SESSION 5: ACID MINE DRAINAGE REMEDIATION

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HYDROLOGIC INVESTIGATION AND REMEDIATION OF A POST-REMINING ACIDIC SEEP[1]

by

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Abstract. Surface remining of coal pillars in abandoned underground workings in the Pittsburgh seam in southwestern Pennsylvania has often resulted in post-remining discharges whose water quality is the same or better than the pre-existing discharges. However, at one such operation in Washington County, PA, an increase in contaminant loading occurred at an outcrop seep after remining. This problem was believed to be at least partly related to a small unstripped area of the old deep mine workings immediately upgradient from the seep. A hydrologic investigation that included a chemical tracer test, slug tests in the remined spoil, and water quality monitoring indicated that the mine pool in the old workings discharged through the seep. However, the water in the mine pool and much of the remined spoil was consistently alkaline; this suggested that the acidic water may have originated in other areas of the spoil and old workings, and passed rapidly to the seep through a highly transmissive portion of the spoil. Acting on this assumption, the mine operator successfully implemented a remediation scheme in which the spoil was excavated to intercept the acidic spoil water. The excavation was then re-emplaced with an anoxic limestone drain at its base. The drain now serves both to add alkalinity to the water and to divert the seep to an area where metals can be removed easily via precipitation in wetlands.

Additional Key Words: mine hydrology, mine spoil

Introduction

A great deal of uncertainty and confusion often exists with respect to the origin of contaminated "off-site" seeps which emanate from unmined areas near reclaimed surface mine spoils. The hydrology of the spoil material and surrounding strata is often only poorly understood, and the potential sources of contamination within and/or around the spoil are usually not well-defined. The situation is complicated even further in remining situations or when other surface mines exist on adjacent properties. In these cases, the local hydrology may have already been altered by the previous mining. The consequences of this uncertainty become critical in the context of SMCRA enforcement, where a regulatory agency must make a determination as to whether a mining permit holder is responsible for the remediation of the contaminated off-site discharge.

The degree of uncertainty associated with the origin of an off-site discharge can sometimes be reduced by conducting a preliminary hydrologic investigation at the mine site. While the investigation may still not reveal

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the exact source of the contamination, the information may be sufficient to narrow the differences of opinion which had existed between the permit holder and the regulatory agency. This paper describes how a preliminary hydrologic investigation was used to help a mine operator identfy the potential source of a contaminated off-site seep, implement a cost-effective remediation scheme, and avoid a protracted litigation process.

Mining History

The study site is located in Washington County, Pennsylvania, about 15 miles southwest of Pittsburgh. As shown in Figure 1, the entire Pittsburgh coal seam in the general area had been mined by underground methods prior to 1940. Portions of the deep mine barrier pillar at the Pittsburgh coal outcrop adjacent to the eastern side of the mine permit area had also been strip mined previously during the early 1950's. However, enough coal still remained in the deep mine pillars to allow an economically viable surface mine operation within the permit area shown in Figure 1.

Figure 2 shows the topographic contours and a cross section of the mine permit area prior to the most recent period of surface mining. This mining took place between 1985 and 1990, beginning at the coal outcrop area shown in Figure 2 and progressing to the southwest, southeast, and northwest until the permit boundary or an uneconomic overburden depth was reached. The overburden consisted mostly of shale, with some sandstone. A persistent limestone bed of 5-10 ft thickness was located approximately 40 ft above the Pittsburgh coal. This limestone was believed to be responsible for the alkaline discharges that were produced from remining operations in the vicinity of the study site, despite the fact that the deep mines had discharged acidic water prior to remining. Because of this, the mine operator sought a permit under SMCRA regulations rather than under the Pennsylvania remining program. Therefore, while the subject mine was a remining site in a physical sense, it

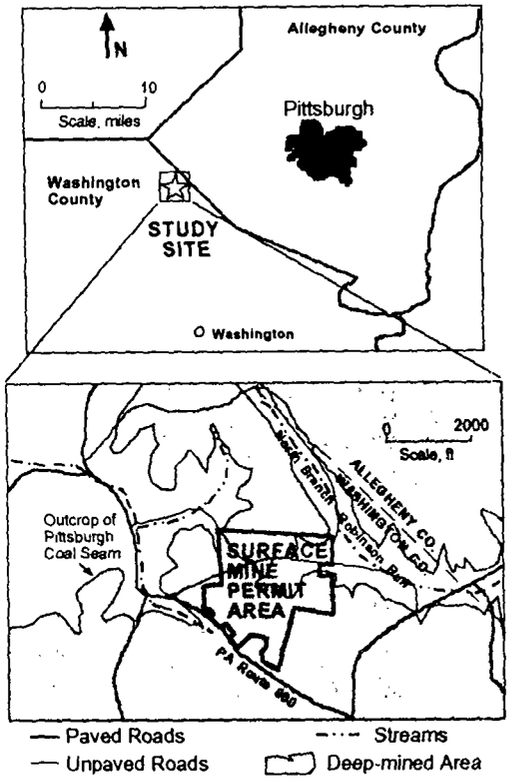

Figure 1. Location Map of Study Site

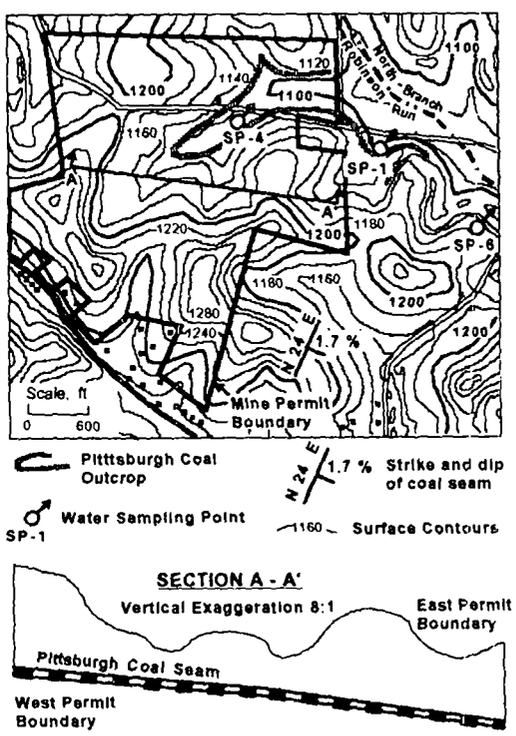

Figure 2. Pre-remining Topography and Sampling Points

was not defined as such in the regulatory arena.

Water Quality Changes

Although no ground water elevation data were available for the 1985-90 period, it can be assumed that the local ground water flow direction was from northwest to southeast due to geologic structure, and was dominated by the presence of the active surface mine and the mined-out Pittsburgh coal seam (see cross-section in Figure 2). Figure 2 also shows the locations of the three surface water sampling points which were closest to the downgradient edge of the mine permit boundary. Sample point SP-4 was intermittent and consisted mostly of surface runoff; it did not show evidence of mining-related contamination before or after the period of mining. Sample point SP-6, located about 1000 ft southeast of the permit boundary, was moderately acidic before, during and after mining. This discharge occurred at the side of a collapsed mine portal structure, and it was obviously connected to a deep mine pool; however, its relationship to the surface mining operation could not be determined. The sampling point of greatest interest was SP-1; prior to mining, this discharge originated as seepage from a swampy area in a natural hollow near the east permit boundary. However, for compliance purposes, sampling was performed at the outlet of a concrete culvert that carried the discharge under the road. Samples were collected on approximately a quarterly basis from 1984 through 1994. Table 1 summarizes the changes in pH, flow rate, and the concentrations of acidity, iron, manganese, and sulfate that occurred at sample point SP-1 before, during, and after the 1985-90 period of surface mining. Note that the discharge was slightly acidic with elevated contaminant levels before mining occurred, and became progressively worse during and after mining. It was unclear whether the source of contamination was the abandoned deep mine workings, the 1950's surface mine spoils just to the east of SP-1, or the new surface mine spoils. Although the discharge did not emanate directly from the surface mine spoil, it was close enough to suggest that a hydrologic connection existed; therefore, the state regulatory agency required the mine operator to initiate treatment of SP-1.

However, the mine operator pointed out that another factor besides the surface mine may have been controlling the degradation of SP-1. At some time shortly after the cessation of surface mining, the landowner to the east of the permitted area made several excavations that began to discharge acidic water at a rate that was greater than that of the original SP-1. Flow from the original SP-1 decreased concurrently. As shown in Figure 3, these post-remining discharges (Seeps A and B) eventually passed through the SP-1 compliance monitoring point. The mine operator contended that the excavations were tapping a portion of the deep mine pool that had not been impacted by surface mining, and that the mining company should not be held responsible for treatment of the discharge.

Initial remediation efforts

The mining company conducted temporary chemical treatment of SP-1 by

Table 1. Water Quality Changes at Sample Point SP-1

Period	# of Samples	Statis-tic	Flow gpm	Lab pH	Net Acid mg/L CaCO3	Total Fe mg/L	Mn mg/L	Sulfate mg/L
Pre-remining	6	Median	4.5	5.00	11	0.44	2.85	520
1/84 - 1/85		Mean	5.4	4.78	43	0.76	3.17	527
During remining	13	Median	1.5	4.90	46	0.90	4.90	790
1/85 - 1/90		Mean	2.2	4.04	132	2.79	4.24	872
After remining	16	Median	18.0	3.27	111	17.49	10.75	1623
1/90 - 1/94		Mean	20.1	3.24	145	21.49	11.22	1355

placing sodium carbonate briquettes in the contaminated stream; however, this was not viewed as a viable long-term solution by either the company or the regulatory agency. To supplement this treatment, the mining company injected a large quantity of anhydrous ammonia into the abandoned mine voids which were believed to be the source of the discharge. The injection wells, labeled A-1 through A-4 in Figure 3, were located between the surface mine highwall and the mine permit boundary, and penetrated the mine voids within 300 ft of the post-remining seeps. It was expected that the alkalinity and aeration introduced via the ammonia injection would eliminate the acidity of the seeps and cause precipitation of metals to occur within the mine voids. However, the water quality of the discharges showed no appreciable change after ammonia injection, thus causing the mining company to review its approach toward remediation.

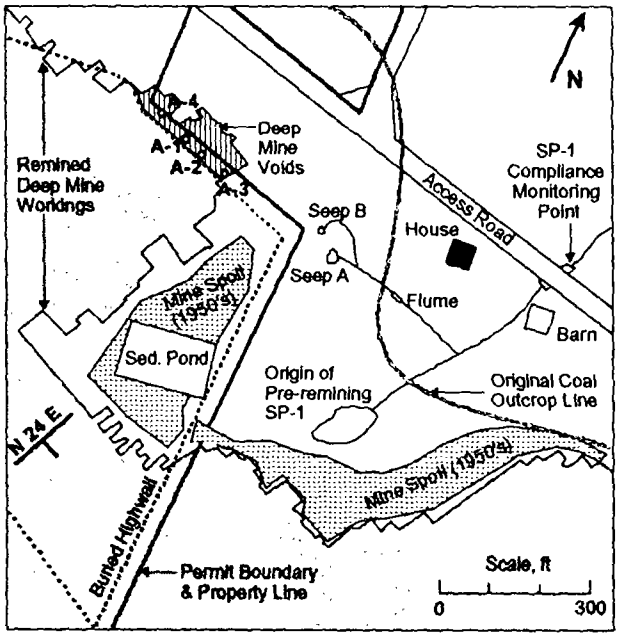

Figure 3.Post-remining Discharge Area

Hydrologic Investigation

During January 1994, the mining company agreed to cooperate in a preliminary hydrologic investigation at the site, with the intent of determining why the initial ammonia injection had failed, and whether the desired remediation could be achieved by injecting cement kiln dust into the abandoned deep mine voids. The following sections describe the data collected and analyzed by the U. S. Bureau of Mines in support of this effort.

Preliminary Data Collection

Water elevations in the mine void wells were measured weekly from March through June of 1994; the combined flow rate of Seeps A and B was also measured weekly with an H-type flume (Figure 3). Water quality samples were collected once every two weeks from the void wells and the seeps during the same period. Site conditions precluded the direct measurement of the flow rates of these seeps, but estimates were obtained via ion mass-balance methods described previously by Aljoe (1995). Concurrently with these efforts, a chemical tracer test was conducted by injecting a concentrated sodium bromide solution into two of the four ammonia injection wells. The following sections describe the results of these investigations.

Water Elevations and Flow Rates. Water elevations in wells A-1, A-2, and A-3 were almost identical (Figure 4), suggesting that these wells penetrated the same mine pool. The mine voids were only partially flooded, with about 2 ft. of water in a void height of about 7 ft. By June 14, the mine void at Well A-1 became dry. It was inferred that a small mine pool existed in the voids penetrated by these three wells, and that the pool was drained by a consistent discharge source.

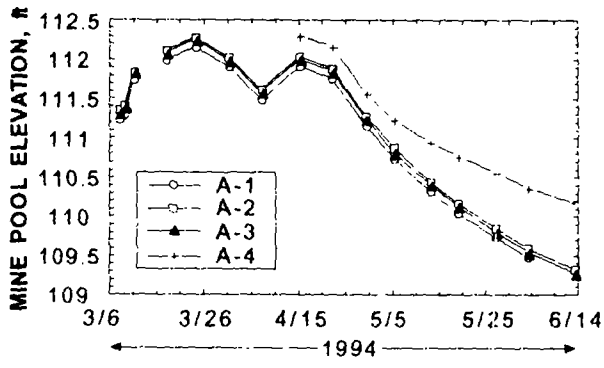

Figure 4. Water Elevations in Mine Void Wells (arbitrary reference datum).

The water elevation in Well A-4 was consistently higher than in the other three mine void wells by 0.5 to 1.0 ft; this difference was considerably greater than the error that could be attributed to surveying and level measurement. Also, the decline in the water elevation at Well A-4 was less steep than in the other three wells during May and June 1994. From these data, it was inferred that another small mine pool existed in the portion of the deep mine penetrated by well A-4. The degree of hydrologic connection between the two pools could not be confirmed; however, the behavior of Well A-4 during May and June suggested that this pool was not directly connected to the same discharge source as the pool penetrated by the other three wells.

The combined flow rate from seeps A and B was directly related to the elevation of the mine pool at wells A-1, A-2, and A-3 (Figure 5). This relationship was not surprising, given that both the pool elevation and flow rate would be similarly influenced by precipitation. Figure 5 shows that the mathematical relationship at this site was exponential (linear plot on log scale); however, mine pool elevation-discharge plots at other sites had exhibited a direct linear relationship (Aljoe, 1994).

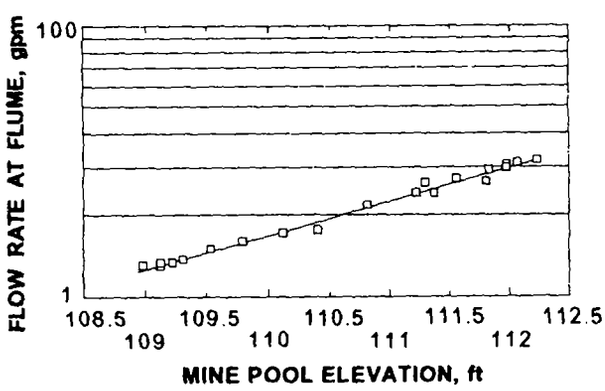

Figure 5. Mine Pool Elevation vs. Discharge Rate.

Another deviation from past experience was that the total discharge rate, about 30 gal/min for much of the study period, was much larger than would be expected from such a small postulated recharge area (about 2/3 acre of surface area above the mine voids). The lack of a visible physical connection between the seeps and the mine voids also suggested that more evidence had to be gathered to verify the hydrologic connection between the mine pool and the contaminated seeps.

Tracer Test. One of the most direct ways to verify the hydrologic connection was to inject a chemical tracer into the mine voids and monitor the seeps for its arrival. The bromide ion was chosen as the tracer because of its conservative behavior in mine waters, the lack of detectable bromide concentrations in the mine voids and the seeps, and the ease of application in the form of a concentrated bromide salt solution. On March 8, 1994, a total of 6.0 kg of NaBr salt (4658 g of Br^-) was added to the mine voids; half of this total was added to Well A-1, and the other half to well A-3. These wells were chosen because Well A-2 still possessed large quantities of ammonia and Well A-4 had not been found at the time the tracer test was begun. If the extent of the pool were limited to the area occupied by the mine voids (approx. 433,000 gal), this amount of bromide would have been sufficient to raise the bromide concentration in the mine pool to a level that was about 15 times the laboratory detection limit of 0.1 mg/L, even if the solute became uniformly distributed within the pool. This ensured that if the mine pool and seeps were indeed hydrologically connected, bromide would be detected at the seeps even if a substantial degree of dilution were occurring.

In general, the results of the tracer test showed that there was a distinct hydrologic connection between the mine pool and the seeps, but that the connection was not as direct or exclusive as first anticipated. Figure 6 shows the bromide concentrations (a) and loads (b) at the three discharge locations. If the mine pool were indeed the only source of water to the seeps, the high discharge rate would result in a pool turnover time (complete passage of the tracer cloud

through the seeps) of about 10 days. However, the peak bromide cncentration did not occur until the twelfth day, and the total time required for the bulk of the tracer to pass through the seeps was about 50 days. This suggested that one or both of the initial assumptions about the flow system was incorrect, i.e., the mine pool was much larger than the area of open mine voids, and/or the monitored portion of the pool was not the only source of water to the seeps.

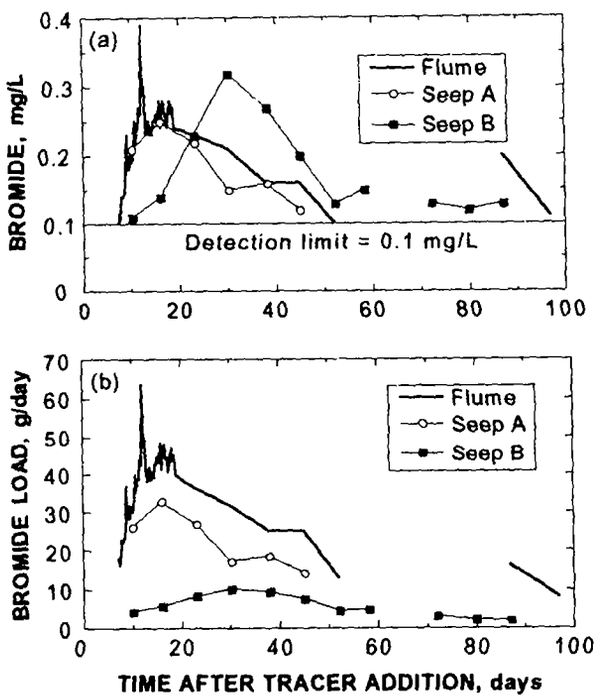

Figure 6. Results of Bromide Tracer Test (a) concentrations; (b) loads.

From the peak bromide concentration and load shown in Figure 6, the average flow velocity from the bromide injection wells to the seeps was estimated to be 12 to 27 ft/day. This velocity is more than an order of magnitude lower than found by Aldous and Smart (1988) for underground mine workings with pure conduit-type flow. Instead, the velocity is closer to those for sealed underground mine workings (Aljoe and Hawkins, 1993), mine spoil (Hawkins and Aljoe, 1992), or glacial sediments (Grisak, et al., 1977). These results suggested that the tracer cloud moved through relatively resistive material (mine spoil and/or unmined, fractured strata) between the injection wells and the seeps.

Analysis of tracer data gathered weekly from the injection wells and seeps showed that the mine pool was hydrologically connected to both seeps, but the degree of connection was different for each seep. Seep A, which consistently accounted for 75% to 80% of the flow at the flume, also appeared to be the most direct outlet for the mine pool. As shown in figure 6, the bromide profiles of Seep A generally paralleled those of the flume, and the bromide load at Seep A was generally greater than at Seep B. Higher bromide concentrations were often found at Seep B, but the path from the mine voids to Seep B appeared to be less direct. The peak concentration occurred two weeks later than at Seep A; Seep B also had a less-pronounced loading peak, and concentrations at Seep B remained detectable until almost 90 days after the test was begun. This suggested a slower, more evenly distributed release of tracer through Seep B.

Figure 7 shows the bromide concentrations in the injection wells over the sampling period, along with the flume concentration curve. The consistently lower concentrations in Well A-3 were attributed to the greater amount of flushing water that had been used in this well. The rates of concentration decline in the two wells were very similar, but the higher initial concentration in Well A-1 allowed bromide to remain detectable until the mine void became dry.

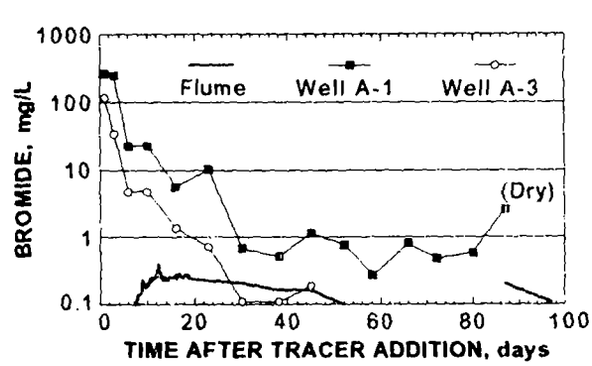

Figure 7. Tracer concentrations in Mine Pool and Discharge.

The fact that bromide concentrations in part of the mine pool were on the order of 1 mg/L while seep concentrations were undetectable indicated that dilution was occurring between the mine voids and the seeps.

Water Quality Data. Initial water quality data collected at the site showed that the most critical difference between the water quality in the monitoring wells and the seeps was the net acidity over the study period, as depicted in Figure 8.

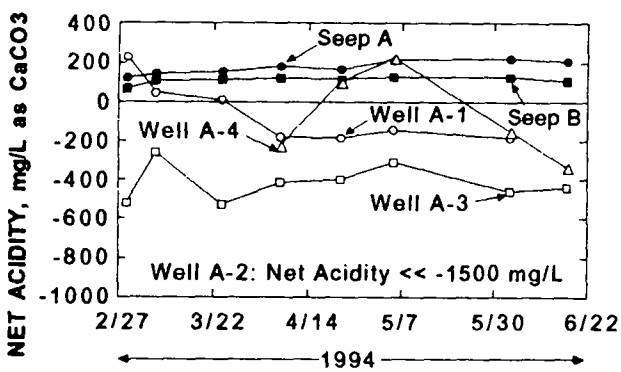

Figure 8. Net Acidity in Mine Pool and Seeps.

Net acidity at the seeps was very stable at 100 - 200 mg/L over the study period; conversely, the mine voids generally possessed strongly alkaline water (negative net acidity = net alkalinity). Although wells A-1 and A-4 were acidic on several occasions, they showed temporal fluctuations that contrasted markedly with the stable pattern of the seeps. Furthermore, Well A-3, which was closest to the seeps and was shown to be hydologically connected to the seeps via the tracer test, was consistently net alkaline by more than 400 mg/L. In order for the seeps to be net acidic, while still receiving recharge from the alkaline mine pool (as verified in the tracer test), one or both of the following must have been occurring: (1) significant geochemical changes were occurring along the flow path; or (2) another source of recharge that was more acidic and probably larger in volume than the mine pool was present.

Table 2 lists the average values of the other important mine water quality parameters over the study period, along with the average cation/anion ratios calculated from the laboratory analyses. The substantial differences in water quality within the mine voids and the lack of tracer detection in wells A-2 and A-4 suggested that there was very little geochemical mass transfer within the mine pool. It would therefore be inappropriate to combine the parameter values across different wells to obtain "average" values for the pool as a whole. In fact, it may be justifiable to exclude Well A-2 completely from the analysis; its anomalous characteristics were attributed to the continued presence of ammonia from the previous injection. Water samples were not routinely analyzed for ammonia; however, the presence of ammonia (as the NH_4^+ cation) was suspected when the very low cation/anion ratio of Well A-2 (see Table 2) was first noted. Several subsequent samples from Well A-2 were found to contain ammonia concentrations of greater than 1000 mg/L. The cation/anion ratio of Well A-3 was also significantly lower than unity, so it is possible (though not verified by laboratory analysis) that ammonia was

Table 2. Average Water Quality Parameters, March - June 1994

Location	pH	Fe, mg/L	Ca, mg/L	Mg, mg/L	Al, mg/L	Na, mg/L	Mn, mg/L	SO4, mg/L	Cations /Anions	Notes
SEEP A	4.37	43.0	324	133	6.0	19.2	13.2	1483	1.00	
SEEP B	3.62	20.2	370	170	20.8	12.6	16.4	1903	0.93	
Well A-1	6.68	73.0	528	227	5.7	17.6	14.4	2203	1.03	Tracer Inj.
Well A-2	8.40	0.8	98	150	0.1	22.7	1.3	2999	0.13	High NH3
Well A-3	6.67	7.7	459	191	0.9	21.2	13.4	2188	0.75	Tracer Inj.
Well A-4	6.40	198.0	532	267	4.4	14.6	21.4	2654	0.97	

also partially responsible for its alkaline character. However, wells A-1 and A-4 had cation/anion ratios near unity even when they were net alkaline, indicating that ammonia concentrations were very low. Therefore, except for Well A-2, it was concluded that the ammonia injection alone was not responsible for the predominantly alkaline character of the mine pool.

Some of the water quality differences shown in Table 2 could have resulted from geochemical reactions along the flow path from the wells to the seeps; however, these reactions alone cannot explain all the differences. For example, the pH and iron concentrations were generally higher in the wells than at the seeps, while the aluminum concentrations were lower. There were also significant decreases in net acidity (Figure 8), calcium, magnesium, and sulfate. Magnesium in mine drainage has been found to be particularly conservative in almost all situations (Hedin, et al., 1994); calcium and sulfate would also be expected to be conservative under these site conditions (Bencala, et al., 1987). The most reasonable explanation for these decreases would be dilution by other recharge sources whose concentrations of these ions were lower.

Additional Data from Spoil Wells

Given the results described above, it was clear that the mine voids and seeps were hydrologically connected, but that the flow rate and water quality of the seeps were heavily influenced by one or more other sources. The most likely other source was the mine spoil; however, in the initial analysis, no hydrologic data were available for the spoil. In order to investigate this possibility, the mining company installed four monitoring wells in the spoil (Wells B-1 through B-4) as shown in Figure 9. Water level and water quality data were collected from the spoil wells for a short period after their installation (from June 17 through August 9, 1994). Slug injection tests were performed to determine the relative hydraulic conductivity of the spoil at the well locations. Longer-term data from these wells were not collected. However, the initial data generally supported the conclusion that ground water in the spoil was contributing to the seep discharges, and formed the basis of the coal company's subsequent remediation effort.

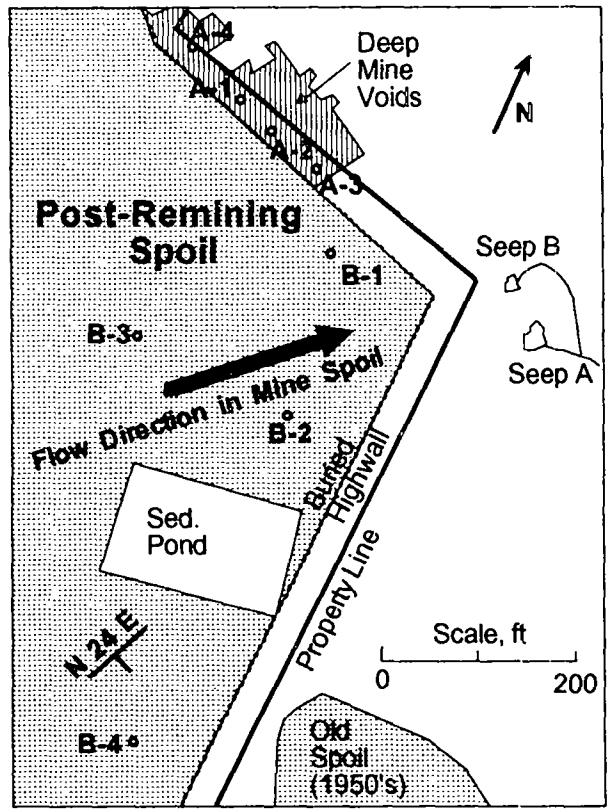

Figure 9. Mine Spoil Well Locations.

The water level in the monitored mine pool was about the same as that of Well B-3, and about 0.5 to 1.0 ft above the levels in wells B-2 and B-1. The water elevation in Well B-4 was 3 to 4 ft below those of the other wells; however, because of its physical separation from the other wells and the seep areas, and the tendency of mine spoil to have multiple flow paths, Well B-4 was considered to be relatively unimportant to the flow system in the seep area. Figure 9 shows the local ground water flow direction as determined from the water levels in wells B-1, B-2, and B-3. Note that the flow direction did not parallel the dip of the pit floor, but was directed toward the seeps.

Table 3. Average Water Quality Parameters, June - August 1994

Location	pH	Net Acid, mg/L CaCO3	Fe, mg/L	Ca, mg/L	Mg, mg/L	Al, mg/L	Na, mg/L	Mn, mg/L	SO4, mg/L	Cations /Anions
SEEP A	4.82	95	52.5	403	170	2.95	23.86	13.25	1788	1.01
SEEP B	3.55	186	41.5	446	216	15.44	14.58	16.10	2207	0.97
Mine Void Wells										
Well A-2	7.29	-2685	0.2	162	167	<0.1	18.44	1.65	2116	0.24
Well A-3	6.56	-422	3.6	496	208	<0.1	19.71	13.63	2141	0.82
Well A-4	6.65	-419	158.1	479	239	<0.1	14.78	18.77	2497	0.85
Spoil Wells										
Well B-1	5.86	-89	84.9	555	213	0.56	26.33	18.41	2091	1.12
Well B-2	**4.28**	**52**	**66.9**	**382**	**153**	**0.72**	**30.18**	**12.57**	**1617**	**1.09**
Well B-3	6.64	-152	89.6	647	211	0.11	31.73	17.34	2111	1.18
Well B-4	7.19	-284	1.2	346	75	1.07	34.85	2.36	878	1.05

Table 3 summarizes the water quality data (average of 2 to 4 samples per well) collected during the study period after the spoil wells were installed. Like the mine voids, the spoil contained primarily alkaline water at the well locations. However, the well closest to the seep area (Well B-2) contained water that was consistently net acidic; although the concentration of acidity was not as great as that of the seeps, it confirmed that acidic water was indeed present in the spoil. Furthermore, the concentrations of the calcium, magnesium, and sulfate in Well B-2 were lower than those of the seeps, as would be expected if the mixing scenario postulated above were taking place.

Table 4 summarizes the hydraulic conductivity data collected from slug injection tests in the spoil wells. As would be expected for mine spoil, the hydraulic conductivity values had a broad range; the hydraulic conductivities of the wells closest to the seep area (B-1 and B-2) were more than an order of magnitude greater than those of the other two wells. Although the range of influence of a slug test is not large (on the order of a few feet), the fact that the hydraulic conductivity of the acidic well (B-2) was the greatest suggested that it could lie along or near a preferred flow path for acidic water originating in other parts of the spoil and/or the undisturbed deep mine workings upgradient of the remined area.

Table 4. Hydraulic Conductivity of Mine Spoil Wells

Well	Hydraulic Conductivity, ft/sec
B-1	3.91E-04
B-2	6.12E-04
B-3	3.28E-05
B-4	9.27E-08

Conceptual Description of Flow System

While the data collected in the hydrologic investigation were far from conclusive, a preliminary conceptual description of the flow system at the site was developed from the available data. Given the high carbonate content of the mine overburden, the most likely source of the acidic water at the seeps was the large undisturbed portion of the abandoned deep mine workings outside the remined area (see Figures 1 and 3). Recharge from the mine voids to the spoil could occur either from unflooded workings northwest (upgradient) of the spoil, or lateral (along strike) inflow from a large mine pool to the southwest of the mine permit area. Existence of such a mine pool could be inferred from the large, consistent, acidic discharge at SP-6 (see figure 2). Under "normal" conditions, the resistance to flow of the mine spoil and the undisturbed material at the eastern edge of the remining permit boundary would have

been much less than that of the areas where the mine voids were very close to the surface (such as at SP-6). As such, very little flow would be expected at the east permit boundary. However, the excavations made by the landowner could have decreased the overall resistance to flow in that area. Under these conditions, acidic water that entered the spoil from the deep mine could have passed relatively quickly, and without much chemical alteration, through large conduits that commonly exist in spoil to emerge at Seeps A and B.

The predominantly alkaline character and associated ion concentrations of the water in the mine spoil and void wells (except for the influence of ammonia in well A-2, as discussed earlier) were indicative of mine drainage that had been neutralized by calcium carbonate. Under the flow scenario described above, much of the recharging water would follow a comparatively direct path to the seeps, with relatively little modification of water quality resulting from its contact with the alkaline mine spoil. The water quality of Well B-2 may be indicative of a portion of the spoil that is relatively close to one of these conduits. Another percentage of the inflowing water would follow a more circuitous path to the seeps; the pH and alkalinity of the water would increase in proportion to the contact time with the alkaline spoil. Calcium and perhaps magnesium concentrations would increase, while other indicators of mine drainage contamination (sulfate and manganese) would remain high. The behavior of iron would be much more complex; for example, ferrous iron in the mine water would be relatively unaffected by passage through the alkaline spoil under anoxic conditions. However, ferrous iron that oxidized to the ferric state would precipitate immediately due to the high pH conditions. Water that entered the small pocket of mine voids at wells A-1 through A-4 could "pool" in this area prior to exiting through the seeps via the unmined strata and/or the spoil in the vicinity of Well B-1.

Remediation Efforts

The results of the hydrologic investigation indicated that although the evidence was not clear-cut (i.e., a source of water of extremely acidic character was not positively identified) the the acidic water at the seeps was almost certainly passing through the mine spoil. Conditions of the mining permit dictated that since the seeps were hydrologically connected to the mine spoil, the discharges had to be treated to SMCRA effluent standards. Since the acidic quality of the seeps probably resulted from the lack of sufficient contact time between the mine water and the alkaline spoil material, treatment of the seeps via an anoxic limestone drain (ALD) was chosen. In January 1995, the mining company excavated a trench within the spoil (Figure 10) to intercept the inferred area of acidic water, and installed an ALD along the base of the old pit floor.

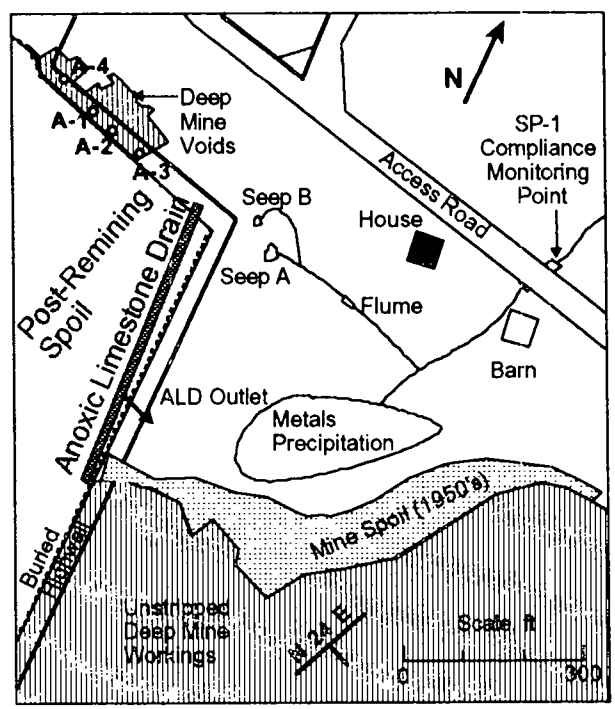

Figure 10. Location of Anoxic Limestone Drain in Remined Spoil.

This approach was considered to be technically feasible because the iron at the flume location was almost entirely in the unoxidized (ferrous)

state, and the aluminum concentrations were not excessive. Furthermore, permission of the adjacent landowner was not required for this activity because it took place within the original permit boundary.

As the excavation of the trench progressed northward, flow rates from the trench increased suddenly to several hundred gallons per minute. This suggested that water had pooled in the spoil, and was released as the primary storage conduit(s) were intercepted by the trench. Flow rates remained very high for almost a week before decreasing to the rate that existed before the excavation began (about 15-20 gpm). The bottom of the 500 ft long, 12 ft wide trench was filled with 500 tons of limestone (bed depth approx. 2 ft). Piping was installed above the limestone to allow it to remain inundated while diverting the discharge away from seeps A and B. The drain pipe discharged into the swampy area of the original SP-1, where sufficient space for precipitation of metals was available. After backfilling of the trench was completed, discharge from the ALD outlet pipe continued while flow from seeps A and B ceased. Flow rates from the ALD were not measured; however, visual estimates by both the state inspector and the mine operator indicated that the flow was about the same as that of the seeps prior to construction of the ALD.

Table 5 summarizes the water quality data at the ALD outlet and SP-1 during the 5-month period after the drain was completed. As expected, alkalinity concentrations at the ALD outlet were consistently greater than 100 mg/L. Iron concentrations were lower in the ALD outlet than in the spoil wells during the previous year (Table 3), suggesting that iron may have been precipitating in the ALD. There were no concurrent spoil well data to compare to those in Table 5, however, so this could not be concluded definitively. It was clear that almost all of the iron leaving the ALD was being precipitated prior to reaching SP-1. It also appeared that significant amounts of manganese were being precipitated; this is consistent with the results of Hedin, et al. (1994) which indicate that manganese can be removed in wetland systems if ferrous iron concentrations are very low.

Discussion

The remediation effort described above, which appears to be successful thus far, may not have been attempted without the additional knowledge gained through the hydrologic investigation. When the contaminated off-site seeps first occurred, there was a substantial difference of opinion between the mine operator and the regulatory agency with respect to the origin of the seeps and the responsibility for their abatement. At first, the investigation yielded results that were somewhat contradictory. Although a chemical tracer test confirmed the hydrologic connection between the seeps and a portion of abandoned deep mine workings that were not disturbed by the mineoperator's remining efforts, other hydrologic and water quality data

Table 5. Water Quality Parameters after ALD Installation, March - August 1995

Location	# of Samples	Statis-tic	pH	Total Alk. mg/L CaCO3	Net Acid mg/L CaCO3	Fe mg/L	Al mg/L	Mn mg/L	SO4 mg/L
Anoxic drain outlet	16	Mean	6.28	172	4	20.85	1.48	10.33	1506
		Median	6.25	174	0	17.45	0.93	10.55	1511
Culvert outlet SP-1	11	Mean	7.49	208	0	0.99	0.64	4.48	1336
		Median	7.50	146	0	0.42	0.50	5.67	1331

Alkalinity values in this table are total alkalinities; they are not directly comparable to the "negative net acidities" shown in Table 3 and Figure 8 because of differences in laboratory measurement procedures

suggested that the seeps were influenced more heavily by other sources that had not yet been identified. This explained the failure of the mine operator's initial remediation effort and discouraged further remedial efforts involving the abandoned mine voids. Further investigation revealed that the ground water in the mine spoil was somewhat acidic; this was in direct contrast to the mine operator's experience at several other remining sites in the same area. The degree of acidity found in the spoil water was not as severe as that of the seeps, but the hydrologic and water quality data were sufficient to convince the mine operator that remedial measures would have to be taken. The mine operator used the available data to implemement a remediation scheme which involved re-excavating the spoil to intercept the acidic water and routing the water through a passive treatment system (ALD and wetlands). Through these efforts, a situation which could have resulted in lengthy litigation and a legally enforced, inefficient temporary treatment scheme was resolved by a relatively cost-effective, long-term treatment system.

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WATER QUALITY IMPROVEMENTS RESULTING FROM FBC ASH GROUTING OF BURIED PILES OF PYRITIC MATERIALS ON A SURFACE COAL MINE

by

Joseph Schueck, Mike DiMatteo, Barry Scheetz, and Mike Silsbee

Abstract. A 37 acre surface coal mine in Clinton County, Pennsylvania, was mined and reclaimed between 1974 and 1977. Buried pyrite-rich pit cleanings and tipple refuse were found to be producing severe acid mine drainage (AMD). The pyritic material is located in discrete piles or pods in the backfill. The pods and the resulting contaminant plumes were initially defined using geophysical techniques and confirmed by drilling. Isolating the pyritic material from water and oxygen will prevent AMD production. A grout, composed of fluidized bed combustion (FBC) ash and water, was used in two different approaches that attempted pyrite isolation. Pressure injecting grout directly into the buried pods to fill the void spaces within the pods and coat the pyritic materials with a cementitious layer was the first approach. In the second approach, pods that would not accept grout because of a clay matrix were capped with the grout to isolate the pyrite from percolating water. The grout was also used in certain areas to blanket or pave the pit floor to prevent dissolution of clays, which are a suspected primary source of high aluminum (Al) concentrations at this site. Monitoring wells have been sampled since 1990 to monitor changes in the water quality resulting from grouting efforts. Grouting occurred during the summers of 1992 and 1993. Statistically significant water quality improvements have been noted as a result of the grouting, although results are varied. Any water quality improvements resulting from the grouting are expected to be permanent because of the nature of the cementitious grout.

Additional Key Words: Magnetometry, Electromagnetic Terrain Conductivity, VLF, AMD, Acid Mine Drainage, Abatement, Fluidized Bed Combustion Ash, Grouting, Trace Metals

Introduction

Effective in-situ abatement technology requires that the source(s) of the AMD production first be located. AMD source location can be done with little difficulty on many surface coal mines using geophysical mapping techniques (Schueck, 1988, 1990, 1994). Pyritic material such as tipple refuse or pit cleanings are often placed in discrete piles and buried. When placed in discrete piles or pods and not properly isolated from infiltrating precipitation or groundwater, severe localized AMD production may result. Under these conditions geophysics can detect the pods and the resultant AMD plume. Geophysical detection of the AMD sources would be less successful on sites where the pyritic material was disseminated throughout the backfill.

Abatement technology can be applied once the precise locations of the acid producing materials buried within the backfill are determined. The contact of pyrite with oxygen and water is needed to produce AMD. In-situ AMD abatement will result through permanent removal or isolation of any one of these three (pyrite, water, or oxygen). Fluidized bed combustion (FBC) ash grout was used to isolate pyrite from oxygen and water in this research effort.

This paper provides further information on an AMD mitigation effort that was described in the 1994 ASSMR Proceedings (Pittsburgh, Pa.). This earlier paper should be referenced, for detailed discussions of the geophysical methods and grouting techniques used. The primary purpose of the current paper is to discuss water chemistry data.

Site Description

The project site is located in north-central Pennsylvania in the Sproul State Forest, Clinton County. This site was permitted and mined by the mountain top removal method between 1974 and 1977. The Lower

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Kittanning coal seam was present in two splits separated by 10 to 20 feet of clay. Only the upper split was mined, leaving a thick underclay as pavement. The coal was overlain by black shale capped by a sandstone unit. The black shale is thought to be pyritic and acid producing. Infiltrating precipitation is the only source of groundwater. Acidic discharges developed soon after reclamation and were first noted after a fish kill in 1978. The discharges (surface and underground), estimated to average 35 gpm, destroyed five miles of native trout streams. The operator was unable to maintain treatment facilities and forfeited $9,400 in bonds.

Technical Approach

The primary objective of this AMD abatement approach was to isolate pyritic material from water and oxygen. Geophysical investigations were used to locate pods of acid-producing materials, evaluate local hydrology, and monitor grout propagation. Monitoring wells were used to evaluate water quality across and adjacent to the site. Water quality was also monitored at a toe-of-spoil seep and in receiving streams.

Fluidized bed combustion (FBC) ash was the material selected to be used in this isolation approach. FBC ash was chosen primarily because of its pozzolanic (or cementitious) properties as well as for economic reasons. A low viscosity grout was pressure injected into the geophysically identified zones (pods) as a means of encapsulating the pyritic materials with a cementitious coating. Diversion grouting was also used. This approach included capping of some of the pods and pit floor paving. The grouting should generate zones of low permeability and redirect groundwater flow, significantly reducing water contact with the pyrite. Although the spoil across the entire site was thought to be acid producing, the grouting effort was directed only toward reducing the AMD being produced by the buried piles of refuse and pit cleanings. The ultimate goal was to restore five miles of lost stream by improving the quality of the discharges. Final evaluation of the receiving streams has not yet been completed.

Pre-grouting Investigations

Geophysical Investigation

Several geophysical mapping techniques were used for site characterization. These techniques included electromagnetic terrain conductivity (EM), magnetometry, and very low frequency (VLF). EM was used to map the location of the AMD plume throughout and off the site. The piles of buried refuse and pit cleanings were located with magnetometry. VLF was used to map bedrock fracture zones beneath and adjacent to the site (Schueck, 1994).

EM mapping and drilling data indicate the general groundwater flow path through the site to be from the northwest to the southeast (Figure 1). This is the down-dip direction. EM mapping indicates pooling of pit water in the down-dip portions of the site. These down-dip portions are referred to as the east and south lobes. The EM mapping further indicates groundwater pollution plumes from the site at three locations where toe-of-spoil (surface) discharges were not present. VLF mapping indicates the presence of fractures in the pit floor which coincide with the pollution plumes.. These fractures apparently channel AMD from the mine spoil to a major joint system beneath the site. The joint system then conveys the AMD discharges to Rock Run as base flow, some 250 feet lower in elevation and east of the site.

A toe-of-spoil discharge is present beyond the south lobe. The discharge varies from 2 to 20 gpm and appears as a diffuse seep. It is at an elevation equal to the lower, unmined split of coal. This discharge flows into Camp Run, a tributary of Cooks Run.

Magnetometer mapping was used to determine the locations and configurations of concentrated pods or piles of pyritic materials such as tipple refuse. Magnetic anomalies indicate the aerial extent of the pods of pyritic material buried beneath the surface. In Figure 1, polygons are used to indicate the location and extent of the pods of pyritic material and to show the extent of grouting.

When the magnetic anomaly map was overlain with the EM map, it was observed that conductivity values were highest at or adjacent to the magnetic anomalies. The conductivity values gradually decreased in the direction of groundwater flow. This observation is consistent with severe AMD production within the buried pods of pyritic material, followed by dilution as the AMD migrates further away from the pods.

Water Sampling

Forty two monitoring wells were drilled on and adjacent to the site. The wells were located using the results of the combined geophysical mapping. Wells located on the site were drilled through spoil to the pit floor, with depths ranging from 10 to 40 ft. Monitoring wells located adjacent to the site were drilled into the unmined lower split of the Lower Kittanning coal seam. This initial drilling effort also confirmed the locations of the pods of refuse and pit cleanings identified with

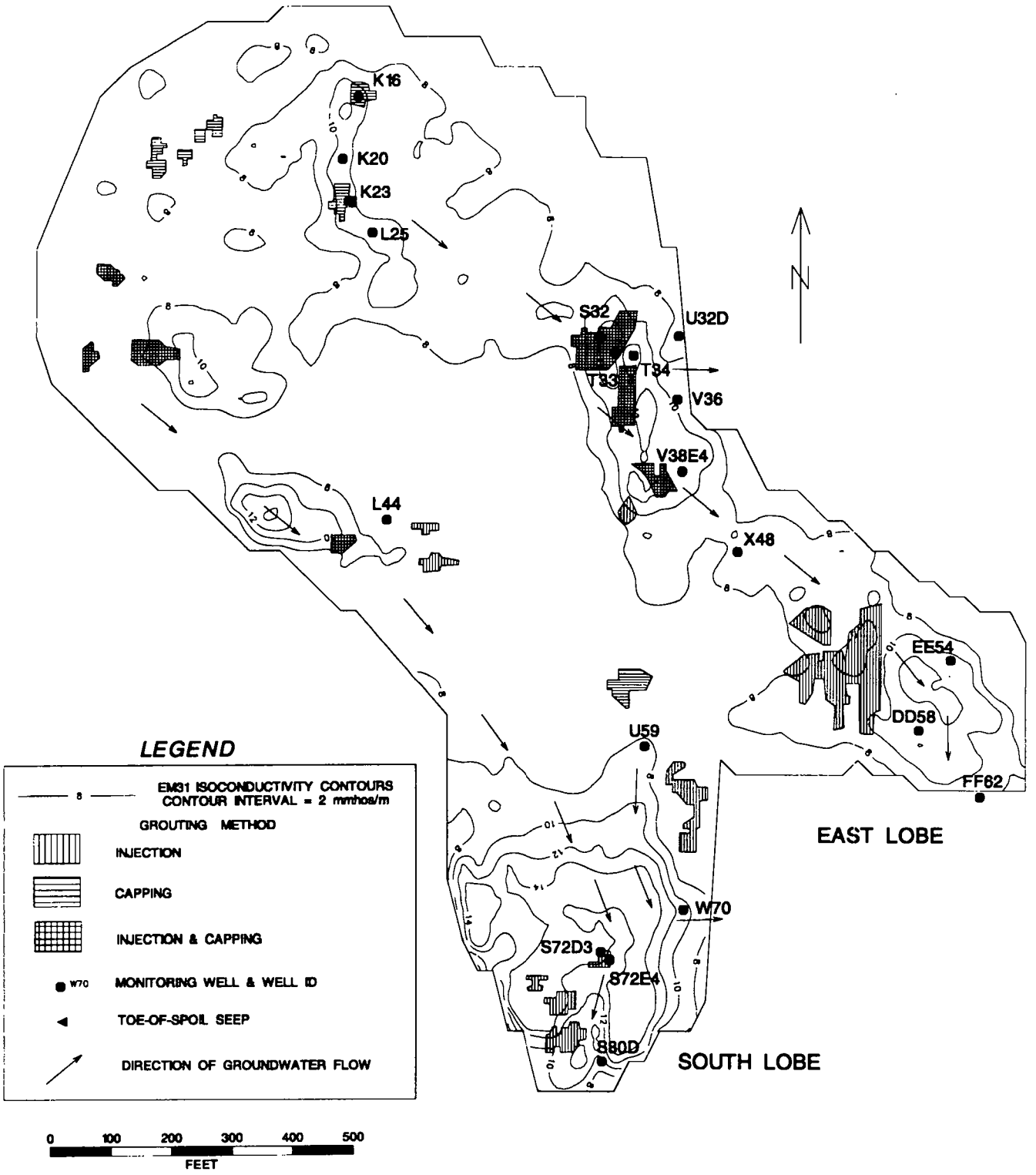
K16
K20
K23
L25
S32
U32D
T33
T34
V36
V38E4
L44
X48
EE54
DD58
FF62
U59
W70
S72D3
S72E4
S80D
EAST LOBE
SOUTH LOBE
N
LEGEND
EM31 ISOCONDUCTIVITY CONTOURS
CONTOUR INTERVAL = 2 mmhos/m
GROUTING METHOD
INJECTION
CAPPING
INJECTION & CAPPING
W70 MONITORING WELL & WELL ID
TOE-OF-SPOIL SEEP
DIRECTION OF GROUNDWATER FLOW
0 100 200 300 400 500
FEET

FIGURE 1

D3

magnetometry. Water quality monitoring was initiated in 1990 and continued through 1995. The grouting occurred during the summers of 1992 and 1993. Sampling of the monitoring wells was done on approximately a monthly schedule from April through November each year. The site is generally not accessible during the winter months. Monitoring wells discussed in this report are shown on Figure 1. Water sampling was also performed at the only surface discharge, D3, which is a toe-of-spoil seep located 200 feet south of the site.

Water Quality

Table 1 lists pre-grouting water quality for the toe-of-spoil seep and selected monitoring wells which are considered to be representative of the site (Figure 1). High, low, and mean pH values and metals concentrations are presented. These data are based on 13 to 21 sampling events.

The toe-of-spoil seep, labeled D3, and well FF62 represent the pre-grouting water quality which exits the site from the south and east lobes, respectively. Well FF62, located off-site and adjacent to the east lobe, intercepts a subsurface discharge plume (as identified by EM survey) suspected to enter Rock Run as base flow. Also, well FF62 samples water in the lower, unmined split of coal. The poor water quality demonstrates fracture communication between the pit floor and lower coal seam. D3 also appears to be coming from the lower coal seam. Comparison of the mean concentrations indicates that the water discharging from the east lobe (D3) is of poorer quality than that discharging from the south lobe (FF62). Drainage from the majority of the pods of pyritic material flows towards the east lobe.

Monitoring Point D3--Toe-of-spoil seep area N=16

	Lab	TDS	SO_4	Acid	Fe Tot	Fe^{+3}	Al	Mn	Cd	Cu	Cr	Zn	Temp
	pH	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	ug/L	ug/L	ug/L	mg/L	deg C
High	2.7	8828	3749	3520	543	385	348	62.3	66	852	269	4.2	n/d
Low	2.4	4540	1245	2220	183	149	205	28.4	1.9	399	125	2.5	n/d
Mean	2.49	6475	2571	2995	321	254	268	48.3	25.5	612	200	3.4	n/d

Monitoring Well FF62 - East Lobe - Groundwater Discharge Point N=15

	Lab	TDS	SO_4	Acid	Fe Tot	Fe^{+3}	Al	Mn	Cd	Cu	Cr	Zn	Temp
	pH	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	ug/L	ug/L	ug/L	mg/L	deg C
High	2.6	12706	5773	6440	1500	1294	562	67.3	167	1110	301	7.5	13.1
Low	2.2	3404	1272	1940	386	246	114	14.8	29	611	142	2.1	11.6
Mean	2.32	7970	3477	4088	876	737	256	39.2	83	806	221	4.3	12.0

Monitoring Well L44 - Lower Kittanning Spoil N=21

	Lab	TDS	SO_4	Acid	Fe Tot	Fe^{+3}	Al	Mn	Cd	Cu	Cr	Zn	Temp
	pH	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	ug/L	ug/L	ug/L	mg/L	deg C
High	3.1	16376	5376	7020	1390	1346	493	66.6	190	1300	229	12.0	15.7
Low	2.2	1555	828	1120	221	14	120	13.7	19	286	70	2.5	11.2
Mean	2.47	7920	2958	3828	747	598	236	48.1	111	751	163	6.8	12.9

Monitoring Well K23 - Severe AMD Production in Pods N=13

	Lab	TDS	SO_4	Acid	Fe Tot	Fe^{+3}	Al	Mn	Cd	Cu	Cr	Zn	Temp
	pH	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	ug/L	ug/L	ug/L	mg/L	deg C
High	2.2	128205	25110	23900	5690	2320	2240	79.0	1190	7410	1816	39.0	14.9
Low	2.0	33706	9868	18280	3320	120	281	30.3	128	3360	593	10.8	10.2
Mean	2.1	46352	15639	21315	5437	1200	1515	60.5	610	5950	1108	27.6	13.3

Monitoring Well X48 - Combined Spoil and Pyritic Pods N=14

	Lab	TDS	SO_4	Acid	Fe Tot	Fe^{+3}	Al	Mn	Cd	Cu	Cr	Zn	Temp
	pH	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	ug/L	ug/L	ug/L	mg/L	deg C
High	2.8	25372	9950	9760	2210	1816	690	125	368	3370	687	10.5	13.8
Low	2.2	947	4763	3780	342	0	299	7.8	11	1680	492	6.2	11.2
Mean	2.37	14085	6991	7470	1707	439	492	72.8	227	2543	559	8.7	12.7

Table 1 Pre-grouting Water Quality

Monitoring well L44 represents the pre-grouting water quality resulting from the Lower Kittanning spoil. L44 is not located downgradient of buried refuse or pit cleanings. Monitoring well L44 is considered a suitable control well to monitor normal water quality variations on the site because it is not influenced by the grouting activities. Flow from L44 would be toward the south lobe and eventually to the toe-of-spoil seep.

Monitoring well K23 demonstrates that the pods of refuse or pit cleanings can be sources of severe, localized AMD production. Concentrations of the mine drainage parameters in the water in and adjacent to these piles are often several times greater than the concentration of the same parameters in the discharge or elsewhere on the site. K23 is located within a pile of buried tipple refuse. It is located on the up-dip portion of the mine site and is also at the upper end of a pollutional plume as defined by EM. The mean concentrations of the AMD parameters at K23 are four to six times greater than the concentrations of the same parameters in L44, which represents AMD generated by the spoil alone. This implies that enhanced AMD production from the pyritic material at K23 and similar locations significantly contribute to the degradation of the final discharge quality. The isolation of these subsurface pods of pyritic material from water and/or oxygen should improve the final discharge quality. This was the premise for this research effort.

Monitoring well X48 is located several hundred feet downgradient of piles of pyritic material, but is within the flow path of mine drainage as it migrates through the site towards the east lobe. The water quality sampled from this well would be influenced by both the Lower Kittanning spoil as well as AMD formed in the buried pods of pyritic materials. Note that the mean concentrations of the mine drainage parameters in well X48 are about double the mean concentrations of L44. X48 indicates dilution of the severe AMD as it migrates and mixes with less severe mine drainage.

Certain trace metals also contribute to the pollution from this site. Elevated concentrations of zinc, copper, chromium, cadmium, and arsenic were common in the drainage from this site. The concentrations of other trace metals, such as lead, nickel, and selenium were generally below detection limits.

FBC Ash Characterization

The quality of the coal combustion ash is extremely important, particularly when it is being placed into an acidic environment. A poor quality ash which leaches undesirable trace metals could make an existing environmental problem worse. The characterization of the FBC ash used at the site was completed at the Penn State Materials Research Lab (Zhao,1993). Chemical analysis of the ash is as follows: Al_2O_3 - 12.51%, CaO - 38.03%, SiO_2 - 23.91%, SO_2 - 16.02%. The ash was tested using the EPA's Toxicity Characteristic Leaching Procedure (TCLP). All elemental contents of the ash fell within the established guidelines of the TCLP.

Mixed with only water, the FBC ash forms a low strength cement. After 20 days, at a water to solids ratio of 0.5, an unconfined compressive strength of 1920 psi is developed. The compressive strength continues to increase slowly to slightly over 2000 psi in 90 days (Zhao, 1993).

Field Operations

Grout Applications

Only those pods of pyritic material identified with magnetometry were targeted for grouting. The grout injection wells were installed on 10 foot centers using 2 1/2 inch, perforated, schedule 40 PVC casing. The injection wells were installed in August 1992. Grouting operations began September 1, 1992 and continued through the end of October 1992. The grouting operation resumed in June 1993 and was completed in August 1993. Grout injection wells were located within the polygons indicated in Figure 1. The amount of grout accepted by the wells ranged from less than 0.3 to 83 yd^3. Approximately 4500 yd^3 of grout were used on this project.

Originally only pressure injection directly into the pods was planned for the isolation of the pyritic materials. However, soon after the grouting operations began, it became evident that this method would not work for all the pods within the site. Several of the piles refused to accept grout. Excavation within these pods showed the pyritic material was within a clayey matrix. These piles were capped with grout to divert infiltrating precipitation. The spoil above the piles was excavated. The excavated area was then pooled with fly ash grout. After the grout hardened, the excavated area was backfilled and regraded. However, the capping would not be effective in preventing lateral flow along the pit floor from coming into contact with the pyritic materials. Several of the pods were both capped and grouted. This combined application occurred where several of the wells within the pod accepted little or no grout.

Aluminum concentrations in excess of 1000 mg/l at various locations within the spoil suggested that the clay pit floor is a primary source of Al. Therefore, paving areas of the pit floor with a grout slurry was another water diversion technique applied at this site. The purpose was to isolate the pit floor clays from contact with the AMD within the spoil. Success in this approach depends upon a high permeability of the spoil materials covering the pit floor. Well L25 shows the results of the paving activity and is discussed later in this report.

Post Grouting Operations

Water Quality Changes

Grouting occurred during the summers of 1992 and 1993. Water quality was monitored on approximately a monthly basis, April through November, from 1990 through 1995. In order to test the effectiveness of fly ash injection on water quality improvement, a series of one-tailed t-tests were computed for the water quality variables sampled from the monitoring wells. A t-test represents a test of significance that compares the mean and standard deviation of one group of samples to that of another to test if both groups came from the same population. The one-tailed t-test further compares not only if there is a significant difference between the two groups but if one group mean is significantly greater than the other. The $p <= 0.05$ level of significance was used as the rejection level of the null hypothesis for all tests. Readers are referred to Davis (1986) and Krumbein and Graybill (1965) for additional information regarding the t-test.

For the tests, the water quality data for the respective monitoring wells were divided into two groups: the data sampled before fly ash injection occurred and the data sampled after fly ash injection was completed. It was obvious in some of the wells that the grout supernatant was impacting the water quality during and shortly after the grouting effort. These water samples were excluded from the data analysis.

During the summer of 1995, drought conditions existed at the site. The water quality of the control well, L44, changed dramatically. Mean SO_4 values increased four-fold during the summer of 1995 and concentrations of TDS, acidity, Al, and Fe more than doubled. Moderate increases in concentrations of the mine drainage parameters were noted in most of the monitoring wells across the site during 1995. However, the increases are slight when compared to L44. The conclusions within this paper are based on mean values of water chemistry parameters including the data from the summer of 1995. No effort has been made to correct this data for the drought conditions. Water monitoring at the site is planned for several more years.

Table 2 lists the percentage reduction in mean concentrations for several of the mine drainage parameters for the three different applications. The applications included 1) injection only, 2) capping only and 3) a combination of injection and capping Data are included for both wells located within the pod (IP) and for wells located downgradient (DG) of the pod. The percentage change in concentrations for L44, the control well, are included for comparison.

Data for the first four wells in Table 2 reflect water quality changes resulting from injection grouting only. There is within-pod water quality data for only one pod that was subjected to grout injection. There are two wells located within this pod, S72D3 and S72E4 (Figure 1). Both wells exhibited modest reductions in the mean concentrations of the common mine drainage parameters ranging from 23 to 52%. These reductions are statistically significant with the exception of SO_4 in well S72E4. Significant reductions in trace metal concentrations from 42 to 88% were observed as well. This suggests that AMD production was reduced within the pod as a result of the grout injection. Wells EE54 and DD58 are located downgradient of a pod that was only pressure injected. These wells exhibited 16 to 37% statistically significant reductions in mean concentrations of the common AMD parameters. The exception is SO_4 which remained virtually unchanged. Significant trace metal reductions were also noted, although percent reductions were less than observed in the within-pod wells. Wells EE54 and DD58 are situated where the flow of AMD from the site can influence them, however.

The second situation are those pods that would not accept the pressure injected grout and were therefore capped. Wells K16 and K23 are located within pods that were only capped. The changes that occurred in this situation are quite mixed, ranging from a 44% non-significant increase in mean SO_4 concentration in well K23 to a 37% decrease in mean Al concentration in well K16. Few of the chemical changes in these two wells were statistically significant Decreased infiltration because of capping may have abated some of the AMD production occurring in the upper portion of the pod. However, lateral flow of water along the pit floor can still react with the pyritic material at the base of the pods

Application: Injection Grouting Only													
Well	Loc*	TDS	SO_4	Acid	Fe Tot	Fe^{+3}	Al	Mn	Cd	Cu	Cr	Ca	Temp
S72D3	IP	***39%***	***30%***	***40%***	***36%***	***52%***	***41%***	***50%***	***88%***	***54%***	***47%***	***-83%***	***5%***
S72E4	IP	***35%***	23%	***35%***	***39%***	***52%***	***27%***	***42%***	***85%***	***42%***	***44%***	***16%***	***7%***
EE54	DG	20%	3%	***21%***	***29%***	21%	***21%***	***30%***	***82%***	***22%***	***32%***	7%	***12%***
DD58	DG	***16%***	-4%	***20%***	***25%***	***26%***	***23%***	***37%***	***76%***	***22%***	***26%***	***-52%***	***6%***
Application: Capped Only													
Well	Loc *	TDS	SO_4	Acid	Fe Tot	Fe^{+3}	Al	Mn	Cd	Cu	Cr	Ca	Temp
K16	IP	0.2%	1%	5%	-0.4%	-15%	***37%***	-40%	***88%***	32%	26%	***-122%***	4%
K23	IP	21%	-44%	***13%***	11%	-35%	19%	1%	***75%***	11%	***26%***	***-62%***	2%
K20	DG	***51%***	***60%***	***57%***	***53%***	***50%***	***47%***	33%	***90%***	***56%***	***50%***	6%	7%
U59	DG	***29%***	12%	***34%***	***30%***	***33%***	***32%***	***33%***	***87%***	***38%***	***44%***	14%	***10 %***
Application: Grouted and Capped													
Well	Loc *	TDS	SO_4	Acid	Fe Tot	Fe^{+3}	Al	Mn	Cd	Cu	Cr	Ca	Temp
T33	IP	***42%***	30%	***46%***	***59%***	***64%***	***52%***	***44%***	***88%***	***62%***	***66%***	***-236%***	***7%***
T34	DG	***93%***	***94%***	***95%***	***92%***	***91%***	***97%***	36%	***97%***	***97%***	***91%***	***50%***	9%
V38E4	DG	19%	4%	***34%***	***40%***	***-169%***	***43%***	***38%***	***87%***	***53%***	***52%***	***-63%***	6%
Application: Control Well — No Grouting Influence													
Well		TDS	SO_4	Acid	Fe Tot	Fe^{+3}	Al	Mn	Cd	Cu	Cr	Ca	Temp
L44		***-106%***	***-248%***	***-122%***	***-165%***	***-208%***	***-103%***	-7%	17%	***-67%***	-34%	-8%	-2%

Table 2. Percent reductions in mean concentrations as a result of the three grouting applications. Negative values indicate a percent increase in mean concentration. Statistically significant changes where P <=0.05 are indicated in bold italics. Control well L44 is included for comparison. *Location IP=In-pod DG=Downgradient

Monitoring well K20 is located between the K16 and K23 pods and may receive drainage from both, based upon the EM mapping. Significant reductions in mean concentrations of 47 to 60% are observed in K20 for the common AMD variables, with the greatest reduction being that of SO_4. It is thought that a decreased groundwater contribution as a result of capping pods K16 and K23 is responsible for the observed improvement in K20 rather than AMD abatement within the pods, i.e. a reduction in load.

U59 is downgradient of a capped pod. Significant decreases in mean concentrations of 29 to 34% are observed in U59. Unlike the pods at K16 and K23, the pod upgradient of U59 is believed to be located high in the spoil and free of influence from lateral groundwater movement. Improvements in water quality in U59 are likely a result of AMD abatement in the upgradient pod because of capping. The reductions in well U59 are similar to those observed for wells DD58 and EE54. Trace metal reductions are also quite significant.

The final case is where pods were both injection grouted and capped. Well T33 is located within a pod that accepted grout quite well, but was capped as an assurance measure. Significant decreases in mean concentrations range from 42 to 64% within the pod, which suggests a reduction in mine drainage production. Well T34 is immediately downgradient of this pod. Reduction in concentrations of 43 to 97% are noted for this well. The data suggest a reduction in AMD production within the pod and minimal migration of mine drainage from the pod toward the discharge points.

Well V38E4 is situated downgradient of another pod which was both grouted and capped. Improvements noted here are less dramatic than in well T34. In well V38E4 significant reductions in concentrations of 34 to 53% were noted with a 4% non-significant reduction in mean SO_4 concentration. This suggests that grouting of this pod was somewhat less successful than the grouting of the pod at the T33 well location. However, the results are similar to the downgradient well observations for the grouted only situation, wells DD58 and EE54. It should be noted that prior to grouting, virtually all of the iron present in this well was in the form of Fe^{+2} and a small increase in Fe^{+3} concentrations post-grouting is causing the 169% increase.

The observed changes in SO_4 concentrations are not statistically significant for most of the wells monitored. In several of the wells, the SO4 concentrations exhibited little change or even increased. However, most of the wells show a decrease in the concentrations of the other mine drainage parameters. The lack of reduction in SO_4 concentrations is not consistent with the premise that AMD production has been reduced as evidenced by the reductions of the other mine drainage parameters.

Dissolution of sulfate salts is believed to be the reason for the lack of change in sulfate concentrations. Precipitates on the black shales are abundant on the site. Other studies indicate these are likely sulfate salts, most commonly Pickeringite, $MgAl_2(SO_4)_4 \cdot 22H_20$, and Halotrichite, $Fe^{+2}Al_2(SO_4)_4 \cdot 22H_20$ (Brady, 1996). Re-dissolving of these salts would explain the observations. Continued, long term monitoring will test this hypothesis.

There has been concern over the use of FBC ash because of the possibility of trace metals leaching from the ash once it is in place. Trace metals concentrations are not normally determined in routine mine drainage analysis. However, they were determined on this project and their concentrations are presented in Tables 1 and 3 for several of the wells. It should be noted that the concentrations of these metals produced on the site prior to FBC ash introduction are often orders of magnitude higher than the concentrations of the same metals which leached from the ash in the TCLP. Of perhaps greater significance is the reduction in concentrations that were observed as a result of using the ash. These data are presented in the tables. Although not included in the data, arsenic was also present in the mine drainage in concentrations greater than 2 mg/L. Reductions in arsenic concentrations similar to those of copper were common. In this case, the benefits of using the FBC ash far outweigh the concerns with respect to metals leaching from the ash.

It has be questioned whether post-grouting reductions in concentrations of the AMD parameters are a result AMD abatement or a continued neutralization by the grout supernatant. During the grouting operation it was common to note spikes in calcium concentrations along with significant rises in pH and dramatic reductions in concentrations of other mine drainage parameters due to neutralization reactions. If the supernatant was still present and was responsible for the changes, then we would expect to see statistically significant increases in calcium concentrations everywhere there was a significant decrease in the concentrations of the other parameters. This is not the case. The data in Table 2 show significant reductions in concentrations of the mine drainage parameters regardless of whether the calcium increased or decreased. Also, the noted spikes in pH usually disappeared within a few months after grouting indicating a flushing of the supernatant. Subsequent increases in calcium concentrations are thought to result from leaching of the grout.

The concentrations of ferric iron generated from the pods of pyritic material must also be considered. Garrels and Thompson (1960) have shown that pyrite is rapidly oxidized by ferric iron in the absence of oxygen and at low pH values:

$$FeS_2(s)+14Fe^{3+}+ 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \quad \text{(eq. 1)}$$

According to the monitoring well data, Fe^{+3} concentrations from these pods commonly exceed 1000 mg/L with pH values close to 2.0. Once the water exits from the pod, such as the K23 location, it must migrate through 1500 feet of spoil before discharging from the site. The Fe^{+3} is available to rapidly oxidize pyrite located along its flow path to the discharge point. Reduction in Fe^{+3} formation should thus result in reduced pyrite oxidation. It can be seen from the data in Table 2 that reductions in Fe^{+3} concentrations closely paralleled those of total Fe.

Considering that the overburden on the site is acid producing, as demonstrated by the control wells such as L44, evaluation of the various grouting techniques used is difficult, since many of the grouted pods were within the flow path of the AMD as it migrated downdip towards the discharge points. The dramatic increase in concentrations in the control well during the summer of 1995 clouded the evaluation as well.

It is necessary to examine the changes in the water quality which discharges from the site to evaluate the overall effectiveness of the grouting effort.. When reviewing the data it is important to keep in mind that only 2 of the 37 acres (5% of the site) was directly affected by the grouting effort. Table 3 presents the pre- and post-grouting mean concentrations for several of the parameters tested, along with the percent reductions. A negative value indicates the concentrations increased rather than decreased.

There are five monitoring wells which intercept AMD discharge plumes, as identified by the EM mapping, Figure 1. All of these wells are located along down-dip portions of the mine site and reflect the quality of water leaving the site from the lower split of the Kittanning seam. However, all five wells indicated a wide range in water quality variations. During the spring the water quality is historically much better than during the summer and fall months. The lower split of the Lower Kittanning seam extends beyond the limits of the mining on the north and west sides. The winter snow pack is normally up to five feet thick. It appears that as the snow pack melts water infiltrates to this lower split of coal and migrates down dip, influencing the quality of the monitoring wells. It is believed that many of the water quality changes noted in Table 3 are not statistically significant because of the wide scatter in the data even though the percent change exceeds 30%.

Monitoring Well FF62 Mean Concentrations

Condition	Lab pH	TDS mg/L	SO_4 mg/L	Acid mg/L	Fe Tot mg/L	Fe^{+3} mg/L	Al mg/L	Mn mg/L	Cd ug/L	Cu ug/L	Cr ug/L	Ca mg/L	Temp deg C
Pre-Grout	2.3	7970	3477	4088	876	737	256	39.2	83.6	806	221	58.1	12.0
Post-Grout	2.5	5780	3110	2879	527	373	173	24.7	29.3	813	168	61.4	11.7
% Reduction	***-7%***	***27%***	11%	***30%***	***40%***	***49%***	***32%***	***37%***	***65%***	-1%	24%	-6%	3%

Monitoring Well S80D Mean Concentrations

Condition	Lab pH	TDS mg/L	SO_4 mg/L	Acid mg/L	Fe Tot mg/L	Fe^{+3} mg/L	Al mg/L	Mn mg/L	Cd ug/L	Cu ug/L	Cr ug/L	Ca mg/L	Temp deg C
Pre-Grout	2.4	9951	3500	5096	937	749	394	45.5	108.5	1542	394	66.4	12.7
Post-Grout	2.7	7222	3483	3230	530	254	282	32.4	24.9	771	232	58.7	12.7
% Reduction	***-9%***	***27%***	1%	***37%***	***43%***	***66%***	***28 %***	***28%***	***77%***	***50%***	***41%***	12%	0%

Monitoring Well W70 Mean Concentrations

Condition	Lab pH	TDS mg/L	SO_4 mg/L	Acid mg/L	Fe Tot mg/L	Fe^{+3} mg/L	Al mg/L	Mn mg/L	Cd ug/L	Cu ug/L	Cr ug/L	Ca mg/L	Temp deg C
Pre-Grout	2.6	9689	3695	4611	735	606	397	49.4	60.2	985	221	81.9	11.3
Post-Grout	3.0	4795	3327	2348	268	185	180	21.8	17.3	635	156	56.3	10.9
% Reduction	***-17%***	***51%***	10%	***49%***	***63%***	***69%***	***55 %***	***56%***	***71%***	34%	30%	***31%***	4%

Monitoring Well V36 Mean Concentrations

Condition	Lab pH	TDS mg/L	SO_4 mg/L	Acid mg/L	Fe Tot mg/L	Fe^{+3} mg/L	Al mg/L	Mn mg/L	Cd ug/L	Cu ug/L	Cr ug/L	Ca mg/L	Temp deg C
Pre-Grout	2.7	6777	3568	3624	570	396	316	63.7	57.3	526	104	83.1	11.4
Post-Grout	3.1	5330	3111	2351	380	263	212	33.8	21.6	689	149	71.9	10.9
% Reduction	-13%	21%	13%	35%	33%	34%	33 %	***46%***	***62%***	-30%	-44%	13%	4%

Monitoring Well U32D Mean Concentrations

Condition	Lab pH	TDS mg/L	SO_4 mg/L	Acid mg/L	Fe Tot mg/L	Fe^{+3} mg/L	Al mg/L	Mn mg/L	Cd ug/L	Cu ug/L	Cr ug/L	Ca mg/L	Temp deg C
Pre-Grout	2.5	5163	1868	2840	649	602	222	24.3	59.4	1185	245	51.2	10.0
Post-Grout	2.7	4838	2852	2235	356	317	130	13.7	16.1	638	142	185.6	10.8
% Reduction	-6%	6%	-53%	21%	45%	47%	41 %	43%	***73%***	***46%***	42%	-262%	-8 %

Table 3. Pre- and post-grouting mean concentrations of mine drainage constituents and percent reduction in mean concentration for wells located in discharge plumes. Statistically significant % reductions are indicated in bold italics. A negative value indicates a % increase.

Well S80D is located between the limit of mining on the south lobe and the toe-of-spoil discharge, D3. To date, the quality at D3 has remained fairly constant. However, S80D shows marked improvement which should eventually show up at the toe-of-spoil seep, D3. It should also be noted that, for all the wells in Table 3, the percent reductions in concentrations are similar to those observed within the spoil. In addition, changes in SO4 concentrations were generally minor and not statistically significant. This condition was also noted in the on-site wells

Chemical Interactions Between AMD and FBC Ash Grout

Monitoring well L25 provides a fairly clear picture of the chemical changes which occurred as a result of the ash injection into an acidic environment. L25 is located in the AMD plume downgradient of the pod of pyritic material at the K23 location. Pre-grouting water quality indicated the presence of severe AMD. Three injection wells were drilled within 50 feet of well L25 to accommodate a pit floor paving experiment. Only the bottom of the casing was open so that all of the injected grout would be directed to the pit floor. The two adjacent wells accepted a total of 90 yd^3 of grout and a third located 50 feet downgradient accepted 20 yd^3.

The following graphs illustrate the chemical changes which occurred when the grout interacted with the AMD. The first graph, Figure 2, depicts the changes which occurred to pH. Prior to the grouting, the mean pH was 2.3. Grouting occurred on day 1520. The pH increased immediately to 8.9 because of the highly alkaline supernatant. Over the next several months, the pH value gradually dropped. In 1994 the mean pH was 2.8 and in 1995 the mean pH was 2.4, close to pre-grouting levels.

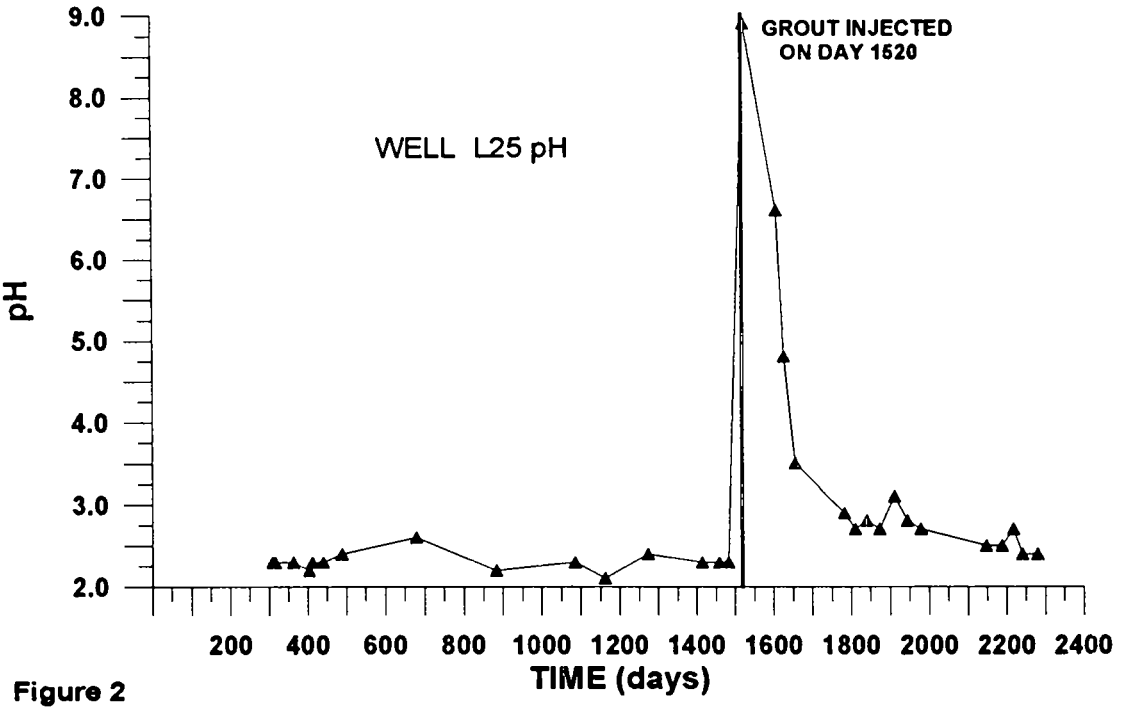

Figure 2

Figure 3 is a graph of SO_4 and acidity concentrations over time. These two variables likewise show a response to the grout supernatant. Sulfate concentrations averaged 6496 mg/L prior to grouting. After grouting, the concentrations were close to 1500 mg/L for the next four months. Since that time, the SO_4 concentrations have gradually risen to pre-grouting levels. Acidity also dropped dramatically as a result of the supernatant. In fact, the alkalinity determination 90 days after the grouting was 766 mg/L. During 1994 and 1995 the acidity concentrations have risen but remain at below pre-grouting levels.

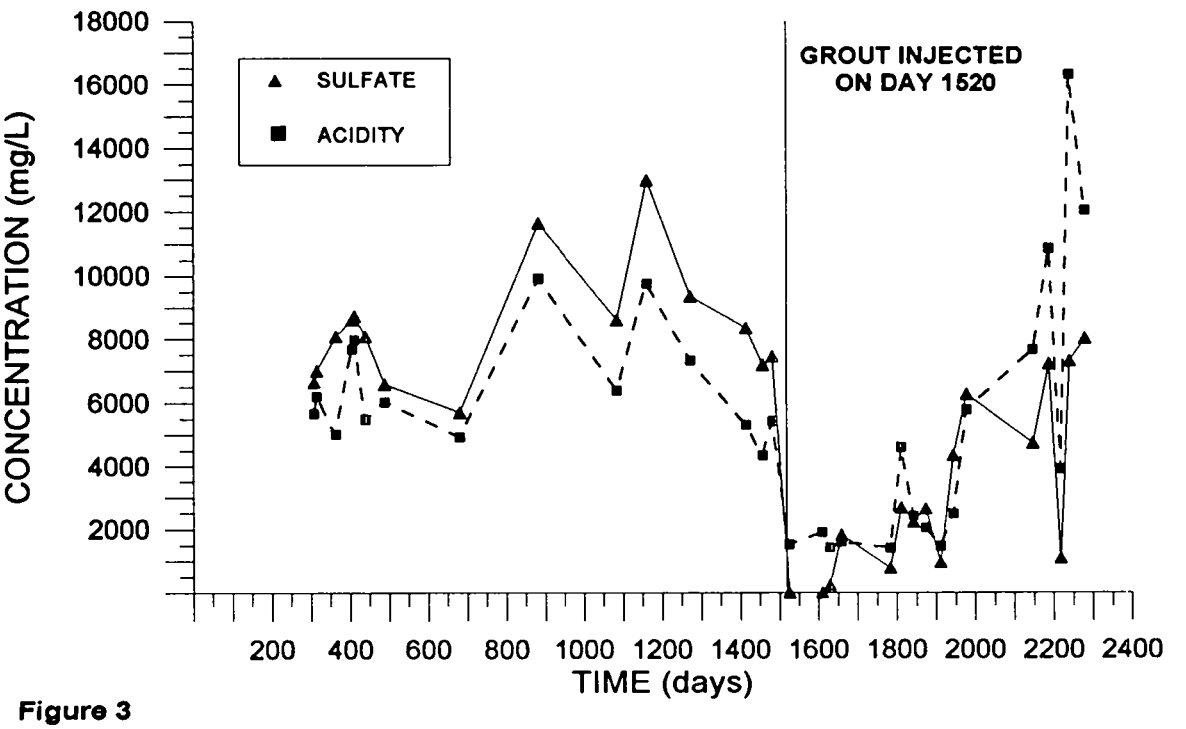

Figure 3

The third graph, Figure 4, illustrates the behavior of the trace metals: arsenic, cadmium, and barium. Throughout the history of sampling on this site, arsenic and cadmium behaved in similar fashion. Following the injection of the grout on day 1520, the concentrations of these two metals decreased dramatically and remain well below pre-grouting levels. Barium, on the other hand, increased in concentration from a background of less than 10 ug/L to 106 ug/L. It was common to note increases in barium shortly after grouting on other areas of the site. However, barium has since returned to pre-grouting levels.

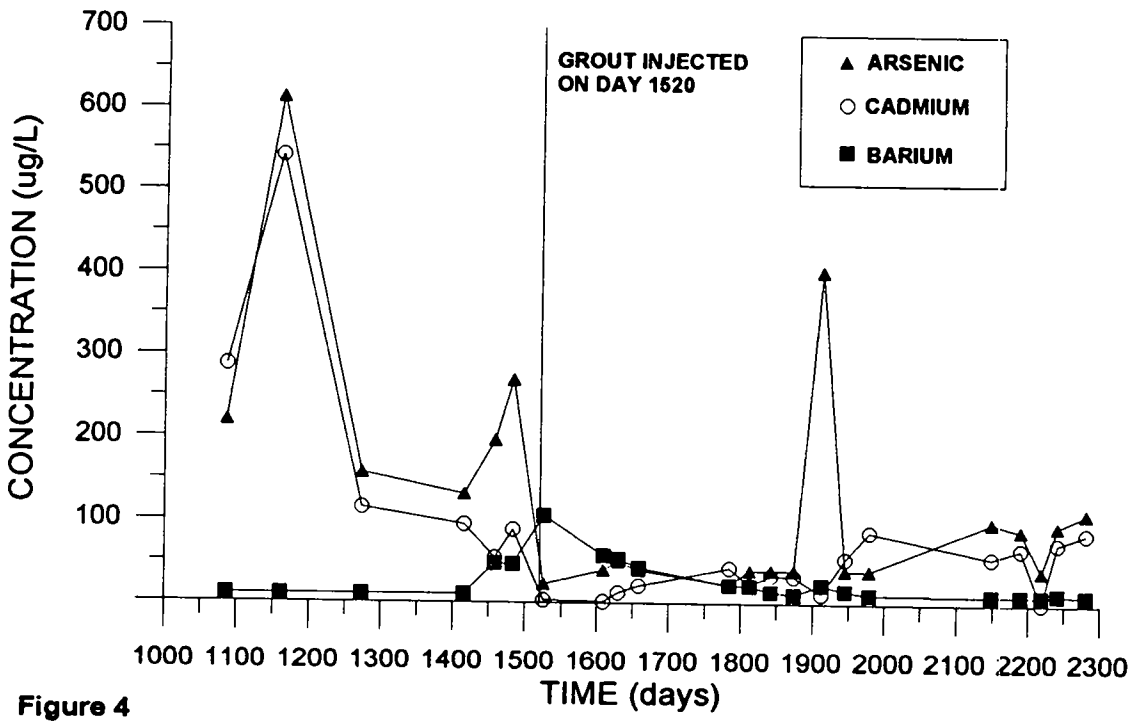

Figure 4

Calcium and aluminum concentrations are included on the final graph, Figure 5. Shortly after grouting, Al concentrations dropped to a low of 8 mg/L but have since returned to near pre-grouting levels. Calcium shows a rather different behavior. The mean Ca concentration prior to grouting was 72 mg/l for well L25. After injection, the concentration rose sharply to over 700 mg/L as a result of the supernatant. Since then, the mean concentration has averaged 350 mg/L, well above the pre-grouting value.

Based upon testing performed in the laboratory by the Penn State Materials Testing and Research Lab, there is an explanation for this. Within the grout, the calcium is normally present in three chemical phases . These include, in the order of decreasing solubilities, calcium hydroxide (logK=-5.05), calcium aluminum silicate hydrate (log K=-8.16 to -22.54), and calcium aluminum sulfate or ettringite (log K=-44.5). The high calcium concentrations are most likely a result of the dissolution of the calcium hydroxide. The calcium aluminum sulfate and the calcium aluminum silicate hydrate are likely to leach over time, but at a much slower rate than the calcium hydroxide. These reactions are similar to what would be expected if Portland cement had been injected instead of the fly ash (Silsbee, 1995).

A second possible source of the high calcium content might be the ash cap placed over and beyond the limits of the pile at K23. The ash which remained on the surface near the mixing bin was incorporated into this cap. Much of this was placed in the dry state and would be subject to leaching by infiltrating precipitation. The edge of this cap is only 30 feet away from the location of the L25 well.

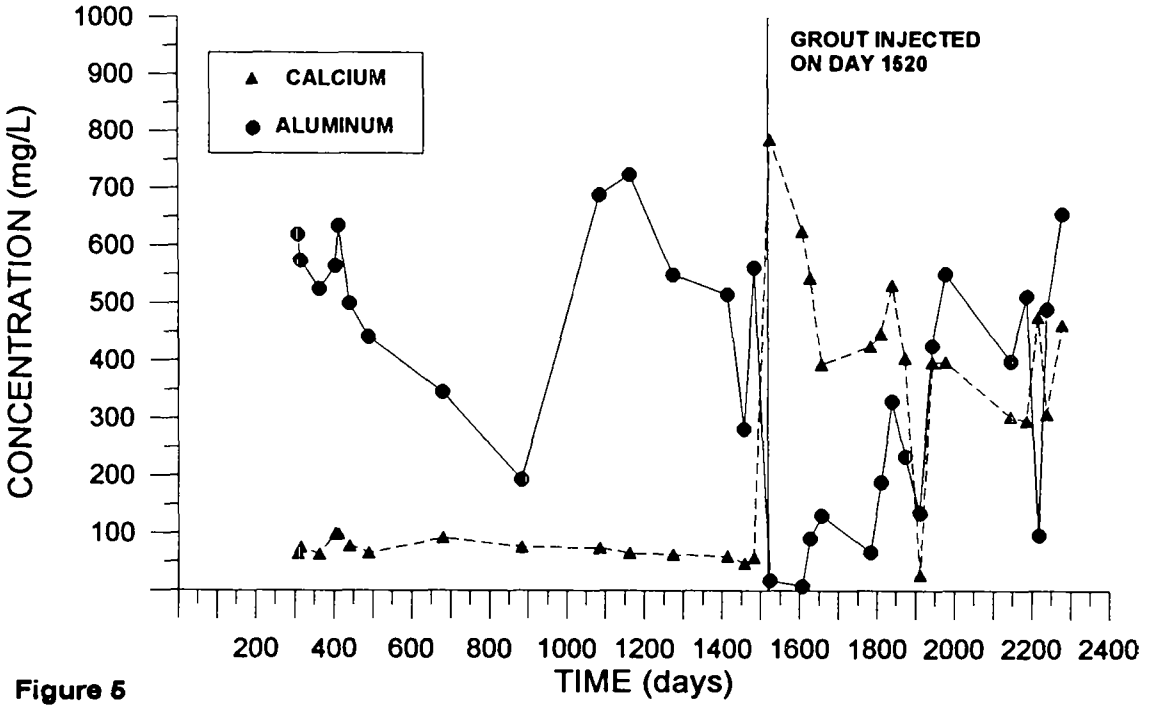

Figure 5

The purpose of the pit floor paving was to prevent the AMD from reacting with the clays to leach aluminum. The area where this was attempted exhibited high permeability. Unfortunately, this application occurred near the end of the project when the ash was in short supply. Consequently, several of the wells installed for this part of the project were not grouted.. Post grouting Al concentrations are 20% lower in L25 than they were pre-grouting. The data reflecting the presence of supernatent were excluded for making this determination. A downgradient monitoring well did not reflect this change, however. This is likely due to the limited aerial extent of the pit floor paving. Because of the limited extent of this application, insufficient data exists for the authors make recommendations on its use or non-use.

Conclusions

The pods of pyritic material were treated with FBC ash grout in three ways: 1) injection only, 2) capping only, and 3) both injection and grouting. Based on the water chemistry, the combination of injection grouting and capping produced the most favorable results, followed by injection only. Capping produced the least favorable results. The combined approach inhibits contact between water, oxygen, and pyrite by limiting infiltration as well as diverting lateral flow around the pods. Injection limits contact via lateral flow, but may not inhibit vertical infiltration. Capping is most applicable in situations where the pods are located high in the spoil and above the level of water table fluctuations within the backfill.

The inability to control final grout placement is a major drawback of the injection process. Pseudo karst conditions become established during backfilling operations (Hawkins, 1993). Because the gout is a viscous fluid, it will tend to flow into high permeability zones when pumped into spoil under pressure. If the permeability within the pod is low, the injected grout may flow away from the pod instead of filling the voids within the pod as intended or else the well will accept very little grout. When this happens, AMD abatement will be limited or will not occur at all.

The placement of the grout in the capping operation is controlled by the operator and is a direct approach. The ability to control infiltration zones is dependent upon the area of excavation and grouting. This approach is appropriate where the pyritic material cannot come into contact with water moving along the pit floor.

Use of the FBC ash grouting techniques on this site resulted in an overall improvement in water quality. Although percent reduction in mean concentrations vary, concentrations of the comon AMD parameters generally decreased by 30 to 40% and reduction of trace was usually higher. This is significant because the grout application occurred on only 5% of the site. The research effort was to demonstrate that FBC ash grout could effectively reduce the severe AMD production within the pods of pyritic material buried within the spoil. The noted water quality improvements indicated this goal has been met; however, the degree of improvement is somewhat less than what the researchers had hoped for. Any changes in water quality which resulted from the grouting are expected to be permanent because of the pozzolanic nature of the grout It was known that the entire site generated AMD and there was no pretense of eliminating all AMD production. Hopefully the reduction in pollutant loading discharging from the site will be sufficient to provide for stream recovery. Final stream evaluation remains to be completed.

Despite less than total success at AMD abatement, the authors view injection grouting as a viable AMD abatement technique worthy of application on sites which meet certain criteria. This technology is perhaps best indicated for those sites which would normally produce net alkaline drainage but improper placement of refuse or pit cleanings has resulted in an acidic discharge. In addition to reclaimed sites, the use of FBC ash is recommended on active surface mines and refuse disposal sites as a preventative measure. FBC ash grout can be used in a controlled approach on active sites. The ash grout can be applied directly to or mixed with refuse and pit cleanings to create monolithic structures capable of diverting water away from the pyritic materials.

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REMEDIATION OF ACID MINE DRAINAGE WITHIN STRIP MINE SPOIL BY SULFATE REDUCTION USING WASTE ORGANIC MATTER [1]

Jeralee Stalker, Arthur W. Rose and Louise H. Michaud[2]

Abstract: Many treatment options for AMD, like wetlands and anoxic limestone drains, are limited by acidity, metal loadings, flow rate or areal requirements so as to be inapplicable at many sites. *In-situ* bacterial sulfate reduction is proposed as a solution for certain settings. Requirements for successful *in-situ* bacterial sulfate reduction include dissolved sulfate, an organic substrate, permanent anaerobic conditions, a mixed culture of bacteria, appropriate nutrients, and a sufficient AMD contact time. These requirements can be provided within mine spoil by injection of waste organic matter into an extensive zone of saturated spoil.

Laboratory experiments on cheese whey, lactate, non-degraded sawdust, partially degraded sawdust, pulped newspaper and mushroom compost have all yielded sulfate reduction, increased alkalinity and iron sulfide precipitate in AMD with pH < 4.0. The addition of a small amount of dolomite to the organic matter creates alkaline microenvironments that facilitate the initiation of sulfate reduction. The rates of sulfate reduction using cellulose materials are slow but the rate for milk products is much more rapid.

A field test utilizing partially degraded sawdust is underway. A total of 11.3 tons of sawdust mixed with 5% dolomite, 5% sewage sludge and a mixed bacterial culture was successfully injected into 4 drill holes in mine spoil as 13% w/v suspension. The spoil had enough coarse porosity for injection into the saturated subsurface at about 300 L/min. Data on *in-situ* SO_4 reduction rates and water quality are being collected in preparation for a full remediation program at the site, which has an extensive zone of saturated spoil 10-20 m thick.

Additional Key Words: acid mine drainage, sulfate reduction, *in-situ* remediation, organic addition

Introduction

Although generation of acid mine drainage (AMD) at new surface coal mines has been largely eliminated by changes in federal and state regulations, many previously mined sites release severe AMD that contaminates streams in western Pennsylvania and other coal mining areas. "Passive" methods such as wetlands, compost wetlands, anoxic limestone drains (ALD) and alkalinity producing systems (APS) are beginning to provide methods for treating these AMD flows (Hedin et al., 1994). However, aerobic wetlands satisfactorily mitigate only AMD containing net alkalinity. Weltands also require a large area and become less effective in cold weather. ALD's can neutralize a maximum of only about 250 mg/l acidity, and require considerable area and length for large flows, as do compost wetlands and APS. This paper describes the injection of waste organic matter into strip mine spoil to promote bacterial sulfate reduction as an additional passive method. Figure 1 schematically illustrates a situation in which *in-situ* sulfate reduction may perform satisfactorily.

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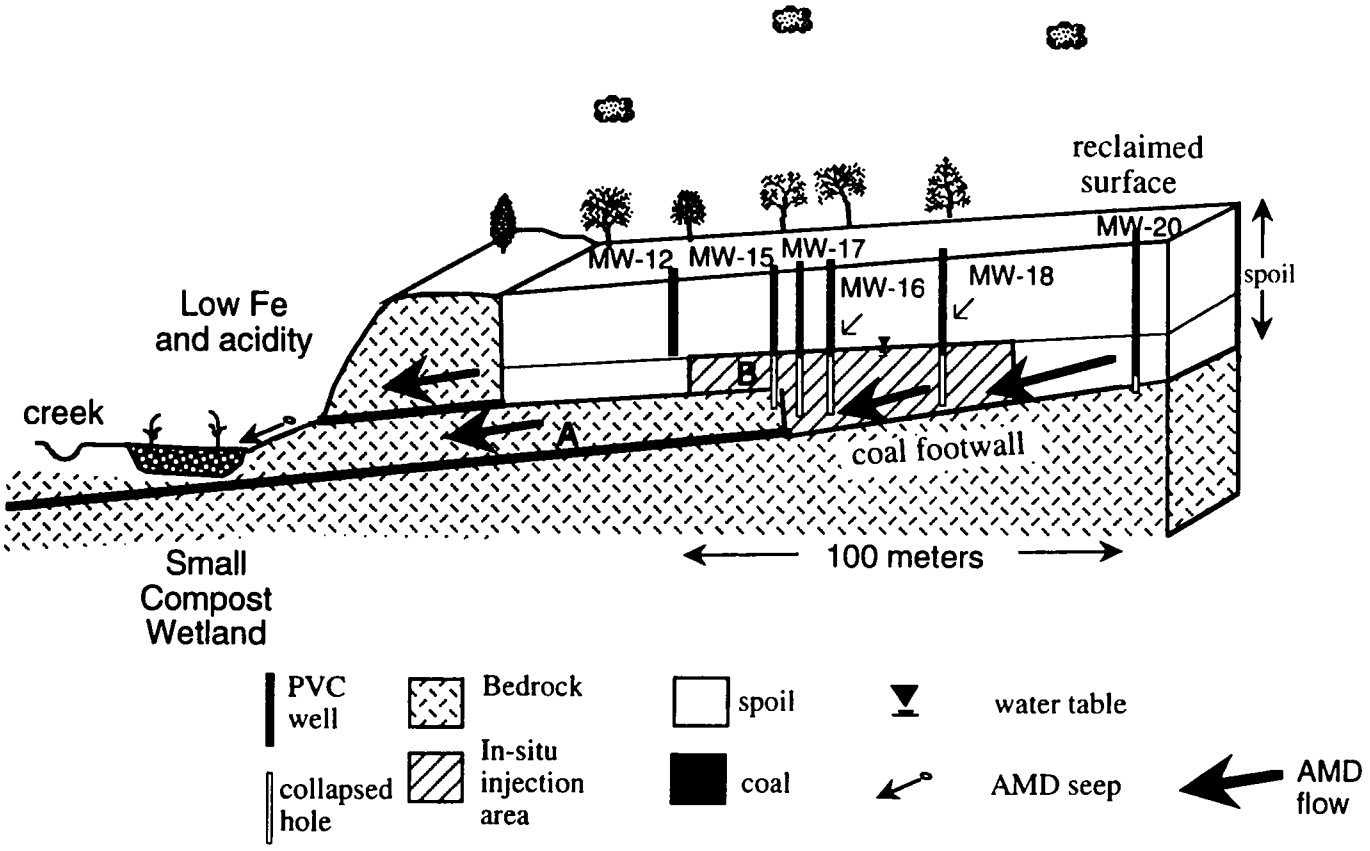

Figure 1. Schematic diagram of the area of in-situ sulfate reduction. Wells at the site are indicated. A hypothetical wetland is included in the diagram. Thick arrows indicate possible ground water flow paths. A) AMD may flow between the Mercer and Brookville coals in a sandstone unit and emerge as seeps along the crop line. B) This may be an area of little flow. Due to the shallow water table in this area, anaerobic conditions may not be maintained here.

To investigate the applicability of *in-situ* sulfate reduction, laboratory experiments were conducted on several waste organic materials to determine rates of sulfate reduction and to investigate limitations on the process, such as pH. Based on successful results of the laboratory experiments, a field test at a reclaimed strip mine was designed and implemented, and is being monitored.

Sulfate Reduction

Sulfate reduction is accomplished by several species of bacteria that obtain metabolic energy by reacting sulfate with simple organic compounds such as lactate, pyruvate, ethanol or acetate (Brock et al, 1994). They require an O_2-free environment because aerobic bacteria deplete the levels of these organic substrates to levels too low for utilization by sulfate reducing bacteria (SRB). In general, the SRB produce H_2S (or HS^-) and alkalinity (HCO_3^-). The H_2S reacts with dissolved Fe to precipitate FeS or a similar compound.

SRB cannot break down complex organic substrates; they rely on other bacteria, mainly fermenting bacteria, to provide substrates like acetate and lactate from larger organic molecules such as glucose or cellulose (Chapelle, 1993).

An example of the reaction accomplished by SRB on a lactate substrate at slightly acid pH (4 to 4.5) follows:

$$SO_4^{2-} + 2CH_3CHOHCOO^- + 4H^+ = H_2S + 2CH_3COOH + 2H_2CO_3 \quad (1)$$

Given the pK's for dissociation of lactic acid (3.8), acetic acid (4.75) and carbonic acid (6.5), the nature of the products depends on pH. At alkaline pH (pH>6.5), the products would be acetate (CH_3COO^-) and HCO_3^-, and no H^+ would be consumed but alkalinity would be produced. Some SRB are able to utilize acetate to reduce sulfate (Brock et al., 1994):

$$SO_4^{2-} + CH_3COO^- + 3H^+ = H_2S + 2H_2CO_3 \quad (2)$$

The total oxidation of lactate by sulfate is thus:

$$3SO_4^{2-} + 2CH_3CHOHCOO^- + 8H^+ = 3H_2S + 6H_2CO_3 \quad (3)$$

If H_2S does not degas or complex with other species, it can dissociate to HS^- and/or react with dissolved Fe^{2+} to precipitate FeS:

$$H_2S = H^+ + HS^- \quad (pK = 7.0 \text{ at } 25°C) \quad (4)$$

$$Fe^{2+} + HS^- = FeS + H^+ \quad (5)$$

An overall reaction generating FeS from SO_4 and lactate at pH 4.75 to 6.5 is:

$$3SO_4^{2-} + 2CH_3CHOHCOO^- + 3Fe^{2+} + 2H^+ = 3FeS + 6H_2CO_3 \quad (6)$$

Under certain conditions, sulfate reduction has the capability of producing pyrite from AMD, though the reaction is generally slow compared to FeS precipitation. In fact, bacterial sulfate reduction during sedimentary diagenesis was responsible for the formation most of the original pyrite in the rocks that produce AMD. Pyrite has been observed in several AMD localities undergoing sulfate reduction (Hedin et al., 1988).

In contrast to anoxic limestone drains, sulfate reduction is not limited in the amount of alkalinity that can be produced by SRB. The main limitations are the rate of the process, which may be relatively slow, especially if fermentative bacteria are necessary to break down cellulose or other complex organic compounds to simpler coumpounds metabolizable by

SRB. The pH may also be a limitation, since SRB prefer pH values above 5 (Zajic, 1969).

Materials and Methods-Laboratory Study

Prior to the *in-situ* test of sulfate reduction at the Pot Ridge mine, several organic substrates were tested in the laboratory. Initial substrate selection was based on a combination of characteristics including availability, cost, longevity and previous work indicating ability of SRB to degrade the substrate. Tuttle et al, (1969a, 1969b) showed that flow of AMD through a sawdust pile accomplished some remediation, and that cellulose could reduce SO_4 in lab experiments. Compost wetlands and APS accomplish some of their effect by sulfate reduction. Composted organic matter, hay, spent mushroom compost and other inexpensive organic materials have been used as organic substrates for sulfate reduction (Bechard et al., 1994, Bechard et al., 1995, Eger and Wagner, 1995, Dvorak et al., 1991, McIntire et al., 1990, Hammack and Edenborn, 1992, Borek et al., 1995). Waste whey from cheese production was initially tested as a substrate. Later substrates tested included fresh and degraded sawdust, newspaper, and spent mushroom compost.

In initial experiments with sawdust and pH 3.85 AMD, sulfate reduction had not started at day 217, but addition of 10% by weight dolomite led to fluctuating decreases in sulfate in 6 days and sustained decreases in sulfate in about 50 days. The dolomite particles apparently furnished alkaline microenvironments in which the bacteria could thrive. Therefore, dolomite particles (100 mesh) or alkaline fly ash was added to later experiments.

Intial experiments also indicated that low redox conditions are absolutely necessary to stimulate sulfate reduction. Several types of plastic tubing were used in systems for circulating AMD through substrate-filled columns, but all were found to be permeable to O_2 , resulting in Fe-oxide precipitation and slow to negligible sulfate reduction. The most useful data was obtained in glass systems completely closed to air except during brief addition of fresh AMD.

Bacteria from waste water at the Penn State Sewage Treatment Plant were initially cultured with cheese whey and an $FeSO_4$ solution. After sulfate reduction was observed in this medium, the culture was divided into several closed containers and fed lactate and $FeSO_4$ periodically. Later experiments were inoculated with 10 ml of this culture.

The lactate and whey experiment included 1 liter of synthetic AMD ($FeSO_4 \cdot 7H_2O$) and whey initially, then reagent grade calcium lactate. This experiment was circulated through a flask filled with glass beads (Figure 2A) by bubbling a constant stream of ultra high purity (UHP) N_2 through tubing connecting the bottom and top of the column. Samples were collected weekly from one of the top openings under a stream of UHP N_2 using a pipet.

The experiments with solid substrates were run in glass ion chromatography columns (2.2 cm diam x 50 cm length) (Figure 2B) with 125 mL of AMD from the Pot Ridge site and variable amounts of substrate (Table 1). Sawdust, spent mushroom compost and newspaper were tested. Table 1 indicates the organic substrates tested, the alkaline material added to the experiment, the volume of organic substrate added and the initial sulfate concentrations. Weekly, 20 ml was drained from the bottom and analyzed, and 20 ml of fresh AMD was added to the top of the columns.

The pH, Eh, and temperature were measured *in-situ* for the lactate experiment and immediately after the effluent was drained from the columns for the solid substrates. Alkalinity

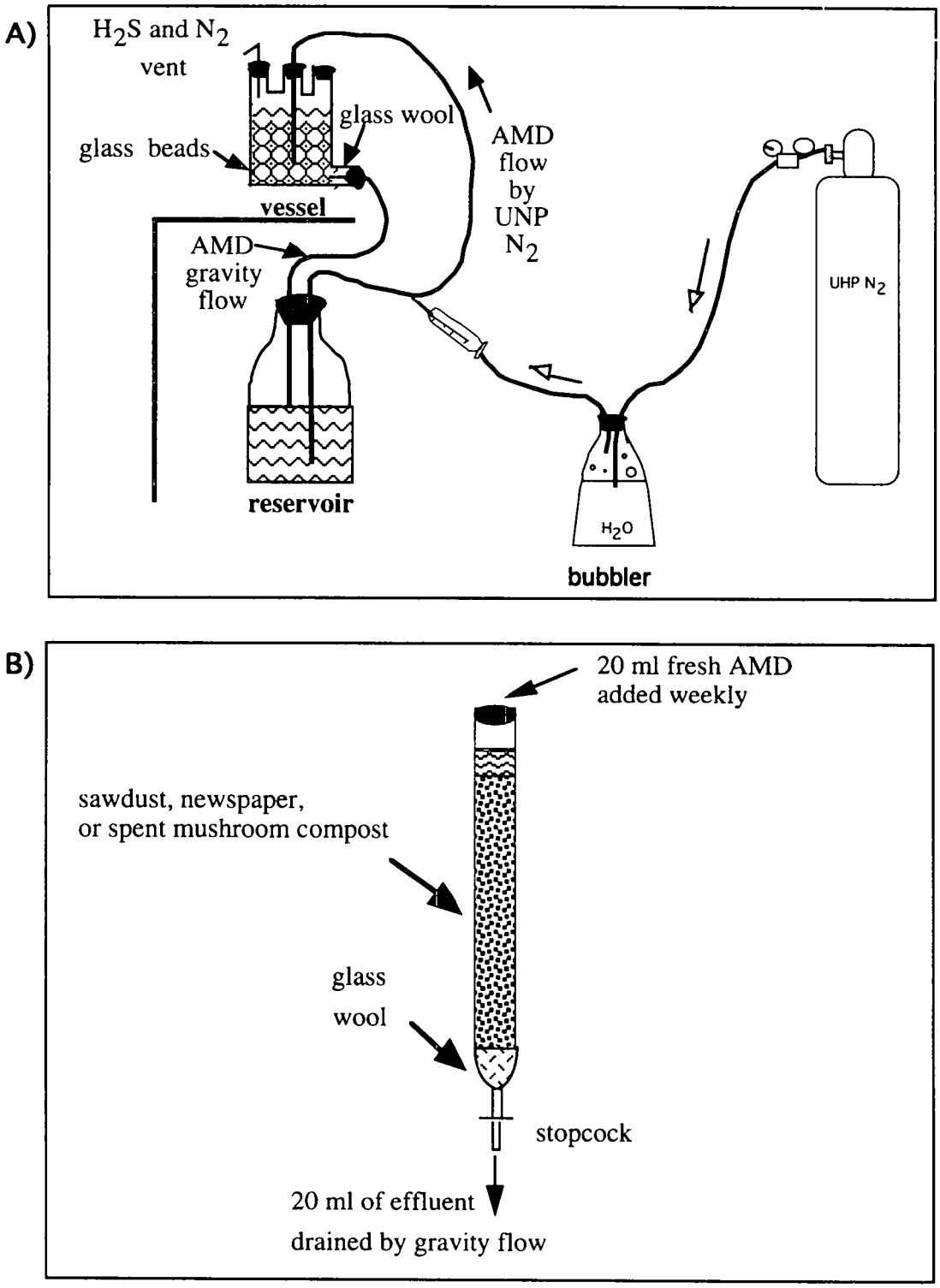

Figure 2. A) Reaction vessel and reservoir . B) Column design. Weekly, 20 ml of effluent was drained from the stopcock and fresh AMD was replaced at the top.

Table 1. Organic substrates, alkaline and AMD sources for each experiment.

Organic substrate	Alkaline source	Amount of Substrate	SO_4 mg/L	AMD source and amount
Fresh sawdust	FBC fly ash (10%)	3.84 cm^3	641 mg/L	150 ml AMD
Degraded sawdust	FBC fly ash (10%)	24.05 cm^3	641 mg/L	150 ml AMD
Spent mushroom compost	limestone	22.65 cm^3	641 mg/L	125 ml AMD
Newspaper	dolomite	5.37 cm^3	641 mg/L	125 ml AMD
Lactate	------	2400 mg/L	1585 mg/L	1L $FeSO_4$

was determined immediately after sampling and was followed by hot acidity. Methods are summarized in Table 2. Samples were diluted for ICP analysis using a ratio of 6 ml sample: 1 ml concentrated HCl: 23 ml distilled deionized water. All samples were filtered through a .45 micron filter directly after dilution and prior to chemical analysis by ICP.

Results of Laboratory Studies

In general, sulfate reduction was observed for all substrates after varying lag periods. For example, Figure 3 illustrates the behavior of SO_4, Fe and pH in the experiment using lactate. Initially, the low pH solution and high redox conditions inhibit sulfate-reducing bacteria. In a system closed to the atmosphere, O_2 is utilized rapidly by aerobic organisms, lowering the Eh. Fermentation then breaks down the complex organics matter into simpler substrates. Sulfate reducing bacteria utilize the simple organics via equation 6 or a similar reaction involving simple organic matter and sulfate. The bacteria thus create alkaline microenvironments within low pH AMD. Figure 4 summarizes results in the form of percent gains and losses for SO_4 and Fe for each substrate normalized for changing influent concentrations and different

Table 2. Analytical Methods

Method	Procedure
Alkalinity	Method 410 (Fishman and Friedman, 1989)
Acidity	Method 305.1 of E.P.A. (1979) using boiling and H_2O_2 to oxidize Fe
pH	Combination Ag/AgCl electrode standardized with pH 4 and 7 buffers connected to an Orion 205A or a Fisher Scientific Accumet pH Meter
Eh	platinum electrode with an Ag/AgCl reference electrode
Mn, Al, Fe,S Ca, Mg, Na, K	Plasma Spectrometry (ICP)

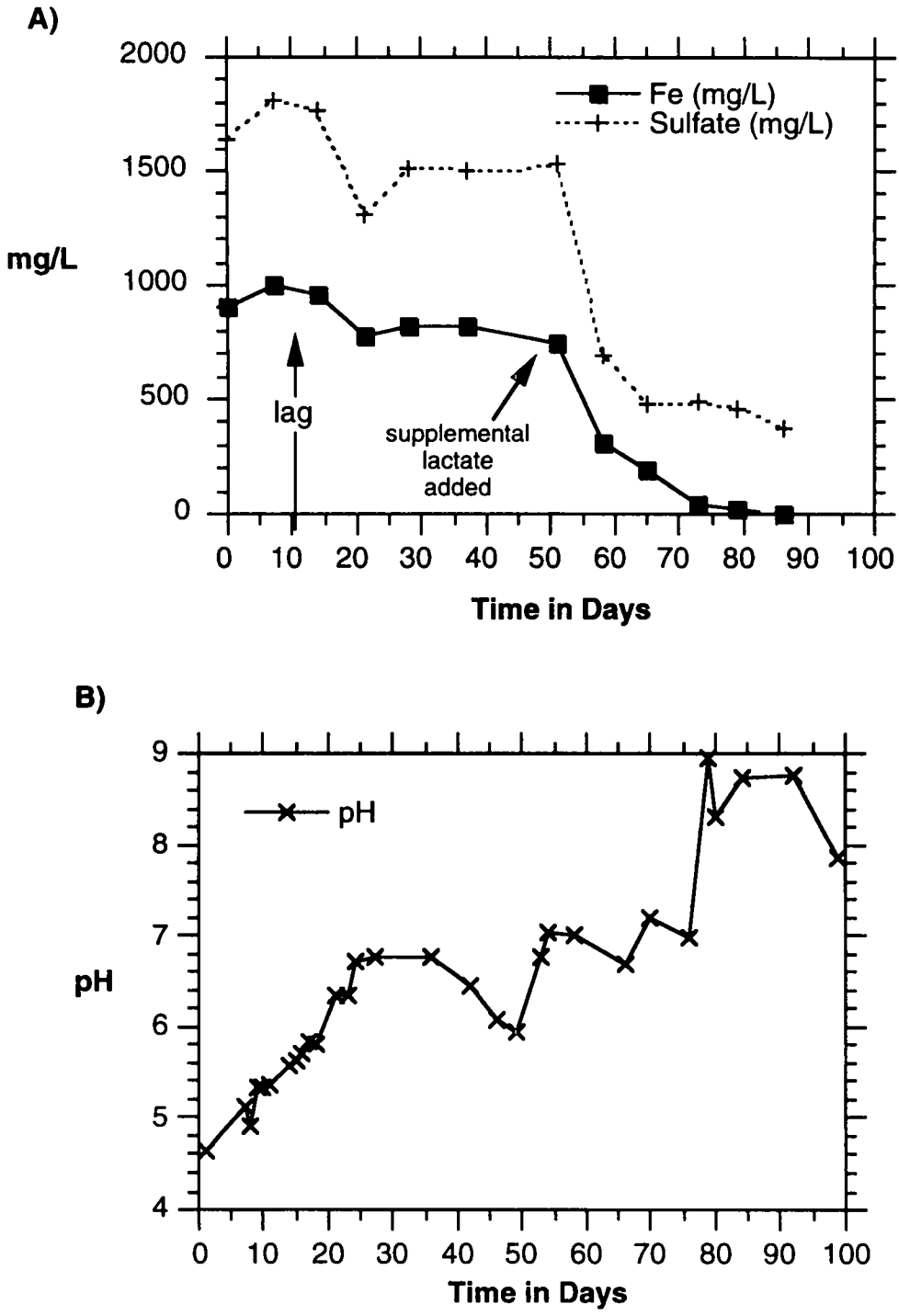

Figure 3. Plot of sulfate, iron (A) and pH trends (B) over time for the lactate experiment as an example of the raw data. The lag time before sulfate reduction is between day 0 and day 15. Sulfate decreases rapidly after this period. The ceasing of sulfate reduction from day 30 to day 55 represents a period of negligible organic matter concentrations. Sulfate decreases again when lactate is added on day 46.

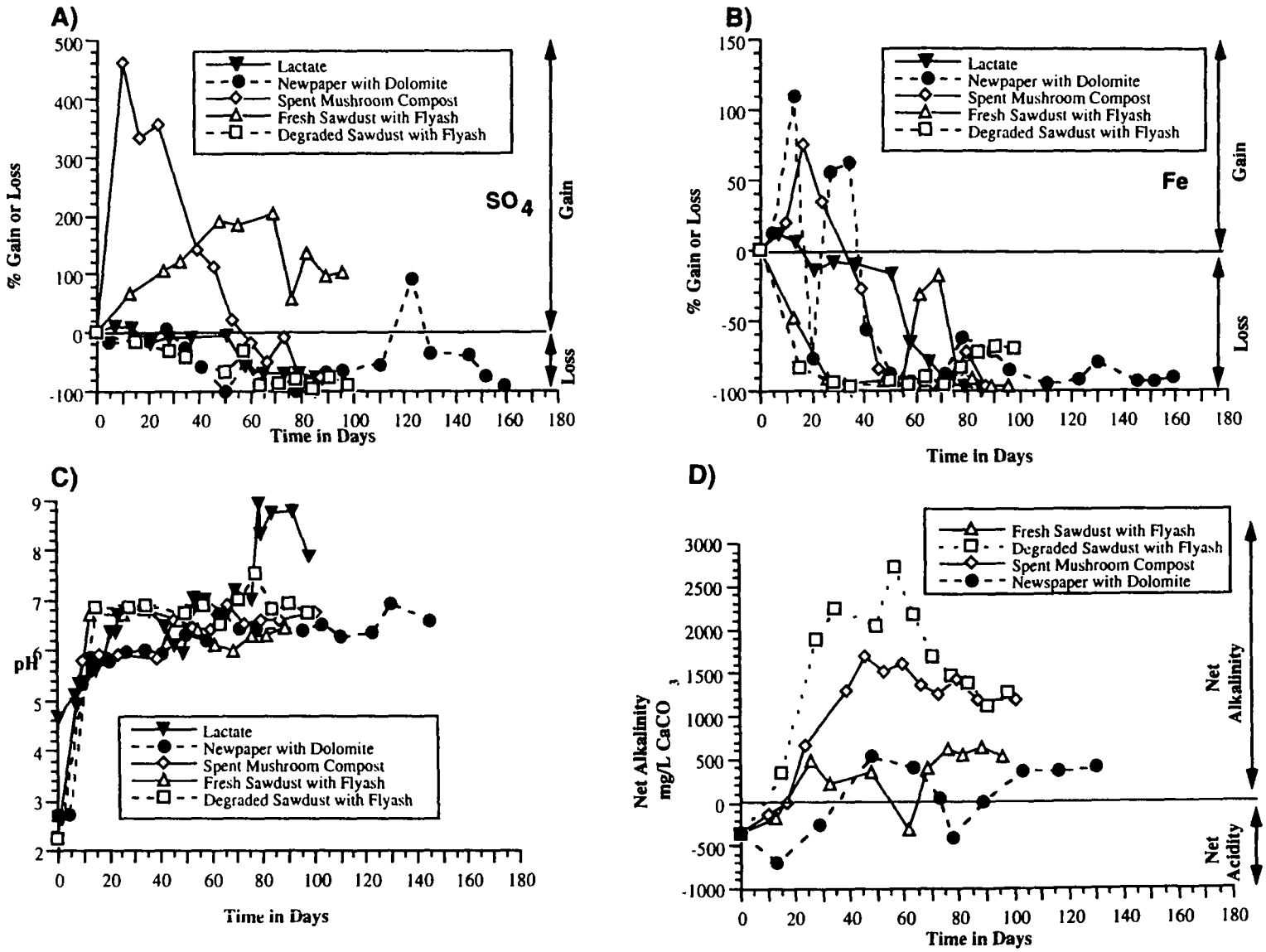

Figure 4. Experimental data for various organic substrates tested in the lab. A) and B) Gains and losses for sulfate and iron are expressed in % relative to the influent concentrations; C) pH over time; D) Net alkalinity over time.

substrate volumes. The influent concentrations of Fe and SO_4 for the lactate experiment were 870 mg/L and 1585 mg/L respectively. For the other experiments which used solid substrates, the influent concentrations of Fe and SO_4 were 38 mg/L and 641 mg/l respectively.

Several experiments showed increases in sulfate and other solutes during an early leaching period. An increase in SO_4 was observed in the mushroom compost due to the dissolution of gypsum and in the fresh sawdust amended with fly ash due to the leaching of sulfate from the fly ash. No excess sulfate was observed for the degraded sawdust with fly ash; however, cation concentrations for Ca, Mg, K and Na increased in both substrates suggesting that these constituents were being leached from fly ash in both degraded and fresh sawdust substrates. The cation leaching period lasted for the entire length of the experiment for both sawdust substrates. Although some leaching of Fe is indicated in Figure 4 for the newspaper with dolomite and the spent mushroom compost, nearly 100% of the Fe was removed in all experiments to once sulfate reduction began. Erratic patterns for some substrates may be due to disturbance of the anaerobic environment.

Average sulfate reduction rates were calculated for each of the column experiments using the decrease in sulfate concentrations over time per gram of substrate (Table 3). Rates were calculated for the lactate experiment using the decrease in sulfate concentrations over time per liter of AMD. Gypsum dissolution in the sawdust experiments that contained fly ash yielded excess SO_4 in these columns. In order to obtain sulfate reduction rates that reflected this additional SO_4 concentration, the analytical data was corrected using the molar ratio of $Ca:SO_4$ from control experiments (Stalker, 1996). The sulfate reduction rates for fresh and degraded sawdust were calculated using corrected SO_4 values. The sulfate reduction rates obtained for the degraded sawdust with fly ash experiment are probably underestimated, as both the sulfate leached from fly ash and the sulfate in influent AMD are reduced. Rates of sulfate reduction for the mushroom compost and newspaper with dolomite experiments were determined during the later portion of the experiments, after leaching. The alkalinity and pH trends over time indicate that all experiments went from acidic to near neutral pH levels with a concomitant rise in alkalinity (Figure 4). Alkalinity was not measured during the course of the lactate experiment, but a net alkalinity of 260 mg/l $CaCO_3$ was measured at the culmination of the experiment.

All experiments produced effluents with high alkalinity. However, since some alkalinity could be furnished by carbonate dissolution or consumed by precipitation of Fe and Al hydroxides, the source of alkalinity deserves consideration. Based on the increased Ca and decreased SO_4 in solution, dissolution of added dolomite, and alkaline components of fly ash and mushroom compost is estimated to contribute 70-

Table 3. Calculated sulfate reduction rates for the experimental organic substrates.

Substrate	Average SO_4 Reduction Rate
Lactate	197 mmol/L/day
Newspaper with dolomite	69 nmol/g/day
Spent Mushroom Compost	60 nmol/g/day
Fresh sawdust with fly ash	20 nmol/g/day
Degraded sawdust with fly ash	148 nmol/g/day

90% of the alkalinity, especially during the early stages of the experiment. However, some alkalinity was attributable to sulfate reduction in each experiment.

Site of the Field Test

The Pot Ridge mine located near Dunlo, PA, U.S.A. was the focus of the field study. The mine is a 198.3 hectare strip mine that was reclaimed approximately 10 years ago. Forty-four highly acidic AMD seeps emerge near the cropline of the Brookville coal and flow into nearby Paint Creek.

In the central part of the Pot Ridge mine, ground water is ponded against an internal highwall bounding an up dip zone where the deeper Mercer coal as well as the Brookville and Clarion coals were mined (Figure 1), and a down dip mine where only the upper two coals were mined (Figure 1). A saturated zone up to 13 m thick is ponded in the up dip mine over an area of about 400 m x 300 m. Rainfall infiltrating into the spoil in this up dip area becomes acid in the unsaturated zone, migrates downward and down dip in the spoil to the ponded zone, and then slowly leaks out through the crop barrier and a barrier between the mines to emerge as a major group of seeps.

This saturated zone appears to satisfy the requirements for *in-situ* sulfate reduction if organic material is introduced. The thick zone of ponded groundwater should lead to a thick anoxic layer overlain by a thin aerobic layer just beneath the water table in which dissolved O_2 is consumed by aerobic bacteria. Flow through the ponded zone is slow, estimated at .4 m/day giving time for sulfate reduction. Although the water table fluctuates by 1 to 2 m over the year, the ponded zone appears permanent, which is essential to prevent re-oxidation of FeS and regeneration of AMD.

The results from the laboratory experiments were used to implement a field test for *in-situ* sulfate reduction. Nearly 11.3 tons of sawdust mixed with 5 % by volume dolomite and 5 % by volume sewage sludge (to supply nutrients) were injected as a slurry with 13% solids into the saturated spoil at the Pot Ridge mine. A total of about 20 liters of an SRB culture was mixed into the slurry as it was injected. The slurry was injected through the drillstem into 4 drill holes spanning about 33 m (Figure 1). Previous efforts to complete drill holes using casing with coarse perforations were unsuccessful due to caving before the casing could be inserted. The slurry was mixed in a hydroseeder and pumped into the drill hole with a grouting machine or the hydroseeder pump at rates of about 300 L/min (75 gal/min). Little or no back pressure was encountered; the slurry seemed to flow into the hole essentially by gravity, indicating high porosity and large pores.

The sawdust was derived from a pile left from a sawmill near Portage, PA and was considerably degraded and mixed with soil (79.8% loss on ingnition, LOI) in comparison to fresh sawdust that was 99.7% LOI. Because of appreciable stone, bark and other coarse pieces, it was sieved to less than 1 inch to remove these materials.

The extent of spoil containing the sawdust slurry is not clear, but little sawdust could be noted in holes 10 m from the injection holes. If the spoil has 30% porosity, calculations indicate that 2.7% of the porosity is filled with sawdust.

Preliminary results after about 7 months indicate an inital rise in pH and alkalinity, and appreciable decrease in SO_4 in the injection area compared to an up dip well (Figure 1). Table 4 presents *in-situ* data for a monitoring well (MW-17) in the injection area and an up dip well (MW-20).

Table 4. Results for an *in-situ* injection well (MW-17) and an up dip monitoring well (MW-20). MW-17 was dry between days 51-107 due an extremely dry summer. Day 0 is July 26, 1995.

Injection well (MW-17)

Days	m SWL	pH	mS/cm Cond.	mg/L $CaCO_3$ Acid.	Alk.	mg/L SO4	Fe	Mn	Al	Ca	Mg	TOC
37*	13.96	7.40	2560	0	686	1010	155	65	.1	352	154	251
51*	14.42	6.60	1090	0	407	1019	177	54	9.3	295	175	155
107*	13.87	5.66	1350	408	180	595	239	83	.8	191	147	83
145		4.60	1840	440	8.0	1534	86	90	17	171	197	2.1
189		3.30	2480	440	0	784	37	93	24	164	199	3.5
210**		3.70	1275	--	--	--	--	--	--	--	--	--

Up dip well (MW-20)

Days	m SWL	pH	mS/cm Cond.	mg/L $CaCO_3$ Acid.	Alk.	mg/L SO4	Fe	Mn	Al	Ca	Mg	TOC
37*	18.50	3.90	6600	1540	0	4085	381	131	67	329	320	5.0
51*	18.93	4.00	6450	1660	0	3651	446	124	94	212	338	3.7
62		4.20	6690	1230	18	3088	404	132	84	258	337	4.9
76*	19.45	4.40	6500	1364	28	3082	477	128	91	261	338	6.4
90		5.00	5280	680	22	2400	247	114	14	306	252	3.2
107*	18.47	4.18	2950	1412	0	1275	467	126	100	236	202	NA
111		4.90	5960	962	18	3238	319	132	23	338	326	3.2
145		4.80	6370	1080	20	2946	284	126	13	363	323	3.0
189		3.20	7440	1940	0	1772	467	159	94	256	456	3.8
210**		4.60	3400	--	--	--	--	--	--	--	--	--

* Denotes PSU sampling dates. All other dates sampled by Mahaffey Labs, Grampian, PA.

** Monitoring is continuing and the samples from day 210 are being analyzed.

If the difference in SO_4 concentrations between the up dip well and the injection well was due to SO_4 reduction and the precipitation of FeS, then equal molar decreases in Fe would be expected. Redox potential was low enough (140 mV) within the injection area to support sulfate reduction, but persistent high concentrations of Fe suggest that sulfate reduction may not have been responsible for the large difference in SO_4 concentrations between MW-20 to MW-17. A decrease in TOC over time in MW-17 may suggest bacterial activity or dilution in the injection area. Increases in alkalinity and pH suggest that some acidity-consuming reactions are occurring. In addition to sulfate reduction the dissolution of dolomite is probably occurring. The possibility also exists that the organic matter in the sewage sludge adsorbed Fe, other metals and/or sulfur compounds. This could explain why the ratio of decreases in Fe to SO_4 are not concomitant.

A significant problem may be that MW-17 had only about 0.7 m of water at most sampling dates, whereas most sawdust was injected from 1 to 8 m deeper. Sulfate reduction may have been occurring beneath the completed portion of the well where anaerobic conditions are inferred to be prevalent. Figure 1 indicates that the geometry of the injection area may greatly influence the test results.

Another possible explanation for lack of clear evidence for SO_4 reduction is that deep water in MW-20 does not flow to the other monitoring wells. The water that is sampled from MW-20 may leak through sandstone units associated with the Brookville and Mercer coals and emerge as seeps to the northwest without mixing with overlying water. Because of this MW-20 samples may not reflect the up dip chemistry of the monitoring wells.

A third possibility is that there is little flow in the injection area, especially at MW-15 where the ponded area thins over the Brookville coal pit floor.

Discussion

Although the most rapid rate of sulfate reduction was obtained with whey (and lactate), this material has the disadvantage of being liquid, so it would presumable flow out of the spoil with the groundwater and would have to be replaced continuously. The possibility of organic outflow has been raised as a concern, though if appropriate concentrations were added the effluent concentration should be negligible. However, because of these potential problems, this option was not pursued, though it has potential. Discussions with milk processors indicate that whey is difficult to dispose of, and considerable quantities might be obtained.

Addition of alkalinity can stimulate the initiation of sulfate reduction. However, leaching from the alkaline material may initially increase concentrations in the effluent. For example, some fly ash and mushroom compost contains readily soluble $CaSO_4$. Over time the leaching will slow and eventually concentrations will decrease to less than or equal to influent concentrations. Initial alkalinity and increased pH in both the lab and field experiments is most likely the result of carbonate dissolution. Subsequent alkalinity generation is mostly the result of sulfate reduction.

Clearly, fresh sawdust did not support sulfate reduction as well as the degraded sawdust. This was also evidenced by Tuttle et al. (1969b) where partially degraded wood dust yielded more consistent sulfate reduction rates over a longer period of time than fresh sawdust in flask experiments. Here, the degraded sawdust with fly ash provided enough carbon to reduce not only all of the generated SO_4 from the fly ash, but also some of the influent SO_4 as well. This observation suggests that the degree of degradation of sawdust can affect sulfate reduction rates. Sulfate reduction using fresh sawdust may be limited by lignin, which protects plant cells from degradation. Also, the degraded sawdust may have been significantly broken down by fermentation of cellulose into simpler organics that SRB can use, but not so degraded that all of the reactive carbon is gone. Newspaper, mushroom compost and lactate all support sulfate reduction at similar rates.

Based on the average rate of SO_4 reduction obtained in the lab experiments, the reduction of sufficient SO_4 to create alkalinity adequate to neutralize the very high acidity of 1500 mg/L $CaCO_3$ found at the Pot Ridge mine would require a contact time of 500 days assuming 30% spoil porosity, 2.7% of porosity filled with sawdust and 2 moles of alkalinity for each SO_4 reduced. This very long contact time is not practical at the Pot Ridge site. However, several possible means of improving this performance can be suggested. Injection of higher sawdust concentrations, to perhaps 10% of the porosity, should proportionately increase the reduction effect. Also, the possibility of using milk processing wastes, which react more rapidly, exists.

An important question remaining is whether cellulose-type substrates will continue to degrade and react at rates similar to those measured. Eger and Wagner (1995) found that sulfate reduction markedly decreased in the third year of experiments with compost and sawdust and ceased in the fourth year, despite considerable carbon still available. Middelburg (1989) summarizes research on sulfate reduction in marine sediments indicating that the rate of organic carbon

decomposition in recently deposited marine sediments decreases with time according to the equation:

$$\log k = -0.95 \log t - 0.81 \qquad (7)$$

where k is the rate of carbon decomposition by sulfate reduction (yr^{-1}), and t is time (yr). If this relation applies, then the rate of organic-sulfate reaction is predicted to decrease by a factor of about 9 between year 1 and year 10. To the extent that the organic matter in marine sediments is land-derived (which some undoubtedly is), then this rate of decrease might apply to the AMD system. This first order relationship follows the multi-G model which asserts that organic matter consists of many groups of compounds with different degradation rates (Westrich and Berner, 1984; Jorgensen, 1979). Marine organic matter tends to be more reactive than land plant wastes and the pH in the marine environment is higher than most AMD environments. Fe occurs as solid Fe-oxides rather than in solution in AMD, so the rate may decrease at a slower rate for the conditions applicable in this study. Tarutis and Unz (1994) showed similar trends for organic matter in wetlands exposed to AMD. Also, the rate of AMD generation probably drops off with time, so the required rate may be smaller.

Based on these data, the reaction rates we have derived should probably be considered a maximum rate, with a progressive decrease over a period of years. Probably only a field experiment over a long time period will be able to determine the long-term behavior of sawdust or similar materials exposed to AMD.

The sulfate reduction rates obtained in this study for cellulose and related materials are probably not the optimum that can be attained. The breakdown of the wood material by fermenting bacteria is probably the rate limiting step. Further experiments are needed to find fermenting bacteria that can accomplish this reaction more rapidly at acid pH values.

Conclusions

Bacterial sulfate reduction is capable of removing iron from AMD solutions and furnishing alkalinity to neutralize the acidity. Considerable sulfate is also removed. The process has no inherent maximum concentration that can be removed, in contrast to anoxic limestone drains. A variety of organic substrates can be used, including several forms of organic waste products such as milk processing wastes, sawdust, compost, and paper. If a sizable zone of anaerobic water-saturated spoil exists or can be created at a reclaimed surface mine, then AMD generated in the overlying unsaturated spoil can be partly or completely remediated within the spoil, thus obviating the need for surface treatment.

Experiments indicate that bacterial sulfate reduction can be initiated even at pH less than 3, though the rate is slow until about pH 5 is reached. Initial results from a field test show that slurries of organic particles can be injected into strip mine spoil in large quantities. Initially, there was a large rise in alkalinity and pH in the injection area, however these parameters have leveled off to pre-treatment values. It is possible that the monitoring wells are not deep enough to penetrate the anaerobic zone. Deeper wells are being drilled and sampled to ascertain the effects of sulfate reduction on AMD at depth in the spoil.

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IMPROVING GROUND WATER QUALITY IN THE BACKFILL WITH ALKALINE ADDITIONS

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Abstract. Skyline Coal Company, a wholly owned subsidiary of Cyprus Amax Coal Company, initiated surface mining of the Sewanee seam of coal in Sequatchie County, Tennessee, in September, 1987, pursuant to the terms of a duly approved surface mining permit. The mine was named after an adjacent creek, Glady Fork. The engineering and geological studies conducted in the preparation of the surface mining permit application indicated that the mine could be operated with a minimum of concern for the generation of adverse impacts to the hydrological regime outside of the permit area. On July 5, 1990, however, the mine was cited for polluting Glady Fork with iron laden seeps. Shortly thereafter, comprehensive hydrogeological, geochemical, and operations management investigations were launched. Furthermore, laboratory testing procedures were scrutinized and modified to address the "siderite masking" of overburden data generated from standard acid-base accounting techniques. These investigations culminated in the preparation of a detailed Toxic Materials Handling Plan (TMHP) which incorporated "state of the art" ground water management plans and water quality assurance programs. In light of the lithologic distribution of the problematic strata and the reliance on both blast casting and dragline equipment for overburden movement, the TMHP placed a heavy emphasis on the timeliness of certain activities, the collection of detailed pre-mining information, and the application of heavy doses of alkalinity in the form of crushed limestone. The permit area has been mined out and is currently in the final reclamation phases of pit closure. Data collection from various ground water sources support the validity of the concepts and practices undergirding the TMHP. Significant alkaline recharge of the backfill ground water resource has been realized. More importantly, the alkaline additions of the TMHP have yielded substantial reductions in both iron (Fe) and manganese (Mn) concentrations in the post-mine ground water regime.[1][2][3]

Introduction

Activities aimed at the prevention or abatement of poor quality mine drainage must be based upon a well designed, fully implemented Toxic Materials Handling Plan (TMHP). The plan should be site specific in nature. Its overall effectiveness in meeting desired abatement objectives will be contingent upon the prudent factoring of key hydrogeologic, geochemical, and operational considerations into its design and field application. In this case, alkaline additions through imported limestone were a key component to the success of a TMHP developed specifically for the Glady Fork Mine. This paper will document the merits of adding limestone amendments to the backfill in coordination with surface coal mining and reclamation activities. Emphasis is placed on the benefits

[1]Paper presented at the 1996 Annual Meeting of the American Society for Surface Mining and Reclamation, Knoxville, May, 1996.

[2]Vance Patrick Wiram, Supervisor of Environmental Services of Cyprus AMAX Coal Company, Brazil, IN and Hans E. Naumann, Senior Vice President, Marshall Miller & Associates, Lexington, KY.

[3]Publication in this proceedings does not prevent authors from publishing their manuscripts, whole or in part, in other publication outlets.

derived from adding the alkaline materials along identified hydrologic flow-paths in the backfill.

Statement Of Purpose

The purpose of this paper is to share the experiences of Skyline Coal Company with the coal mining industry. In particular, the writers wish to address the following points of significance:

- The methodologies involved with limestone incorporation to the backfill in synchronization with the surface mining and reclamation process require a detailed knowledge of the operation of the mine.

- Limestone additions, with respect to both quantity and placement in the backfill must be based on overburden geochemical data. These data must be routinely gathered in advance of mining.

- Time spent in identifying the post mining ground water regime and direction of flow is essential in developing concepts and defining the needed "building - blocks" to achieve overall effectiveness of the TMHP.

- The benefits of alkaline additions can be directly measured or observed by monitoring the ground water quality of the backfill.

Background

Skyline Coal Company is a small surface operation (<500,000 tons/year) located in Sequatchie County, approximately 15 miles northwest of Dunlap, Tennessee. The subject mine is the Glady Fork Mine. Mining was initiated at the Glady Fork site in September, 1987, in the lower third of the mining permit by use of endloaders and trucks. A box cut was prepared using that equipment. Once the box cut was in place, a walking dragline was placed into the sequence, and the front end loaders and overburden trucks were subsequently phased out. Cast-blasting was later introduced to the operations and subsequently the remainder of the permitted area has been developed with a combination of both dragline and cast-blasting as the primary mode for overburden movement.

The coal-bearing sequence developed at Glady Fork are Pennsylvanian Age rocks of the Crab Orchard Group. *Figure 1* shows the overburden strata to consist of the Newton Sandstone and Whitwell Shale Formations. The coal seam being mined is the Sewanee Coal Member of the Whitwell Shale Formation. The surface mine is in a broad upland divide area of the Cumberland Plateau. It lies between major drainage systems which dissect the plateau surface. The major stream adjacent to the former mine site is Glady Fork Creek.

In mid-1990, Skyline Coal began experiencing water problems at Glady Fork. The water concerns were in the form of off-site seepage emanating from the mine site into the adjacent creek. The seepage consisted of slightly acidic to alkaline, manganese (Mn) enriched, ferruginous waters. Seepage flows were defined as originating from the mine disturbance areas with movement to the creek via natural fracture systems or other stratigraphic flow paths existing in the stream buffer zone and stream bed itself. Although the overall impacts of the seepage to the adjoining streams were limited to aesthetics (red staining) and temporary benthic aquatic habitat concerns (iron sediment coatings), the discharge was defined as a pollution source to waters of the State and therefore implementation of remedial action plans was required to eliminate or minimize degradation potentials.

The range in primary water quality parameters of the seeps at the

time of discharge were as follows: pH = 3.4 to 7.5; alkalinity = 0 to 121 mg/l; total iron (Fe) = 4.8 to 48.6 mg/l; total manganese (Mn) = 2.3 to 34 mg/l; and, sulfate (SO_4) = 8 to 812 mg/l.

Skyline embarked on an intensive investigative program so that enough information could be collected to identify the cause of the apparent disparity between the projected and actual water quality parameters. This information was also deemed necessary in order that a reliable materials handling plan could be developed which would satisfy both the regulatory authorities and corporate custodians. This program included extensive core drilling, testing of overburden samples, and modifying the testing procedures to account for "siderite masking" of acid/base overburden characterization objectives (Wiram, 1992), re-examining the hydrogeological and geochemical structure of the overburden, and consulting with experts in the field of mine drainage. Contrary to earlier permit findings, the additional site investigations identified potential acid-producing strata that were previously ill-defined or non-existent based upon acid/base laboratory procedures that did not account for the abundance of siderite ($FeCO_3$) common to the overburden shale sequence.

Using modified analytical procedures to account for the "siderite masking", three stratigraphic horizons in the overburden were identified as being potentially acid-producing in character. The three horizons were (listed in descending order):

1) upper shales (<5.0') at the top of the Whitwell Shale Formation;
2) lenticular sandy shales (0 - 20') within the Whitwell; and,
3) pit floor or underclay of the Sewanee Seam.

A fourth type of material, the "coal cleanings" (an admixture of coal and underclay), generated in the coal extraction process, was also identified as being acid-producing in character and was subsequently targeted for proper handling and disposal during mining.

Although the different materials were demonstrated to possess pyritic materials and a lack of inherent neutralizing potentials, the acid producing character of the various strata was only sporadic in nature. With the exception of the "coal cleanings", it was not uncommon to see both acid and alkaline characteristics within the respective strata.

Typical ranges in % pyritic sulfur ($\%P_S$) contents and modified net neutralization potentials (MNNPs, expressed as tons of $CaCO_3$ /1000 tons material (Wiram, 1992)) for identified acid producing units were as follows:

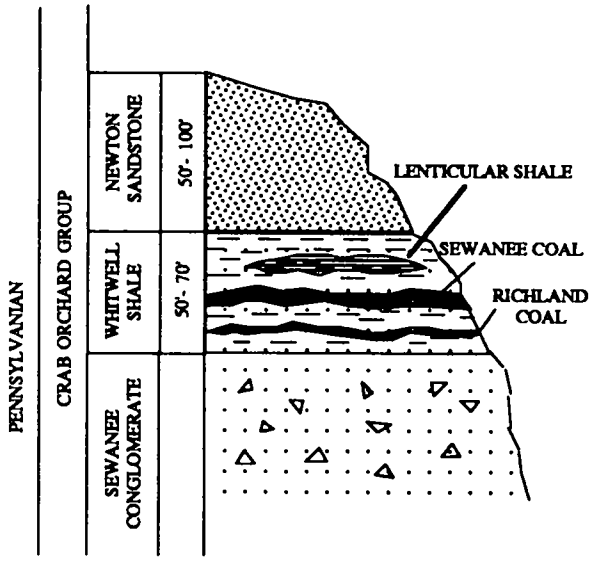
1) Upper shales: $\%P_S$ = <0.1 to 1.64, and MNNP = -26 to +55.
2) Sandy shale: $\%P_S$ = <0.1 to 1.78, and MNNP = -48 to +14
3) Underclay: $\%P_S$ = 0.12 to 0.78, and MNNP = -19 to +20

The typical range in both $\%P_S$ and MNNP observed for the coal cleanings were 0.73% to 1.60% and -45 to -24 tons $CaCO_3$/1000 tons material respectively.

Throughout the reserve area, the lower Whitwell Shale interval above the coal seam demonstrated consistently low $\%P_S$ and was alkaline in character. The Newton Sandstone, the rock unit comprising the majority of the stratigraphic column of the coal sequence, was shown to be basically inert from the standpoint of acid or alkaline producing potentials due primarily to its indurated, quartzitic cementation. An exception to the general rule for the sandstone interval existed when, on an occasional basis,

the quartzitic cementation was replaced by sparry calcite. Although the calcite cementation was sporadic in occurrence, when present, such sandstone material demonstrated excess alkalinity characteristics with MNNP values commonly in the range of 100 to 130 tons of $CaCO_3$/1000 tons material.

Figure 1
Stratigraphic Sequence in Permit Area



Eventually, these investigations, mine planning efforts, negotiations with the regulatory authorities, and protracted hearings at the administrative law level, generated a TMHP which was attributed the highest probability of success. The balance of this presentation describes the results of the application of this TMHP.

The Mining Method

Skyline's method for selectivity handling and disposing of potentially acid-producing materials involved a combination of operating techniques. Overburden movement was achieved by a combination of direct cast-blasting, tractor pushing, and dragline placement with the mine's Bucyrus-Erie Model 1300 stripping machine.

Skyline modified some phases of its traditional mining methods to accommodate the TMHP developed for the site. An important element of change was that Skyline moved the backfill-side operating bench level of the dragline from 50 feet or less off the pit floor to 85 feet above the coal. That change enhanced the machine's capabilities of handling an increasing volume of shale (i.e., problematic shale) to be placed on the bench pad as well as expanding the machine's ability to place the best shale materials in the graded backfill. Both activities were deemed important to the success of the TMHP.

The mining sequence was initiated with the cleaning of the mined out pit, placement of cleanings against the toe of the machine bench, and where appropriate, constructing a hydrologic flow-path (chimney drain) to move subsurface water off the dragline bench itself. As other sections of this paper will discuss, this phase of the mining/reclamation sequence was also the recipient of alkaline additions. The pre-blast configuration as well as the generalized geochemical characterization of the overburden are depicted in *Figure 2*.

Figure 2
Configuration of Pit Prior to Blast Cast

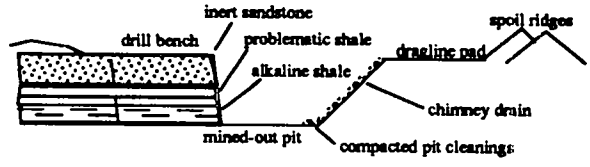
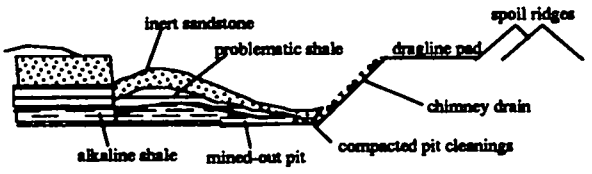


Figure 3 illustrates the position of the muck pile (shot overburden) following a normal cast-blast shot. (The shape and the distribution of the shattered rock ("the bread loaf") was established by field measurements. Thereafter, the services of blasting specialists using high speed movie cameras were also secured. An examination of the film using the "stop frame" capability of a special projector supports these initial field

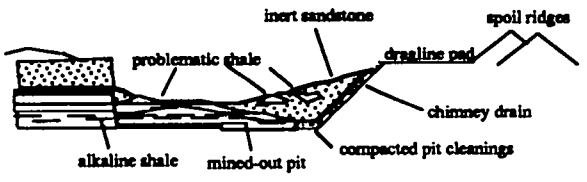
observations.) Note that the problematic shale extends across the former pit floor. However, the bulk of the acid-forming shale lies toward the highwall side of the pit and thus in a more advantageous position for selective handling with the dragline. Lastly, it is important to note that the shot rock underlying the entire length of the muck pile consists of alkaline shale materials derived from the basal section of the original overburden profile.

Figure 3
After Blast Cast



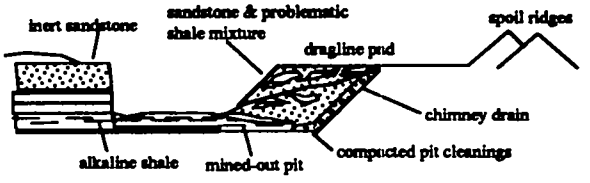
Once the overburden material was cast, tractors were used to push the upper sections of the muck pile ("the bread loaf") from the highwall side toward the adjacent backfill bank. Eventually the tractors would cut into the shattered problematic shale and the pushed material would become an admixture of problematic shale and inert sandstone. This unique configuration is depicted in *Figure 4*.

Figure 4
After Tractor Push



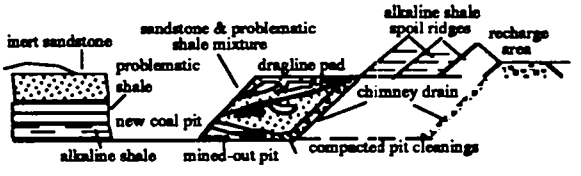
Following the tractor push of primarily inert rock materials, the dragline was used to build its dragline bench out of mostly problematic shale materials. As a practical way of providing in-field identification of the position of the problematic shale materials in the muck pile following cast blasting, stakes with notes affixed were placed along the dragline bench. Information pertaining to estimated depths to the base of the problematic materials was provided by these notes. The dragline operators would rely on the information on those stakes to control stripping depths to the base of the problematic shale. *Figure 5* shows the position of the pad relative to the other components of the mine backfill.

Figure 5
Configuration After Building Dragline Bench



Final pit excavation consisted of placing the alkaline shale materials in spoil ridges behind the machine on the dragline bench. As shown in *Figure 6*, only an extremely small portion of problematic shale materials had the opportunity of actually being cast into the spoil ridges. Overburden sampling of the graded spoil ridges at this mine proved the validity of the method. As the dragline bench has progressively moved higher into the backfill, the geochemical quality of the graded backfill interface steadily improved.

Figure 6
Final Overburden Distribution



Tractors regraded material no more than three spoil ridges behind the active cut. *(See Figure 6.)* This material was graded in lifts approximately 8 feet thick. The spoil ridges were continually worked with

tractors until the area was regraded to the approximate original contour, or slightly elevated due to the swell of the overburden. Final grading was conducted parallel to the contour in sloped areas to minimize erosion and to provide a more stable surface for redistribution of topsoil.

As a summary comment, the majority of the problematic shale ended up on or directly beneath the dragline bench. At a minimum, Skyline targeted placing 90% of the acid- producing shale materials on or below the dragline bench horizon. An estimated 30 - 40% of the acid-producing materials remained permanently buried in the cast-blast profile. As will be discussed later, limestone applications above and below the direct cast-profile were designed to prevent and/or substantially minimize acid production from this zone of the backfill.

Design Objective Of Alkaline Additions

The limestone applications had to meet both interim and long-term requirements. A synopsis of the key amendment objectives follows:

1. To subdue bacterial pyritic oxidation activities and neutralize acidities generated from unavoidable reactions occurring when potentially acid-producing materials (i.e., Whitwell interface shale and lenticular sandy shale deposits, coal cleanings, underclay materials, etc.) are exposed to the atmosphere between stripping cycles to control similar reactions in these materials once disposed in the backfill.

2. To focus alkaline recharge capabilities along pre-defined hydrologic flow-paths (i.e., dragline bench, graded backfill/topsoil interface, pit floor, etc.) to enhance a long-term alkaline availability in the backfill for the purpose of counteracting unfavorable acidity build-up. (Coarse-sized ($1^1/_2$" x 0") limestone was used in order to sustain longevity of the alkaline resource.)

3. To enhance the chemical stability of siderite ($FeCO_3$) common to the shale materials comprising the overburden sequence. Limestone additions were expected to provide high alkalinity/acidity ratios in the backfill and to thus maintain favorable pH/alkaline conditions which would prevent and/or minimize the mineral dissolution of siderite constituents in the backfill.

4. To complement the in situ alkaline shale materials at the base of the muck pile. The combination of imported limestone and native alkaline shale at the base of the muck pile was to ensure the availability of alkaline products of sufficient quantity and distribution to effectively accommodate the chemical reactions and subsequent metal-loading activities that could accompany natural backfill weathering processes (i.e., "wetting" and "drying" cycles) associated with backfill ground water re-establishment.

Key Methods, Parameters, And Assumptions

1. Overburden was sampled ahead of mining on a close-spaced grid (approximately 500 feet) using air-rotary or core recovery methods. Individual samples were collected at 5-foot vertical intervals in each exploratory hole.

2. All amendment rates associated with alkaline additions to the backfill were determined by utilizing the modified neutralization potential (MNP) (Wiram, 1992) procedure for the purpose of eliminating "siderite masking". MNP was expressed in terms of tons $CaCO_3$/1000 tons of material.

3. The standard multiplication factor of 31.25 times the pyritic sulfur content was used in calculating potential acidities (PAs) of the various overburden materials. Potential acidities were expressed in terms of tons $CaCO_3$/1000 tons of material.

4. Modified Net Neutralization Potential (MNNP) was defined as the difference between MNP and PA (MNNP = MNP - PA).

5. In defining its lime requirements, Skyline Coal used a 2,300 tons/ac.-ft. factor for estimating in situ tonnages of overburden shale and pit cleanings to be encountered in stripping. This is a "Caterpillar Performance Handbook," (Edition 17, October, 1986) value. A 250 foot radius around each hole was used to estimate the total quantity of alkalinity required.

6. Limestone application rates were based on "negative MNNP" zones identified through the 5-foot sampling and testing interval in each borehole. (These were also denoted as "net deficient" zones in other communications on the subject.) Each zone was presumed to be 5 feet thick and to occupy an area reaching half the distance to each adjacent borehole (typically 250 feet). Zones demonstrating negative MNNP values equal to greater than 5 tons $CaCO_3$/1000 tons of material were selected for the subsequent calculation of limestone application rates for the area around the borehole. The limestone application rates for each 5-foot zone demonstrating negative MNNP's equal to or greater than 5 tons of $CaCO_3$/1000 tons of material were then accumulated to arrive at the total quantity of limestone applicable t the area around each borehole.

7. The alkalinity of "net neutral" zones in each exploratory hole was not factored into the limestone quantity estimation calculations.

8. Limestone application rates were based on a stone quality of 90% purity.

Alkaline Addition Placement In The Backfill

The "building blocks" needed to develop a workable TMHP relative to the following issues began to accumulate as the investigations proceeded. These "building blocks" included the following:

1. The water quality characteristics of the earlier mined and backfilled portions of the mine, as evidenced by both post-mine ground water data and off-site seepage water quality;

2. The refinement of pre-mine/post-mine positioning of potentially acid-producing materials in the stripping sequence; and,

3. The establishment of a basic understanding of the hydrologic flow-paths in the backfill.

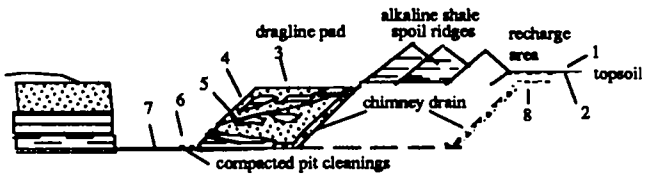
It quickly became evident that alkaline additions to the backfill would play a major part in the TMHP. These additions were to have the dual role of minimizing and/or preventing acidic reactivity in the backfill and to enhance the alkaline-loading of the reemerging ground water presence in order to meet the long-term post-mine drainage objectives following reclamation. The overall concepts for the design and planned installations of alkaline-loading mechanisms for the TMHP are credited primarily to the past research works and technical papers of Caruccio and Geidel, 1988 and 1989. The ideas and technical support for incorporating the limestone materials into the backfill in conjunction with the stripping and reclamation process stem primarily from the works of Byerly (1990) and Infanger and Hood (1980).

Eight zones in the backfill were targeted for alkaline additions. As

shown in *Figure 7*, the zones of alkaline additions are (in descending order from the reclaimed surface):

1) replaced topsoil;
2) topsoil-graded backfill interface;
3) backfill-side dragline bench;
4) pit-direct cast overburden;
5) pit-direct cast understory;
6) coal cleaning;
7) pit floor underclay/shale; and,
8) surface alkaline recharge structures (SARS).

Figure 7
Alkaline Addition Areas



Because of the substantial quantities of limestone to be applied to the backfill to account for the neutralization deficiencies identified for the involved strata and to compensate for possible unforeseen short-comings in the mine's overall success at achieving total selective handling in the backfill, Skyline split the limestone application into three equal portions. Each split was placed within a specific position within the backfill. Correct proportioning in the field was assured by use of "zone of influence" boundaries marked along the dragline bench.

The three sections of the backfill receiving the limestone amendments are as follows:

1) topsoil/backfill interface;
2) backfill dragline bench; and
3) direct cast profile.

The portion of lime placed on the topsoil/backfill interface was in addition to the amount of lime already added to compensate for possible "hot-spots" identified on the graded backfill in advance of final soil replacement.

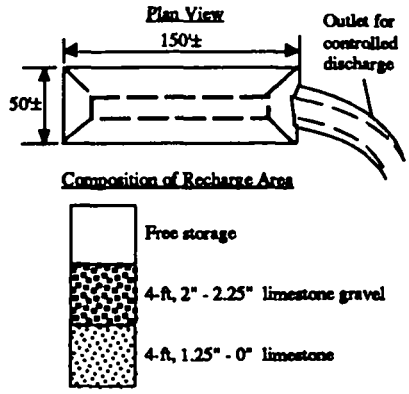
Skyline further split the lime targeted for the "direct cast profile" of the muck pile into two separate applications. Half of the required lime amount was dumped on the pit floor and spread in a uniform lift. The remaining half of the lime planned for the direct cast profile was placed and spread over the tractor push area of the muck pile.

Backfill Alkaline Recharge Structures

To enhance the introduction and subsequent movement of alkaline waters into and through the backfill, Skyline constructed a network of surface alkaline recharge structures (SARSs). *(See Figure 8.)* The SARSs were installed during final reclamation and were designed to afford maximum watershed inflow into the backfill. Furthermore, wherever possible, these surface features were positioned to overlay chimney drains installed in the backfill. In that manner, the potential for the alkaline/oxygen loading of the backfill ground water was enhanced. The key objective of this initiative was to induce metal precipitation within the backfill.

Typically, each SARS was first excavated and shaped to match the existing contours of the reclaimed land. Usually, this would result in a backfill excavation with volume of approximately 1.8 acre-feet. Limestone with a calcium content of 90% or greater was placed into the excavation. The first four feet of limestone consisted of a 1.25" x 0" "crusher-run" produce. The next four feet consisted of 2" x 2.5" gravel. The resulting loosely packed, bowl-shaped, recharge areas were anticipated to have a water holding capacity of 1.3 acre-feet, almost double the volume expected from the design precipitation event (2-year, 15 minute event).

Figure 8
Detail of Alkaline Recharge Facility



Ground Water Monitoring Results

The application of the TMHP is now running into its fourth year. *Figure 9* shows the general location of where the TMHP was implemented at Glady Fork. The TMHP was initiated in August 1992. Skyline Coal continued full implementation of the plan through final pit closure in 1995.

Prior to entering into a discussion of the water quality data of the mine site, it is important for the reader to understand that the basis for this paper is "ground water well" data and not "seepage" data. This is a practical off-shoot of the company's seepage abatement program which was initiated in October, 1990. At that time, the ground and surface water paths to the identifiable seeps to Glady Fork were intercepted, and as a result, the seeps have ceased to exist. The multi-source water captured in the process is being pumped back to the mine site. This method of control of the former seeps is expected to continue until the company installs a passive, wetland-based, water control system. Among the many objectives of this wetland is the accommodation of those seepage flows, should they in fact re-emerge following final reclamation of the mine site.

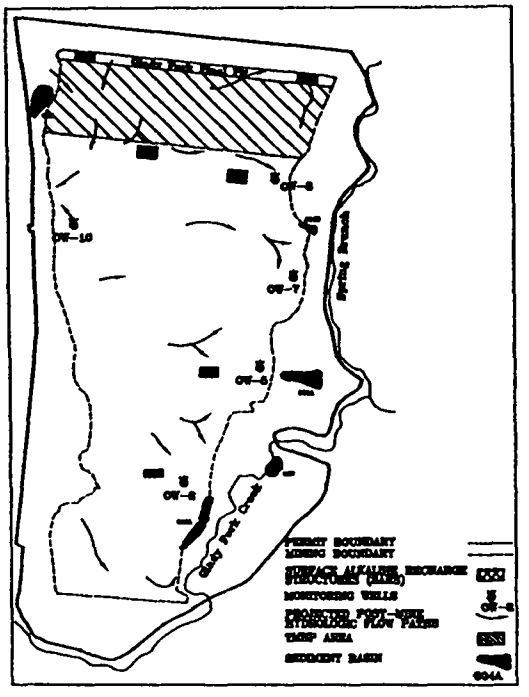
A review of the water quality trends from the majority of the backfill monitoring wells indicates an overall amelioration of the ground water associated in areas mined prior to the application of the TMHP. The improvement in ground water quality in the areas mined prior to full implementation of the TMHP initiative primarily reflects the combined benefits of contemporaneous reclamation and the backfill's inherent capabilities to control the chemical reactions which generate poor quality water. The water quality trends within and adjacent to those areas that had the direct benefits of the TMHP clearly demonstrate the prevention of significant deterioration of the ground water. The following discussions and graphic presentations summarize these observations.

Water quality data generated from five backfill ground water wells are presented here. The five wells (listed in order from south to north through the mined reserve) are OW-2, OW-5, OW-7, OW-10, and OW-8. *Figure 9* shows the respective positions of the ground water wells relative to the projected post-mine ground water flow paths in the backfill. Also, delineated on the generalized map are the TMHP and non-TMHP areas as well as locations of the installed SARS. Some discussion of the location of ground water wells relative to the SARS, TMHP area, and post-mine hydrologic flow paths is required.

- Wells OW-2, 5, 7, and 10 are similar in that they fall well beyond the boundary of the fully implemented TMHP area. These four wells reflect non-TMHP backfill conditions for approximately 90% of the total area mined at Glady Fork.As shown on *Figure 9*, ground water wells OW-2 and 5 share additional likenesses in that both are located down gradient from SARSs. The SARS up-gradient of OW-2 was installed in March, 1991. The

SARS located above OW-5 was constructed in October 1991.

Figure 9
General Location Map of Ground Water Wells, TMHP Area and SARS



- OW-7 is located approximately 1,300 feet northeast of OW-5 and along the easternmost highwall perimeter of the mined area. The well is positioned over a structural low area on the former pit-floor and is within the projected post-mine hydrologic flow-path from the TMHP area in the backfill.

- OW-8, located approximately 1,300 feet south of the final pit, is located immediately down gradient of the TMHP area and is positioned hydrologically in the backfill to effectively monitor the overall influence of the fully implemented TMHP on the ground water regime. Although OW-7 lies down gradient of OW-8, both wells are hydrologically connected in that the location of each well falls within the overall post- mine hydrologic flow pattern.

- OW 10 is offered here as a stark contrast primarily to OW-7 and OW-8. This observation well was deliberately placed in a shallow backfill area, known for its preponderance of problematic shales, and its anticipated high position in the ground water regime of the backfill. It was concluded early on, that this well would at best monitor the results of contemporaneous reclamation and possibly the influence of previous backfill/interface liming activities only. The area around this well was not the beneficiary of the direct application of the TMHP, and it had little or no chance of enjoying TMHP benefits through ground water migration.

Five ground water quality parameters are discussed here for the purpose of demonstrating the overall effectiveness of the TMHP in meeting the desired post-mine reclamation goal of minimizing backfill ground water deterioration. The five parameters to be highlighted are alkalinity, pH, sulfate (SO_4), total manganese (Mn), and total iron (Fe). With the exception to the sulfate, all the parameters chosen for comparative evaluations align with the mine's current post-mine NPDES effluent standard requirements. For sake of brevity, the comparative discussions offered below address the overall performance of the different quality parameters from a time-trend perspective. The graphic presentations provided depict a statistically computed trend line reflecting overall performance of the respective parameters as measured since initiation of monitoring at the individual wells involved.

The trend lines of the various water quality parameters presented here have been developed using a statistical software program within Harvard Graphics 2.3. The trend lines of the parameters have been statistically derived by a least squared fit of the data. The sample population of each parameter ranged from a minimum 26 to 49 data points depending on the age of installation of the respective ground

at OW-7. The ground water accumulated in the vicinity of OW-7 has not only been the beneficiary of alkaline-loading from the up-gradient TMHP area, it has also been the recipient of alkaline-loading from both surface alkaline recharge as well as backfill/interface liming initiatives. These additional sources of alkaline-loading explain the observed high alkalinity levels recorded at OW-7.

Observation wells OW-5 and OW-2 are functionally similar in that both measure backfill ground water conditions at a considerable distance (3,000 feet and 4,500 feet respectively) from the TMHP area. However, both wells are positioned down-gradient of SARSs. They demonstrate alkaline-recharge in those areas of the backfill where basically no limestone additions have been made. Data derived from both wells show favorable increases on alkalinities with time. Average alkalinity levels observed for ground water at OW-5 and OW-2 are 159 mg/l and 140 mg/l respectively.

The elevated alkalinity trend observed for OW-5 reflects the dissolution of limestone within the SARS under the influence of both natural precipitation and operational pump-back recharge to the backfill. Surface water pump-back activities to the SARS above OW-5, began in late summer, 1994, and has continued to the present. Both surface and spoil ground water which accumulates in Basin 002A is routinely pumped back into the backfill to prevent basin discharge of possible non-compliant effluent. The pump-back mechanism allows for natural "air-stripping" of both iron and manganese prior to re-entry to the backfill ground water resource.

Contrary to OW-5, the overall trend line for OW-2 is flat to slightly negative. The character of this trend line reflects the long-term influence of continuous backfill dewatering activities associated with pumpage at Basin 002A and past sediment pond modifications. Changes in pond structure were implemented in the Fall of 1991 for the dual purposes of controlling pond discharge and to establish a framework for ultimately developing a permanent passive wetland system for the backfill discharge area. Basin 002A modifications resulted in significant lowering of water levels in the pond and related backfill ground water. Since modification, Basin 002A has been under a continuous pump-back mode. The continuous pumping at 002A has resulted in considerable ground water fluctuations in the adjacent backfill over time. The sustained mechanical manipulations of the ground water is primarily responsible for the trend character observed for alkalinity at OW-2.

Ground water in the vicinity of OW-10 displays a slight negative trend in alkalinity. This trend undoubtedly reflects the consumption of alkalinity in response to past and/or current natural acidification/neutralization activities in the backfill. Despite the apparent decline in natural alkalinity depicted by the graph, the inherent backfill carbonate resources appear to be effective in maintaining favorable alkalinity levels in the ground water.

Backfill Ground Water - pH

The benefits of the alkaline additions to the backfill can also be discerned from a trend line graph of pH values *(See Figure 11)* for the ground water collected from the selected wells.

The pH values at both OW-7 and OW-8 ground water wells have remained within the 6.0-7.0 range. The slight negative trend in pH observed for OW-8 reflects pit-dewatering/final closure activities. No pH conditions have been recorded which might indicate adverse

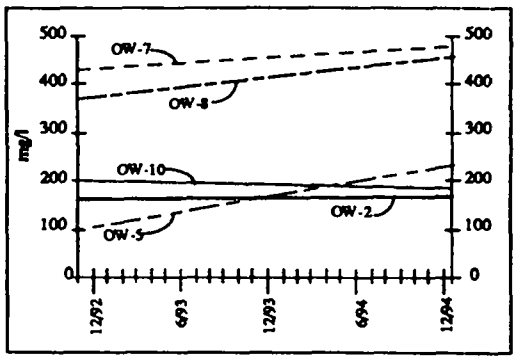
water monitoring wells involved. For example, the trend line derived for OW-8 was based upon the least number of data points (i.e., 26) per parameter due to the fact that the monitoring well in question is the younger of all the wells. Ground water well OW-2 is one of the older wells installed at Skyline Coal's Glady Fork Mine, therefore, a greater population density of data points (i.e., 49) exists for this well. The frequency of data collection of all the ground water monitoring wells discussed in this paper is monthly. Because of the population density of the data involved and the desire to present legible graphics absent data cluttering, a decision was made to present only trend line information of the various parameters at this time. It is recognized that the trend line presentations cannot be subjected to rigorous interpretation without further statistical analysis beyond which is currently offered here, however, the information provided does afford the reader with a preliminary overview of the favorable geochemical responses of adding alkaline materials to the backfill for the purpose of improving post-mine ground water quality conditions. Such transfer of information despite its preliminary nature is the ultimate objective of this paper.

Backfill Ground Water - Alkalinity

Figure 10 depicts the various alkalinity trends established for the selected wells in the backfill.

The elevated positions of the trend lines for the hydrologically connected wells OW-7 and OW-8 clearly illustrate the positive effects of the alkaline additions. Although not discernible from this simplified graph, up until March, 1994 (the date of initiation of pit dewatering for pit closure),the slope of the alkalinity trend for OW-8 was greater than that of

Figure 10
Glady Fork - Backfill Ground Water - Alkalinity



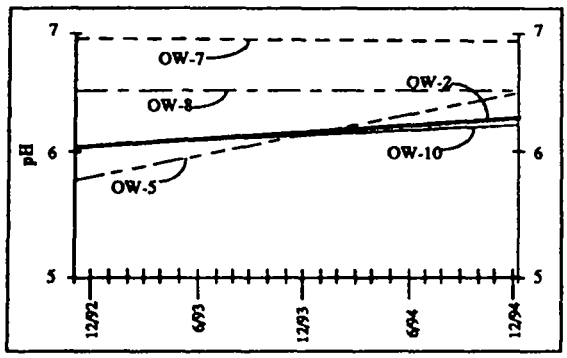
OW-7, and individual readings actually were higher that those of OW-7. Pit dewatering activities associated with final pit closure, however, lowered the next series of readings for OW-8 by an estimated 50 to 60 mg/l during the summer and fall of 1994. This temporary operational impact explains the currently observed position of the OW-8 alkalinity trend below that of OW-7. Despite these unavoidable operational manipulations, the average alkalinity value for ground water in the vicinity of OW-8 is an impressive 433 mg/l. The maximum recorded alkalinity for the 2 1/2 year time period of monitoring is 537 mg/l.

As previously mentioned, both OW-7 and OW-8 wells are positioned within the primary post-mine hydrologic flow-path in the backfill. OW-7 is located in an area which had not been subject to the TMHP. OW-8, on the other hand, is located within a TMHP area. OW-7 pre-dates OW-8 and is hydrologically down-gradient of OW-8. Despite the fact that OW-7 lies approximately 2,100 feet from OW-8, its high ground water alkalinity values reflect down-gradient migration of alkaline charged waters from the TMHP area.

North-to-south ground water movement has resulted in a significant "pooling" of alkaline-loaded waters in the structural low area in the backfill

acidification activities in this part of the Glady Fork backfill.

Figure 11
Glady Fork - Backfill Ground Water- pH



The steady pH performance observed at OW-7 reflects the cumulative benefits of both recharge contributions from the SARSs and subsurface ground water recharge from the TMHP area. OW-7's distance from any significant draw-down impacts associated with pit/dewatering activities provides a further explanation of the consistency of the pH values observed at this well location.

OW-5 is located in backfill that had not been the recipient of the TMHP. It is located down-gradient of an SARS. Considering the past backfill-dewatering activities and the subsequent manipulations of the ground water regime nearby (in the vicinity of OW-2) it is apparent that the surface alkaline recharge structure up-gradient from this well has played a beneficial role in maintaining steady state pH conditions in the backfill. Evidence indicates that the backfill ground water conditions have gone from acidic pHs (<6.0) to more favorable pHs (>6.0) in less than a 2 1/2 year period following reclamation.

A major segment of the monitoring well-screen for OW-10 is positioned in pit cleanings. The steady pH recorded for OW-10 (pH = 6.0± range) reflects the presence of natural alkaline resources in the backfill and the benefits derived from the inundation of coal-cleanings positioned at the base of the backfill.

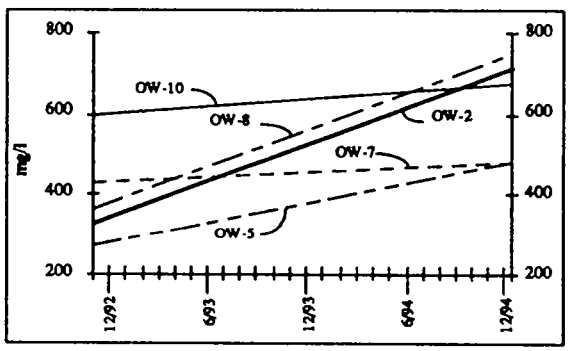
Backfill Ground Water - Sulfates (So_4)

The sulfate data is openly presented here for the purpose of allowing the readers to formulate their own opinions regarding possible geochemcial reactions occurring in the backfill, in particular, the case for suppression of pyrite oxidation. Commonly, observed increases in sulfate concentrations are automatically attributed to pyrite oxidation in the backfill and that sulfate concentrations are expected to decline with time if indeed pyrite oxidation is being prevented. However, the authors suggest that caution be used in the broad application of this "axiom" of AMD technology in the interpretation of the sulfate trends being presented here as well as any other backfill water quality investigations. There exist other possible sources of sulfate productivity in the backfill besides pyrite oxidation that can and most likely are contributing to the observed sulfate increases to date in the Glady Fork Mine study. In light of the marine/freshwater paleo-environment source (i.e., distributary channel/backwater embayment setting) of the former sediments comprising the overburden in the Glady Fork Mine area, other mineralogical sources of sulfates can be expected to be present. When considering the degree of overburden fragmentation involved with the mining process coupled with the past and present ground water mechanical manipulations (i.e., sediment pond dewatering, continuous spoil pump-back activities, final pit closure dewatering, etc.) of the backfill, natural increases in sulfate concentrations are expected to occur. The mere cyclic "wetting and drying" and subsequent "flushing" phenomena associated with the mechanical manipulations of the backfill ground

water resource yields sulfate loading from multiple mineralogical sources.

Figure 12 depicts the various trend-lines for sulfates measured at the respective well locations in the backfill. All of the sulfate trends illustrate increases in concentrations with time. The only differences in sulfate performance between wells are in degree, as indicated by positioning of respective trend-lines on the graph, and the rate of productivity (kinetics of reactivity), as measured by the respective slopes of the individual trend lines.

Figure 12
Glady Fork - Backfill Ground Water - Sulfate (SO_4)



The sulfate trend-line for OW-7 shows elevated sulfate conditions in the backfill. The flattened slope of the line, however, reflects rather stable conditions relative to actual acid/base reactivity in the backfill. Another possible explanation for the observed flattened slope is that equilibrium conditions have been reached between a mixture of waters having varying degrees of sulfate concentrations. The sulfate performance observed here reflects the cumulative effects of recharge to the backfill ground water originating from the previously identified up-gradient SARS and the migration of ground water from the TMHP area.

The sulfate trend observed at OW-8 exhibits a response to pit-dewatering/pit closure activities. Up to March, 1994, the sulfate levels recorded at OW-8 were historically lower than those observed at OW-7 and the overall slope aspect of both trend-lines were essentially the same. Shortly after the initiation of full scale pit pumping in early March of, 1994, sulfate concentrations at OW-8 increased steadily. This is attributed to the "flushing" of the backfill materials as ground water levels in the backfill near that hole were caused to fluctuate. One significant observation that can be made from the data is that sufficient alkaline materials are present in the backfill to mitigate the effects of the acidic reactions. Thus both acid-loading and metal-loading have been minimized or prevented.

The slopes observed for the sulfate trends measured at both OW-5 and OW-2 somewhat mirror the trending sulfate levels observed for OW-8. As with OW-8, the overall sulfate trends for both wells reflect significant influences from past and present mechanical manipulations of the ground water regime. Surface water pump-back activity to the SARS up-gradient of OW-5 has induced frequent "flushing" of the backfill. Both pump-back and backfill-dewatering has significantly influenced the overall sulfate-loading in the vicinity of OW-2. Undoubtedly in both situations, some backfill acid/base reactivity has accompanied such mechanical influences. The ground water quality data supports the conclusion, however, that the overall impacts of undesired reactions have been minimized by the alkalinity releases from the SARS and the natural alkaline resources of the backfill materials.

In comparison to measurements made at all other observation wells at Glady Fork, the sulfate concentrations at OW-10 have been consistently higher. The elevated sulfates coupled with the slight increase in sulfate productivity

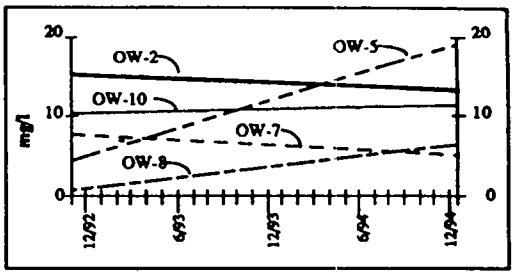
over time is associated with a backfill situation where greater than normal proportions of pyritic-bearing backfill and coal-cleanings are present and the benefits derived from fully implemented TMHP are lacking.

Backfill Ground Water - Metal Loading Fe And Mn

The benefits of alkaline additions is further evidenced by the significant reductions in metal-loading to the backfill ground water regime. Trend comparisons of metal concentrations of both Fe and Mn reveal the positive effects of the alkaline additions in preventing or significantly minimizing development of undesirable acid conditions and restraining metal dissolution in the backfill. Although the company collects both total and dissolved metal data routinely, only total values are shown here. Total iron and manganese data are presented here for the purpose of illustrating the "worst case" scenario of backfill ground water conditions. It is understood that suspended solids can conceivably create a negative bias in the metals data which is independent of the alkaline additions to the backfill, however, the idea is to present favorable conditions resulting from use of total metal information knowing that use of dissolved metal data would only show a much better case. *Figures 13 and 14* illustrate the overall trends of both metals for each of the wells under consideration here. The following discussions briefly highlight key observations made from the trend analyses provided.

Manganese (Mn). Compared to background Mn levels in the majority of the non-TMHP areas of the backfill, a significant reduction in Mn-loading is observable at OW-8. Using a calculated mean of 14 mg/l for Mn data generated at OW-10 for comparison purposes, a 3.5X to 4X fold reduction in manganese dissolution has been achieved at OW-8.

Figure 13
Glady Fork - Backfill Ground Water - Total Manganese (Mn)



This favorable reduction is noted despite the fact that the trend shown for OW-8 is negative. Over the 2.5 year time-period of monitoring at OW-8, the Mn levels have fluctuated from 1.8 to 8.1 mg/l and averaged 3.7 mg/l. As depicted in *Figure 13*, the Mn trend-line at OW-8 is climbing. This negative trend is skewed upward by recent pit-dewatering/final pit closure activities. Prior to the pit dewatering events at Glady Fork, the Mn performance fell in the range of 1.8 to 4.0 mg/l. These values are consistent with post-mine NPDES effluent discharge standards and are anticipated once again following final pit closure.

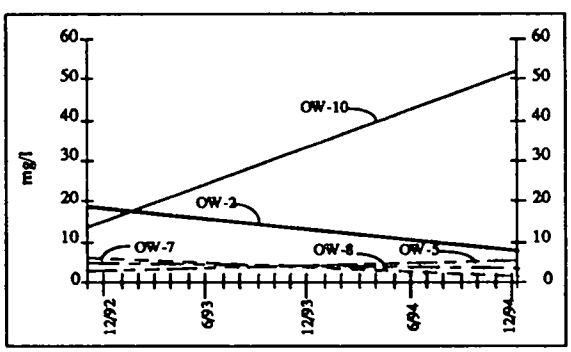
The progressive decline in Mn concentrations observed at OW-7 reflect the positive effects of highly alkaline, low Mn-bearing ground water generated in the TMHP area migrating southward toward OW-7. At OW-7, a 2.5X to 3X fold reduction in Mn levels can be observed when compared to ground water quality at OW-10. From initial monitoring at OW-7, the Mn levels have varied from 1.80 mg/l to 9.30 mg/l. The last year values cluster around 5 mg/l and are trending downward.

The continued mechanical manipulation and associated "flushing" of the backfill as a result of pump-back activities and pit dewatering have influenced the overall Mn trend-lines for both OW-5 and OW-2. Their concentrations of Mn are high. A favorable trend in Mn reductions at OW-

2 was noted following the halt of pump-back and backfill dewatering activities. This suggests that this parameter will be reduce with time once passive wetland systems are finally established and backfill pumping activities are permanently terminated.

Iron (Fe). The alkaline additions element of the TMHP has played a significant role in reducing the concentrations of iron and subsequent acid productivity in the backfill. Although it cannot be definitely proved by the information gathered to date, the positive trends in reduction of both acidity and iron levels lends support to the proposition that the alkaline additions have played a role in suppressing pyrite oxidation in the backfill. The effects of the alkaline additions on such backfill reactivity are best illustrated by observing the major reductions in Fe loading shown in *Figure 14*.

Figure 14
Glady Fork - Backfill Ground Water - Total Iron (Fe)



Using OW-10 data for comparisons, a 10X fold reduction in iron levels observed at both OW-7 and OW-8 can be tied directly to the influence of the limestone additions of the TMHP. The average Fe values observed for both OW-8 and OW-7 are 3.4 mg/l and 2.8 mg/l respectively.

As mentioned in the preceding discussions of Mn-loading, the on-going pit-dewatering/pit closure activities have caused "flushing" of the backfill and as a result have impacted the ground water quality in the vicinity of OW-8. However, despite an observed "spike" in Fe levels following the draw-down events, the overall trend is toward significant reduction of ferruginous water in the backfill.

Once final reclamation at Glady Fork is complete and the backfill ground waters receive the full benefits of the "workings" of the TMHP, Fe concentrations are expected to drop and remain below 3.0 mg/l iron on a permanent basis. Backfill water quality data collected during the interim of final pit inundation (March 1993 - March 1995) provides a technical basis in support in of such a favorable post-mine ground water quality projections. Prior to final pit dewatering, the iron levels at OW-8 averaged 2.4 mg/l. With final pit closure the post-mine ground water quality should stabilize in the 2.4 to <3.0 mg/l range.

The on-going pump-back/surface alkaline recharge activities associated with OW-5 provides a plausible explanation for the slight negative trend in iron-loading associated with this well. A reversal in trend can be expected once these operations are halted. Iron concentration trends depicted for OW-2 provides a technical basis for that expectation. As indicated in *Figure 14*, OW-2 Fe concentrations show a steady reduction over time. This favorable trend was accelerated following completion of pump-back and backfill -dewatering activities in the vicinity of that well.

When all mechanical manipulations of the backfill ground water regime are terminated, it is expected that continued declines in iron-loading will be achieved. Such favorable trends in the backfill ground water will ensure long-term effectiveness of passive wetlands designed for handling post-

mine water quality discharges from the southern end (Pre-TMHP area) of the Glady Fork Mine.

Conclusions And Recommendations

In review of the overall design objectives of the TMHP, in particular the element of limestone additions, the ground water data generated from monitoring the ground water in the Glady Fork backfill indicate significant benefits have been derived. In fact, the monitoring data reflect that all of the basic design criteria and related objectives built into the TMHP are being met. The following summary highlights salient observations, interpretative inferences, and conclusions drawn from the monitoring data collected to-date.

- The alkaline additions have made significant inroads toward achieving major reductions in the concentrations of acidity, iron, and manganese. Iron concentrations in amended backfill are up to 10 times less than those in unamended backfill. While manganese levels are 2.5 - 3.0 times lower.

- The consistently high alkalinity levels recorded and the observed steady rise of ground water alkalinity with time provides substantial evidence that limestone placement along pre-determined hydrologic flow-paths in the backfill has generated the desired alkaline-loading. In areas where limestone has been added, observation wells had alkalinity concentrations that were 2 to 3 times greater than those of a well (OW-10) located in the backfill where no alkaline amendments have been made.

- Favorable alkaline-loading accompanied by reductions in metal concentrations are observed to be associated with the SARS. The ground water data from points down-gradient of the SARSs show steady increases in alkalinity and corresponding decreases in metal levels (both Fe and Mn).

- Because of the observed significant reductions in levels of acidity, iron, and manganese, it can be inferred (not proven) that limestone additions to the backfill have been effective in subduing bacterial pyritic oxidation activities during and following mining. The observed persistent high alkalinities, lowered metal contacts, and the complementing favorable pH conditions in the backfill have undoubtedly minimized or prevented pyritic oxidation reactions. Further, the same favorable water quality parameters have undoubtedly assisted in maintaining a more favorable stability field for siderite in the backfill.

Suggested Future Investigative Efforts

All of the favorable trends referenced above point to achievement of the desired long-term goal of preventing damage to the environment.

The results of the ground water data generated to-date raise technical questions, which if answered through additional on-site investigations, would expand the knowledge base for achieving workable solutions to effective AMD abatement and control. The following are suggested investigative efforts.

- The high alkalinities (400-500 mg/l range) observed as a result of the limestone additions to the backfill, suggest that the basic geochemical mechanisms of the passive anoxic limestone drains (PALDs) are at work at the Glady Fork Mine. These high levels of alkalinity can only be achieved through the accelerated dissolution of the added limestone. This in turn suggests the involvement of CO_2 in the backfill. Further investigative efforts are needed to document the role of CO_2 in the

backfill and its ability to enhance the solubility of limestone.

- Further studies are needed to document the effectiveness of the limestone additions along defined hydrologic flow-paths in the backfill. Such investigative efforts should focus on development of technical guidelines which will facilitate the application of this attractive alkaline-loading method.

- Investigation and formal documentation of the workings of the SARSs are in order. Technical guidance documents should be developed subsequent to this investigation so that the application of such facilities to other mines can be better evaluated.

Conclusions

In conclusion, this paper provides documentation of the benefits of planned placement of alkaline additions to the backfill. The limestone materials added to the Glady Fork Mine in combination with the synergistic workings of all elements of the TMHP have been effective in minimizing and/or preventing acid drainage development in the backfill. Further, the fully implemented TMHP has been effective in substantially curtailing the dissolved metal concentrations in the backfill ground water regime.

Post-mine NPDES effluent standards will be achieved for the areas under the immediate influence of the TMHP. This is supported by the current ground water quality trends in the backfill. Therefore, in the unlikely event that seepage discharges were to occur from the TMHP section of the backfill, off-site damage in the form of AMD will not occur.

With respect to the southern portions of the mine where the TMHP was not applied, the benefits of alkaline-loading and metal-loading reductions derived from the TMHP area, the alkalinity contributed by the SARS, and the inherent alkaline resources within the backfill material itself positions these portions of the mine for meeting post-mine NPDES discharge objectives.

Acknowledgments

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THE USE OF SEDIMENT SAMPLING TO EVALUATE THE SUCCESS OF HYDROLOGIC RECLAMATION [1]

by

ROBERT G. LIDDLE [2]

Abstract Surface water monitoring efforts usually involve random, infrequent, grab sampling of the water column. This method may not detect irregular or infrequent pulses of pollutants and may be ineffective in assessing the physical and chemical quality of the benthic zone. The benthic zone can accumulate metals and often supports the aquatic insects essential to a healthy aquatic ecosystem. Sediment analysis was conducted on two mine-project sites in Kentucky and Tennessee to supplement existing chemical and biological sampling of streams and lakes. Sediments were analyzed for 15 metals and trace elements (Al, Sb, Ar, Be, Cd, Cr, Cu, Fe, Pb, Mn, Ni, Se, Ag, Tl, and Zn) and fine-particle size analysis was done using air elutriation methods. Each sediment sample was analyzed using total metal extraction, EPA's Toxicity Characteristic Leachate Procedure (TCLP), and a four-step sequential extraction procedure. The four-step sequential extraction procedure provided the most meaningful indication of metals and trace elements that could be of concern. The results showed distinct sediment chemistry and particle-size distribution between mined and unmined streams. Sediment chemistry mirrored pore-water chemistry and aided interpretation of the stream water and biological data in mined and unmined streams that was not otherwise apparent by sampling the water column alone. Sequential sediment analysis and fine-particle size analysis shows promise in assessing the success of hydrologic reclamation at mined sites.

KEY WORDS: Trace Elements, Water Quality, Coal, Mining

Introduction

Hydrologic Reclamation includes, but is not limited to, the restoration of baseline water quality and sediment quality to support the aquatic ecosystem and other potential water users. Assessing hydrologic impacts and hydrologic reclamation typically includes sampling of the water-column and comparing it with ambient criteria or water-quality standards. This method alone may ignore the condition of the benthic zone that can be critical to the aquatic ecosystem. In addition, the spacial and temporal nature of water column sampling may not represent the acute or chronic water chemistry of the stream affecting aquatic life.

This report summarizes the results of stream and lake sediment sampling programs at watersheds having active and proposed coal mines. The results were used to compliment the other physical, chemical, and biologic surveys done at the sites. It was intended that the sediment sampling would reduce the time and cost of obtaining ambient water conditions over water column sampling alone and be more representative of in-field conditions. The physiochemical environment at the sediment level is generally ignored in typical coal mine stream sampling. Yet the benthic zone is host to much of the food source used by higher aquatic life such as fishes. The bottom dwelling aquatic insects rely on the sediment pore-water quality as much as the water column itself.

The effects of mining on sedimentation loads has been well documented (Walters, 1995; EPA, 1981). Stream pollutants and sediments from mining may occur in

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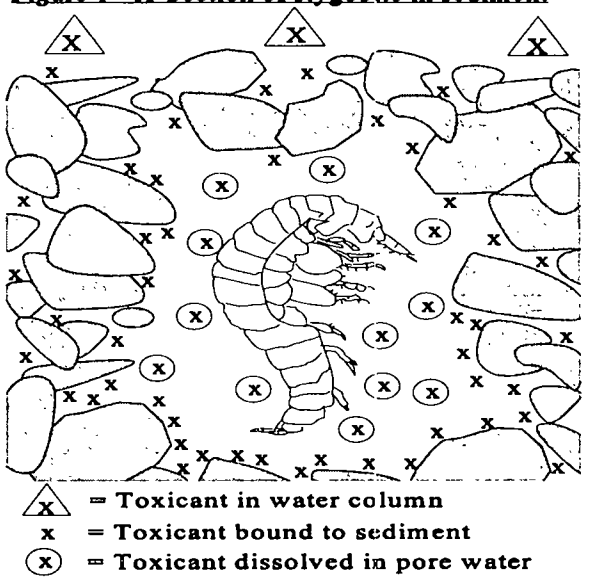
pulses due to the nature of sediment distribution and transport and also operational considerations such as the periodic opening and closing of treatment system discharge valves. Periodic random water column sampling may or may not represent the true pollutant load placed on a stream since it ignores bedload sediment (Horowitz, 1991). Frequent and composited stream water sampling is needed to characterize the stream-water-column environment fully; however, use of diffusive gradients in thin films (DGT) technology is helping fill the gap (Zhang, 1995, p. 3391). Sediment sampling aids in filling in the gaps between periodic water-column sampling and presents a more complete picture of the quality of the aquatic environment. A previous regional study in Tennessee has shown that water sampling alone only identifies 75 percent of the mine impacted drainages (O'Bara, 1993, p. 87). Another regional study in Virginia concluded benthic impacts from copper and zinc were occurring in coal mined drainages despite regulatory water column monitoring (McCann, 1993).

Several literature reviews on recent sediment research are provided by Fuller (1995, p.164) and Clement (1985, p. 236R). Sediment sampling can include both bioassay (Ingersoll, 1995A) and direct chemical analysis. Stream and overbank sediment sampling is useful in evaluating mining-related stream impacts (Ridgway, 1995; Wielinga, 1994; Prairie, 1994; Coupe, 1993).

Metal and trace element contaminants may be dissolved or settle as particulate matter. They may be adsorbed to sediments, precipitated, coprecipitated, bonded organically, undergo cation exchange, or be incorporated into the crystal lattices of sediments that coat the bottom of the stream channel. The type of sediment dictates the ability to bind with other metals. Horowitz (1991, p.41) found the relative capacity of collectors in freshwater systems were: Amorphous Iron Oxides > Total Extractable Iron > Total Organic Carbon > Reactive Iron > Clay Minerals > Total Extractable manganese > Manganese Oxides. Horowitz (1991, p. 69) also studied the relative importance of selected physical and chemical factors on sediment trace-element chemistry; he found: Amorphous Iron Oxides > Surface Area > Total Organic Matter (LOI) > total Extractable Iron > Other Organic Matter > Percent less than 63 μm > Reactive Iron > Total Organic Carbon > Percent less than 125 μm > mean grain size > percent clay minerals > percent less then 16 μm > percent less than 2 μm > Total Extractable Manganese > Manganese Oxides.

The sediment pore-water quality is a function of both the sediment and the overlying water quality (Burton, 1992). Figure 1 shows this relationship. Unless the benthic zone is restored after mining, the aquatic ecosystem will not be restored to baseline levels.

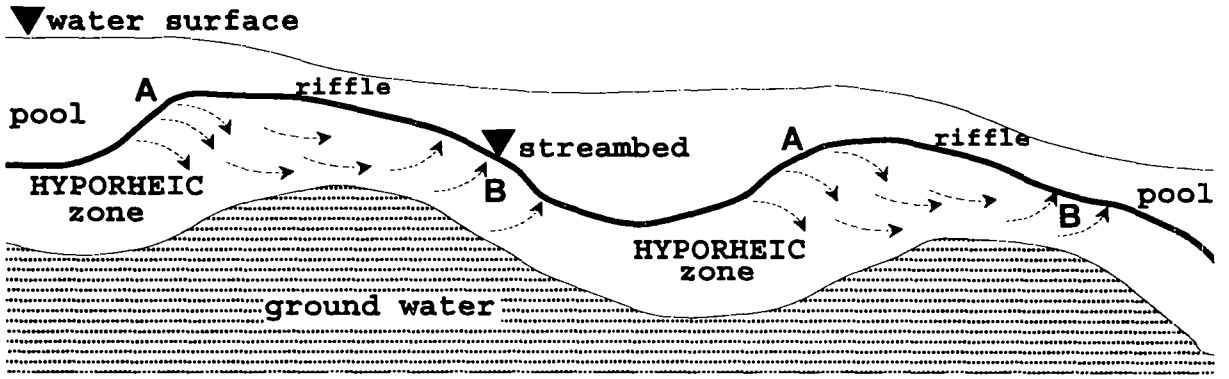
Figure 1 - X-Section of stygobite in sediment



After Burton, 1992

The sediment zone contains a reservoir of metals, trace elements, and nutrients that can be re-suspended in the water column by diagenic processes (Buffle, 1994, Horowitz, 1991, p. 49) such as floods or bioturbation, changes in physiochemical conditions (pH, eH, DO, temperature, *etc.*), and biochemical reactions (bacteria, humic substances, *etc.*) that increase toxicity or solubility (e.g., methylization of mercury). The sediment layer is often the location of the ground water and surface-water interaction zone, termed hyporheic zone (See Figure 2), which fluctuates seasonally and supports a diverse ground-water ecosystem (Hendricks, 1992; White, 1992, Gilbert, 1994, Dahm, 1992). Polluted ground waters recharging a stream in this zone can adversely affect the interstitial waters of the sediment without detectable change in the water quality of the water column. Therefore, the use of benthic and interstitial

Figure 2 - Conceptual Model of Hyporheic Zone



A = Zone of Down-welling **B** = Zone of Up-welling → = Direction of water
After Hendricks, 1992. (Vertical exaggeration)

invertebrates, such as stygobites, can also be used as indicators of ecosystem damage, along with sediment analysis (Plenet, 1992; Gilbert, 1994).

Heavy metals and trace elements such as Al, Cd, Cu, Se, Pb, Ni, and Zn are known to be associated with coal mine drainages (EPA, 1981; Liddle, 1994; Liddle, 1995). Often these minor elements are not monitored since it is incorrectly assumed they either do not exist in high concentrations or they are removed during the iron and manganese treatment process. For example, metal transport through the spoils to streams via fractures is unaffected by surface-water treatment ponds, yet this groundwater is seldom monitored at minesites unless it forms springs. Another example is aluminum, which is often reported in the literature as having a low (<1 mg/l) concentration at mine sites. However, it was not until August 1988 that EPA promulgated the aquatic freshwater criteria of 0.087 mg/l for aluminum (53 FR 33178). And recently the EPA is considering reducing the drinking water standard for arsenic from 0.040 mg/l to 0.006 mg/l, because of carcinogistic concerns (Eaton, 1994). Since many trace-element water-quality criteria have not been determined until recently, and EPA criteria are very low, one must guard against assuming only iron and manganese are of concern. The sediment-analysis methods presented here show techniques that can be used to determine the amount of metals available for bioaccumulation and the amount of metals easily taken back into solution in the pore water or water column. The absence of these metals in the sediments is a good indicator they are not significant in the water column.

Methods

At project site #1, sediment, biological, and water sampling was conducted in four watersheds with similar geology and topography and with little or no non-mining development: 1) 18.4 km^2 (7.1 mi^2)Little Yellow Creek in north Tennessee; 2) nearby 25.9 km^2 (10 mi^2) Little Clear Creek in southern Kentucky; and 3) Bennett Fork, and Langley Branch). Little Yellow Creek watershed is proposed for surface coal mining and the others have been mined since the late 1970's. As such, they are excellent locations to evaluate true baseline conditions with post-SMCRA mining impacts. Little Yellow Creek and Little Clear Creek historically contained a large population of the endangered Blackside Dace. However, the mined watershed has been without the Blackside Dace since 1985, according to stream surveys. Mining is suspected of causing this extirpation. Complete information on the hydrology of the sites is available from OSM (Liddle, 1995A). A second project site is Bruce Creek above Cove Lake State Park. The stream was sterilized by metal contamination in 1993 emanating from an anoxic drain in coal spoils (Sugar Ridge Mine, 200 acres) north of Knoxville, TN. While water quality has since improved due to treatment, the question of restoration of the benthic zone remains unanswered.

About 15 to 20 sediment samples less

than 4 cm deep were taken at each site and composited. Five sites were sampled on each stream at the base of a riffle zone during low streamflow (Burton, 1992, p. 89; USGS, 1995, p. 20; USGS, 1970, p. 53). These five composites were then combined to produce one sample felt to represent the stream. It was important to take many samples, because stream sediments from coal mines are spatially and seasonally variable (Gunten, 1994) and lab analysis was to be done on only a few grams of each sample. Sediments were stored at or near freezing until analyzed, which took several months. This may have produced errors; recent research has shown samples should be frozen and analyzed immediately to prevent biochemical changes (Becker, 1995). The less toxic the sediments the more susceptible they are to changes.

The sampling procedures followed recommendations of Burton (1992, p. 32), Ingersoll (1995) and the specifications of ASTM standards D3974-81 and D3976-92 (ASTM, 1993, Vol. 11.02). ASTM Standards D4822-88, D4823-88, D5074-90, and D3976-92 were also followed depending on the stream being studied (polluted vs. unpolluted). Sampling and laboratory practices generally followed the USGS procedures (USGS, 1982; USGS, 1993).

Particle size analysis was done using sieves and air elutriation methods to obtain very fine particle analysis to 0.0015 mm. Samples were analyzed in three ways: 1) total metals were extracted using hydrochloric and nitric acid digestion; 2) the EPA Toxicity Characteristic Leaching Procedure (TCLP); and 3) a 4-step sequential extraction method. The sequential extraction method is based on Tessier's (1979) work, and has been modified to fit geochemical extractions of inorganic metals and trace elements common in mining investigations (Tessier, 1979; Chao, 1983; Chao, 1984; Horowitz, 1988; Horowitz, 1990; and Horowitz, 1991a). The sequential extractions were done on samples screened to less than 0.63 micron to allow clearer comparisons based on particle size (See Horowitz, 1991a). No grinding or crushing of particles was done.

Results of Grain Size Analysis

The sediment grain-size distributions showed that the mined watershed of Little Clear Creek had more fine clays and silts than the unmined watershed of Little Clear Creek (See Figure 3). Field investigations included suspended sediment sampling during storm events to develop a sediment graph for both streams. The results revealed that during storm events the coal-mine haul roads were a significant source of sediment loads to the stream since most of the haul-road drainage entered the Little Clear Creek untreated.

The grain-size distributions for Bruce Creek revealed that stream sediments had less clays at greater distances away from the mine site. Since clays have the highest surface area per particle, and sediment surface area is directly proportional to the capacity to capture and retain metal and trace elements (Horowitz, 1991, p. 16) the grain-size distribution can shed light on the potential for metal retention.

Results of Sediment Chemistry Analysis

The total digestion of the samples with nitric and sulfuric acid did not show any meaningful trends between mined and unmined streams or downstream from the anoxic drain at Bruce Creek. This is because the amount of metals contamination was very low. In high contamination sites such as hazardous waste sites, concentrations of metals are large enough to show differences between natural and contaminated sites. The EPA TCLP extractions confirmed that none of the sediments came close to meeting EPA toxic criteria. The metals contamination at coal mines would be expected to be more subtle. The total digestion of sediments does not distinguish between metals held in the crystal lattice of the rocks, metals bound organically, metals precipitated, or metals adsorbed. Consequently the total metals results show more about the mineral content of the sediments than about the bioavailability of metals.

The total metal extraction (TME) analysis is somewhat useful as a quality check on sequential extraction methods. If a total extraction with hydrofluoric and nitric acid is conducted on ground sediments, then all metals including those in the crystal lattice should be released. (Note Hcl, HNO_3, H_2SO_4 alone will not extract all metals without HFl) One could then analyze the remaining sample after the sequential extractions to determine what metals were not released. The quality check then becomes:

$$TME = E_1 + E_2 + E_3 + E_4 + E_n \ . \ . \ . + TME_e$$

Where E_1 to E is the mass of metal released from the first to last sequential extract, respectively, and TME_e is the mass of metal remaining on the extracted sediment after all sequential extracts are completed. In this study, our contract laboratory would not do the HFl extractions due to safety concerns, therefore we were unable to obtain this quality check step. Instead, splits were run on the samples to ensure reproducible results.

The sequential extractions were designed to mimic the physiochemical processes that would strip sediments of metals and trace elements from successively higher energy orders. Use of sequential extractions, while not an exact science, has been used extensively by the metal mining community for geochemical prospecting (Chao, 1983, 1984). Extraction #1 is designed to extract exchangeable, adsorbed, and carbonate metals using 1 gram residue per 8 ml 1M Sodium Acetate adjusted to pH 5 with Acetic Acid, agitated for 1 hour. Extract #2 is designed to release metals easily bound to manganese oxides and reactive iron using 1 gram of residue per 50 ml of 0.1 M Hydroxylamine Hydrochloride in 0.1 M HNO_3, shaken for 30 minutes at 25°C. Extract #3 is designed to release tightly bound metals from amorphous iron oxides and manganese using one gram residue to 250 ml solution of 0.25 M Hydroxylamine Hydrochloride in 0.25 M HCl, heated and shaken at 50°C for 30 minutes. Extract #4 should release organically bound metals using 3 ml of 0.02 M HNO_3 and 5 ml of 30% H_2O_2, adjusted to pH 2 with HNO_3, heated and occasionally shaken at 85 °C for 2 hours. Then adding a 3 ml aliquot of 30% H_2O_2 adjusting to pH 2 with HNO_3 again and heated and agitated for 3 more hours. After cooling, add 5 ml of 3.2 M Ammonium Acetate in 20 % v/v HNO_3 , then dilute with distilled water to a 20 ml volume, shake at 25°C for 30 minutes, then analyze. Each extract was separately analyzed for Al, Sb, Ar, Be, Cd, Cr, Cu, Fe, Pb, Mn, Ni, Se, Ag, Tl, and Zn.

The results of total digestion of the samples for the first project site are listed below in mg per kilogram dry weight (Figure 1). The results show the difficulty in comparing multiple sources of sediments using total sediment analysis. For some parameters such as arsenic, the unmined watershed was highest. In unmined Fern Lake the lead concentration was highest probably due to the use of lead fishing sinkers. Mining affected streams were higher in zinc, nickel, copper, and chromium. However, this method may be useful for screening out elements that are too low to consider further such as Ar, Ag, Se, Tl, Sb, Be, and Cd.

Table 1 - Total Digestion of Sediment

	L. Yello Creek	Fern Lake	Benn-ett Fork	L. Clear Creek	Lang-ley Br.
mg/kg	UNMINED		MINED		
AL	2290	14 K	2210	3410	6580
Sb	0.5	0.5	0.5	0.5	0.7
Ar	9.4	5.6	4.2	0.7	2.2
Be	0.4	1.1	0.2	1.0	0.8
Cd	0.1	0.2	0.2	0.1	0.02
Cr	5.6	8.7	8.3	8.3	9.9
Cu	5.6	20.6	15.7	10.8	15.8
Fe	12 K	40 K	9900	12 K	26 K
Pb	4.5	204	6.9	8.6	144
Mn	260	347	254	426	1220
Ni	10.4	30.3	15.7	13	32.6
Se	0.3	0.2	0.2	0.2	0.2
Ag	0.1	0.1	0.1	0.1	.001
Tl	0.1	0.2	0.2	0.1	0.1
Zn	29	107	40	49	83

The results of the first sequential extractions in mg/kg dry weight are as follows:

Table 2 - SEQUENTIAL EXTRACT #1

	Yello Cr	Fern Lake	Benne -t Cr	L. Clear	Lang-ley
mg/kg	UNMINED		MINED		
Al	263	192	34	20	87
Cu	8000	7310	1540	1010	480
Fe	331	1210	35	16	61
Pb	832	1550	29	69	47
Mn	840	304	121	509	613
Ni	12	8	4	5	10
Zn	165	1100	304	200	99

These results show concentrations in the 63μm fraction of sediment and are useful in correlation studies. The USGS has used similar procedures to find relationships between chemical and physical parameters with sediment chemistry on a regional basis. If a good correlation is found, then concentrations of the elements can be predicted for similar regions. Examples of the USGS national sediment models are:

$$Cu = 0.52\ LOI + 0.351\ Al + 0.395\ Ti + 0.875$$

and

$$Ni = 0.963\ Al + 0.248\ TOC + 0.003$$

(See Horowitz, 1991, p. 79)

To evaluate the total effects of the metals in the environment, one must consider the total metal available, not just the 63 μm fraction. Since the previous data shows mined watersheds were higher in clays, the total contribution of metals must be recalculated, based on the percentage of clays to the total sediment. One could reanalyze the total sediments, but research has shown the contribution from sands and silts to be negligible in most cases (Horowitz, 1991). The results of this comparison follow:

Table 3 - SEDIMENT TOXICITY: Extracts 1 + 2

	L. Yello	Bennett	L. Clear	Langley
mg/kg	Un-Mined	MINED WATERSHEDS		
Al	90	57	188	266
Fe	275	192	830	551
Mn	84	46	279	405
Zn	37	99	105	71
Cu	872	1120	643	373
Pb	105	12	50	46
Clay	8.9%	28.5%	37.8%	52.2%

Assuming the sediments have similar bulk densities and assuming the first two sequential extractions represent the bioavailable fractions; the results show that the mined watersheds are higher in some metals. Lead is higher in the unmined watershed, owing to lead fishing tackle, while zinc and aluminum are generally higher in mined watersheds. Some element concentrations are not significantly different in the sediments (e.g., copper). Pore water samples taken by centrifuging sediments from Langley Branch below a strip mine revealed dissolved aluminum concentrations of 1.68 mg/l, well above the EPA chronic aquatic standard of 0.087 mg/l (53 FR 33178, 8/30/88), while the maximum concentration in the water column was only 0.02 mg/l. The dissolved iron concentration in pore water was 2.17 mg/l, which is above the 1.0 mg/l EPA threshold (EPA, 1985); the maximum iron content in the water column was 0.028 mg/l. The zinc pore water concentration was 0.053 mg/l, which is near the EPA aquatic life chronic criteria of 0.059 mg/l (52 FR 6214, 3/2/87). The water column concentration of dissolved zinc was 0.03 mg/l. The sediment analysis failed to correlate with the elevated lead concentrations of 0.006 mg/l in the pore water, which is above the EPA chronic aquatic criteria of 0.0013 mg/l (50 FR 30791, 7/29/85); the dissolved lead concentration in the water column was 0.002 mg/l.

At the second project site at Bruce Creek, sediment samples were taken at treatment ponds below an anoxic drain and in several places in the receiving stream. The purpose was to assess how far downstream the metal contamination had spread. Water from the anoxic drain flows from 0.25 to 2 cfs and contains several toxic concentrations of metals, as compared with aquatic receiving-stream standards. The following table compares concentrations from the anoxic drain with receiving-stream standards:

Table 4 - Anoxic Drain Quality

	Total Metals	Dissolved Metals	Aquatic Criteria[1]
Cu	20 μg/l	1 μg/l	6.5 μg/l
Al	1810 μg/l	940 μg/l	87 μg/l
Cd	26 μg/l	0.5 μg/l	4.6 μg/l
Fe	85 mg/l	40 mg/l	1.0 mg/l
Mn	35.4 mg/l	35 mg/l	none
Ni	470 μg/l	430 μg/l	88 μg/l
Zn	388 μg/l	190 μg/l	59 μg/l
Hg	2.3 μg/l	-	.012 μg/l

[1] EPA Freshwater Aquatic Chronic Criteria.

Although the water is now being treated under a bond forfeiture situation, the stream was already contaminated to the point where no aquatic life was found (Turner, 1995). Recent stream-water-quality sampling of the water column about 0.2 km (1/8 mile) downstream

revealed aluminum, copper, iron, nickel, and zinc are still at the EPA aquatic life chronic criteria. Water samples taken about 3.2 km (2 miles) downstream showed aluminum, nickel and zinc were still at EPA freshwater aquatic life chronic criteria. The results of the sediment analysis showed decreasing metal concentrations as one sampled downstream:

Table 5 - Sediment Toxicity: Extracts 1 + 2

mg/kg	Upper pond sedimnt	Lower pond sed.	1.75 mi down stream	2 mi. Down stream
Al	575	399	242	22
Cu	584	664	466	43
Fe	4975	2223	433	74
Mn	5726	1113	725	234
Ni	104	7.5	4.5	1.5
Zn	153	221	113	10
Clay	80 %	35 %	22 %	3 %

If one looked at total metals analysis, and even TCLP data, the results would not show this trend. For example, aluminum total digestion results for the upper pond to the lower segment were 4080 mg/kg, 8460 mg/kg, 5640 mg/kg, and 3070 mg/kg respectively. Total zinc concentrations were 180, 39, 37, and 49 mg/kg respectively. Similar results were noted with Cu, Mn, and Ni. Since biological data shows aquatic life survival increases the further downstream from the anoxic drain one samples, and the water column sampling shows a similar trend in improvement, one could logically hypothesize that the availability of metals in the sediments would also increase. Pore-water sampling and biological assays would be needed to support this hypothesis.

Additional information was obtained from the sediment data. Sequential extract #11 implied that the unmined watersheds had higher available metals (i.e., easily adsorbed metals and carbonates) than the mined watersheds studied. This could be the result of the mined watersheds adding iron to the stream that resulted in higher-energy binding of metals and trace elements to the sediment. The second extractions showed much more metals in the mined watersheds. The EPA TCLP extractions did not mimic any of the sequential extractions, as might have been expected. A comparison of sequential extractions from both project sites indicates metals would likely be a problem at levels greater than 100 mg/kg total.

Evaluation of the sediment quality data currently is done using comparisons of affected and unaffected reaches. The EPA has only recently established sediment-quality criteria for several organic constituents; metal criteria are still lacking, and bioassay has been historically used in evaluating dredged sediments (EPA, 1987, Zarba, 1988, Mancini, 1992, and Iannuzzi, 1995). Some States have developed threshold criteria based on comparative sampling (Kelley, 1984) and Canada has issued Provincial Guidelines for Sediment Quality (Prairie, 1994).

CONCLUSIONS

The EPA TCLP extractions were not very useful for estimating pore-water chemistry or as indicators of affected drainages. This test was designed based on municipal waste leachate testing (Kimmell, 1988). Most coal mine drainage will not result in metal contamination that would be high enough to be classified as "toxic" according to this EPA test.

The total metals analysis was not useful in predicting either the availability of metals and trace elements or comparisons of affected verses unaffected drainages. The total metals analysis may serve as a check on the results of sequential extractions.

Sediment sequential extractions shows promise in identifying the availability of metals and some trace elements. Sequential extractions #1 and #2 were particularly useful; other extracts would be useful in other investigations such as geochemical prospecting or organic contaminants. Sequential extractions are better suited for investigating metals of elevated concentrations (>100 mg/kg) and are less valuable in looking at trace amounts of elements. The OSM is now using a five-step sequential extraction procedure to better define the speciation of metals in sediments.

Partical-size analysis of sediments is important for assessing the quality of the sediments and to evaluate the results of sediment metal extractions.

A lab experienced in sediment analysis should be used so that samples can be quickly analyzed upon collection, otherwise errors can occur. Short delays in getting a sample analyzed, even if the sample is frozen, has been shown to affect the toxicity of the sediment (Becker, 1995).

Additional research is needed in sampling and preparation of both pore-water and sediment from typical high gradient first and second-order streams. More research is needed in establishing standard sequential extraction methods that replicate bioavailable fractions typical of coal mining geochemistry (Horowitz, 1991). More comparative studies are needed of sediment quality, pore-water quality, water quality, sediment bioassay, and aquatic bioaccumulation at mine sites. Additional work is needed in establishing sediment-quality standards.

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