ABATEMENT OF ACID MINE DRAINAGE POLLUTION TO UPPER THREE RUNS BY CAPPING AN ACID PRODUCING RECLAIMED SURFACE MINE WITH FLUIDIZED BED COMBUSTION FLY ASH.

by

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Abstract: A watershed in north central Pennsylvania was being polluted by an acidic mine drainage discharge from a surface coal mining operation. To abate the pollution, application of a 0.91 in thick concrete mix based on fluidized bed combustion fly (FBC) ash was made to the reclaimed surface previous to spreading the topsoil and revegetating the mined area. The FBC ash concrete layer serves as an aquitard which prevents the vertical contribution of groundwater flow due to rainfall from reaching acid forming units in the backfilled mine. The horizontal components of groundwater flow to the site are negligible. Consequently, the formation of acid from the oxidation of pyrite, FeS_2, is inhibited, and the concentrations in the groundwater and the in the surface discharges of Fe, Mn, and Al, metals commonly associated with mine drainage are diminished substantially bellow levels present before the application of the fly ash layer. EPA priority pollutants Cr, Cu, Pb, Ni, and Zn are not present at detection limits in the receiving stream, while only a trace of Se is present. Benthic macroinvertebrate populations have improved substantially since the fly ash application. This reclamation effort offers the promise of abating pollution in numerous surface mine discharges whose primary hydraulic contributor is vertical flow from. rainfall. It is expected that such discharges can be ameliorated to approach discharge limitations, or that their flow rate can be diminished sufficiently to facilitate abatement of pollution in the final discharges with passive treatment.

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Introduction

Acid mine drainage is formed by the oxidation of metal sulfides, primarily the oxidation of pyrite by the familiar mechanism (Stumm and Morgan, 1996):

$$2\ FeS_2 + 7\ O_2 + 2\ H_2O \rightarrow 2Fe^{2+} + 4\ SO_4^{2-} + 4\ H^+ \qquad \text{Equation 1}$$

$$4\ Fe^{2+} + O_2 + 4\ H^+ \rightarrow 4\ Fe^{3+} + 2\ H_2O \qquad \text{Equation 2}$$

$$Fe^{3+} + 3\ H_2O \rightarrow Fe(OH)_3(s) + 3\ H^+ \qquad \text{Equation 3}$$

$$FeS_2(s) + 14\ Fe^{3+} + 8\ H_2O \rightarrow 15\ Fe^{2+} + 2\ SO_4^{2-} + 16\ H^+ \qquad \text{Equation 4}$$

As shown in equations 1 and 2, oxygen must be present to initiate the oxidation. At a low pH level, pH on the order of 3, the ferrous iron oxidation given in equation 2 is accomplished primarily by iron oxidizing bacteria, such as *Thiobacillus ferrooxidans*. This low pH level is promoted by hydrolysis, as shown in equation 3. The overall oxidation reaction in solution is accelerated as shown in equation 4, wherein FC^{3+}, instead Of O_2, is the oxidizing agent.

Guo and Cravotta. (1996) point out that pyrite oxidation occurs mainly in the unsaturated zone of mine spoil. Although infiltrating H_2O carries dissolved O_2 at an equilibrium solubility of between 9.2 mg/L at 20^0C to 14.6 mg/L at 0^0C (Standard Methods, 1996), oxidation by atmospheric O_2 (normal atmospheric volume per cent = 2 1 %, Perry, 1976) is more effective that oxidation in solution, considering the low solubility and the low replacement of dissolved O_2 by molecular diffusion (Diffusivity = 2.5 x 10^{-6} cm^2/scc: at 25 C, Perry, 1976). Guo and Cravotta. observed at a mine where the spoil was compacted, friable shale, the atmospheric oxygen diminished to less than 2 volume % at a depth of about 10 in (33 ft), which suggests that most of the acid mine drainage is formed in the upper layer, approximately 6 in (20 ft), of backfilled spoil.

The remaining pyrite oxidation depends on molecular diffusion Of O_2 from aqueous solution to the pyrite surfaces as well as dissolution of the reaction products (equations 1-4). The Department observes that 40% to 50% of the rainfall at a surface mine infiltrates vertically into the spoils, furnishing the medium for acid mine drainage production. This observation is consistent with a recharge rate of 40% of the precipitation observed at a deep mine underlying the Winding Ridge site in Garrett County MD.

The foregoing discussion suggests that placement of a shallow, relatively impervious barrier as an upper layer of the surface mine backfill would inhibit the formation of acid mine drainage, both by creating an impermeable barrier to atmospheric oxygen and by redirecting the rainfall, the vertical component of the groundwater flow, as shallow runoff. An impermeable barrier could be fashioned from a conventional concrete made from portland cement; however, the cost would prove prohibitive. However, FBC ash in certain cases has the properties necessary to be formed into the necessary shallow, impervious barrier. During the combustion of coal, coal ash in the form of bottom ash and fly ash is formed. The American Coal Ash Association (1991) reports that of the 61.74 million tonnes (68 million US Tons) of coal ash generated in the United States in 1990, only 31% was utilized, the remaining 69% requiring some form of final disposal. Hence, the development of a fly ash cap to abate mine drainage pollution has the added benefit of lessening a serious disposal problem.

FBC ash has been used successfully in several other cases, for example the substantial abatement of mine drainage at the Fran Contracting mine in East Keating Township, Clinton

County, Pennsylvania (Schueck, 1994). Other examples are the ongoing effort by Sky Haven Coal, Inc., to diminish mine drainage and its attendant pollution with a FBC ash cap in Graham Township, Clearfield County, Pennsylvania (mine drainage permit 17810107) and in Boggs Township, Clearfield County (surface mine permit 17820107); also a partial deep mine sealing project (surface mine permit 17880118) in Sandy Township, Clearfield County. Stalker (1996) developed a master's thesis which investigated the mitigation of mine drainage in Somerset County, Pennsylvania using FBC ash. FBC Fly ash has also been used as a backfill material for an abandoned highwall at the Bark Camp Run site in Huston Township, Clearfield County, and as a substrate for oysters in Galveston Bay, Texas. Two projects are currently underway to abate pollution from deep mine discharges, one known as the Omega Mine in Monongalia County WV the other known as the Winding Ridge Site in Garrett County MD.

Fly ash has been used successfully in anthracite coal mine reclamation for over a decade. From 1986 through 1996, 30 permits involving its use were issued by the Pottsville District Office (anthracite mining district) alone. After no less than ten years of monitoring, the Department has not detected any significant off-site water pollution from the use of coal ash in mine reclamation (Scheetz et al., 1997).

Site Description

Original mining on this site began as a Lower Kittanning deep mine, which closed in the early 1950s. Surface mining began in the late 1940s. In 1976, John Teeter Coal Company applied for a mine drainage permit to daylight the Lower Kittanning deep mine and to mine the Middle Kittanning coal seam as well. An updated permit 1779145 was issued to John Teeter Coal Co. 3/18/80, and the permit was transferred to AME enterprises 4/5/92. It was repermitted as 17793044 on 2/19/85 and renewed as River Hill Coal Company on 1/3/91.

The McCloskey surface mining operation, surface mine permit number 17793044, is located in Karthaus Township, Clearfield County, Pennsylvania. Runoff from the mine drains to Saltlick Run; Marks Run (tributary of Upper Three Runs), an unnamed tributary of Upper Three Runs, and directly to Upper Three Runs, all tributaries to the West Branch Susquehanna River, a part of the Chesapeake Bay watershed. During active mining, pit water was pumped and treated, resulting in a temporary abatement of pollution from the mine to Upper Three Runs. However, despite the operator's best efforts, the remining was not able to achieve permanent abatement of the mine drainage. A proposal was developed to secure a surface mine permit for the adjacent area to allow any groundwater from the McCloskey mine to drain via an underdrain to be developed in the new permitted area to Saltlick Run and away from Upper Three Runs, thereby effecting permanent abatement of pollution to Upper Three Runs. The proposal proved not to be feasible when overburden analysis submitted as part of the new permit application predicted the formation of even more acid mine drainage that would discharge to Saltlick Run.

The operator was left with the problem of treating or abating the acid mine drainage that formed within the backfilled McCloskey mine, The operator attempted to passively treat the resulting average 327 m^3/day polluted discharge with a horizontal flow aerobic constructed wetland having an area of 8903 m^2 and incorporating aeration at the inlet. This system has the disadvantage that the mine drainage has to be pumped to the wetland inlet due to space and elevation constraints. Although the 1991 average sample results given in Table 1 show substantial improvement in water quality by the constructed wetland, the wetland was not successful in meeting effluent limits.

Parameter	pH (s. u.)	Alkalinity (mg/L $CaCO_3$)	Acidity (mg/L $CaCO_3$)	[Fe] (mg/L)	[Mn] (mg/L)	[SO_4^{2-}] (mg/L)
Influent	4.8	33	657	230.7	146.3	4766
Effluent	3.3	12	236	31.7	107.9	4752

By letter of August 9, 1991 to the District Mining Manager, Professor Barry E. Scheetz of the Pennsylvania State University, on behalf of the operator, proposed capping the backfilled mine with an impervious FBC ash barrier in an effort to abate the polluted discharge.

Design and Implementation of Fly Ash Cap

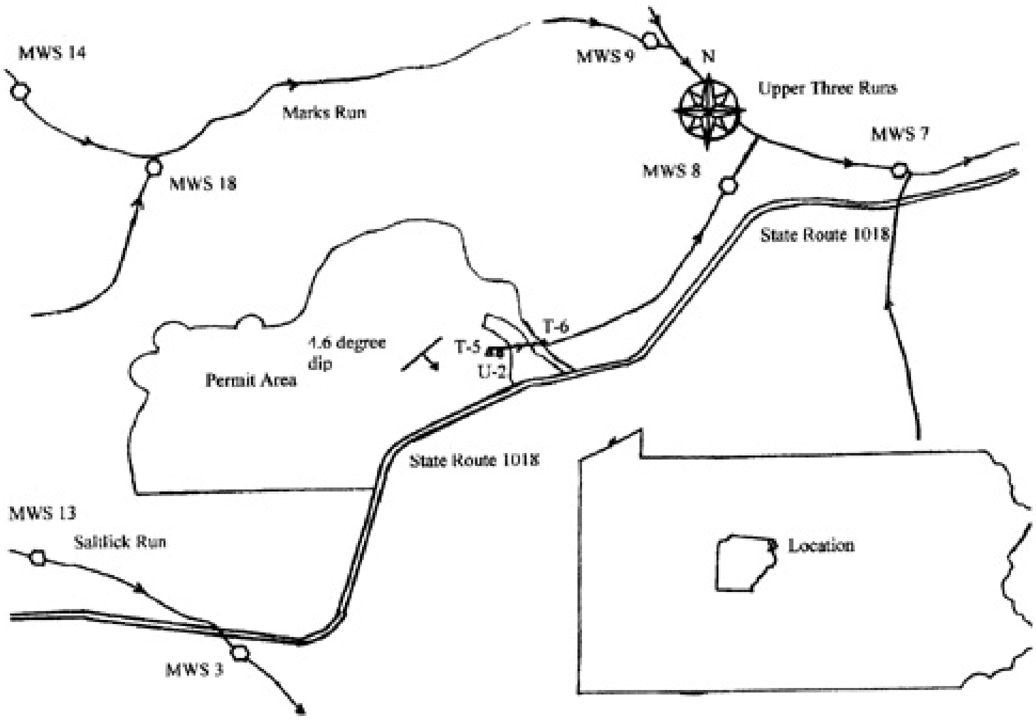

Figure 1: Map of McCloskey Mine Site

A map showing the configuration of the reclaimed area to be capped is given as Figure 1. The mined area is a hilltop surrounded by drainage to the Saltlick Run and Upper Three Runs watersheds. A hydrogeologic (Scheetz et al, 1997, op.cit.).study which considered these and other hydrogeologic constraints and boundary conditions, revealed that there was no apparent horizontal groundwater contribution to the water balance at the site. The rain water falling directly on the site percolates through the spoils almost quantitatively with a detention time of approximately 2 days, with the major portion of the water exiting the site via the seep shown as seep T-5 and some water exiting as seep T-6. This is consistent with the measured strike and dip varying from $N31^{0}E$, 0.7^{0} to $N11^{0}E$, 2.3^{0} for the Middle Kittanning "C" coal and varying from $N43^{0}E$, 4.6^{0} to $N42^{0}E$, 1.5^{0} for the Lower Kittanning "B" Coal. This suggested that placing a FBC ash cap over the reclaimed area would intercept nearly 100% of the water that contributed to the mine drainage flow. On March 3, 1992, the surface mine permit was revised to approve the use of FBC ash grout on site for the purpose of abating the acid mine drainage discharge.

The application of the FBC ash began in July, 1992 as a 1.52 ha (5 ac) experimental project, and has been extended to capping the area described in the next paragraph. The ash is mixed with a waste lime (CaC03) at a rate of 90% fly ash to 10% lime by volume. It is spread and compacted primarily by rubber-tired graders over the reclaimed site. The 0,91 in (36 in) fly ash cap was applied in accordance with procedures developed by Scheetz and Silsbee under the direction of the Department (Scheetz et al, 1997, op. cit.). Water was metered onto the fly ash formulation from water trucks during dry months; otherwise, rainfall furnished the necessary water. The fly ash cap was compacted in 15.24 cm (6 in) lifts to a total thickness of 0.91 in (36 in). The permeability of the ash was determined by laboratory testing to be 10^{-7} cm/sec after a curing time of 515 days. After the Department had satisfied itself concerning the correct application of the cap, the topsoil layer was applied and the area seeded.

The test plot was evaluated by monitoring infiltration. Several 55 gallon drams were buried in the backfill. The drums were filled with clean stone, covered with geotextile fabric. and a standpipe was installed which extended from the bottom of the drum to the surface. Water accumulation within the drums was monitored. Water accumulated in the drums on a regular basis when the cover material was only spoil. However, once the ash cap was in place above the drums, they remained dry. Although a simple test, this monitoring indicated that an ash cap over the entire site should be successful in inhibiting infiltration below the cap.

An area of 37.23 ha (92 ac) has received the fly ash cap, which is to extend to a planned total area of 45.32 ha (112 ac) The cap was applied to a thickness of 0.91 in (36 in) and covered with 0.91 in (36 in) of topsoil or topsoil substitute, which in turn was revegetated to the standards set forth in Pennsylvania's surface mining regulations (Pennsylvania Code, 1998). As estimated 263,320 tonnes (290,000 US Tons) of fly ash has been applied as of February 2, 1998. It is estimated that another 58,112 tonnes (64,000 US Tons) of fly ash will be required to cap the remaining 8.09 ha (20 ac). Based on an annual rainfall of 1040 min (41 in) of which 40% would otherwise have furnished a vertical component of flow through the mine spoils, the annual removal of rainfall contribution over the capped 37.23 ha is expected to be 1.551×10^5 m^3 (4.097×10^7 gal) or an arithmetic average of <u>425 m^3/ </u>(78.95 gal/min) removed from groundwater at the mine site This compares favorably to the value of 327 <u>m^3/day </u>given above for the polluted discharge, supporting the conclusion of the previous hydrogeologic study of the McCloskey site.

The ashes approved for use were from several sources, the first approved source being Public Service Electric and Gas Company's Hudson Generating Station in Jersey City NJ; later authorized were NYE&G Greenwich Plant and Milliken and Goudey Sources and American Ref-Fuel Company in Essex County NJ; also to the Lakeview Coal Bottom Ash Source. Currently ash from the Piney Creek and Scrubgrass cogeneration facilities and the Lancaster Millable Metals site, all in Pennsylvania, are being applied. All of these ashes were approved by the Department prior to their being placed at the McCloskey Operation. Typical chemical characteristics of the ash are given in Table 2 (Data provided by Scheetz).

Parameter	Concentration (mg/L)	Parameter	Concentration (mg/L)
[Al]	0.48	[Mn]	0.0.41
[As]	0.08	[Mo]	0.53
[B]	1.05	[Ni]	0.15
[Ba]	0.41	[Pb]	0.65
[Ca]	970	[Sb]	1.28
[Co]	0.03	[Se]	0.05
[Cr]	0.07	[Si]	9.6
[Cu]	<0.02	[Sn]	0.61
[Fe]	0.06	[Sr]	6.1
[Hg]	0.004	[Ti]	<0.02
[K]	310	[Zn]	0.04
Mg	35	[Zr]	2.39

Table 2: Chemical characteristics of fly ash used at McCloskey site

The beneficial use of fly ash is covered in Title 25 Chapter 287 of the Pennsylvania Code, and it is estimated that approximately 363,000 tonnes (400,000 US Tons) of coal ash is transported annually to sites within both the anthracite and the bituminous coal regions for disposal or beneficial use from a variety of sources including coal fired utilities located in other states (Scheetz et al, 1997, op. cit.).

Results

A sample of the McCloskey discharge was taken by the Mine Conservation Inspector. The results given in Table 3 show the absence of EPA priority pollutants from the discharge which is being mitigated by the fly ash cap.

Parameter	Concentration (mg/L)	Parameter	Concentration (mg/L)
Total Dissolved Solids	5024	[Cd]	<0.0002
Alkalinity as $CaCO_3$	2	[Ca]	326
Acidity as $CaCO_3$	706	[Cr]	<0.004
Cl^-	8	[Cu]	<0.010
F^-	1.7	[Pb]	<0.001
[Fe] total	122	[Mg]	547
[Na]	19.3	[Hg]	<0.001
[NH_3] as N	<0.04	[Se]	<0.007
[NO_3^-] as N	0.43	[Zn]	2.31
[Al]	23.7	[Mn]	127
[As]	<0.004	[SO_4^{2-}]	3386
[Ba]	<0.010		

Table 3: Chemical quality of discharge after fly ash cap was applied

The Pennsylvania fish and Boat Commission on August 12-13, 1997, sampled Upper Three Runs downstream of the fly ash capping project and obtained the results given in Table 4. The Fish and Boat Commission also obtained the benthic macroinvertebrate results given in figure 2 and the electrofishing results given in figure 3.

Parameter	Concentration (mg/L)	Parameter	Concentration (mg/L)
pH	10.8	$[NO_3^-]$	1.23
Spec Cond (umho/cm)	1085	[Al]	0.000926
Total Dissolved Solids	898	[As]	<0.004
Alkalinity as $CaCO_3$	74	[Ba]	0.031
Suspended Solids	40	[Cd]	<0.010
Acidity as $CaCO_3$	0	[Ca]	218
$[Cl^-]$	9	[Cr]	<0.050
$[F^-]$	<0.20	[Cu]	<0.010
[Fe]	0.744	[Pb]	<0.010
[Na]	3.15	[Mg]	2.71
Turbidity (NTU)	122.5	[Ni]	<0.025
[Mn]	25	[Se]	<0.0071
$[NH_3]$	0.17	[Zn]	<0.010

Table 4: Upper Three Runs Water Quality Results (PA Fish and Boat Commission)

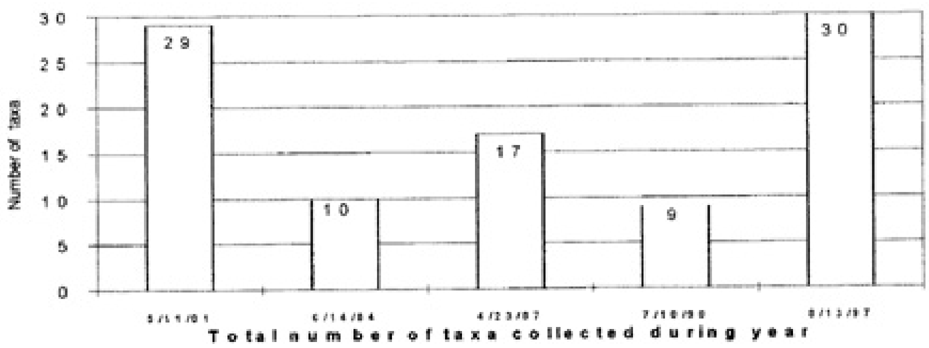

Figure 2: Benthic macroinvertebrates downstream

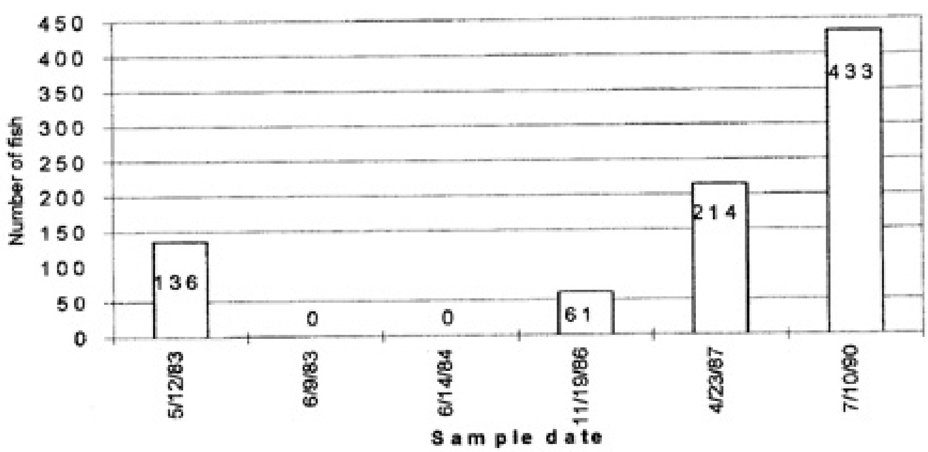

Figure 3: Fish populations downstream

The box and whisker plots given in Figures 4 through 8 illustrate the quality of the main discharge T-5 during four periods of the mining operation.. They illustrate that the rates of acidity and sulfate generation from the McCloskey site have diminished with time.

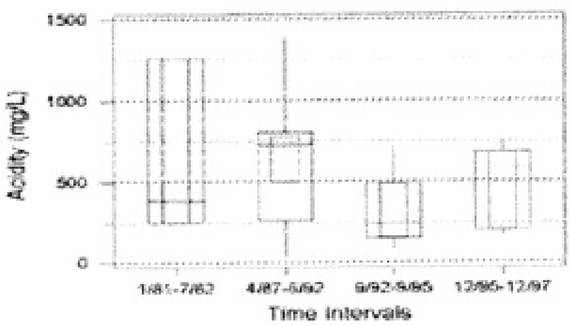

Figure 4: Acidity in the main discharge (T-5) during different time intervals

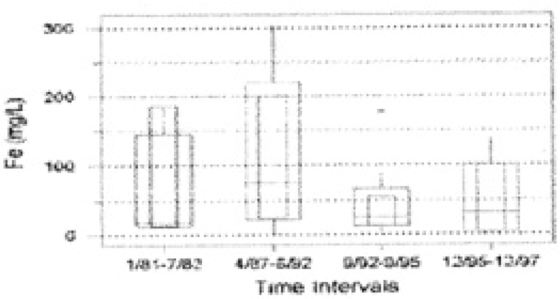

Figure 5: Total iron in main discharge during different time intervals

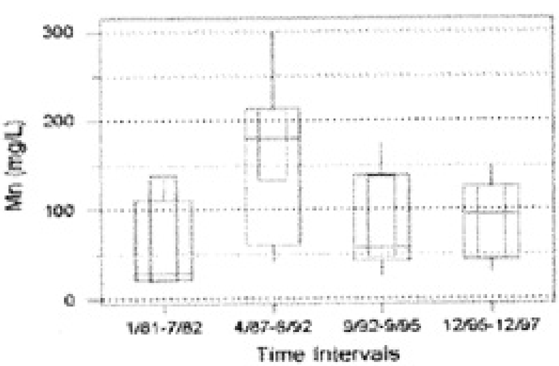

Figure 6: Total manganese in main discharge during different time intervals

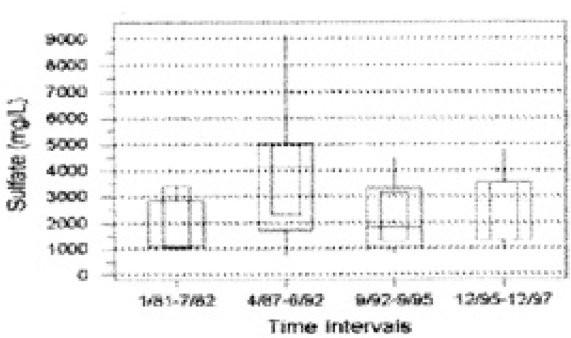

Figure 7: Total sulfate in main discharge during different time intervals

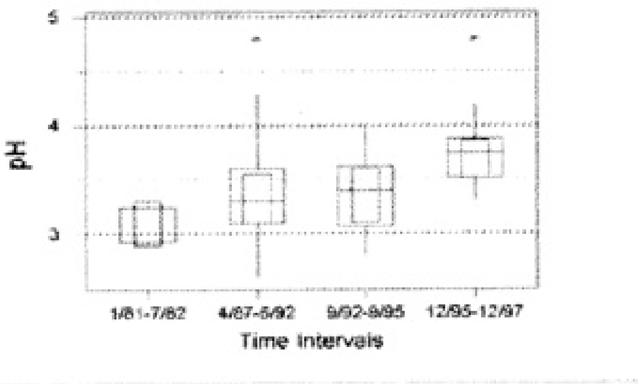

Figure 8: pH in main discharge during different time intervals

The chemical water quality data for the Unnamed Tributary of Upper Three Runs and of Upper Three Runs downstream of the McCloskey Operation as a function of time are from two sources: the operator's file and the Department's Hawk Run District Mining Office file for the permitted area. Figures 9 through 13 depict the behavior of typical mine drainage parameters with time, The acidity in the unnamed tributary of Upper Three Runs has declined with time, and the pH has risen. Iron concentration has declined progressively with time. The significant downward trend in manganese concentration is an indicator that the fly ash project is abating pollution, while the decline in sulfate indicates that the rate of pyrite oxidation has diminished.

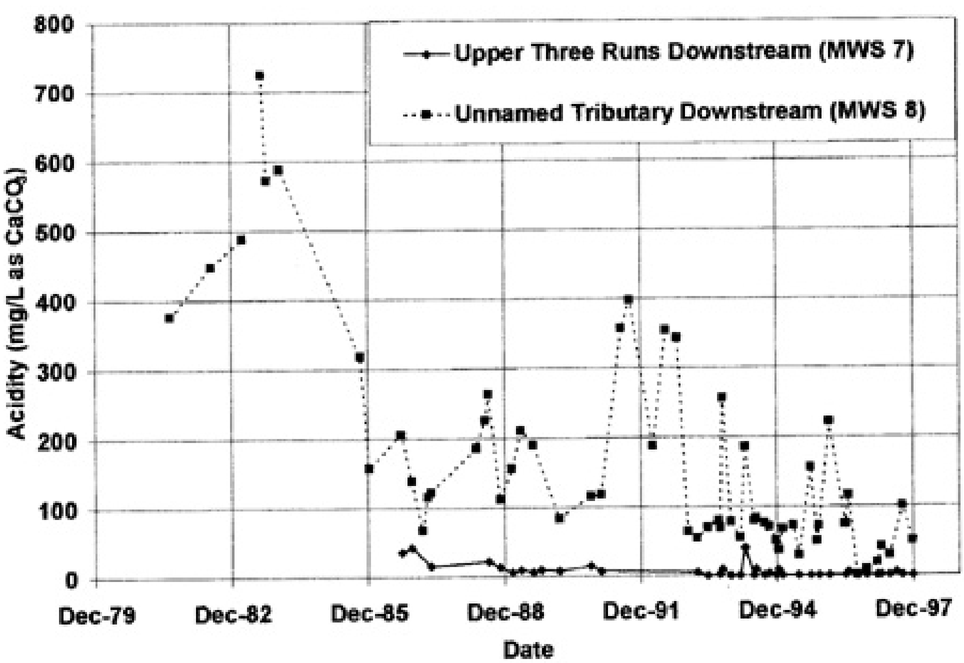

Figure 9: Acidity in Unnamed Tributary and Upper Three Runs

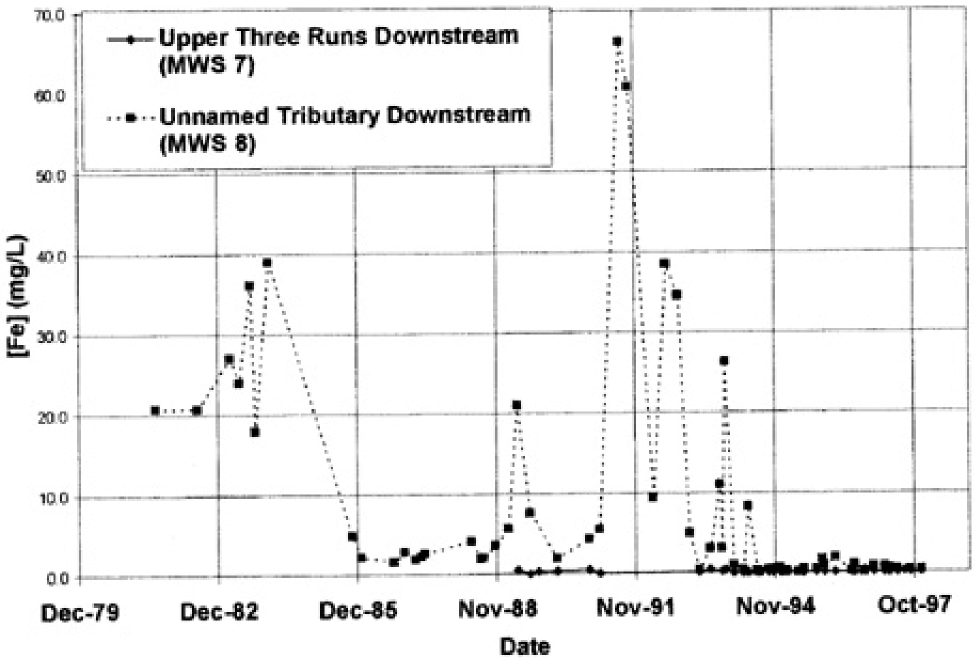

Figure 10: Iron in Unnamed Tributary and Upper Three Runs

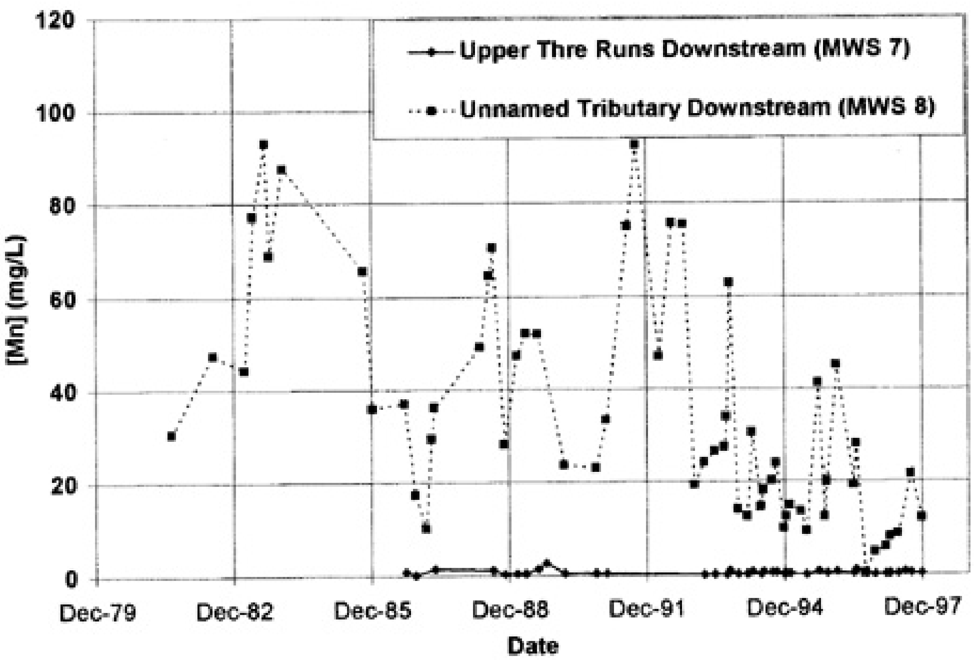

Figure 11: Manganese in Unnamed Tributary and Upper Three Runs

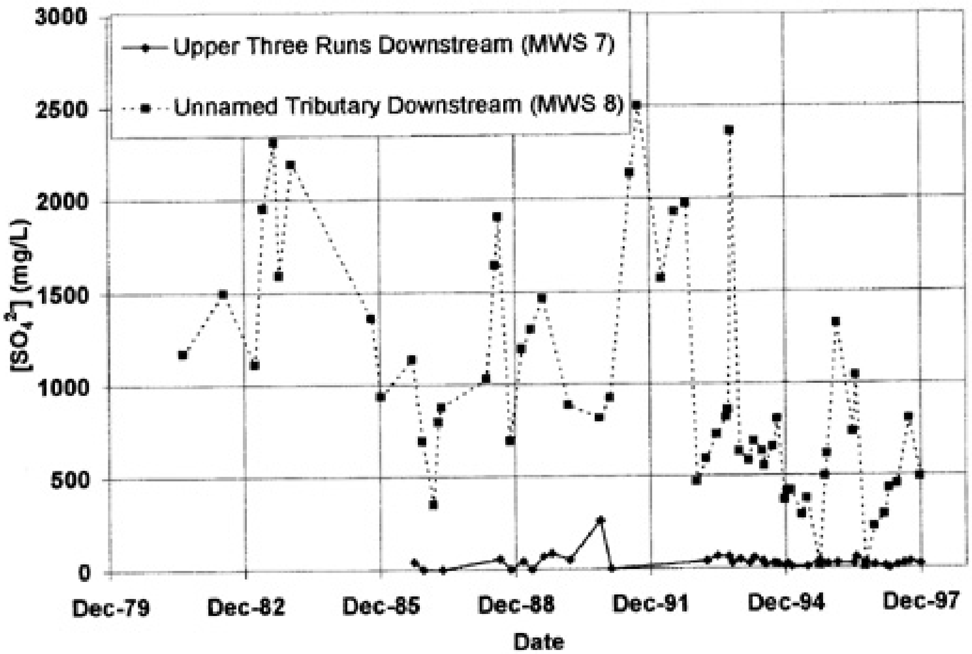

Figure 12: Sulfate in Unnamed Tributary and Upper Three Runs

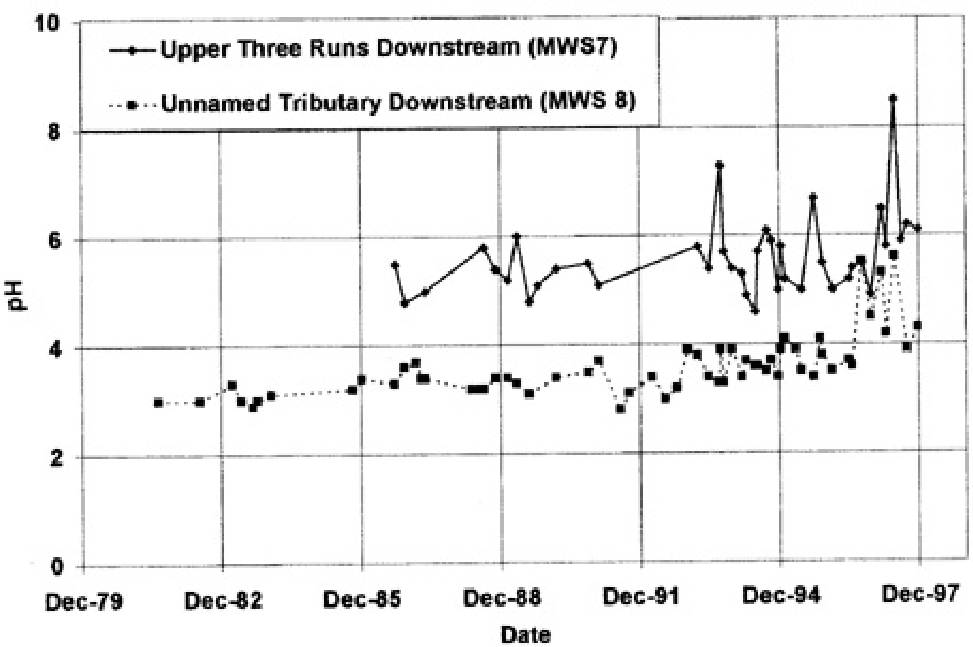

Figure 13: pH in Unnamed Tributary and Upper Three Runs

Much of the information about the flow from this discharge must be inferred, because the operator has been pumping the water into the constructed wetlands. As a consequence, the flow measurements are discrete and are incomplete. However, mine inspectors and company representatives have observed generally that flows from the main discharge T-5 have substantially diminished. The flow rates provided by the operator for the main discharge T-5 have averaged 92 m3/day since June, 1992, possibly confirming the supposed diminution of flow from the discharge. In addition, the operator was spending a considerable sum of money on chemicals to treat the discharge before placement of the ash cap. Currently, with the cap construction being 82% completed, the operator no longer needs chemical treatment as the wetlands alone are able to bring the water to effluent quality.

A significant permanent improvement in the quality of Upper Three Runs is expected from the fly ash cap. Pollution from the mine drainage parameters given in the Department's regulations has been removed, and the stream now supports fish where none were supported previous to the FBC ash capping project. No detectable pollution from other EPA priority pollutants has been found in Upper Three Runs.

Conclusions

1. The fly ash cap at the McCloskey site has enhanced reclamation, abated water pollution, and allowed the population by fish of a stream which otherwise would support no fish.
2. The fly ash cap at the McCloskey site has diverted the vertical contribution from rainfall out of the groundwater flow regime. The horizontal contribution to groundwater flow within the reclaimed spoils being negligible, the fly ash cap has substantially abated the formerly polluted post-mining discharge.
3. The fly ash cap at the McCloskey site has not generated secondary problems in the form of EPA priority pollutants in the receiving stream.

This abatement and reclamation project demonstrated the environmentally safe and beneficial use of what otherwise would be considered a waste product. The project does not demonstrate that a fly ash cap to retard vertical flow would be successful in all cases of mine drainage pollution, and further studies are necessary. For example, if the inflow to a given mine site has a significant horizontal component, retarding the vertical flow from rainfall on the site itself might not be as successful at that site as it has been at the McCloskey site. As another example, insufficient time has elapsed to determine whether, at sites where the natural succession includes plants whose roots might penetrate the cap, a fly ash cap would lose its effectiveness over time or simply limit root zone development. Other studies are currently evaluating the ability and feasibility of a FBC ash grout mixture to fill the voids in a deep mine and prevent pollution that otherwise might emanate from it. These issues are of great importance to mine reclamation and pollution abatement efforts.

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