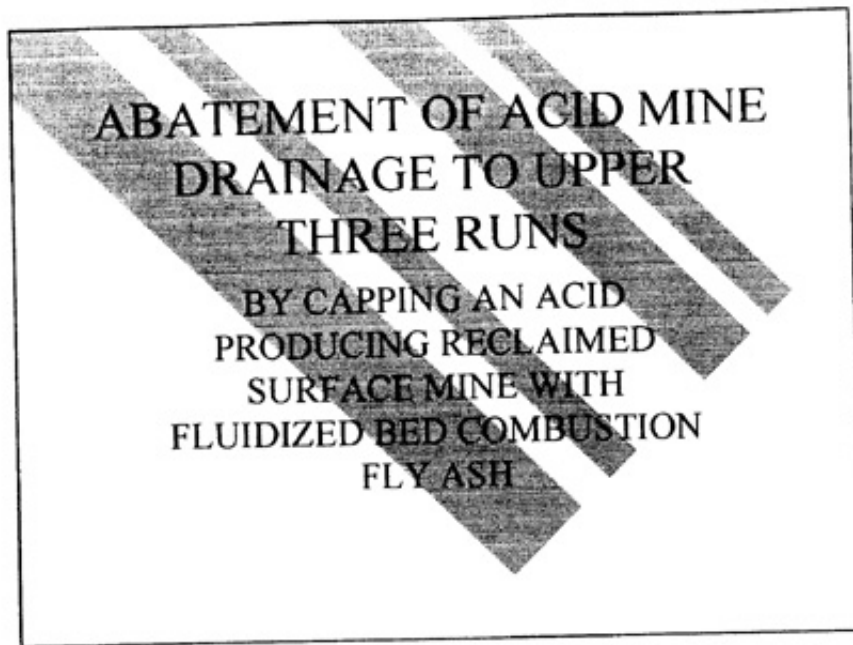


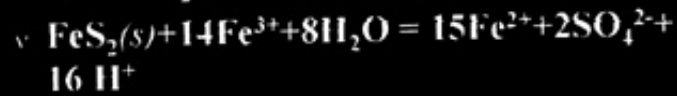
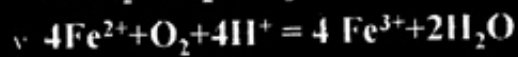
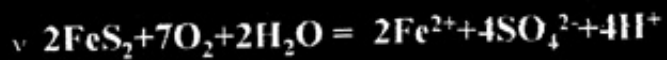
Abatement of Acid Mine Drainage to Upper Three Runs: by Capping an Acid Producing Reclaimed Surface Mine with Fluidized Bed Combustion Fly Ash



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## OXIDATION OF PYRITE



Stumm, W. and J. J. Morgan, 1996. Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters, Third Edition. John Wiley and Sons, New York, NY, 1024p.

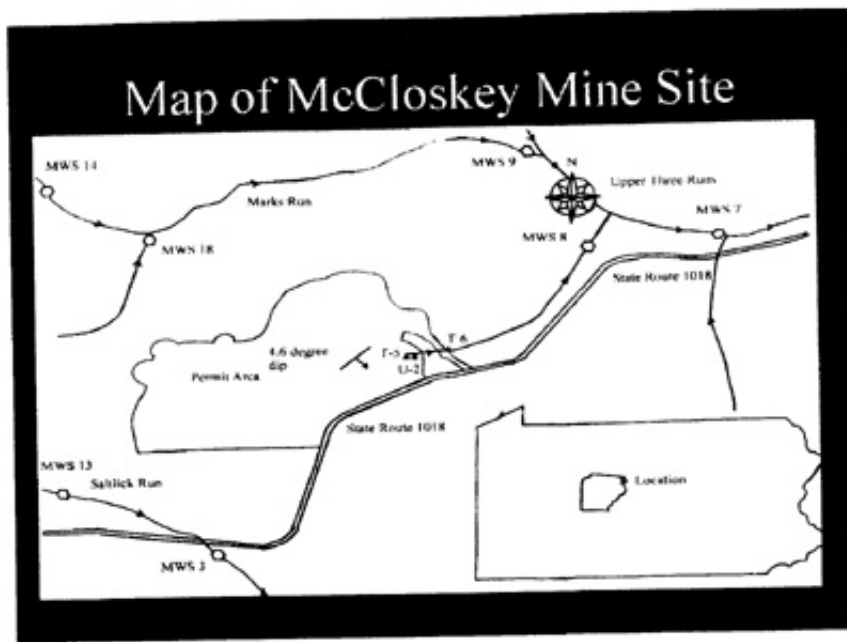
Equation 1 shows that both oxygen and water are needed to initiate the pyrite oxidation reaction.. Sulfuric acid is formed, and the iron remains in the ferrous form.

Equation 2 shows the oxidation of ferrous iron to ferric iron, effected primarily by bacteria such as *Thiobacillus ferrooxidans*.

Equation 3 shows the hydrolysis of the ferric ion.

Equation 4 shows the oxidation of pyrite by ferric ion, showing that the formation of acid can be propagated even under apparently anoxic conditions once sufficient ferric ion concentrations are present.

Oxidation occurs mainly in the unsaturated zone of mine spoil.



River Hill Coal Company, surface mine permit 17793044, McCloskey Operation, Karthaus Township, Clearfield County, PA.

The receiving streams are Saltlick Run, and the tributaries of Upper Three Runs (Marks Run and an unnamed tributary that receives the major discharge from the operation). Saltlick Run and Upper Three Runs are tributaries of the West Branch Susquehanna River, which drains via the Susquehanna River to the Chesapeake Bay.

Major sources of pollution to the upper reaches of the West Branch Susquehanna River occur in the watershed of Clearfield Creek, which flows from south to north and approximately bisects the southern portion of the County; Moshannon Creek, which flows from southwest to northeast and forms most of the eastern boundary of the County; and Bennetts Branch Sinnemahoning Creek, which flows from the northwest part of the County into Elk and Cameron Counties to the north.

Outdoor activities such as fishing , bathing beaches, and boating are very important to the economy of Clearfield County and the Moshannon Valley. Efforts such as this one are important in restoring the water quality of the Chesapeake Bay watershed in general and of the watersheds of our community in particular.

## Performance of Constructed Wetland

Parameter	pH (s. u.)	Alkalinity (mg/l. CaCO <sub>3</sub> )	Acidity (mg/l. CaCO <sub>3</sub> )	[Fe] (mg/l.)	[Mn] (mg/l.)	[SO <sub>4</sub> <sup>2-</sup> ] (mg/L)
Influent	4.8	33	657	230.7	146.3	4766
Effluent	3.3	12	236	31.7	107.9	4752

The major discharge at sample point T-5 had an average flow of 327 m<sup>3</sup>/day and was the source of the major portion of the pollution to Upper Three Runs. The coal operator tried to abate the pollution with a horizontal flow aerobic constructed wetland, and was partially successful. However, the wetland effluent still did not conform to effluent limits without further treatment; and the discharge had to be pumped to the wetland.

The operator was not required to report aluminum concentrations, so data on aluminum are scarce. However, a comparison of the acidity with the iron and manganese concentrations indicated that aluminum is not a major contributor of acidity at this site.

The quality of Upper Three Runs had improved, but Saltlick Run is polluted from acid mine drainage. The operator therefore developed a plan to mine the area south of the McCloskey Operation and construct an underdrain to convey the T-5 discharge to Saltlick Run and away from Upper Three Runs. This had an excellent chance to succeed in maintaining the quality of Upper Three Runs. Marks Run and the reaches of Upper Three Runs upstream of the unnamed tributary represented by MWS 8 are not polluted.

However, the overburden analysis revealed that further pollution was probable if the new mining was permitted. Therefore, an alternative pollution abatement plan was necessary.

## Fly Ash Characteristics

Parameter	Concentration (mg/l)	Parameter	Concentration (mg/l)
[Al]	0.48	[Mn]	0.041
[As]	0.08	[Mo]	0.53
[B]	1.05	[N]	0.15
[Ba]	0.41	[Pb]	0.65
[Ca]	970	[Sr]	1.28
[Cd]	0.08	[Se]	0.05
[Cr]	0.07	[Si]	96
[Cu]	<0.02	[Sn]	0.61
[Fe]	0.05	[S]	6.1
[Hg]	0.004	[Tl]	<0.02
[K]	310	[Zn]	0.04
[Mg]	35	[Zr]	2.39

The abatement method selected was the application of fluidized bed combustion (FBC) fly ash. Dr. Barry Scheetz of the Pennsylvania State University worked with the operator to develop a plan for capping the backfilled mine area with a 0.91 m thickness of fly ash. This ash was intended to form a stratum with very low permeability, thereby depriving the acid forming spoil of water from rainfall directly on the mine area. This would retard or arrest the oxidation of pyrite, as shown in Equation 1. The flow of water contributed laterally from outside the fly ash cap area is negligible, especially flow into the unsaturated zone, as can readily be inferred from the site map.

The planned fly ash application area is 45.32 ha, of which 37.23 ha has already been capped.

The fly ash was tested for the potential pollutants shown. The Department determined that, given the alkaline nature of the fly ash cap and its relative impermeability, there was minuscule probability that these parameters would appear at pollutant levels in the receiving stream.

## Discharge after Fly Ash Application

Parameter	Concentration (mg/L)	Parameter	Concentration (mg/L)
Total Dissolved Solids	9024	[Cd]	<0.0002
Alkalinity as CaCO <sub>3</sub>	2	[Ca]	326
Acidity as CaCO <sub>3</sub>	706	[Cr]	<0.004
Cl <sup>-</sup>	8	[Cu]	<0.010
F	1.7	[Pb]	<0.001
[Fe] total	122	[Mn]	547
[Ni]	19.3	[Hg]	<0.001
[NH <sub>3</sub> ] as N	<0.04	[Se]	<0.007
[NO <sub>3</sub> ] as N	0.43	[Zn]	2.31
[Al]	23.7	[Mo]	127
[As]	<0.004	[SO <sub>4</sub> <sup>2-</sup> ]	3386
[Ba]	<0.010		

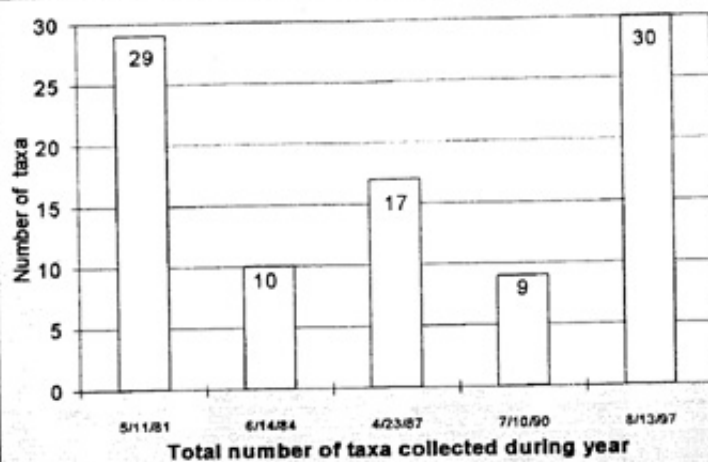
In fact, there has been no pollution of the receiving stream from these trace elements. This table shows the quality of the discharge. I got the alkalinity and acidity reversed in the table.

## Upper Three Runs Water Quality

Parameter	Concentration (mg/L)	Parameter	Concentration (mg/L)
pH	10.8	[NO <sub>3</sub> ]	1.23
Spec Cond (umho/cm)	1085	[Al]	0.000926
Total Dissolved Solids	898	[As]	<0.004
Alkalinity as CaCO <sub>3</sub>	74	[Ba]	0.031
Suspended Solids	40	[Cd]	<0.010
Acidity as CaCO <sub>3</sub>	0	[Ca]	218
[Cl <sup>-</sup> ]	9	[Cr]	<0.050
[F]	<0.20	[Cu]	<0.010
[Fe]	0.744	[Pb]	<0.010
[Ni]	3.15	[Mn]	2.71
Turbidity (NTU)	122.5	[N]	<0.025
[Mn]	25	[Se]	<0.0071
[NH <sub>3</sub> ]	0.17	[Zn]	<0.010

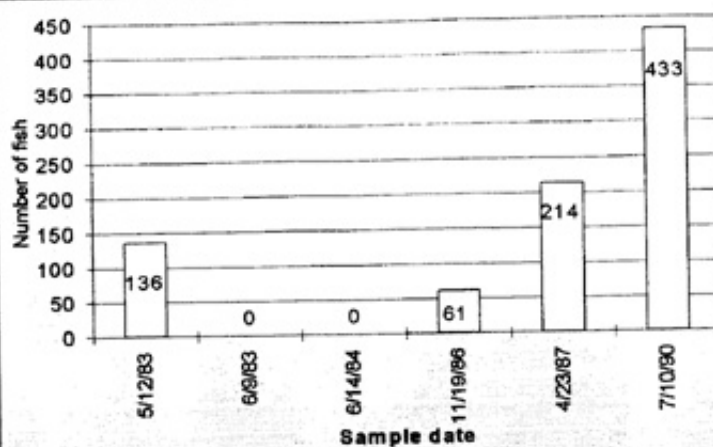
This table shows the results of sampling the unnamed tributary of Upper Three Runs by the Fish and Boat Commission, and shows that there is no pollution from the trace elements.

## Benthic Macroinvertebrates

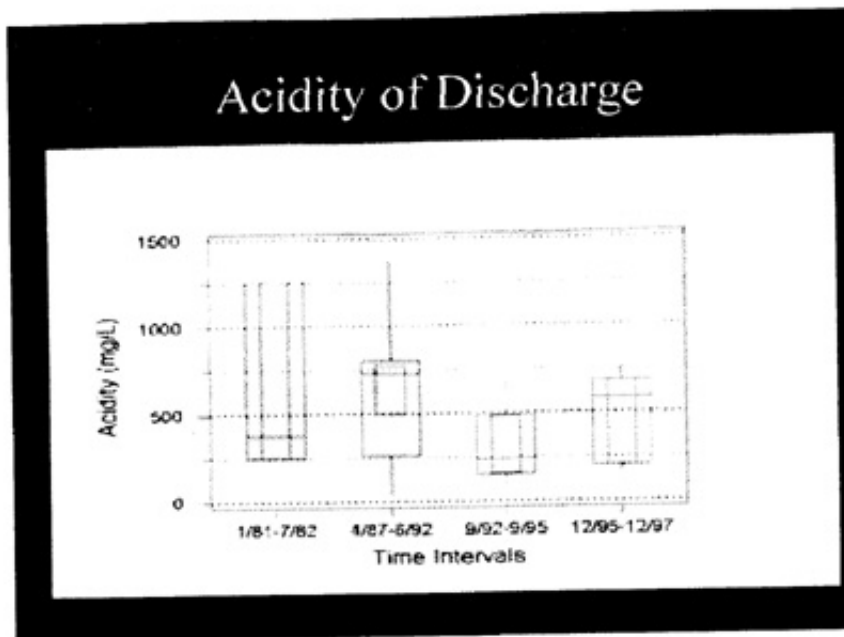


The benthic macroinvertebrate population diversity was 29 during the early stages of mining represented by the sample taken 5/11/81. As the mining continued and the site began to be backfilled, represented by the sample of 6/14/84, the macroinvertebrates declined. The operator's treatment activities caused a rebound in the population (4/23/87), but the wetland alone did not suffice to maintain it (7/10/90). The fly ash capping and the resultant diminution of pollutant loading have contributed to the macroinvertebrate population's restoration to its pre-mining levels (8/13/97).

## Fish Populations



Not unexpectedly, the fish populations follow the macroinvertebrate populations. Both the macroinvertebrate and the fish populations were determined by the Fish and Boat Commission, which in Pennsylvania is entirely independent of the Department of Environmental Protection and is supported from the sales of licenses and publications and by



donations.

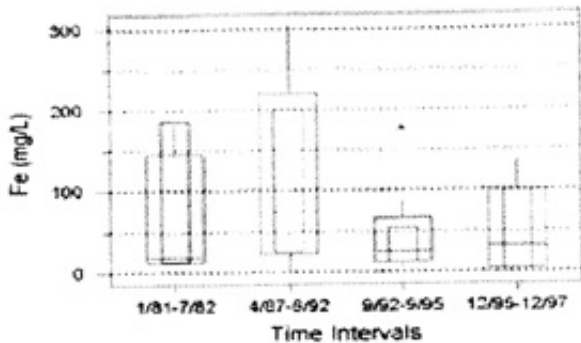
For the original discussion of box and whisker plots, refer to Tukey, J. W., 1977. *Exploratory Data Analysis*. Addison-Wesley Publishing Co., Reading MA. See also Velleman, P. F. , and D. C. Hoaglin, 1981. *Applications, Basics, and Computing of Exploratory Data Analysis*. Duxbury Press, Boston MA. See further Hettmansperger, T. P., and S. J. Sheather, 1986. "Confidence intervals based on interpolated order statistics." *Statistics and Probability Letters* 4, 7579. For a more fundamental discussion, the reader is referred to basic texts, such as Mendenhall, W., and R. J. Beaver, 1991. *Introduction to Probability and Statistics*. PWS-Kent Publishing Co., Boston MA. The actual boxplots were generated by Minitab Software.

A box and whisker plot may be visualized as an aerial view of the distribution curve for a given variable. The horizontal line within the box near its center represents the median value. The ends of the boxes, called "hinges", are approximately equal to the quartile values. The termini of the whiskers are called the "fences" . Data beyond the fences are mild or extreme "outliers", indicative of atypical data.

The confidence limits about the median usually occur near the ends of the boxes. When confidence intervals overlap, the data are not statistically different. Nonetheless, the box and whisker plots seem to indicate a mitigation of the acidity in the discharge (sample point T-5) over time, attributable to the abatement activities.



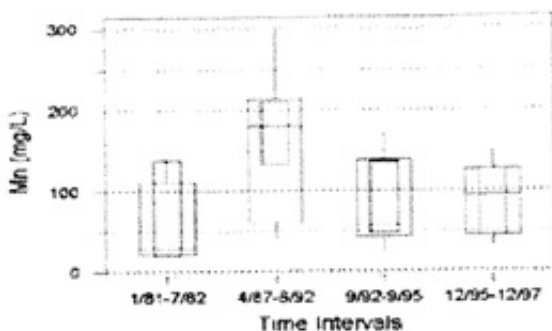
## Iron concentration in Discharge



These box and whisker plots, or simply boxplots, for [Fe] show a mitigation of [Fe] in the discharge (point T-5). Mitigation of [Fe] is very important, because ferric iron tends to form sediments composed of  $\text{FeOOH}$ ,  $\text{Fe}(\text{OH})_3$ ,  $\text{Fe}_2\text{O}_3$ , solid phases which cover the stream bottom. These sediments inhibit the development of macroinvertebrates and prevent fish eggs from hatching.

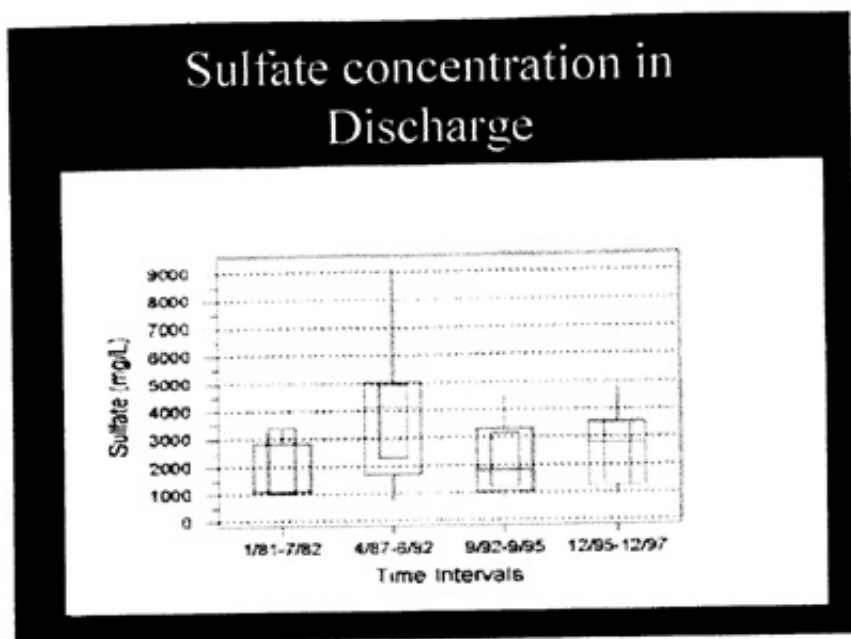
The oxidation of ferrous iron and the hydrolysis of ferric iron were discussed in Equations 2 and 3.

## Manganese concentration in Discharge

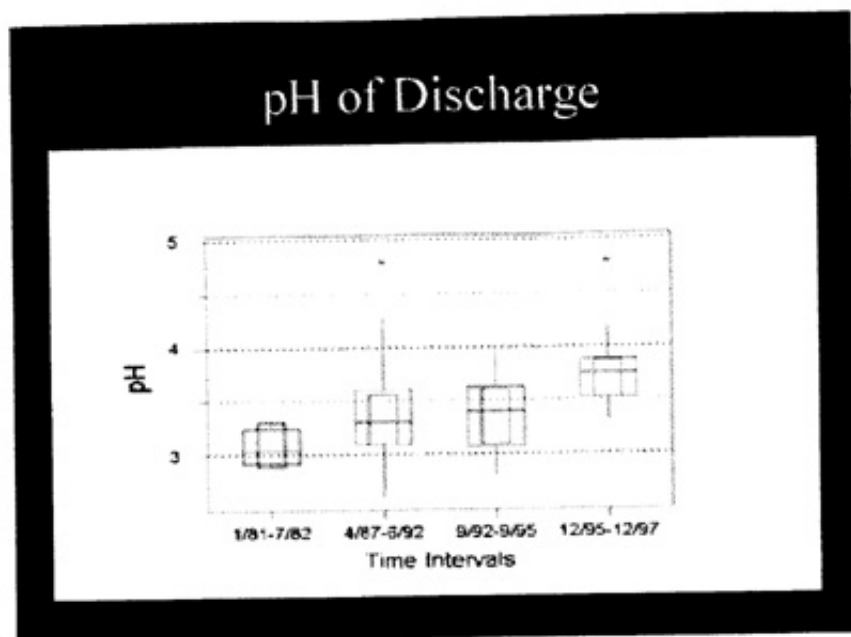


A mitigation of manganese concentrations is also shown. Manganese is removed by oxidation of manganese (II) to manganese dioxide, which is thermodynamically favored under the pH and dissolved oxygen conditions in a good quality trout stream, often resulting in a black coating on the rocks. However, the rate of manganese oxidation is slow at  $\text{pH} < 8$ , and

manganese removal by any abatement measure often is a challenge.

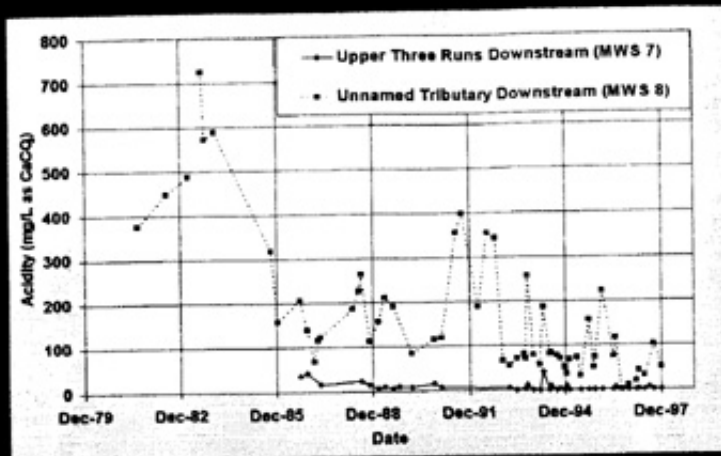


Sulfate concentration has remained elevated, but the median concentration has returned to the pre-mining value.



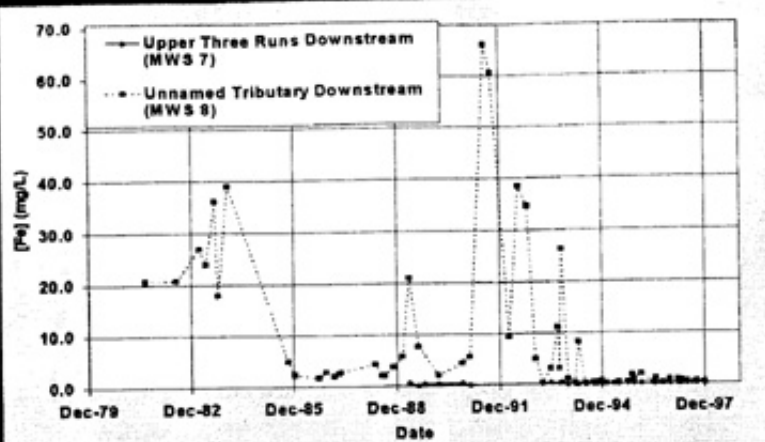
A definite upward trend in pH is shown for the discharge, and the most recent observations show a statistical improvement, which we attribute too the reclamation activities using the fly ash cap.

## Receiving Stream Acidity



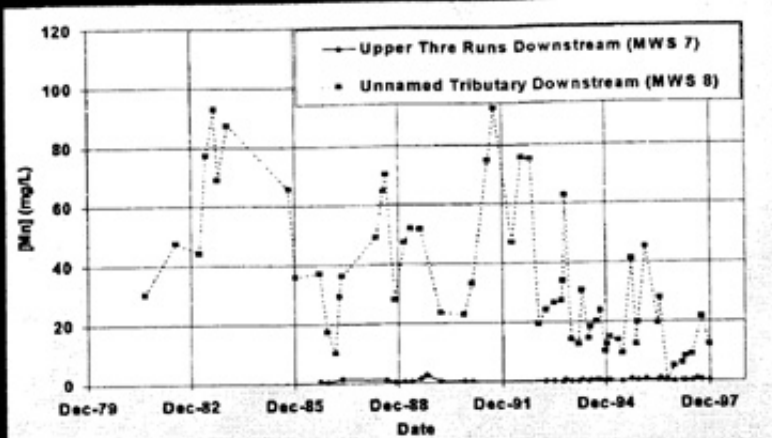
The data show a trend of permanent acidity abatement, suggesting that when all reclamation activities have been concluded, pollution to the unnamed tributary will not cause the lower portions of Upper Three Runs to be rendered again incapable of supporting fish life.

## Receiving Stream Iron Concentration



A similar permanent mitigation effect is observed for Fe in Upper Three Runs. This would indicate that the stream bottom will permanently be capable of supporting the necessary benthic life to support the fish populations once the reclamation has been completed.

## Receiving Stream Manganese Concentration



The mitigating effect on manganese is equally apparent.

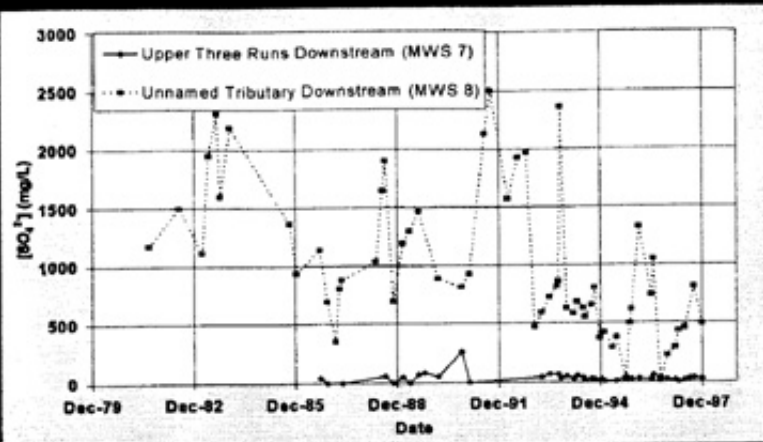
Mathematically, the pollution indicators appear to be following an exponential decline superimposed upon a sine wave which I suspect but do not claim to prove, is caused by seasonal variation in the rainfall.

This would suggest that the concentration of the pollutant as a function of time can be modeled by either a first or second order linear differential equation with a trigonometric forcing function, with a solution that looks like:

$$C = A \exp(-Bt) \sin(\omega t + p)$$

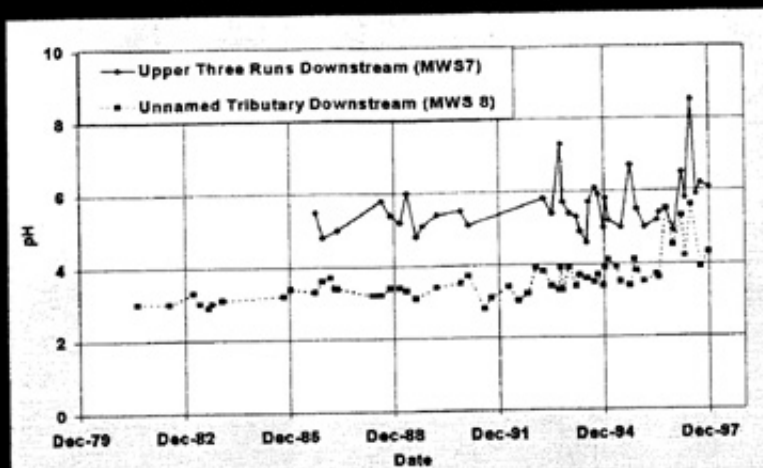
I have observed this effect on other mine sites where sufficient data have been presented to allow the observation. The model would seem to confirm the benefits of good reclamation measures. It is unclear whether a final pollution concentration is being approached asymptotically, much less whether the asymptote represents a concentration conforming to effluent limits.

## Receiving Stream Sulfate Concentration



Sulfate levels have also improved and show a trend similar to that of manganese.

## Receiving Stream pH



The upward trend of pH both in the unnamed tributary and in Upper Three Runs itself is consistent with the improvements seen in acidity, iron, manganese, and sulfate. Trout could not thrive in Upper Three Runs when the pH was depressed much below 6. It now appears that a permanent trout population will remain in the stream once reclamation has been completed.

## Conclusions

- v Enhanced reclamation
- v Abated pollution
- v Abated discharge flow
- v Restored fishery
- v No secondary problems

This project demonstrates the enhancement of reclamation using a combustion product which often has been considered a waste disposal problem. Mine drainage pollution has been abated, both in quality and in quantity, resulting in the restoration of a fishery. No pollution from trace elements has been observed.

Numerous other mine sites, both active and abandoned, lend themselves to the application of this technology. The technology is expected to play an important role in the reclamation of abandoned mine lands, in conjunction with other abatement measures such as passive treatment. Water quality may also be enhanced by active re-mining and reclamation efforts wherein FBC ash caps are utilized..

The Department intends to continue gathering data at the McCloskey site and will follow up this presentation with a more detailed report.

My thanks to Joseph Schueck and to Director Roderick A. Fletcher for their support of this presentation, as well as to M. Gene Wood of River Hill Coal Company for his contribution of time and data.