed, however, no evidence has been found that the resulting caving reached the surface. For this reason, it is believed that a large portion of the water reaching the deep mines enters via the surface mines along the outcrop of the coal seams.

Since the surface mining was done prior to enactment of the recent strip mines laws, the spoil was not regraded and many ponds are to be found along the high-walls. A large portion of the Middle Kittanning excavation lies directly over mined-out workings in the Lower Kittanning seam. The two seams are separated by an average of thirty-six feet ( $\pm$ ) of shale and a three foot thick bed of clay which lies beneath the Middle Kittanning coal. It is probable that in areas where



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surface mining was above the deep mine in the lower seam, the shale and clay separating them is highly permeable.

This assumption is further substantiated by the fact that all of the flows leaving the system do so by way of the Lower Kittanning seam. The strata separating the two veins are apparently quite permeable within the geographic limits of the deep mines and it would be illogical not to expect the same (or even greater) permeability along the outcrop where the strip mining took place.

Observation of the many ponds found along the high walls turned up few that showed any evidence of surface water courses leading away from there. Thus, most surface waters reaching the ponds have to leave by evaporation or percolation.

Two such ponds were observed which were receiving a significant runoff from small water courses above the high-wall but had no outlet at the time. Apparently, all water which did not leave by evaporation was percolating directly into the mines below.

Later investigations revealed that these ponds were directly over an old heading in the Lower Kittanning Seam. Other detailed field exploration would probably reveal the presence of many other such "sink holes" feeding the surface waters into the mine. No attempt was made to catalog all such situations because of the futility of trying to handle the problem by diverting an individual trickle. The potential for such a situation is very high and only major surface restoration can alleviate the problem.

The hills overlying the mine comprise several thousand acres, but a close examination has turned up only two surface streams draining these areas, and most of the flow of these streams emanates from spoil piles. The larger of the streams (McCauley Run) traverses a valley that runs over the mine workings of the Lower Kittanning seam. While the stream flow does not disappear completely, this is certainly a "recharge area" for the mine.



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B. STREAM WATER QUALITY

1. Discussion of Stream Quality and Mine Discharges

The major flows leaving the mine are identified as Sampling Points #1, #2, and #3. (See Appendix B-1) From the Summary attached it can be seen that these three flows contribute 1000 pounds net acidity per day (as CaO<sub>3</sub>) to Brandy Camp Run, These flows are all from the Elbon Mine and are draining from the Lower Kittanning seam.

Sampling Point #4 is located on Brandy Camp Run just upstream from its junction with Toby Creek and the data reveals that dilution by surface waters is significantly lowering the acid concentration. Part of the reduction is undoubtedly due to the natural alkalinity of the surface streams.

Sampling Point #5 is located at an old coal tipple at the foot of the ridge between McCauley Run and Curry Run. The flows leaving the mine at this point were very low and although the drainage was strongly acidic, the total load in pounds acid per day was insignificant.

The surface streams draining the areas over the mine are in relatively good condition, in spite of the extensive strip mining in the area. Sampling Points #6 and #7 are located on McCauley Run and indicate that the acidity and iron are not a problem in spite of the fact that most of the runoff must pass through old strippings before it reaches the valley floor. Sampling Point #11 on Curry Run revealed the same situation. It should be noted, however, that the sulfate concentrations show that a moderate amount of acidity had been formed and was subsequently neutralized.

Sampling Point #8 is located at an old heading near Hays Run at the eastern extremity of the Elbon Mine. The flow was very low, being on the high side of the mine, and probably originated in the overburden near the entrance to the heading. Because the heading has been caved at a point further in, the localized flow was forced toward Hays Run.

Sampling Point #9, on Hays Run, indicated the effect of a discharge originating in the old Kyler Mine located on the east side of Hays Run (not a part of this project). At times this discharge was milky white in color, possibly due to intensive lime applications in a strip mine operation further to the northeast, in the vicinity of the Kyler Mine.



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Sampling Point #10 is on Toby Creek above its junction with Hays Run and the low pH and high acidity is a result of the drainages from the mines in the Coal Hollow area.

Sampling Point #12 is also on Toby Creek near Brockport above the junction with Johnson Run. The pH is still low but the net acidity has been reduced due to the effect of runoff from several streams draining the south slopes of the valley.

The water quality at these locations was monitored for a period of one year, with flow being monitored for the major mine discharges. The flows in the streams were not measured because of the large weir structures which would have been required.

Problems were encountered at Sampling Point #2, where the measuring weir was destroyed by vandals on one occasion and torn out on another. At Sampling Point #3, the monitoring was discontinued after the property owner ordered company personnel off the property.

## 2. Statistical Analysis of Discharge Quality

A linear regression equation was computed for the data points obtained when acid load (lbs/day) is plotted against flow for discharge #1. The resulting equation was as follows:

$$Y = 5 + 2044X$$

Y represents acid load in pounds per day (as  $\text{CaCO}_3$ ) and X represents flow in M. G. D. The correlation coefficient was 0.9812 and the coefficient of determination was 0.9659, indicating that for the data analyzed (and within the range of flows sampled), 96% of the variability in acid load can be attributed to the variation in the flows observed.

It should not be concluded, however, that flow alone is the responsible agent. It is possible that some combination of factors related to flow is the controlling factor in the chemical-biological process by which the acidity is generated.

The analysis does indicate, though, that for a reduction of flow we can expect a corresponding reduction in acid discharged from the mine.



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This being the case, the proper method to be used to abate the pollution would be the elimination of the flows passing through the mine.

This assumption must be carefully examined for two reasons. First, there is no practical way to exclude 100% of the water from the mine. Second, at the nearby Blue Valley-Elk Mine complex the flow continues almost as it did on the day the mines closed in 1966 but the flow character has become alkaline. This spontaneous improvement in the Blue Valley-Elk Mine discharge is of considerable interest since the geologic setting was quite similar to that of the Elbon Mine.



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C. COMPARISON OF ELBON MINE AND BLUE VALLEY-ELK MINE

1. Physical Comparison

The details of the Blue Valley-Elk Mine complex are as follows:

The Elk Mine, located on the west side of Route #219 just above the village of Elbon, is an old mine which was abandoned several decades ago and the entries were closed by collapsing the overburden. The entry adjacent to Route #219 became the drainage point for the mine and also served to drain the more recent and larger Blue Valley Mine to the north. The drainage prior to 1967 was acid and contained a considerable amount of iron.

In December 1966 the Blue Valley Mine closed and all entries were closed.

The two mines are in the Lower Kittanning Seam and, at present, are only partially flooded. (The smaller Elk Mine is almost completely flooded, but the Blue Valley Mine is only 40% flooded.) It is notable that extensive caving took place in the Blue Valley Mine thus facilitating the downward migration of ground waters into the mine. Some strip mining of a higher seam (Middle Kittanning) has taken place over the western portions of the Blue Valley Mine (300 acres approximately) but the situation differs significantly from the Elbon Mine in that these workings were backfilled in accordance with the new law.

To summarize the above comparison, it appears that the nature of the two mine networks, Blue Valley-Elk versus Elbon, is very similar. Both mines are partially flooded; both have been caved to a large extent; both have strip mines over the deep mine workings. Both are in the same seams with the same geologic strata over-lying the mine workings. On major difference is evident. The Elbon Mine is overlain by strip mining almost none of which was restored, since it took place in the period of 1945 to approximately 1955, and the Middle Kittanning Seam was also mined out. No deep mining was done in the Middle Kittanning seam over the Elk-Blue Valley Mines.

During the course of the project, field personnel for this firm have been taking samples of a discharge exiting from the abandoned Elk Mine, located on the west side of Route #255 at Elbon.





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When the Blue Valley Mine was closed in December 1966, the character of the drainage was as follows:

pH	5.1
Total Alkalinity	2 mg/l
Total Acidity	140 mg/l
Total Iron	30 mg/l

The following is a summary of the average values for analyses of 23 samples obtained between April 1969 and April 1970:

pH	6.22
*Net Alkalinity	46 mg/l
Total Iron	24.1 mg/l
Total Manganese	6.48 mg/l
Sulfates	725 mg/l

An analysis of the stratigraphic profile of the overlying rock might provide the necessary information to determine the reason for the alkalinity. Recent bore-hole reports (Appendix "C") by drillers doing coal surveys make no mention of limestone but several seams of "light sandy shale" were reported. Since these holes were drilled for the purpose of locating and measuring coal seams, it is presumed that the drillers were not overly concerned with the true nature of the other strata through which they drilled. A search of geologic literature yielded the report of survey work done in the area in 1878 by Mr. Charles Ashburner, as a part of the Second Geological Survey. Ashburner commented in his report that the Johnstown Cement Bed, as found in the air shaft of the Dagus Mine "could easily be mistaken for anything but limestone". He places the Johnstown Cement as lying 91 feet above the Lower Kittanning seam. This is still 50 feet ( $\pm$ ) below the Lower Freeport Seam.

Ashburner also reported a three foot layer of limestone in the vicinity of Kylers Mine which he thought to be the Lower Freeport Limestone. Ashburner failed to find (in Fox Township) the Upper Freeport Limestone which was reported by James Hodge for the First Geological Survey. Ashburner did find the Upper Freeport Limestone in Meade Run just west of the Blue Valley Mine, but due to its higher elevation the limestone probably is not present over any

\*Alkalinity minus Acidity

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substantial portion of the area. It appears, however, that two persistent seams of limestone might be present in the strata overlying these mines, namely the Johnstown Cement and the Lower Freeport Limestone.

2. Analysis of Mine Discharges

Because of the significant differences between the drainage from the Elbon Mine and the nearby Elk Mine, it was considered important to seek the reason for the difference.

While an analysis of the geology could serve as a starting point in the evaluation, a more complete examination of the discharges is necessary.

Probably the most significant observation was the presence of high levels of  $\text{Ca}^{++}$  in BOTH discharges, indicating that natural alkalinity is being generated in both ground water systems. It is possible, of course, that some calcium is present in the rocks as gypsum ( $\text{CaSO}_4$ ) but this has been largely discounted as a major source of the calcium ions found in the discharge. Geological surveys make no mention of gypsum in the overlying strata, but several seams of  $\text{CaCO}_3$  have been cited by Ashburner as being present in the overlying strata.

For comparison a sample of ground water was also obtained from a small system of springs which supply water for the village of Elbon. These springs are above the Middle Kittanning seam and lie directly over the abandoned Williams Mine (see Sheet #1 of the Topographic Drawings). No mining has been done on the hilltop and the forest cover is complete and undisturbed. The following results were obtained from a chemical analysis of the water sample:

pH	6.8
Alkalinity	60 mg/l
Acidity	0 mg/l
Total Hardness	90 mg/l (as $\text{CaCO}_3$ )
Calcium Hardness	45 mg/l (as $\text{CaCO}_3$ )
Sulfates	23 mg/l
Fe (total)	0.2 mg/l
Mn	0.60 mg/l
Ca	18 mg/l (calculated)
Mg	10.9 mg/l

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From the above analysis it can be noted that the sample contained only a moderate amount of alkalinity probably due to mixing with shallow ground waters which had little or no chance to contact the limestone strata.

If this water were allowed to descend, as surface runoff, to the level of the strip pits and then into the deep mine, the limited alkalinity would soon be exhausted in the mine environment. It is also very probable that this water is representative of the best water which enters the deep mines by way of the strip pits. Most important is the low alkalinity of the water. If this flow were to enter the deep mine via the strip mine ponds, the alkalinity would be exhausted very quickly.

The next logical step in the investigation of the geochemical processes taking place in the system would be to obtain a sample of the deeper ground water as it exists just above the deep mines. Unfortunately, however, no means was available to obtain such a sample and no springs or seeps were found which could be considered as representative of these waters. In fact, no discharges were found even from the Middle Kittanning mine headings, a clear indication of the high permeability of the strata between the two coal seams. As a result, the mine discharges from the Lower Kittanning seam must be used to reconstruct the amount of alkalinity actually being generated in the system.

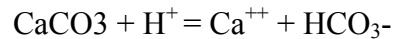
An analysis of a water sample obtained May 11, 1970 from the Elbon Mine is listed below:

Flow	0.461 MGD
pH	4.31
Eh (measured)	+ .387 volts
Acidity (as CaCO <sub>3</sub> )	664 mg/l
Alkalinity (as CaCO <sub>3</sub> )	0 mg/l
Cl	60 mg/l
Organic Nitrogen (as N)	10.0 mg/l
SO <sub>4</sub>	944 mg/l
Fe <sup>++</sup>	52.4 mg/l
Fe <sup>+++</sup>	35.6 mg/l
Ca (as calcium)	180.0 mg/l
Mg	6.6 mg/l
Mn	9.65 mg/l
Si	14.1 mg/l
Na	3.6 mg/l

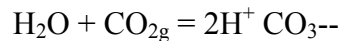


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The calcium content of this sample is of particular interest. Since we might expect that the water obtained its alkalinity before reaching the deep mines, it is important to consider the maximum amount that it might acquire under normal conditions. The chemical equation for dissolution of  $\text{CaCO}_3$  is as follows:



The hydrogen ions (if we exclude the possibility of prior contact with pyrites, etc.) would normally occur as follows:



Thus, the solubility of calcite would be dependent on the partial pressure of  $\text{CO}_2$ . The  $\text{CO}_2$  originates from atmospheric  $\text{CO}_2$  and from a biologically active soil zone. According to Dr. Donald Langmuir of the Pennsylvania State University, the partial pressure of  $\text{CO}_2$  we might expect from this type of environment will be approximately  $10^{-2}$  atmospheres, and the solubility of calcium can be expressed as:

$$\text{Ca}^{++} \text{ (m. mol)} = 8.73 (\text{P}_{\text{CO}_2})^{0.354} \text{ for } T = 25^\circ\text{C}$$

Correcting for a ground water temperature of  $12^\circ\text{C}$  this becomes:

$$\text{Ca}^{++} = 10.91 (10^{-2})^{0.354}$$

$$\text{Solving } = \text{Ca}^{++} = 2.139 \text{ m. mol or } 85.5 \text{ mg/l}$$

It is evident then that the calcium present in the drainage (180 mg/l) is in excess of that which might be picked up from the limestone by the action of carbonic acid alone. For this reason it can be supposed that somewhere in the system some of the waters are coming in contact with limestone after they have picked up acidity from sulfur bearing rocks.

If we examine the characteristics of the flows in McCauley Run (Sampling Points #6 and #7) we can see that neutralization definitely is taking place in that portion of the hydrologic system. While the sulfate concentrations are nearly as high as those emitting directly from the deep mines, the pH is generally between 6.5 and 7.0, and there is usually a net positive alkalinity. This means that the acidity that had formed had been neutralized.



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The flows in McCauley Run are almost totally local flows which originate right in the watershed. Most of these waters percolate through spoil material, but no significant deep mine discharges were found on the watershed. If we discount the natural alkalinity of the surface waters as they run off the hillsides, then the source of the alkalinity must be the strip mine spoil piles. In the earlier discussion of the geology of the region it was noted that Ashburner located the Johnstown Cement approximately 91 feet above the Lower Kittanning coal seam. This would then place it only 40 ( $\pm$ ) feet above the Middle Kittanning seam. From the effect observed on the waters in McCauley Run there must be a considerable amount of this limestone buried in the strip mine spoil.

The following analyses were taken from the report of the Second Geological Survey:

Upper Freeport Limestone

(Sample from J. S. Hyde Farm west of Village of Toby)

Carbonate of Lime	80.4%
Carbonate of Magnesia	1.6%
Oxide of Iron & Alumina	3.6%
Phosphorus	.08%
Insoluble Residue	12.3%

Lower Freeport Limestone (3 to 4 feet thick in region)

(Sample from Chamberlin Farm at Village of Challenge)

Carbonate of Lime	81.8%
Carbonate of Magnesia	7.2%
Oxide of Iron & Alumina	2.7%
Phosphorous	.06%
Insoluble Residue	6.5%

The Johnstown Cement Bed was also analyzed by the Second Geological Survey but it appears that an error slipped into the printing. The analysis reported is identical to that shown for the Upper Freeport Limestone and it is presumed that this was a printing error, since there is little chance that the two samples from two different formations would have an identical assay. It is not likely that Ashburner mistakenly identified one of the seams since he describes the Upper Freeport Limestone as a bluish gray "coarse grained brittle limestone". Further-



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more, the Upper Freeport limestone is found only at the higher elevations and it is not likely that it was mistakenly identified.

Returning to the consideration of alkalinity, the total alkalinity (lbs/day) can be calculated as follows:

180 mg/l of  $\text{Ca}^{++}$  is equivalent to 450 mg/l  $\text{CaCO}_3$

For a flow of 0.45 MGD the total alkalinity generated would be 450 mg/l (as  $\text{CaCO}_3$ ) x  $0.46 \times 10^6$  gal/day x 8.33 lbs/gal = 1724 lbs. alkalinity per day.

Since this alkalinity has all been exhausted, we can equate this to 1724 pounds of acidity, in addition to the acidity still present in the discharge. This means that at a total flow of 0.46 MGD (the flow at the time the sample was obtained) the total acid generated is 930 pounds + 1724 pounds = 2654 lbs/day (as  $\text{CaCO}_3$ ).

Now we are faced with the problem of determining how much alkalinity would reach the deep mine if the drainage from the strip mines were excluded. These flows are probably carrying very little alkalinity as they enter the mine, judging from the quality of the water at Sampling Point #6, on McCauley Run. They do, however, add to the total acid load as revealed by the statistical analysis of the acid load at Sampling Point #1.

Evaluation of the effects of excluding these waters is made difficult, if not impossible, because we are not able to determine how much of the calcium in the discharge could be attributed to alkalinity entering the system and how much originated in the strip mine spoil. Appendix F-1 represents a simplified flow schematic of the waters involved.

Because the inputs to each side of the flow diagram cannot be accurately determined, we are not able to determine the quantity of flow reaching the deep mine via the strip mines. Nor can we determine how much alkalinity reaches the deep mine because of the probability that some of the calcium in the water is a product of the direct reaction of acid with limestone.



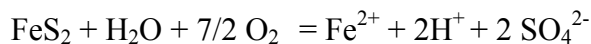
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If funds were available it might be enlightening to drill test wells into the overburden and to take ground water samples at various depths to determine how much alkalinity is actually being generated in the limestone seams. Of particular interest would be the quality of the ground water just below the Johnstown Cement. Unfortunately, however, funds are not available for this type of investigation so we must look elsewhere for answers to the question of what is happening in the mine.

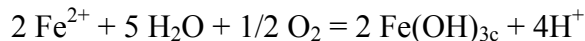
This leaves us with the statistical analysis of the deep mine flows as the most significant indication of the factors controlling the formation of acid. This analysis does not answer the complicated question of which reaction controls the formation of acid but it does give us an indication of what might be done to reduce the quantity of acid produced.

### 3. Chemistry of Acid Formation

In the last few years much attention has been focused on the chemical reactions which create acid mine drainage and the result is a number of equations representing possible chemical reactions. Oxidation of pyrite takes place as follows:



Additional hydrogen ions could then be released by the reaction:



These reactions are both dependent upon oxygen, a relationship which has led to the theory that exclusion of air from a mine, by air sealing, would reduce the amount of acid formed. This procedure is unfortunately dependent on a ground water flow that is also free of dissolved oxygen. In the case of the Elbon Mine system, the waters entering the deep mine through the strip mine are in contact with atmospheric oxygen pressure until they percolate into the spoil. Lack of a biologically active soil cover allows this dissolved oxygen to enter the mine where it is available for reaction with pyrites.

Wash-outs: Another possible contributor to the acid load, according to Langmuir, is the formation of  $\text{Fe}_2(\text{SO}_4)_3$  and  $\text{Al}_2(\text{SO}_4)_3$  effluences on the surfaces of exposed reactive materials. Fluctuation of the ground water flows would periodically inundate some of these reaction sites, dissolving the mineral salts and increasing the acid load being carried by the drainage. This mechanism could explain



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why some mine discharges actually carry heavier acid concentrations during high flow periods than during normal flow periods.

This wash-out of accumulated sulfate deposits would be dependent upon the following factors:

- (a) Peak hydraulic flow as compared to average flow.
- (b) Condition of mine roof, as related to the exposure of sulfur bearing materials to air and percolating ground waters.
- (c) Condition of mine floor (i.e. the amount of sulfur bearing material lying on the mine floor) and in the flow channels.

Obviously, a fully retreated mine will not only expose more sulfur and more reaction sites, but the former roof material, in its new position on the mine floor, can interrupt drainage and periodically flood large volumes of sulfur bearing rocks. It is likely that this results in the dissolution of much sulfur and is responsible, in a large measure for the "slugging" effect noted of some mine discharges.

In the case of the Elbon Mine, this effect was not significant, probably because only a small portion of the mine area was retreated, and the major drainage routes are apparently still open.

Eh - pH Relationships: Investigation of the Elbon drainage with respect to its Eh and pH and the iron concentrations suggest that the discharge is in equilibrium with ferric hydroxide (Fe(OH)<sub>3</sub>).

As a check on the Fe<sup>+++</sup>/Fe<sup>++</sup> ratio, the standard free energy was determined for the oxidation of Fe<sup>++</sup> to Fe (OH)<sub>3</sub>. This was used to determine the standard potential E° from the relationship

$$E^{\circ} = \frac{-\Delta G^{\circ}}{nF}$$

Since the reaction is reversible and it is assumed to be at equilibrium in this case, the oxidation rate equals the reduction rate and the Eh can be calculated using the Nernst equation  $Eh = E^{\circ} + \frac{RT}{nF} \ln K$ .





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The equation was modified to common logarithms and  $[H^+]^3 / [Fe^{++}]$  was substituted for K. After correcting for the temperature of the mine discharge, the equation is as follows:

$$Eh = E^{\circ} + 0.0566 \log \frac{[H^+]^3}{[Fe^{++}]}$$

The ferrous iron activity  $[Fe^{++}]$  was determined from the chemical analysis after calculating ionic strength and using the Debye-Huckel equation to arrive at an activity coefficient ( $\gamma_{Fe^{++}}$ ) of 0.172 for the Elbon Mine discharge.

Substituting  $[H^+]$  and  $[Fe^{++}]$  in the Nernst equation we find a calculated Eh of 0.417. The observed value of 0.387 taken at the mine mouth does not agree precisely with the calculated value but it does confirm that the ferrous iron is in equilibrium with the ferric hydroxides.

Calculation of the stability of the hydroxide was done using the following relationship:

$$pQ = [Fe^{+++}] [OH]^3 - \text{where } pQ \text{ is the activity product.}$$

The resulting value  $-\log pQ + 38.14$  indicates that the hydroxide is amorphous ferric oxyhydroxide and that it is a relatively young precipitate, perhaps only a few hours old. This is probably due to the introduction of fresh oxygen-rich water into the mine through the strip pits on the low side near the point of discharge.

Significance of Eh - pH: The relationship of the ferrous ion concentration and the stability field of the  $Fe(OH)_3$  coupled with the character of the precipitating hydroxide indicates that the water discharging from the mine had recently mixed with oxygen bearing waters, raising the Eh and precipitating the  $Fe(OH)_3$ .

By observing a stability field diagram of the ferric and ferrous species (Appendix F2) we can see the effect of an increase in the pH of the system on the activity of the ferrous iron.

If we were able to raise the pH to the 5.5 to 6.0 range and keep the Eh above 0.4 volts the dissolved iron concentration would be lowered significantly.

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The pH might be raised by maximizing the formation of alkalinity within the mine, and minimizing acid production.

Eh, however, poses a more difficult problem. Introduction of oxygen by contacting the flow with air can raise the Eh to the 350-500 millivolt range (Hem, 1961) but we cannot introduce this oxygen directly into the mine system lest we increase the rate of pyrite oxidation and compound the problem.

Once the drainage leaves the mine, however, a simple cascade might be all that is necessary to raise the Eh and precipitate the remaining iron. A sedimentation pond would also be necessary to allow the ferric hydroxides to settle out of the flow.

In the case of the Elbon Mine, there is ample room for an earthen sedimentation basin, and the nearby strip pits would serve as receptors for the solids when the pond required cleaning. The sludge generated from this type of procedure should not be nearly as voluminous as that from a lime-neutralization operation since there hopefully would be no need for additional pH correction. Present sludge accumulations at the mine mouth probably total 500 cubic yards but this is the result of 20 years of precipitation of ferric hydroxides from water carrying over 100 mg/l total iron. These deposits have compacted well and should not be difficult to handle.



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D. ELK MINE

A detailed analysis was also made of a sample from the Elk Mine discharge on May 11, 1970 with the following results:

pH	5.83
Eh	+0.247 volts
Acidity	32 mg/l (as CaCO <sub>3</sub> )
Alkalinity	76 mg/l (as CaCO <sub>3</sub> )
Chlorides	10 mg/l
Nitrogen (as NO <sub>2</sub> )	0.010 mg/l
Nitrogen (Kjeldahl) as N	11.0 mg/l
Sulfates	429 mg/l
Fe <sup>++</sup>	29.0 mg/l
Fe <sup>+++</sup>	0.0 mg/l
Ca	100 mg/l
Mg	3.0 mg/l
Mn	4.9 mg/l
Si	7.1 mg/l
Na	6.1 mg/l

In this analysis the ferric iron was reported as zero, indicating that the oxyhydroxides had precipitated out prior to the time the drainage left the mine. This might be explained by the fact that the Elk Mine is almost completely flooded and would act as a settling basin for any precipitates.

In the case of the Elbon Mine, the Fe<sup>+++</sup> reported was not dissolved Fe<sup>+++</sup> ions but was reported as such, since sanitary consulting laboratories customarily analyze for ferrous iron and total iron (phenanthroline method) and assume that the difference between the two concentrations is ferric. In this case, however, the dissolved ferric iron should be below detectable limits for both mines.

The Elk drainage was found to have a calculated Eh of +0.150 volts as opposed to a measured value of +0.247 volts. The reason for this large difference is not certain, but it is possible that the discharge was contacting the atmosphere upstream from the sampling point. The flow emerged from a long culvert which was flowing only half full, allowing contact with the atmosphere 40 to 50 feet upstream from the sampling point. The culvert made it impossible to sample where the flow first contacted the atmosphere. We have assumed therefore, that the calculated Eh of +0.150 is the correct value for the



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drainage as it leaves the mine and have plotted this point on Appendix F2.

The rapid rise in Eh to +0.247 would soon cause a reduction in  $[\text{Fe}^{++}]$ . The oxidation of the ferrous iron would produce additional  $\text{H}^+$  but excess alkalinity and subsequent mixing with surface runoff should be sufficient to return the pH to more neutral values.



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### E. BIOLOGICAL OXIDATION

The role of iron oxidizing bacteria has not been considered in the previous discussions because the drainages represent what is considered an equilibrium state as they leave the mines. While the iron bacteria can certainly increase the rate of oxidation, it is not necessary for them to be present for the reaction to go to completion.

An increase in the alkalinity, and a resulting increase in pH, of the mine waters will tend to inhibit the activity of some species, but others can exist at a pH near neutrality (*Gallionella* and *Crenothrix*). The prime requisite for these bacteria is that they are all strict aerobes and depletion of dissolved oxygen in the mine would reduce their activity. Thus, the reduction of flow, and the dissolved oxygen as well, would not only reduce the amount of pyrite being oxidized but would reduce the oxidation of ferrous iron to ferric hydroxide.

An attempt to culture thiobacillus thiooxidans from the drainages of the two mines was not successful but microscopic examination of both cultures revealed large numbers of organisms resembling *Siderocapsa*. These bacteria occurred in colonies of a dozen or more cells surrounded by a brown capsule presumably ferric hydrate.

It is reported by Starkey (AWWA, 1945) that *Siderocapsa* may be strictly heterotrophic and require organic matter. The presence of the nitrates in both drainages indicate that some organic material is reaching the mine.

While the bacteria might not be a critical factor within the mine, they would have a beneficial effect in an oxidation system located at the mine mouth. The increased dissolved oxygen and the abundance of ferrous iron as an energy source would serve to promote the growth of these organisms which, in turn, would accelerate the precipitation of the iron as ferrous hydroxide upon exiting the mine.



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F. SUMMARY

1. Some mine waters originally contain moderate amounts of alkalinity which are subsequently exhausted by acid generated in the mine.
2. Large quantities of limestone are present in strata overlying the mines. (See Appendix A5).
3. Water entering the mines can be considered as coming from two separate sources, one alkaline, the other probably neutral or slightly acid. Acid production (lbs./day) is a linear function of flow. The controlling factor may be the dissolved oxygen in the water.
4. If the neutral flow (that entering through the strip mines) can be diminished sufficiently, the alkalinity of the drainage could possibly exceed its acidity.
5. Iron is in equilibrium with amorphous ferric oxyhydroxide when it leaves the Elbon Mine and a significant increase in pH would effect a considerable reduction in dissolved  $Fe^{++}$ .
6. If the pH of the Elbon discharge can be raised to the same level as the Elk Mine discharge, simple aeration and sedimentation should be sufficient to effect a great improvement in the quality of Brandy Camp Creek, and will diminish the load on Toby Creek.
7. Bacterial oxidation, if actually occurring in the mine, is simply accelerating the oxidation of the ferrous iron to ferric hydroxide. At the pH of the Elbon discharge the ferrous iron is virtually all complexed with hydroxides and thus, oxidation of pyrite by ferric ions is not a significant factor. All oxidation of pyrite would be controlled by the oxygen supply.