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# Use of flue gas desulfurization by-product for mine sealing and abatement of acid mine drainage

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## Abstract

Broken Aro mine is an abandoned underground mine complex last mined in 1910. Acid mine drainage (AMD) from the mine has negatively impacted the water quality in Simmons Run. Re-mining of Broken Aro allowed for recovery of an energy reserve, exposure of the AMD source, de-watering of the mine complex, and simple placement of a continuous mine seal. The fixated FGD scrubber by-product was chosen as the material for mine seal construction due to its low hydraulic conductivity and high alkalinity. The final seal was approximately 2600 ft long, 15 ft wide and was installed in two 4–6 ft compacted lifts for a total height of 8–12 ft. The seal was constructed concurrent with mining activities to maintain a continuous hydraulic barrier. The seal has retained water inside the mine complex and has decreased the contaminant loads to Simmons Run. © 2001 Elsevier Science Ltd. All rights reserved.

**Keywords:** Re-mining; Flue gas desulfurization; Acid mine drainage

## 1. Introduction

The Broken Aro Mine site is located about seven miles west of Coshocton, Ohio on State Route 541 at the Woodbury Wildlife Preserve. An abandoned underground mine complex last mined in 1910, this site forms the headwaters of the Simmons Run Watershed. A No. 6 and a deeper No. 5 coal seam on the 40-acre site have been mined by means of underground mining in the 1910s. The mining operations produced acid mine drainage (AMD) which polluted receiving streams with acidity and heavy metals, killing aquatic and plant life. To prevent this pollution from continuing, a design for keeping the water inside the mine was developed with the cooperation of the Ohio Department of Natural Resources, R&F Coal Company, American Electric Power, and Ohio University. This paper will give a background of the Broken Aro Project, describe the FGD seal design, and demonstrate its effectiveness.

Re-mining was selected as the best option to economically extract remaining coal deposits and provide an opportunity to employ abatement technology. The groundwater was sealed inside the underground mine to inundate the

mine voids with water, removing the air to minimize oxidation and reduce stream pollution. The seal was made from a chemical by-product produced in coal-fired power plants called fixated flue gas desulfurization (FGD) sludge. The FGD seal has a low hydraulic conductivity, which limits water from seeping out of the underground mine. It also has high alkalinity which may neutralize the acidic waters of AMD when water does seep from the mine.

This document gives a brief background of AMD chemistry and its effects, and a discussion of the impact the fixated FGD seal has had on the water quality to date.

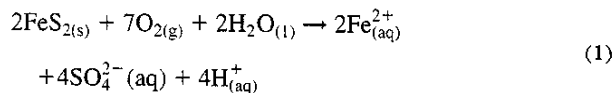
## 2. AMD chemistry

Acid mine pollution is caused by the physical and chemical weathering of iron pyrite ( $\text{FeS}_2$ ), also known as “fool’s gold”. Acidity, ferric iron ( $\text{Fe}^{3+}$ ) precipitation, oxygen depletion, and the release of metals, such as aluminum ( $\text{Al}^{3+}$ ), zinc ( $\text{Zn}^{2+}$ ), and manganese ( $\text{Mn}^{2+}$ ) are aquatic impacts that may be associated with coal mining. The level of acidity and the concentration of the heavy metals is a function of the amount of pyrite in the area around the mine.

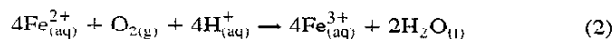
Physical weathering is essential to reduce the grain size of

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the pyrite. The early miners inadvertently accelerated this process by grinding up the ore and dumping the overburden in mine tailings. The next step in the geochemical process is the chemical oxidation of pyrite [1]:



When the pyrite is exposed to oxygen and water, it reacts to form sulfuric acid ( $\text{H}_2\text{SO}_4$ ), which causes a decrease in pH. The  $\text{Fe}^{2+}$  ions (ferrous) are released into the runoff waters from drainage tunnels or tailings piles. Next, the  $\text{Fe}^{2+}$  ions are oxidized to  $\text{Fe}^{3+}$  (ferric) ions, which hydrolyze in water to form iron (III) hydroxide [ $\text{Fe}(\text{OH})_3$ ] as shown in the following reactions:



This process releases more hydrogen ions into the environment, which continues to reduce the pH. The iron (III) hydroxide formed in this reaction is referred to as “yellow boy”, which is a yellowish-orange precipitate that turns the water in the streams an orange-red color and fouls the streambed. The iron (III) hydroxide precipitate kills plants and fish by reducing the amount of light for photosynthesis and smothering aquatic life, their food resources, and spawning beds on the stream bottom.

Pyritic mine tailings leach AMD, in a large part due to the metabolic activity of *Thiobacillus ferrooxidans* [2]. These acid-tolerant bacteria serve to catalyze the oxidation of the pyrite in Eqs. (1)–(3) above, thereby increasing the amounts of acidity and iron released to the environment. Additionally, other chemical reactions may take place. For example, sulfides of copper, zinc, cadmium, lead, and arsenic will undergo similar chemical reactions resulting in the contribution of metals in streams [3].

It is the oxygen requirement in Eqs. (1) and (2) that are exploited in mine sealing for AMD abatement. Notice that, if the iron pyrite is never oxidized or exposed to the atmosphere, the pollution caused by AMD could be eliminated. Therefore, if groundwater could be trapped inside an underground mine to the point of inundation, the air in the mine voids would be forced out. While traces of dissolved oxygen may still be present, the largest oxygen source would be removed. The FGD seal at Broken Aro was designed to retain the groundwater inside the mine to a level above the highest roof elevation, thus minimizing the availability of oxygen and inhibiting the oxidation reaction inside the mine.

### 3. The goal of the FGD seal

The ultimate goal of the seal was to displace the air voids inside the underground mine with groundwater. By

retaining the water inside the mine to the point of inundation, the FGD seal limits the amount of oxygen present in the mine. This inhibits the oxidation reaction and subsequently minimizes the acidic drainage. It would be impractical to expect that all of the water would be restricted only to the mine, especially with the increasing head pressure due to the rising water level. It is expected that some water will continue to seep from the mine complex, primarily through the shale below or reclaim soil over the top of the FGD seal. The expectation is that the small amount of AMD that is produced can be treated by means of natural attenuation in the detention ponds, and therefore it will not be a threat to water quality further downstream.

### 4. Remining for the purpose of FGD seal placement

Re-mining was the strategy used at Broken Aro to benefit the environment, industry, and the public. Re-mining operations ultimately accomplished three goals. First, it recovered remaining coal reserves left from previous mining operations. Second, re-mining allowed for the reclamation of the Broken Aro site and the placement of the FGD seal in order to achieve current environmental standards. Sites that are re-mined and reclaimed reduce environmental pollution, remove health and safety hazards, and considerably improve aesthetic properties [4]. Third, the State of Ohio, American Electric Power, and R&F Coal Company were able to share financial and regulatory burdens so that the re-mining operation was possible. The normal barriers of an insufficient coal reserve, liabilities due to poor, pre-existing water quality, and seal material experimentation can be overcome with this kind of cooperative partnership.

Installation of the FGD seal began concurrent with the continued re-mining effort in June 1997 and was completed by September 1997. The seal design and construction has been described fully previously [5], but will be summarized here. A series of open pits were excavated to recover remaining coal in the re-mining operation. The construction of the seal started adjacent to the exposed highwall with the excavation of a keyway trench which was 5 ft wide and 1 ft deep in the pit floor. The first lift of the seal was constructed by placing the FGD material into the open pit and the keyway trench. The FGD material was forced into mine openings and compacted using a dozer. The compacted first lift was sufficient to cover the face of the exposed coal seam. After the first lift was installed, mine spoil from the adjacent pit was pushed into the current pit floor and used in the leveling of the first lift. This allowed trucks to transport the second lift of FGD without damaging the first. The second lift was placed on top of the first lift, and the FGD material was pushed into the highwall with a dozer to fill and compact the lift. The now, compacted FGD seal was a minimum of 8 ft above the pit floor. The top surface of the second lift was sloped gradually away from the highwall. This was to ensure that infiltration waters flowing

Table 1  
Major and minor constituents in FGD material

Major constituents	wt%	Minor constituents	mg/kg
Calcium oxide	34.9	Arsenic	64.0
Sulfur dioxide	20.9	Zinc	52.4
Silica	9.5	Chromium	51.2
Sulfur trioxide	9.0	Copper	30.0
Iron oxide	7.3	Nickel	24.8
Aluminum oxide	4.4	Lead	21.5
Magnesium oxide	1.4	Selenium	12.6
Potassium oxide	0.2	Molybdenum	9.3
Titanium oxide	0.2	Cadmium	0.7
Sodium oxide	0.1	Mercury	0.2

through the reclaim would be diverted away from the highwall and off the seal.

All deep mine openings that were encountered during seal placement were handled accordingly. Openings were sealed from floor to roof by pushing FGD material as far back into the entrance as possible using a backhoe. Also, care was taken to ensure that there were no gaps between mining pits. This guaranteed that the mine seal was constructed continuously along the length of the highwall. Additional compaction was produced from the placement of overburden above the mine seal from the next pit. The total depth of soil cover was 30–40 ft over the seal.

The FGD material characteristics are presented in Table 1. The material dry weight composition was a 1:1 ratio of fly ash and scrubber filter cake (primarily calcium sulfite) with a 5% lime addition. FGD was delivered to the site as needed with an average water content of 70% (mass water per mass dry solids). It was placed and compacted within ten days of production to achieve optimum performance. The FGD seal itself was constructed in two 4–6 ft lifts, 10–15 ft wide. The width of the seal, along with the placement of soil in the reclaimed area, was designed to allow the seal to withstand the 8–12 ft of hydraulic head which would be generated by the mine water. The natural curing of the FGD increases compressive strength from 100–150 psi to as much as 325 psi over a period of 1–3 months after placement. The hydraulic conductivity also decreases by one order of magnitude over this same time period.

## 5. Environmental monitoring

### 5.1. Sampling locations and methods

A map of the Broken Aro mine site is presented in Fig. 1. On site, there are 15 surface water locations that are sampled and tested which are comprised of underground seeps, ponds, streams, and stormwater runoff from the mined areas. Originally, there were eight monitoring wells situated in four pairs that were drilled into and below the mine. Six additional wells were installed in the reclaim area outside of the seal in August of 1998. The groundwater from each of

these wells is also sampled and tested. Sampling began in April of 1997, prior to the re-mining effort to establish background contaminant profiles. Sampling continued during mining operations and, to date, for over two years after the completion of the FGD seal.

For each stream location, three tasks are performed in the field. First, preserved and unpreserved samples are obtained. Second, field evaluations for water quality indicators are performed. Finally, the flowrate is measured for each stream location. At the well locations, the water level elevation, and the depth of the well is measured first. Then, unfiltered, unpreserved and filtered, preserved groundwater samples are obtained. Finally, field evaluations for water quality indicators are performed. Once samples have been collected from each location, they are transported to an environmental testing laboratory for analysis. This is done at the end of the same day of the sampling event.

### 5.2. Field water quality assessments

The pH, temperature, specific conductivity or total dissolved solids (TDS), and the oxidation-reduction potential (ORP) are measured directly in the field using specific probes. Then, 3% peroxide ( $H_2O_2$ ) is added to the sample cup. Next, the pH and ORP are tested for the oxidized sample to see if it has changed [6]. Most groundwater samples are in a reduced state. For mine water samples that contain a substantial mineral fraction, the peroxide addition causes the release of hydrogen ions ( $H^+$ ) in the oxidation process and thus lowers the pH. This provides the researcher with the ability to predict the potential acidification of a receiving stream once the source has an opportunity to oxidize.

In the streams, volumetric flowrates are determined using different devices such as weirs, flumes, current meters, or culverts. The choice of a flowrate measuring technique depends on the nature (e.g. quantity, site topography, etc.) of the sample location. This enables the calculations of mass loadings from concentration data obtained in the laboratory.

### 5.3. Laboratory water quality assessments

Each water sample is tested in the laboratory for the following constituents: pH, total acidity, total alkalinity, bicarbonate alkalinity, carbonate alkalinity, specific conductance at 25°C, total non-filterable residue, TDS, sulfate, chloride, total calcium, total magnesium, total sodium, total potassium, total iron, total manganese, total aluminum, and hardness. The trace compounds analyzed are: total zinc, phosphate, copper, chromium, arsenic, barium, cadmium, lead, mercury, selenium, silver, cobalt, boron, total nickel, bromide, and total molybdenum. All constituents were analyzed for during the first year. Subsequently, the trace compound series were only analyzed on a quarterly basis.

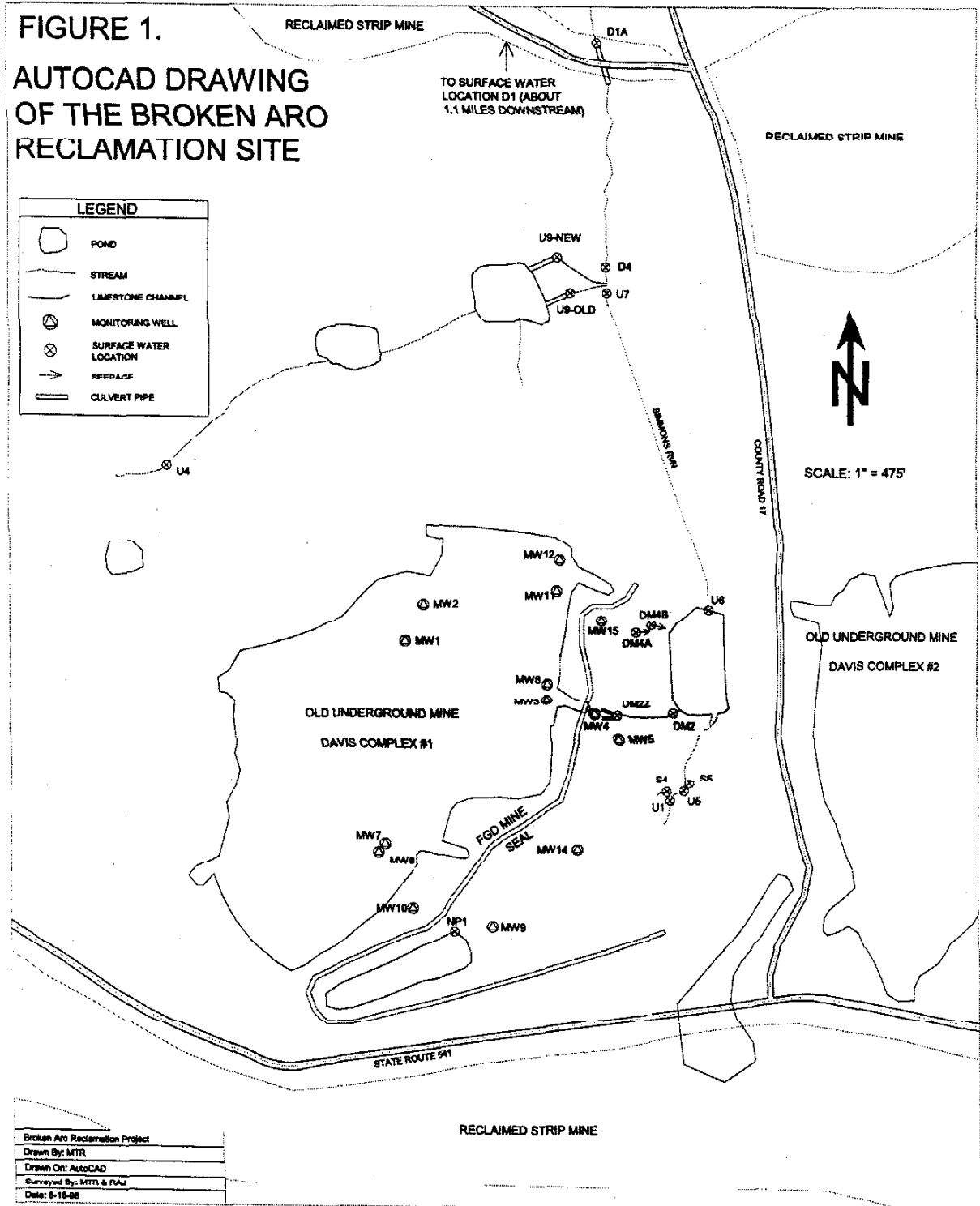


Fig. 1. Site map for Broken Aro Mine identifying the locations of the mine complex, the FGD seal, monitoring wells, and surface sampling sites.

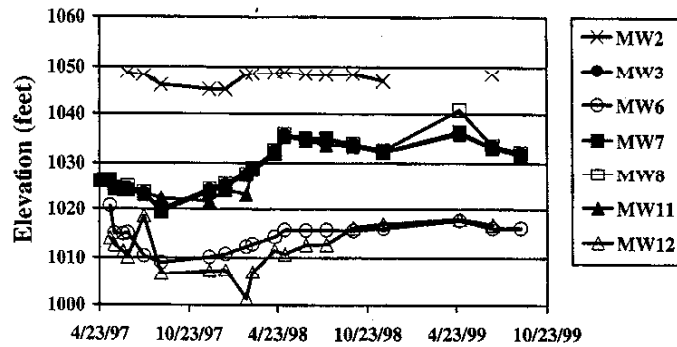


Fig. 2. Water levels in monitoring wells as a function of time.

**6. Effectiveness of the FGD seal**

The effectiveness of the seal to date can be seen via examination of the data collected as a function of time. Sampling events began on a regular basis two months prior to the start of the installation of the FGD seal. Therefore, one can see the effects of re-mining and dewatering activities and any immediate effect the FGD seal had on the AMD pollution. Water level elevations in the monitoring wells will be used to demonstrate how the FGD seal developed and maintained flooding of the underground mines. Chemical concentration profiles in one pair of the monitoring wells will be utilized to demonstrate water quality improvements inside the mine. Contaminant loads at surface water location D1A will be used as an indicator of the FGD seal's effectiveness due to its critical location at the boundary of the mining areas.

Fig. 2 presents the water levels in the monitoring wells as a function of time. The water inside the mine is monitored by wells MW3, MW7, and MW11. Monitoring wells MW6, MW8, and MW12 are screened in a geologic interval under the deep mine, and they describe the water level and water quality below the mine. Monitoring well MW2 is located in a perched aquifer, where the water level is much higher than in the other wells. It should be noted that some vertical

connectivity exist between the mine and MW8 as demonstrated by the fact that the water elevation in that well (below the mine) is the same as the water levels inside the mine.

Prior to dewatering, the water levels inside the underground mine were at an elevation of 1026 ft. During mining operations the water level dropped to 1020 ft due to the fact that the mining activity and the FGD seal construction disturbed some of the mine openings and allowed for dewatering of the underground mine complex. After the completion of the mine seal in August of 1997, the water levels inside the mine complex rose at a rate of approximately 1.5 ft per month to a maximum of 1036 ft in May of 1996. During the drier summer and fall months, the water levels slowly dropped to an elevation of 1032 ft. This decrease of 4 ft was recharged during the winter/spring of 1999. The mine appears to have established a cycle of recharge and loss, which correlates well with the seasonal precipitation. In general, the wells screened within the mine consistently show water levels 6–10 ft above pre-mining levels and 12–16 ft above the dewatered mine levels.

The water quality in the paired wells MW3 and MW6 will be used as typical of groundwater conditions since MW6 is located under the mine and MW3 is located within the underground mine complex. As can be seen in Figs. 3, 5,

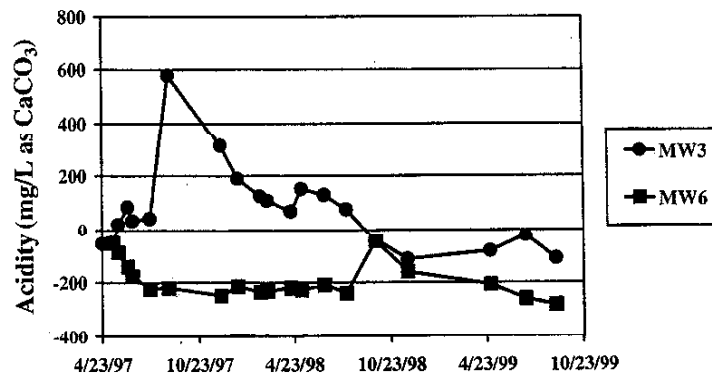


Fig. 3. Total acidity in monitoring wells 3 and 6 as a function of time.

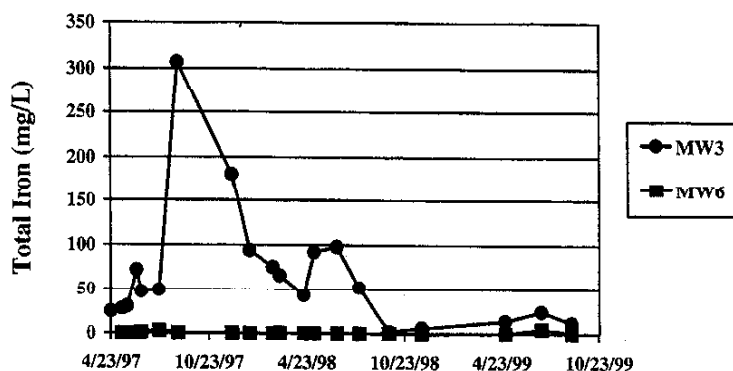


Fig. 4. Total iron concentrations in monitoring wells 3 and 6 as a function of time.

the water quality of MW6 has remained relatively unchanged throughout the testing period with respect to acidity, total iron, and sulfate concentrations. This is a good indicator that the mine waters have remained inside the complex and have not descended into a lower geologic formation. Water quality within the mine after the completion of the seal demonstrated immediate signs of improvement. In MW3, the acidity, sulfate, and iron concentrations have slowly decreased since re-mining and dewatering activities. The improvement in acidity was so dramatic that there are portions of the year in which the mine complex water possesses a net alkalinity. Additionally, calcium concentrations in MW3 have remained unchanged, suggesting that the seal material remains intact and is not dissolving into the mine water.

It is interesting to note that the cycling of the water levels has an impact on the water quality inside the mine. One possible reason for the small increases in the contaminant concentrations in each of the late spring months since the completion of the seal may be attributed to a "roof effect". This would provide confirmation that the mine is inundated after the winter recharge, however, it would also appear that portions of the mine roof become exposed during the fall decline in water elevation. This exposed mineral fraction would then release contaminants into the mine water

when the complex recharges and re-inundates. Another possibility is that the infiltration waters in the winter/spring recharge carry slightly higher dissolved oxygen concentrations which are then able to react in the mine water.

Fig. 6 presents sulfate and total iron loadings at location D1A (site boundary). Sulfate loadings reached a high of 1120 kg/day during the re-mining in May of 1997, but decreased to 370 kg/day by September of 1999. This constitutes a reduction in sulfate load to the watershed of 67%. The iron loadings have decreased in even a more drastic manner, from over 43 kg/day during re-mining operations to about 1.1 kg/day in September of 1999. This is equal to a 97.5% reduction in total iron load off-site. Again, the recharge effect can be seen in the loading profiles as small increases in contaminant loads appear during the spring months. It should be noted that, at no time during the sampling period did concentrations of the trace elements exceed the baseline levels, indicating that the metals present in the seal were not contributing to the contamination in Simmons Run.

Periodic exploration around the mine complex has not identified any new seeps. Three of the original seeps located in the spoil blending area were disturbed during the mining operations and did not flow for the first two years. Recently, one of the seeps has re-surfaced but at a flowrate which is

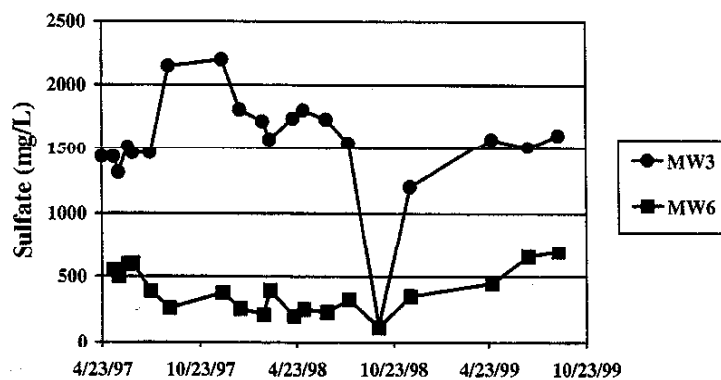


Fig. 5. Sulfate concentrations in monitoring wells 3 and 6 as a function of time.

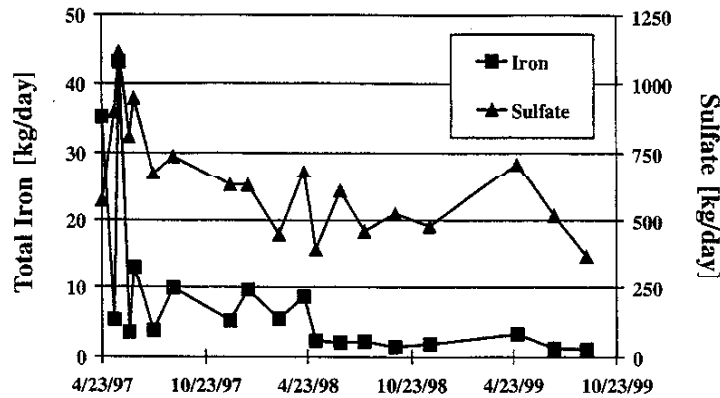


Fig. 6. Iron and sulfate loads at sampling location D1A, the project boundary.

nearly too small to measure. Flowrates at locations DM4A and DM4B remain small and unchanged. Water quality in these seeps is similar to those known to come from the mine, but total contaminant loads from these seeps are negligible in the total load to Simmons Run. Flowrate and contaminant concentrations have both decreased at location DM2, thus lowering the contaminant loads to the watershed.

## 7. Conclusion

The Broken Aro Project will continue to be monitored in years to come to determine the level of success of the fixated FGD seal. The cooperative re-mining effort shared the benefits and liabilities, as well as the costs, of coal recovery and implementation of novel environmental control strategies. To date, the FGD seal has shown that it has improved water quality inside the mine, reduced the quantity of water seeping from the mine, and has reduced contaminant loads to Simmons Run by up to 97.5%. The site still needs to reach its hydrogeologic equilibrium to completely determine the seal's effectiveness. The seasonal cycling of the mine water elevations has had a small, but noticeable, effect on

contaminant profiles. It is important to either lower the concentration of the contaminants or the flowrate so that ultimately the total loading decreases. In this project, both the concentrations and flowrates have consistently decreased due to the mine seal, which is optimal for contaminant load reduction.

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