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

by

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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

1 Paper presented at the 1996 Annual Meeting of the American Society for Surface Mining and Reclamation (ASSMR), Knoxville, Tennessee, May 19-24, 1996. Publication in this proceedings does not prevent authors from publishing their manuscripts, whole or in part, in other publication outlets.

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Proceedings America Society of Mining and Reclamation, 1996 pp 308-320
DOI: 10.21000/JASMR96010308

https://doi.org/10.21000/JASMR96010308

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.

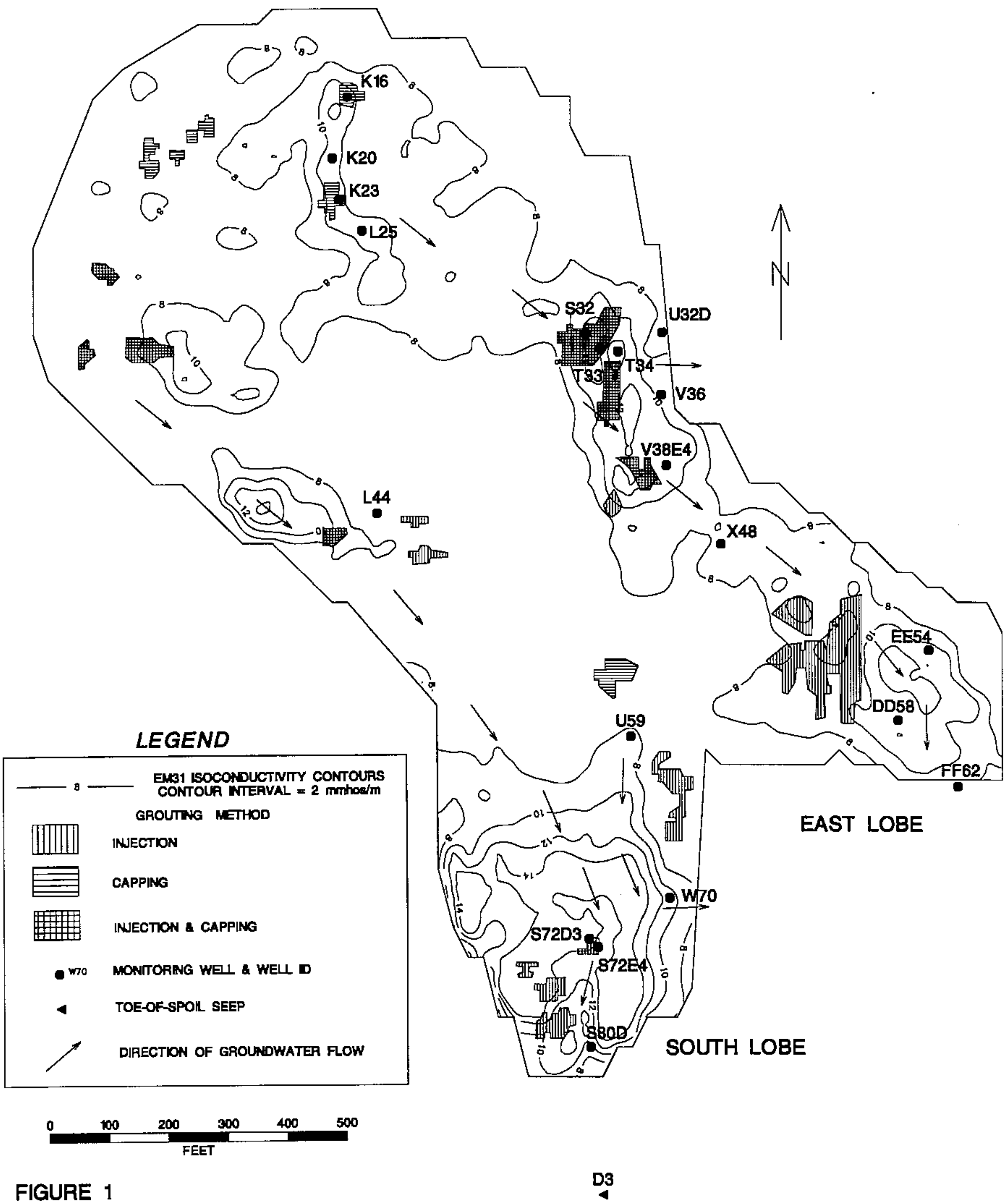
A toe-of-spoil discharge is present beyond the south lobe. The discharge varies from 2 to 20 gpm and appears as a diffuse seep. It is at an elevation equal to the lower, unmined split of coal. This discharge flows into Camp Run, a tributary of Cooks Run.

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
U59
FF62
W70
S72D3
S72E4
S80D
D3
EAST LOBE
SOUTH LOBE
N
LEGEND
EM31 ISOCONDUCTIVITY CONTOURS
CONTOUR INTERVAL = 2 mmhos/m
GROUTING METHOD
INJECTION
CAPPING
INJECTION & CAPPING
MONITORING WELL & WELL ID
TOE-OF-SPOIL SEEP
DIRECTION OF GROUNDWATER FLOW
0 100 200 300 400 500
FEET

FIGURE 1

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 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	Zn mg/L	Temp 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 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	Zn mg/L	Temp 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 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	Zn mg/L	Temp 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 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	Zn mg/L	Temp 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 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	Zn mg/L	Temp 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: $Al2O3$ - 12.51%, CaO - 38.03%, $SiO2$ - 23.91%, $SO2$ - 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

Well	Loc*	TDS	SO_4	Acid	Fe Tot	Fe^{+3}	Al	Mn	Cd	Cu	Cr	Ca	Temp
Application: Injection Grouting Only													
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													
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													
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													
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, $MgAl_2(SO_4)_4 \cdot 22H_2O$, and Halotrichite, $Fe^{+2}Al_2(SO_4)_4 \cdot 22H_2O$ (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	TDS	SO_4	Acid	Fe Tot	Fe^{+3}	Al	Mn	Cd	Cu	Cr	Ca	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
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	TDS	SO_4	Acid	Fe Tot	Fe^{+3}	Al	Mn	Cd	Cu	Cr	Ca	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
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	TDS	SO_4	Acid	Fe Tot	Fe^{+3}	Al	Mn	Cd	Cu	Cr	Ca	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
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	TDS	SO_4	Acid	Fe Tot	Fe^{+3}	Al	Mn	Cd	Cu	Cr	Ca	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
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	TDS	SO_4	Acid	Fe Tot	Fe^{+3}	Al	Mn	Cd	Cu	Cr	Ca	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
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.

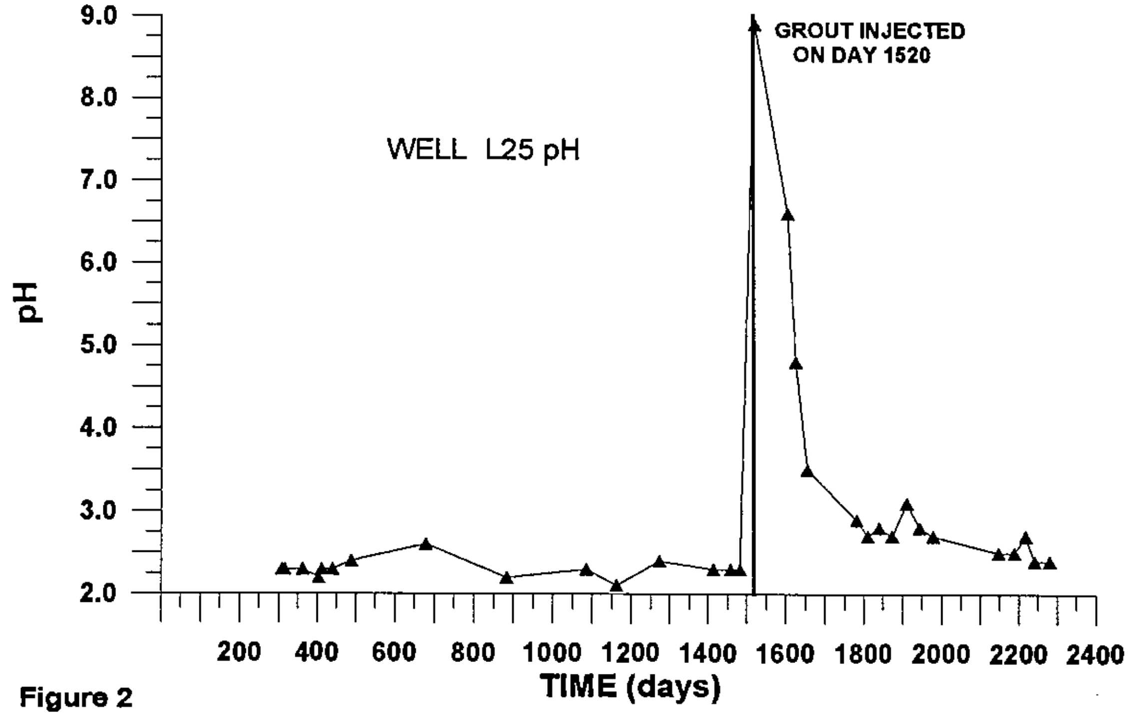


Figure 2

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.

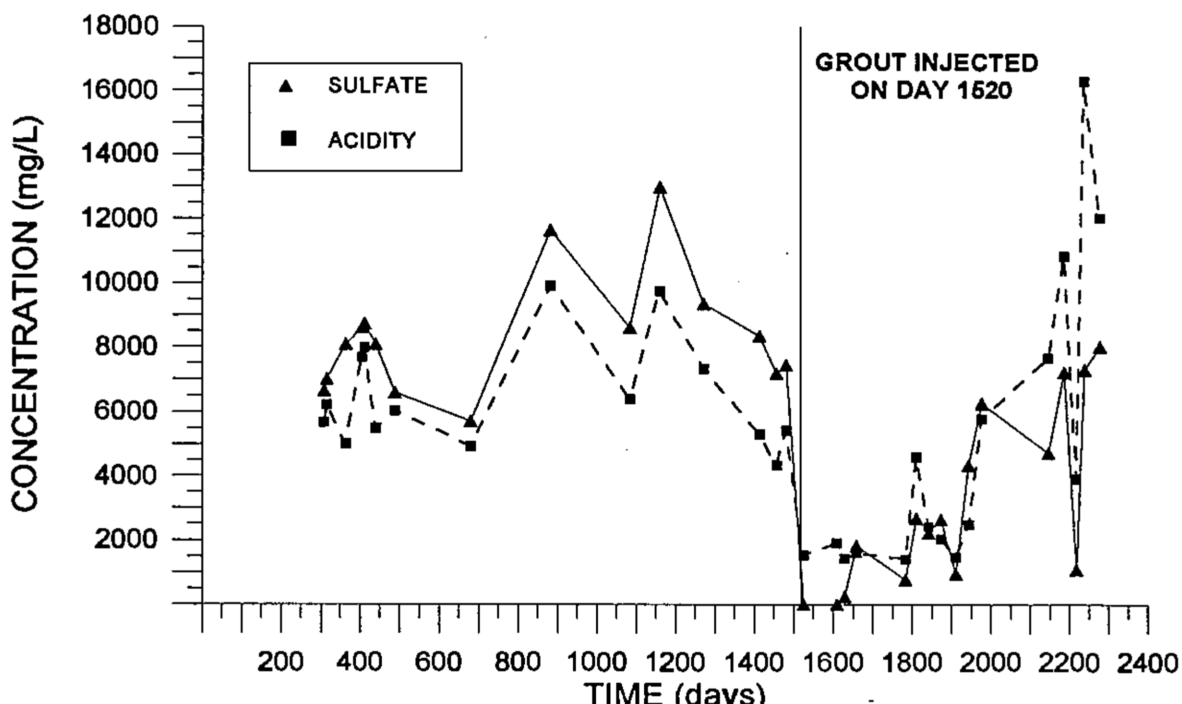


Figure 3

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.

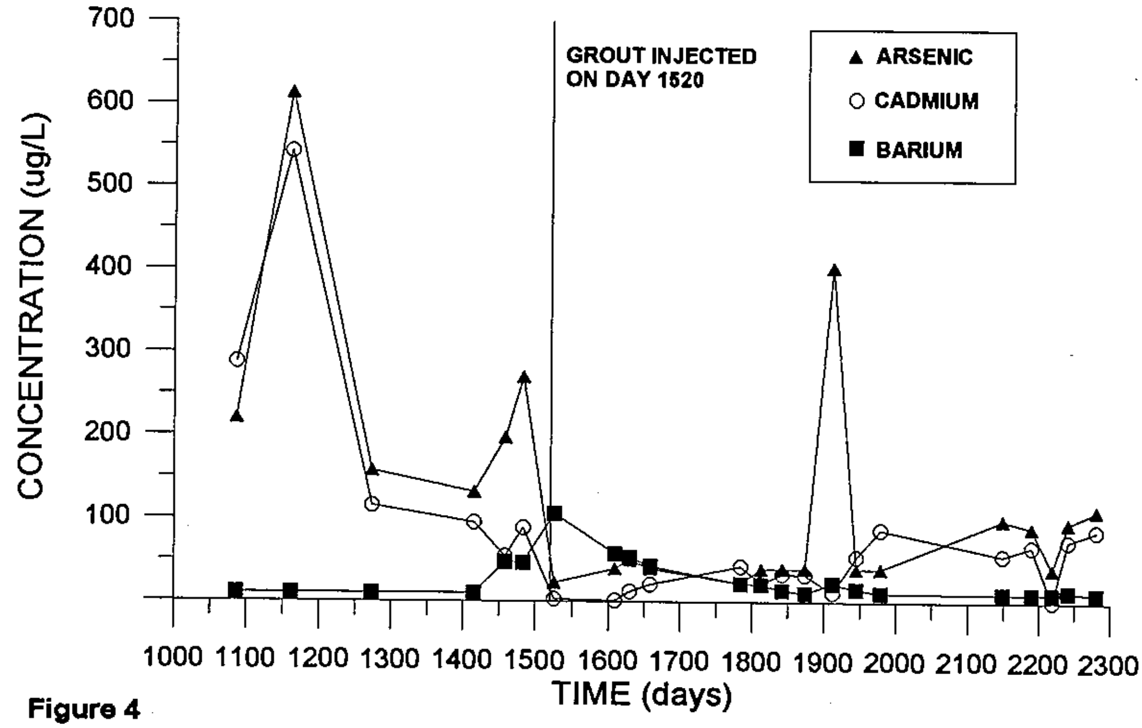


Figure 4

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.

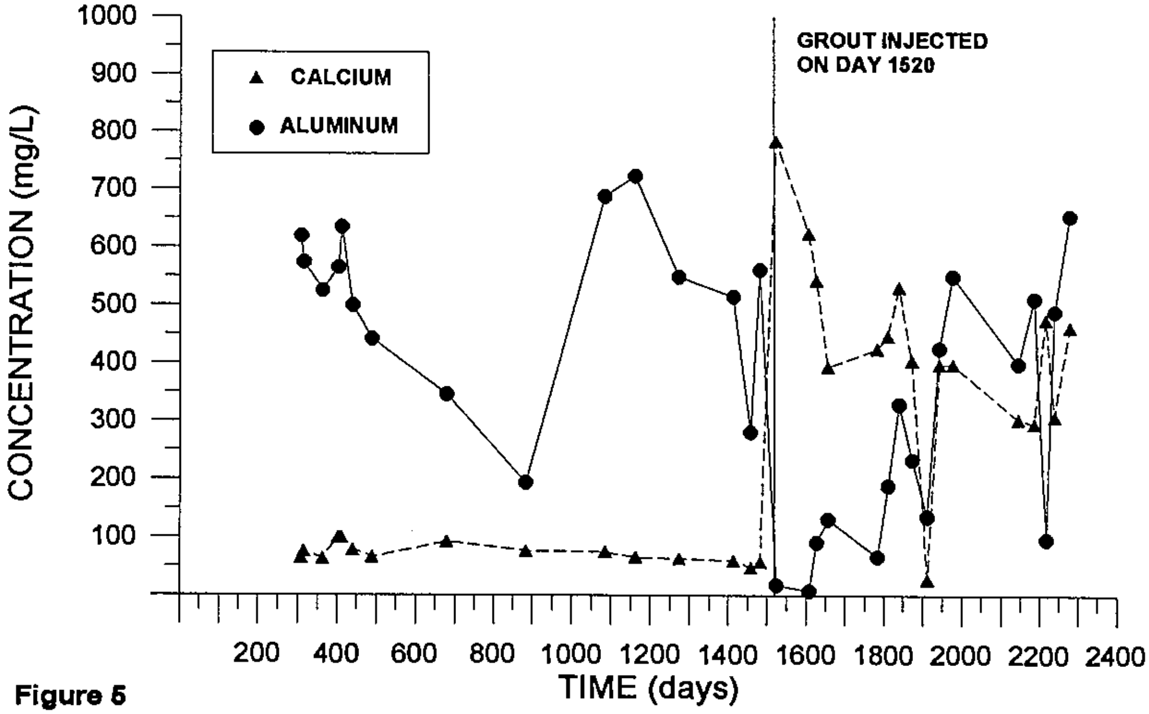


Figure 5

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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