Use of a CCP Grout to Reduce the Formation of Acid Mine Drainage: 10-Year Update on the Winding Ridge Project

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ABSTRACT

The Maryland Department of Natural Resources Power Plant Research Program (PPRP) and the Maryland Department of the Environment (MDE) have formed a partnership with private industry and state and federal agencies to demonstrate the beneficial application of coal combustion products (CCPs) as flowable, self-cementing, environmentally benign grouts to abate acid mine drainage (AMD). Through this partnership, the Winding Ridge Project was initiated as a practical demonstration of AMD abatement. In 1996, 5,600 cubic yards (4,280 cubic meters) of CCP grout was injected into a small, abandoned, deep coal mine in Garrett County, MD. Post-injection monitoring has continued since that time and has included analysis of mine discharge water quality and testing of grout stability. This paper presents a ten-year update of the data for the Winding Ridge Project.

The post-injection monitoring results indicate that the water quality of the mine discharge has improved since injection of the CCP grout and that the grout remains stable within the mine tunnels. Concentrations of iron, magnesium, sulfate, aluminum, manganese, zinc, cobalt, copper, nickel, and acidity in mine discharge have decreased below pre-injection concentrations. The pH of mine discharge has increased by one pH unit, and the estimated rate of acid production in the mine has decreased by as much as 80%. Grout cores collected one and seven years after injection show that the grout has maintained high strength and low permeability within the tunnels.

This Project represents one of very few sites with such an extensive monitoring history. The extensive database of water quality data provides valuable information concerning the geochemical processes responsible for the water quality trends observed.

INTRODUCTION

The Maryland Department of Natural Resources Power Plant Research Program (PPRP) has partnered with private industry to undertake a series of projects to demonstrate the beneficial application of CCPs to create flowable grouts for placement in underground coal mines to reduce acid formation. These demonstration projects are a key component of Maryland's overall ash utilization program to promote and expand the beneficial use of all CCPs on a massive scale. The ultimate goals of these projects are to utilize CCP-based grouts to effect significant acid reduction at large AMD sources in Maryland, such as the Coketon/Kempton Mine Complex (Maryland’s largest source of AMD), and to mitigate subsidence problems associated with lands disturbed by coal mining and natural karst topography.

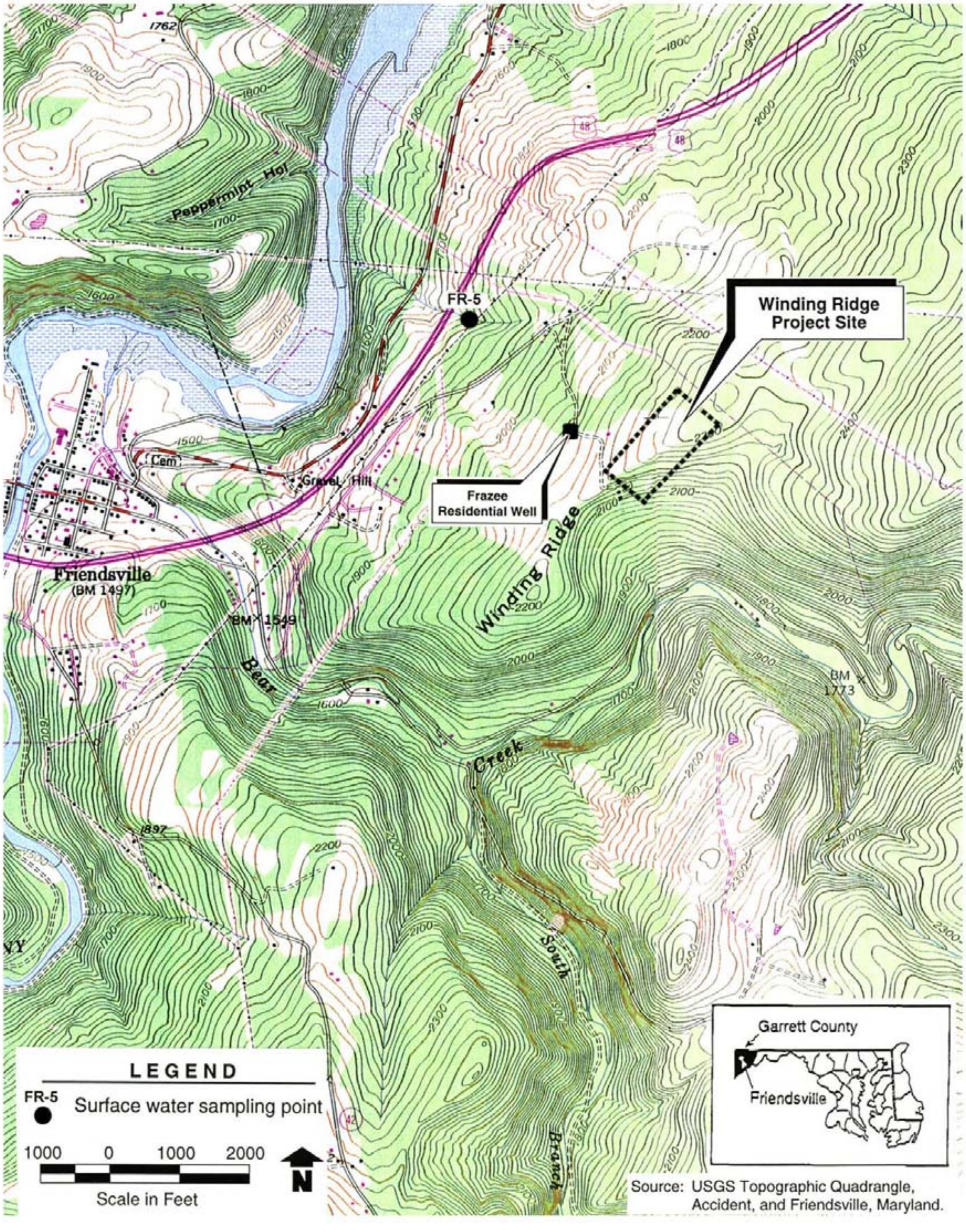
The Winding Ridge Project was the first of these demonstration projects and was initiated in April 1995. The project involved the injection of a 100% CCP-based grout into the Frazee Mine, which is a small 10 acre (40,500 square meter (m^2)), underground coal mine in Garrett County, Maryland (Figure 1). In 1999, the authors reported on the means and methods of the grout injection phase of the project, and presented post-injection water quality data for the first year following injection[1]. In 2001, the authors presented an update on post-injection water quality monitoring including three years of post-injection water quality data[2]. In 2005, the authors presented an update on long term monitoring at the mine[3]. Since that time, additional water quality data has been collected, and monitoring is currently ongoing. As a result, an extensive database has been generated, including a total of ten years of post-injection water quality data. The purpose of this paper is to present the key findings to date regarding post-injection monitoring of the Frazee Mine.

SETTING

The Frazee Mine is located atop of Winding Ridge in Garrett County, Maryland (Figure 1). The mine is a small, hand-dug, abandoned, underground coal mine that was used to mine coal from the Upper Freeport seam from the 1930s to circa 1960. The sulfur content measured in Upper Freeport coal samples from the project site ranged from 1.0% to 3.5%. Acid-base accounting performed on overburden samples indicates that a small, 6 -18 inches (in) (15 to 46 centimeters (cm)) thick, rider coal seam above the Frazee Mine is the only other potential source of acid producing rock besides the Upper Freeport. Total sulfur content of the rider coal seam is about 1.5% to 4.5%. Investigative drilling at the site indicated that the mine consists of two main tunnels, a lower and an upper tunnel, connected by an unknown number of crosscuts (Figure 2). Downhole camera investigations of the mine conducted by the National Energy Technology Laboratory indicated that the mine was in poor condition, the tunnels were poorly timbered and a number of roof falls and collapses were evident.

Ground water monitoring wells installed at upgradient and downgradient locations showed that the Frazee Mine is situated within unsaturated bedrock, and that the regional ground water table is approximately 50 feet (ft) (15 meters (m)) below the mine pavement. The cross section shown in Figure 3 shows the lithology of the Winding Ridge area and the relative elevations of the mine tunnel and mine pool.

Figure 1
Winding Ridge Site Location Map



Source: USGS Topographic Quadrangle, Accident, and Friendsville, Maryland.

Figure 2
Site Layout
Winding Ridge Project
Friendsville, Maryland

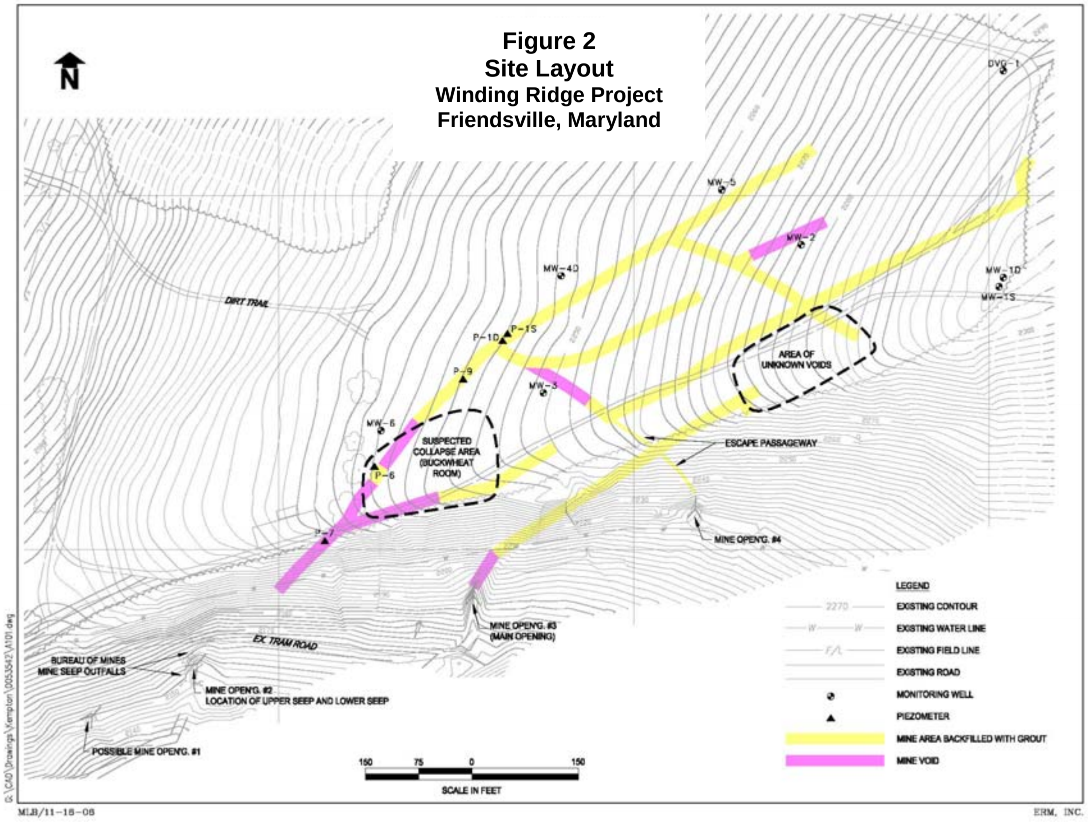
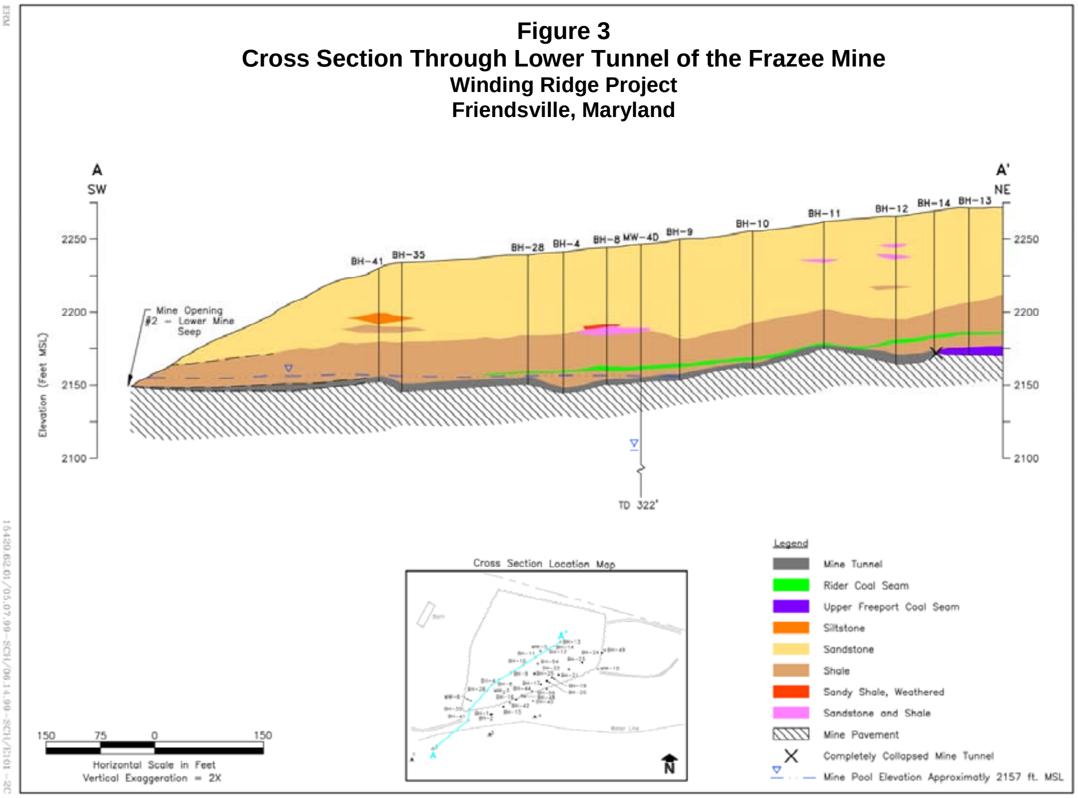


Figure 3
Cross Section Through Lower Tunnel of the Frazee Mine
Winding Ridge Project
Friendsville, Maryland



Infiltrating precipitation impounded within the Frazee Mine created a pre-injection mine pool of at least 550,000 gallons (gal) (2,000,000 liters (l)). This mine pool resides in the lower tunnel, while the upper tunnel is predominantly dry. Although there are four known mine entries, the only mine discharge is from Mine Opening No. 2 (MO2), where AMD flows from an upper and a lower seep. The elevation of the lower seep is about 9 ft (3 m) below the mine pool elevation, and flow is continuous at about 2 gallons per minute (gpm) (0.12 liters per second (l/s)). Flow from the upper seep is intermittent and dependant upon the mine pool elevation. When the mine pool elevation is above the upper mine seep, flow occurs generally at about 3 to 5 gpm (0.19 to 0.32 l/s), although flash events of 20 to 30 gpm (1.3 to 1.9 l/s) have been recorded after rainfalls. Otherwise, the upper seep is dry.

The pre-injection water quality from MO2 was typical of AMD-quality water with an average pH of 2.8 and average total acidity of 1,300 mg/L. The average sulfate, iron, aluminum and total dissolved solids concentrations were 1,300 mg/l, 190 mg/l, 69 mg/l, and 2,100 mg/l, respectively.

GROUT FORMULATION AND INJECTION

The CCPs used for the Project were: fluidized bed combustion (FBC) by-product (commingled bed ash and fly ash), from the Morgantown Energy Associates power plant; Class F fly ash, from the Virginia Power Company's Mt. Storm power plant; and flue gas desulfurization (FGD) by-product, also from the Mt. Storm power plant. The FBC provided the free lime, the fly ash provided pozzolan, and the FGD by-product (mostly calcium sulfite and calcium sulfate with no free lime) was used as a bulking agent.

The mix design consisted of 60% fresh (defined as less than 24 hours old) FBC ash, 20% FGD product, 20% fly ash, and virtually 100% mine water. The FBC was conditioned at the plant to contain about 15% moisture, which resulted in about 3% to 5% free lime content. The final grout moisture content was about 57% on a dry weight basis, and contained about 2% to 3% free lime. Grout samples collected during injection showed a spread of about 8 inches (20 centimeters), and a 28-day unconfined compressive strength of about 550 pounds per square inch (psi) (3.8 megapascals (MPa)).

Full-scale injection began on 7 October 1996 and ended on 8 November 1996. Approximately 5,600 yd^3 (4,280 m^3) of grout were injected into the Frazee Mine. The grout consisted of 3,800 tons (3,400 metric tons) of FBC ash, and 1,200 tons (1,100 metric tons) each of fly ash and FGD by-product. The project used 520,000 gallons (1,970,000 liters) of water, consisting of 449,000 gallons (1,700,000 liters) of untreated mine water (pH of about 3) and 71,000 gallons (270,000 liters) of river water pumped from the nearby Youghiogheny River. The river water was used at the end of injection when grouting precluded any further withdrawal of mine water.

POST-INJECTION MONITORING RESULTS

In-Situ Grout Sampling Results

Two sets of in-situ grout cores have been collected from Winding Ridge. One set of cores was collected in September 1997 (approximately 1 year after grout injection), and a second set of cores was collected in July 2004 (approximately 8 years after injection).

During the 1997 grout coring event, a total of nine coreholes were drilled. These coreholes targeted both wet and dry areas of the mine. Grout was encountered in five of the nine coreholes and four of the five grout cores were submitted for laboratory testing (the fifth grout core was too soft to be tested). Mine tunnel piezometers were constructed within four of the five coreholes that had contained grout in order to monitor the presence and quality of water within the mine tunnels.

During the 2004 grout coring event a total of three coreholes were drilled. These coreholes were co-located with some of the piezometers installed in 1997, in order to better ensure that grout would be encountered during coring. Grout was encountered in two of the three coreholes and one of the two grout cores was submitted for laboratory testing (the second grout core was too soft to be tested).

Table 1 shows the results of laboratory testing for the grout cores collected in 1997 and 2004 as well as samples of grout that were cured at the surface during the injection process.

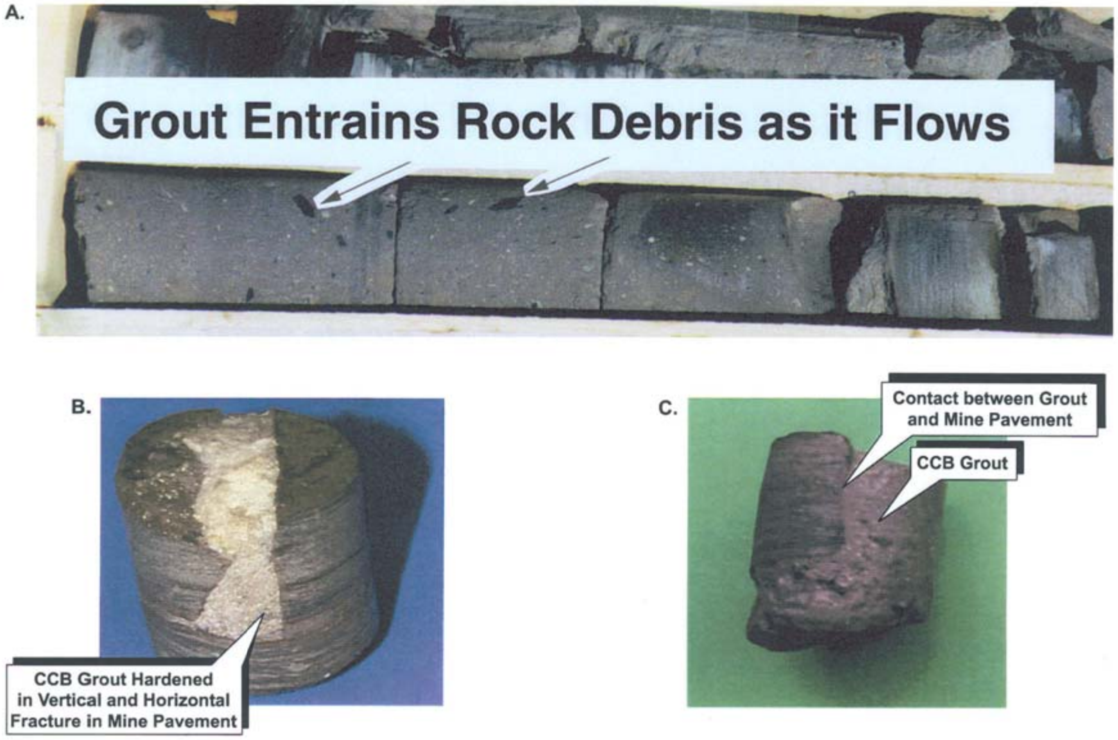
Table 1 Results of Grout Core Analyses

Parameter	**Location**	**Injection Samples**	**CH-3**	**P-1D**		**P-6**		**P-7**	**P-9**
	Label	28-days	CH-3	CH-1	CH-3-04	CH-6	CH-1-04	CH-7	CH-9
	Year	1996	1997	1997	2004	1997	2004	1997	1997
	Depth (ft)	na	71.7-72.8	84.3-85.7	85.5-87.3	83.2-84.4	85.0-86.5	70.0-70.5	85.0-87.1
	Depth (m)	na	21.8-22.2	25.7-26.1	26.1-26.6	25.4-25.7	25.9-26.4	21.3-21.5	25.9-26.5
Strength (psi)		245-850	1,208/1,128	560	773/844	1339	Too soft for testing	Too soft testing	Too soft for testing
Strength (Mpa)		1.69-5.86	8.33/7.78	3.86	5.33/5.82	9.23			
Permeability (cm/sec)		---	2.58E-07	8.89E-06	9.18×10^{-7} 4.14×10^{-7}	1.29×10^{-7}			
Dry Density (pcf)		---	76.8	1.13	80.1/82.7	80.4			
Dry Density (g/cm^3)		---	1.23			1.29			

Notes:
--- - Sample not analyzed for this parameter.
na – not applicable.

In general, the grout cores from both coring events were in very good shape, and had little evidence of in situ weathering caused by the mine environment. The grout cores showed good contact with the mine roof and pavement and showed that the grout was able to entrain mine debris and to fill vertical and horizontal cracks in the mine pavement (Figure 4).

Figure 4
Grout Cores from the Frazee Mine
The Winding Ridge Project
Friendsville, Maryland



The measured permeabilities and compressive strengths for the 1997 and 2004 samples were comparable. In the 1997 samples, the measured permeabilities ranged from 10^{-8} to 10^{-6} centimeters per second (cm/sec). The unconfined compressive strengths ranged from about 560 to 1,400 psi (3.9 to 9.8 MPa). The 2004 sample had a measured permeability of about 10^{-7} cm/sec and a compressive strength of 800 psi (5.5 MPa).

Two grout cores showed possible evidence of in-situ weathering or poor grout curing. The samples from P-7 (collected in 1997) and from P-6 (collected in 2004) were cohesive, but too soft for testing, having the consistency of stiff clay (Figure 5). Both of these sample locations are situated relatively close to MO2 and grout in these areas was injected in contact with water. Water has been present in the piezometers at these locations since they were constructed in 1997. These coreholes were also distant from the injection points and therefore the grout may have been excessively diluted by the mine pool prior to curing.

Figure 5
Condition of Grout within the Frazee Mine
The Winding Ridge Project
Friendsville, Maryland

A. This core has a consistency similar to concrete and is representative of the grout core samples collected at P-1S, P-1D, P-6, P-9, and CH-3-04.

B. This core has a consistency similar to stiff clay and is representative of the grout core samples collected at P-7 and CH-1-04.

Post-Injection Mine Hydrology

AMD continues to flow from the mine from ungrouted areas. Post-injection water level measurements from the mine tunnel piezometers show that the mine pool elevation is essentially the same as its elevation prior to injection, indicating that grout injection has not created new sub-pools or raised the water level to the point that it is contacting the rider coal seam, (which could initiate new generation of AMD). The seep characteristics have changed little since injection. The horizontal location of the lower seep has shifted a few feet, requiring the placement of a new pipe to facilitate sample collection, however, the rate of flow has stayed constant at about 2 gpm (0.12 l/s). The discharge from the upper seep remains intermittent, and dependent upon the mine pool elevation. The upper seep has been dry during approximately 35% of the post-injection monitoring events.

Post-Injection Water Quality Monitoring Program

The water quality of the mine discharge, the water within the mine tunnels and the shallow and deep ground water has been monitored since injection. Tables 2 and 3 describe the monitoring locations, sampling periods, and the analytical parameters included in the Winding Ridge water quality monitoring program.

Table 2 Water Quality Sampling Points and Sampling History at Winding Ridge

Sample Point	Pre-Injection		Post-Injection									
	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006
Mine Tunnel Seeps (Mine Discharge)												
L-2 (Lower Seep)	→	→	→	→	→	→	→	→	→	→	→	→
C-2 (Upper Seep)	→	→	→	→	→	→	→	→	→	→	→	→
Mine Tunnel Piezometers (Water Within the Mine Tunnels)												
P-1D			→	→	→	→	→	→	→	→	→	→
P-6			→	→	→	→	→	→	→	→	→	→
P-7			→	→	→	→	→	→	→	→	→	→
P-9			→	→	→	→	→	→	→	→	→	→
Shallow Monitoring Wells (Shallow Ground Water Outside of Mine Tunnels)												
MW-4	→	→	→	→	→	→	→	→	→	→	→	→
MW-6	→	→	→	→	→	→	→	→	→	→	→	→
Deep Monitoring Wells (Deep Ground Water Outside of Mine Tunnels												
MW-4D			→	→	→	→	→	→	→	→	→	→
DUG-1											→	→

Notes: Monitoring wells MW-1S, MW-1D, MW-2, MW-3, and MW-5 and Mine Tunnel Piezometer P-1S have consistently been dry or contained insufficient water for sampling.

Table 3 Water Quality Analytical Parameters for Winding Ridge Samples

Pre-Injection Monitoring	Injection Period Monitoring	Post-Injection Monitoring
AMD-Related Parameters		
pH Total Acidity Iron Sulfate Aluminum	pH Total Acidity Iron Sulfate Aluminum	pH Total Acidity Iron Sulfate Aluminum
Other Major Cations and Anions		
Calcium Magnesium Sodium Bromide Chloride	Calcium Magnesium Sodium Bromide Chloride	Calcium Magnesium Sodium Bromide Chloride Silica Nitrate/Nitrite
Trace Metals		
Antimony Arsenic Barium Beryllium Cadmium Chromium Cobalt Copper Lead Manganese Mercury Nickel Selenium Silver Thallium Vanadium Zinc	Antimony Arsenic Barium Beryllium Cadmium Chromium Cobalt Copper Lead Manganese Mercury Nickel Selenium Thallium Vanadium Zinc	Antimony Arsenic Barium Beryllium Cadmium Chromium Cobalt Copper Lead Manganese Mercury Nickel Selenium Silver Thallium Vanadium Zinc Boron
Other		
Total Alkalinity Total Dissolved Solids Specific Conductivity Temperature	Total Alkalinity Total Dissolved Solids Specific Conductivity Temperature	Total Alkalinity Total Dissolved Solids Specific Conductivity Temperature

Notes: Boron was added to the analyte list in 2005.

Mine Discharge Water Quality

The lower seep is considered to be most representative of the long-term water quality conditions of the mine water in contact with the grout since its flow is continuous and independent of the mine pool elevation. In comparison, the upper seep is intermittent, and much more susceptible to water quality variation caused by repeated wetting and drying cycles of pyritic strata in the mine roof and walls as the pool elevation fluctuates for this reason, the following discussion is focused primarily on the data from the lower seep (L-2).

AMD-Related Parameters and Other Major Ions

Figure 6 shows the measured pH values for the upper and lower seeps. At the lower seep, pH fluctuated within the historically observed range of values during and immediately after grout injection. Since injection, however, the lower seep pH has exhibited a beneficially upward trend, increasing by about 1 pH unit above pre-injection conditions. The upper seep has not shown any appreciable change in pH since injection. As mentioned above, this observation is attributed to the recharge of hydrogen ions to the mine water as the mine pool rises and falls, exposing pyritic strata to wetting and drying cycles.

Figure 6
pH Results for Upper and Lower Seep at MO2

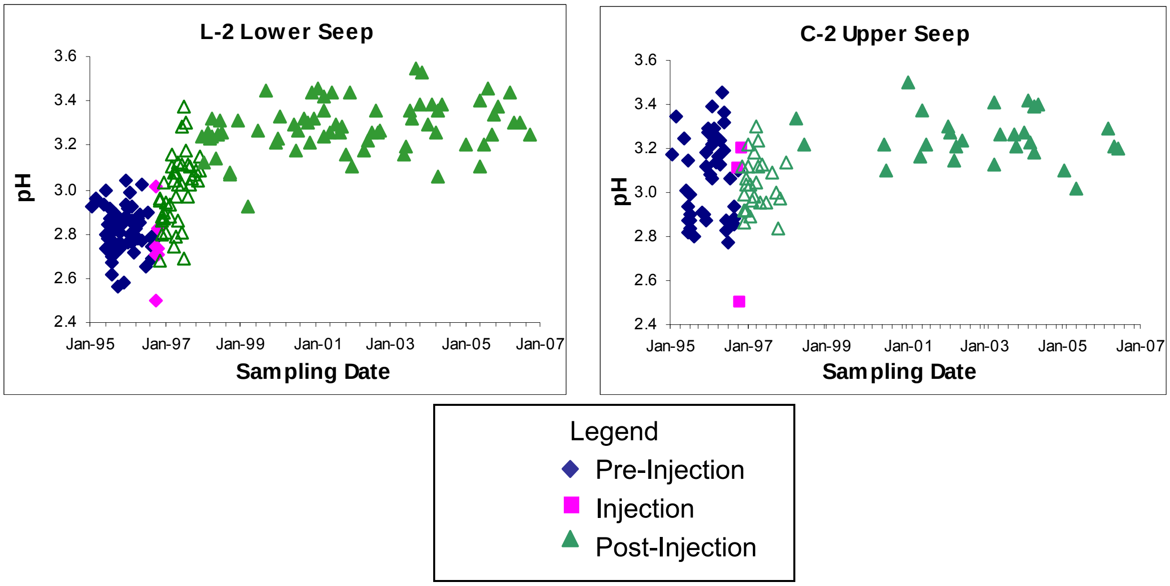
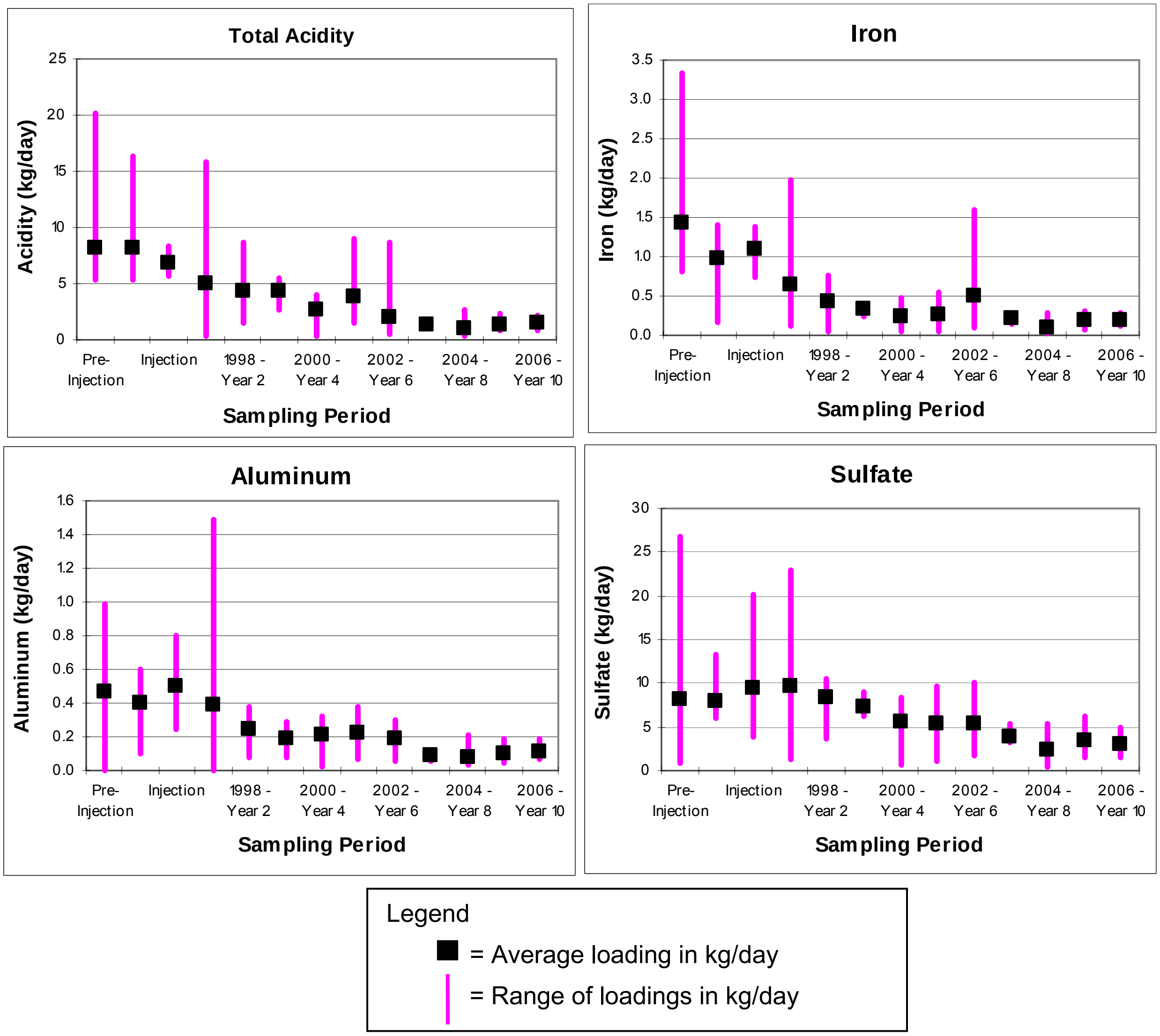


Figure 7 summarizes the loading of other AMD-related parameters (acidity, iron, aluminum, and sulfate) and calcium discharging from the lower seep over time. As noted previously, the flow rate from the lower seep has not changed since the pre-injection monitoring period. Any changes in the loading of any parameters in the mine discharge will be due to changes in the concentration of that parameter and not to changes in the flow rate of the discharge. Therefore, graphs of concentration vs. time for the lower seep show the same patterns as the graphs of loading vs. time shown below.

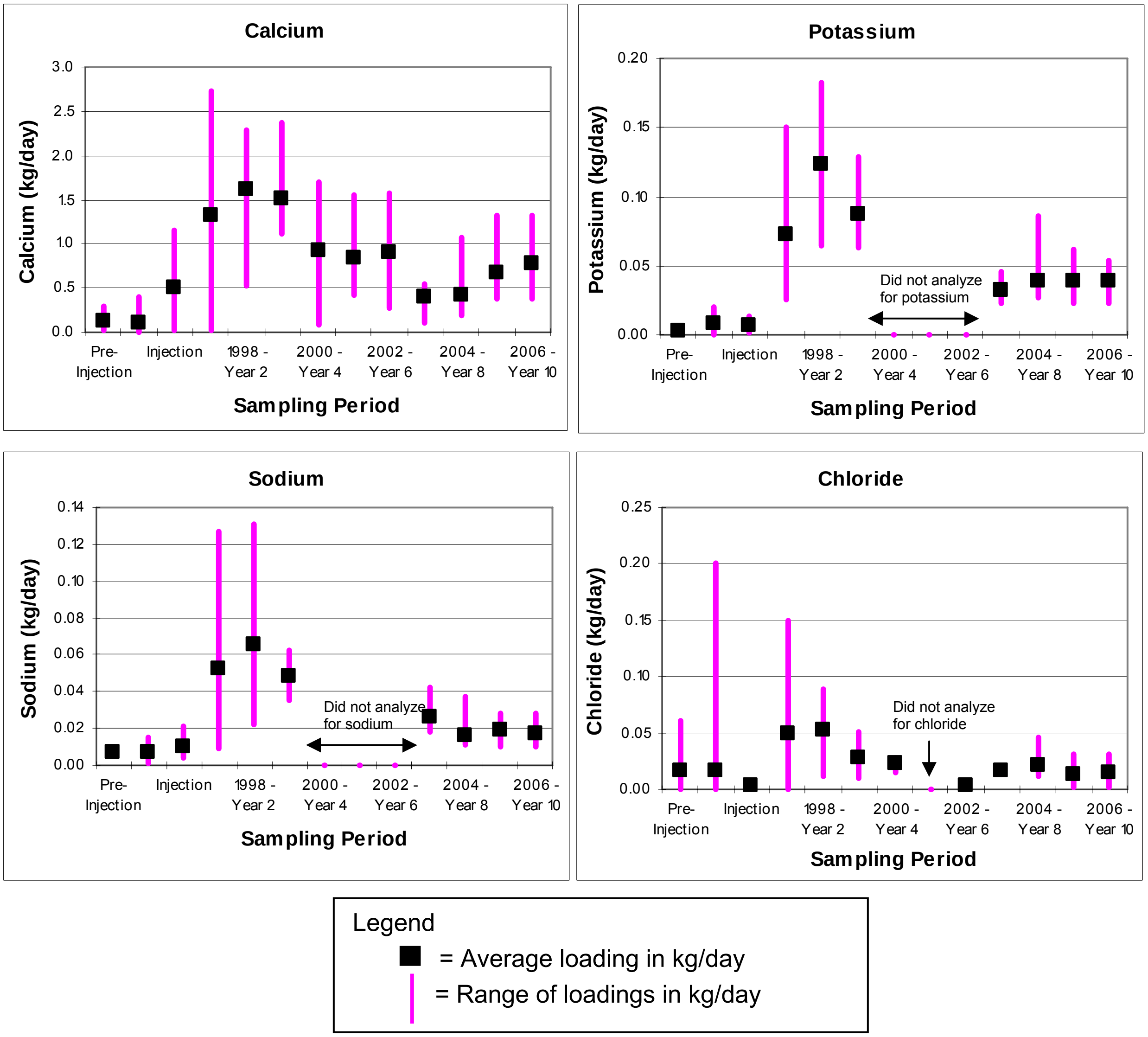
Figure 7
Loading ranges and Averages for AMD Parameters at MO2 Lower Seep



The results show a transient condition of mine water quality during the first year (November 1996 to September 1997) after grout injection. During this time period, the concentrations and loadings for AMD-related parameters increased significantly compared to pre-injection conditions. After that period, the concentrations and loadings gradually decreased to below pre-injection levels. The transient condition is probably due to a combination of factors. One contributing factor is that the grout injection phase could have indirectly caused a temporary increase in acidity when the mine pool was lowered as a result of pumping mine water for grout mixing. The lowering of the mine pool would have exposed previously submerged mine areas to oxidizing conditions, which would have created acid weathering products available for mobilization once the mine pool rose to pre-injection levels. Another contributing factor could have been the re-routing of mine water through previously isolated mine workings. Nonetheless, the water quality data show that the transient condition was a relatively short-lived occurrence.

Figure 8 shows the loadings for other major ions (those not typically associated with AMD) in the mine discharge (calcium, potassium, sodium, and chloride).

Figure 8
Loading ranges and Averages for Other Major Ions at MO2 Lower Seep



The post-injection loadings of calcium, potassium, sodium, and chloride remain elevated compared to pre-injection levels (Figure 8). These are non-toxic elements, and the post-injection concentrations for each of these elements in the mine discharge fall well below their average concentrations in sea water. The post-injection concentration of calcium is less than half of that in sea water (which contains about 400 mg/l calcium). The post injection concentrations of potassium, sodium, and chloride are one or more orders of magnitude below those in sea water (which contains about 400 mg/l potassium, 10,000 mg/l sodium, and 19,000 mg/l chloride).

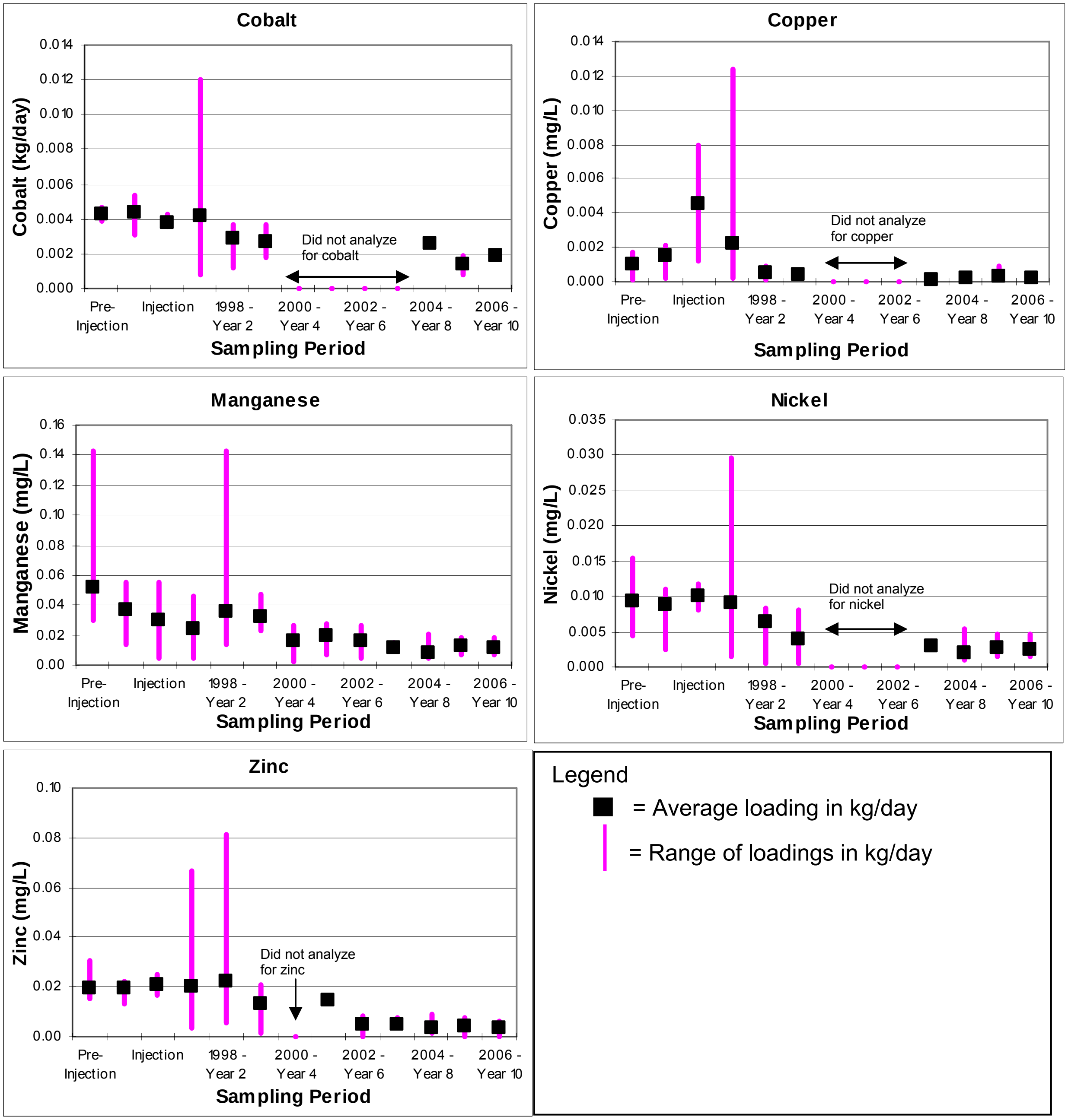
Calcium, potassium, sodium, and chloride are most likely dissolving from the grout into the mine water. Part of the increase in sulfate loading observed during the transition period may also have been due to dissolution of grout components. However, since the grout cores from the mine show that the grout is strong, intact, and competent, dissolution is most likely localized to grout surfaces that are exposed to or in contact with acidic mine waters. In addition, though the levels of the non-AMD major ions remain elevated relative to pre-grouting levels, their concentrations in the mine discharge have gradually decreased in the ten years since injection. This suggests that dissolution rates are slowing. A reduction in the dissolution rate could be due to the formation of a low-solubility surface layer on the grout surface. Such a layer could be formed by the rapid dissolution more soluble grout components from the grout surface, leaving a layer of less soluble grout components, which could behave as a low permeability crust preventing water from reaching the rest of the grout. Another contributing factor could be precipitation and coating by secondary minerals (i.e. iron and aluminum hydroxides) on the grout surface as the chemical conditions within the mine tunnel change.

Trace Elements

Analysis of trace elements in the mine water discharge was also included in the water quality monitoring program, as shown in Table 3. Although a total of 16 trace elements were monitored, the only trace elements that were routinely detected during pre and post-injection monitoring were cobalt, copper, manganese, nickel, and zinc. The water quality data show that there have not been any significant increases in trace element concentrations in the discharge from the Frazee Mine and no trace elements have been detected in the mine discharge that were not present in the pre-injection samples.

Figure 9 summarizes the loading data for copper, cobalt, nickel, manganese, and zinc. As with the AMD-related parameters, the plots show a transition period of elevated concentrations and loadings during the first year after grout injection. Since the second year after grout injection, however, the trace elements concentrations and loadings have consistently fallen within or below those observed prior to injection. In particular, the concentration of copper has fallen to the point that it is often reported as below detection levels in the mine discharge samples.

Figure 9
Loading Ranges and Averages for Trace Metals at the MO2 Lower Seep



Water Quality Within Mine Tunnels

Four mine tunnel piezometers (P-1D, P-6, P-7, and P-9) were installed concurrently with the grout coring operations in 1997. Because these piezometers were installed after injection, there is no pre-injection data for water quality within the mine tunnels. With the exception of pH, the post-injection water quality data for the mine tunnel piezometers is very similar to the data for the mine discharge water quality at the lower seep. The pH within the mine tunnels is slightly higher than that at the lower seep, averaging approximately 4.75 in the 2005 and 2006 samples. This is not unexpected as oxidation reactions are responsible for the low pH of AMD and these reactions are expected to accelerate near the mine discharge point, which is open to atmospheric oxygen.

Shallow Ground Water

Of the seven shallow monitoring wells onsite, the only two that have consistently contained water are MW-4 and MW-6 (Table 2). These monitoring wells are situated downgradient of the Frazee mine and are screened at elevations roughly equal to the mine tunnels. The pre-injection analytical data for these wells showed no evidence of AMD impacts prior to injection. The pH of shallow ground water at MW-4 and MW-6 ranged from 5 to 6. Concentrations of acidity, iron, aluminum and sulfate were much lower than those found within the mine tunnel and the mine discharge water. It is therefore considered likely that MW-4 and MW-6 are screened within a perched water table that infiltrates into the mine.

Post-injection monitoring at MW-4 and MW-6 shows that water quality conditions have not changed. This indicates the grout has not impacted the water flow or ground water quality of shallow ground water outside of the mine tunnels.

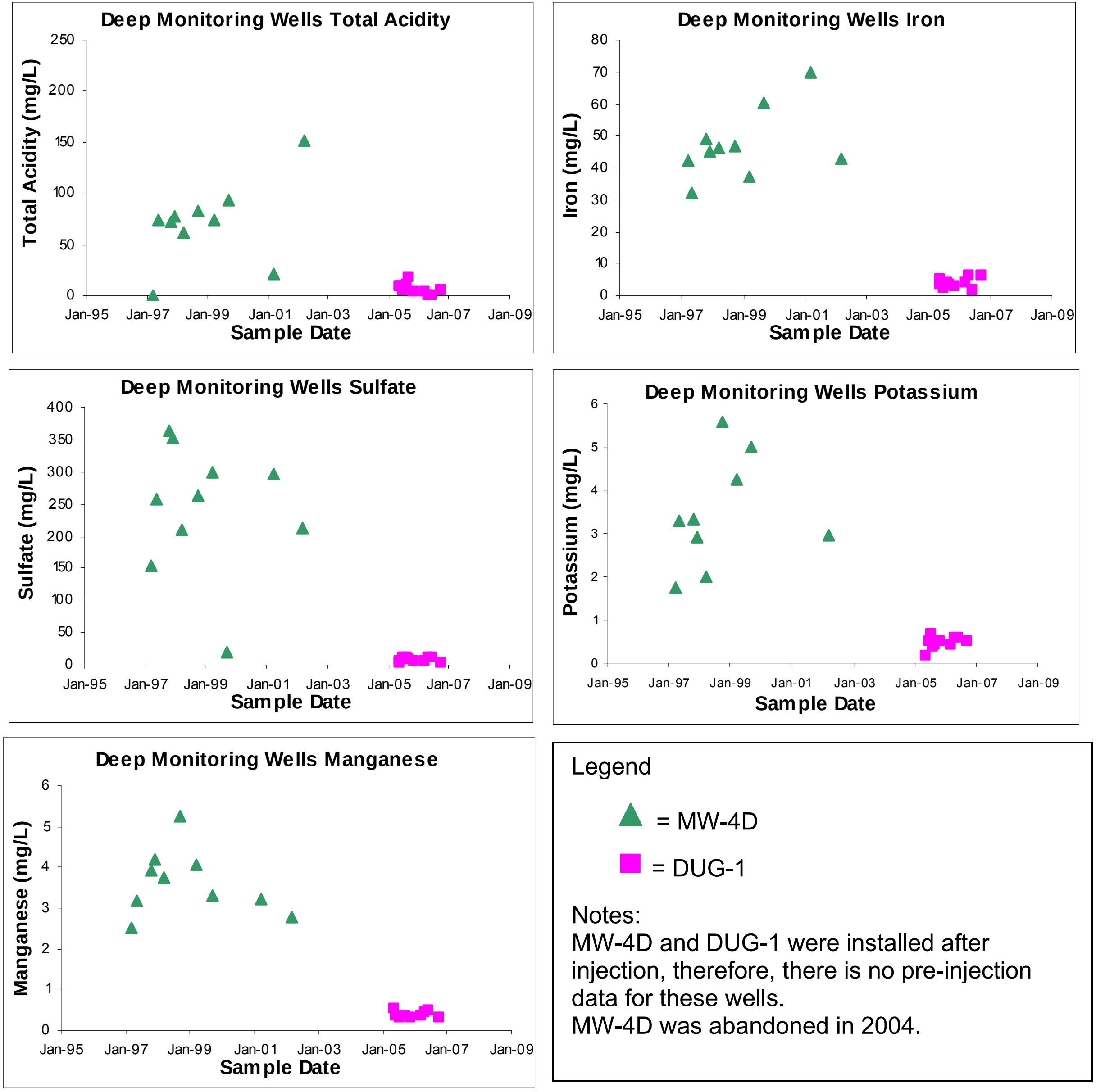
Deep Ground Water

Deep ground water at the site is monitored at wells MW-4D and DUG-1 (Table 2). Both of these deep monitoring wells are screened well below the elevation of the mine tunnels and both were installed after injection was completed, thus, there is no pre-injection deep ground water data for the site. Monitoring well MW-4D was installed shortly after grout injection to monitor the potential for vertical migration of dissolved grout constituents. The well was abandoned in 2004 after a pump became lodged inside it. Deep monitoring well DUG-1 was installed in 2005. This well is situated upgradient of the mine tunnels and provides information about deep ground water that has not been impacted either by AMD or by the grout.

For the most part, the deep ground water data are unremarkable, however it is worth noting that some parameters at monitoring well MW-4D are elevated when compared with the same parameters at well DUG-1. The concentrations of acidity, iron, sulfate, potassium, and manganese are consistently higher at MW-4D than at DUG-1 (Figure 10). Because there is no pre-injection data for the deep wells, it is not certain that these differences are related to grout injection or possibly to vertical leakage of AMD through the bedrock to deeper ground water that may have occurred prior to injection. It does appear, however, that deep ground water quality may have been impacted by AMD and/or by grout constituents. It also appears that the impact, if present, is minor.

Figure 10

Concentration of Selected Parameters in Deep Monitoring Wells



Notes:
MW-4D and DUG-1 were installed after injection, therefore, there is no pre-injection data for these wells.
MW-4D was abandoned in 2004.

DISCUSSION

Mechanisms for Changes in Mine Discharge Water Quality

The goal of the grout injection at the Winding Ridge site was to reduce the formation of AMD within the mine by covering and trapping pyritic mine debris and exposed mine floor and walls with grout, thereby preventing the interactions between water, oxygen, and pyrite, which produce AMD. The changes in water quality observed during post injection monitoring (increased pH, decreased acidity, and decreased concentrations of AMD parameters and trace metals) are consistent with reduced AMD formation within the mine; however, other possible processes that could account for the changes are considered as follows.

Alkalinity Provided by Grout Dissolution

Grout dissolution could improve mine water quality because the grout contains acid neutralizing components such as lime and calcium carbonate minerals. Dissolution of these components consumes hydrogen ions, thereby lowering acidity and increasing pH. The increased pH, in turn, can cause iron and aluminum hydroxides to precipitate, thereby reducing their concentrations in the mine water. Trace metals can often co-precipitate with these hydroxides or adsorb to their surfaces, potentially explaining the reduction in trace metal concentrations as well. These reactions essentially amount to in-situ treatment of AMD, rather than a mechanism to prevent AMD from forming. In addition, although trace metal leaching has not been observed at the Winding Ridge Site, (Figure 9) and little to no trace metal leaching has been observed in laboratory-controlled leaching of CCP-based grout blocks[4]; significant dissolution of the grout material would present the potential to release trace metals from the CCPs into the mine discharge.

The increases in certain major ions after injection (calcium, sodium, potassium, and chloride) suggest that some grout dissolution has occurred at Winding Ridge. However, the grout cores show that, in general, the grout remains intact, strong, and stable after 10 years. In addition, the concentrations and loadings of these major cations have gradually decreased and are asymptotically approaching their pre-injection levels, suggesting that the rate of grout dissolution has slowed.

The decrease in sulfate concentrations over time also suggests that grout dissolution does not account for all of the chemical changes occurring within the mine. Sulfate is present, within the grout, primarily as gypsum ($CaSO4{\cdot}H20$), as well as within the AMD as a product of pyrite oxidation. The behavior or sulfate is not pH dependant, it does not precipitate from solution as iron and aluminum tend to do as pH increases. In addition, the dissolution of gypsum neither consumes nor produces hydrogen ions, meaning that it will neither raise nor lower the pH of the water it dissolves into.

If the acid consuming reactions of lime and calcium carbonate dissolution were entirely responsible for the increased pH and reduced acidity, iron, and aluminum in the mine discharge, one would not expect a similar reduction in sulfate concentrations. In fact, the dissolution of sulfate minerals in the grout, along with the lime and calcium carbonate would continue to release more sulfate. However, the concentration and loading of sulfate in the mine discharge at MO2 has gradually decreased to nearly half the pre-injection levels. This suggests that sulfate production within the mine through AMD-forming reactions has slowed and significant grout dissolution is not believed to be occurring.

Sorption Onto Grout

A second process that could explain the observed increase in pH and decrease in iron, aluminum, and trace metals in the mine discharge is adsorption of these constituents to the grout surface. In this scenario, metal cations adsorb to the predominantly negatively charged grout surface (Figure 11). This mechanism would most likely not affect sulfate concentrations as sulfate is a negatively charged ion.

Figure 11
Adsorption of AMD-Related Cations to a Grout Surface

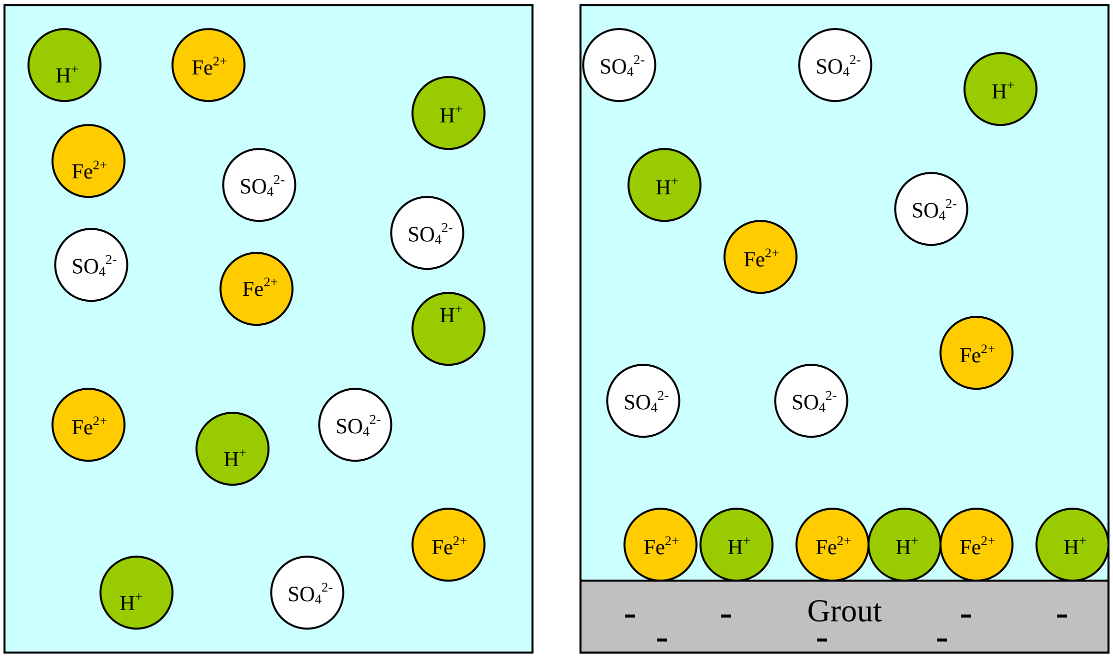
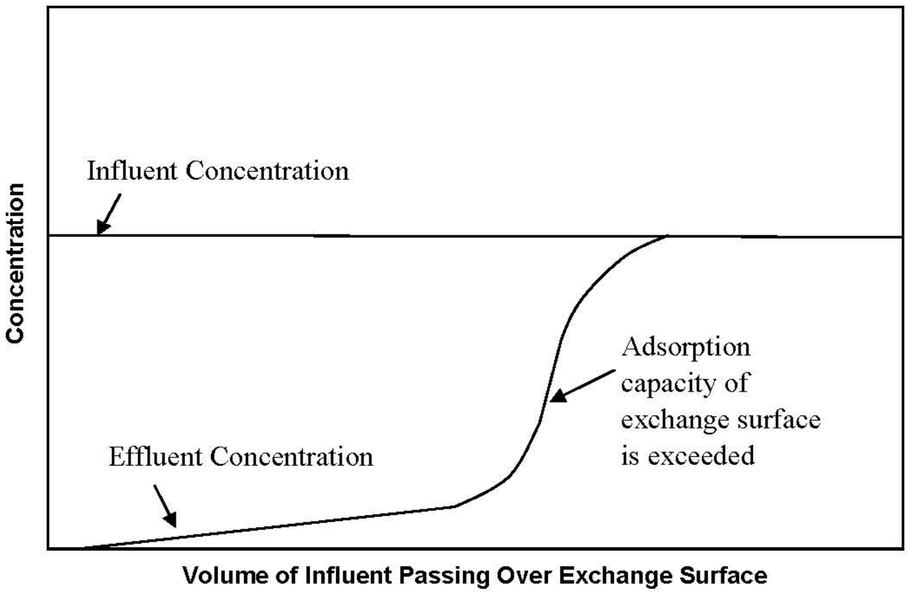


Figure 12 shows a typical curve for the concentrations of a sorbing dissolved parameter after the solution reacts with an exchange surface. An influent solution of constant composition (i.e., water within the mine pool) interacts with an exchange surface having a finite number of exchange sites (i.e., the grout surface). Early on, the exchange surface adsorbs the cationic species (i.e., iron, aluminum, and trace metals) very efficiently, resulting in a very low concentration of these parameters in the early effluent (i.e., the mine discharge). Over time, as the influent solution continues to flow past and interact with the exchange surface, the exchange sites are filled and the grout adsorbs cations less efficiently, leading to gradually increasing concentrations of these parameters in the effluent. At some point, the exchange sites are completely filled, the grout surface can no longer adsorb additional cations, and their concentrations in the mine discharge quickly rebound to match the influent concentration. This phenomenon is sometimes referred to as “breakthrough.”

Figure 12
Typical "Breakthrough" Pattern for Saturation of an Exchange Surface



The concentrations of iron, aluminum, and trace metals observed at Winding Ridge during the last ten years of post-injection monitoring do not match the pattern for a breakthrough curve as described above. The concentrations and loadings of iron, aluminum, and trace metals increased sharply immediately after the grout was injected, then gradually decreased to below pre-injection levels. In addition, as mentioned above, sorption would not be expected to significantly affect sulfate concentrations, but sulfate concentrations and loadings in the mine discharge have decreased by approximately 50%. Therefore, while sorption processes may be occurring within the mine, they alone do not readily explain the water quality patterns observed at Winding Ridge.

Thus, analysis of the water quality data and trends from Winding Ridge suggest that the changes in water quality observed since injection are due, in large part, to reduced AMD formation within the mine as a result of reduced contact between water and pyrite-containing mine debris.

Grout Injection vs. Traditional Treatment Methods

Traditional methods of addressing AMD typically involve pH adjustments at the discharge point where AMD leaves the mine. These methods treat the mine water using acid-neutralizing compounds like limestone, hydrated lime, or sodium hydroxide.

While generally effective at raising the pH of the AMD, they may be less effective at treating other AMD parameters like iron, aluminum, and sulfate. In addition, these methods do not address the source of the problem and they represent potentially perpetual treatments with no end to associated operation and maintenance costs, rather than prevention techniques.

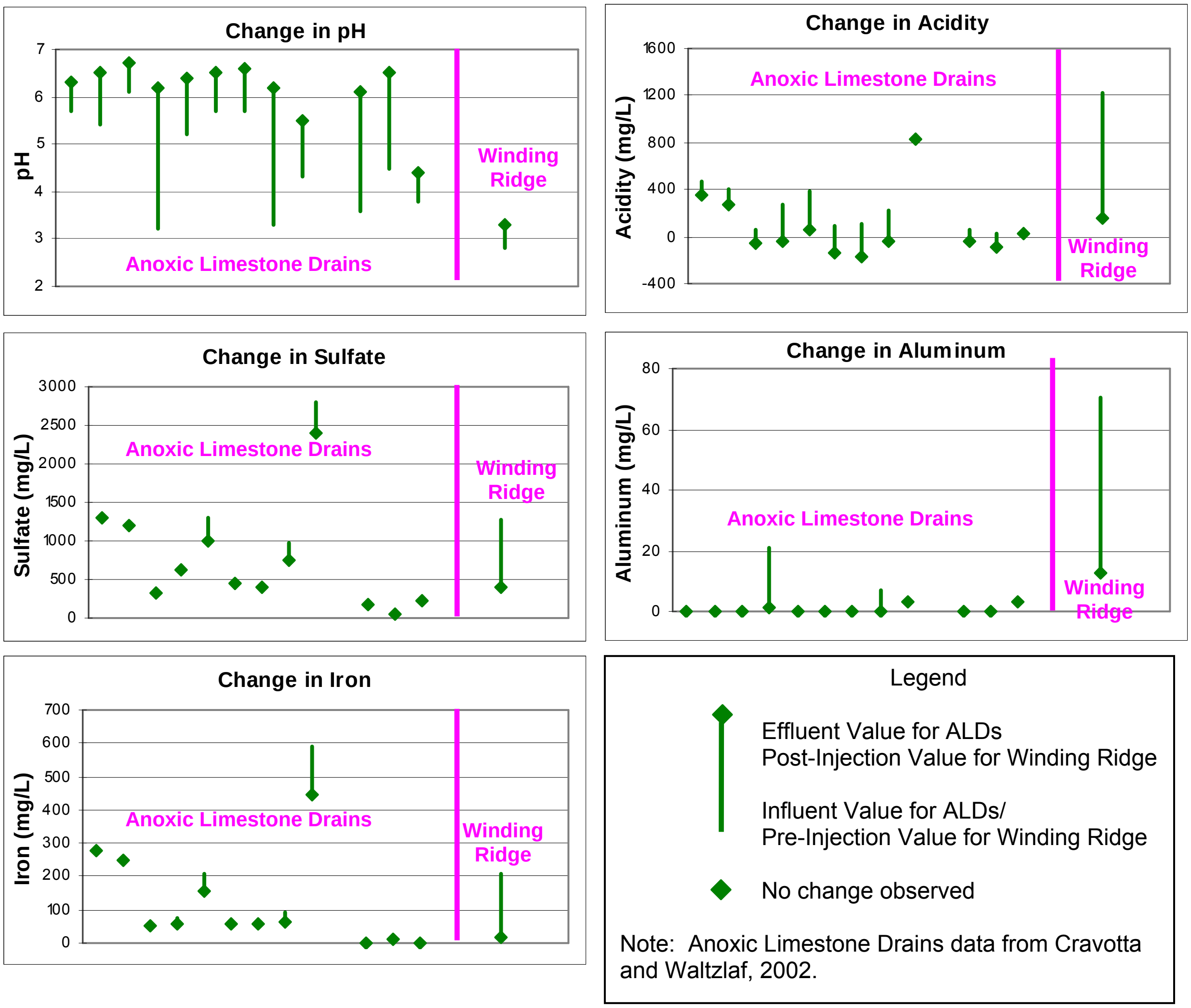
Anoxic Limestone Drains (ALDs)

ALDs are a common passive AMD treatment technique. The AMD is directed through buried limestone channels. As the limestone dissolves, it neutralizes the acidity of the AMD and raises the pH of the water. The channels are buried in order to keep oxygen out of the system. Keeping the system anoxic prevents the precipitation of iron hydroxides within the channels where it would coat the limestone, preventing it from dissolving and eventually causing the system to fail (a phenomenon referred to as "armoring"). These systems work best for AMD discharges that contain little to no dissolved aluminum. Aluminum hydroxides will precipitate with increasing pH just as iron hydroxides do, however, unlike iron hydroxides, their precipitation cannot be prevented by maintaining anoxic conditions. Armoring due to precipitation of aluminum hydroxides is a common cause of ALD failure.

Figure 13 summarizes the total changes in water quality observed at the lower seep at Winding Ridge compared with published changes in water quality observed for AMD that has been treated using ALDs[5]. The bars for Winding Ridge represent long-term changes (average pre-injection concentrations vs. average 2006 concentrations) whereas the ALD bars represent the average quality of water entering the ALD vs. the average water quality exiting the ALD.

While the Winding Ridge project has not achieved the increases in pH or alkalinity observed with most of the ALD systems, the Winding Ridge project has, over time, achieved much more significant reductions in acidity, sulfate, iron, and aluminum than typically observed at ALD systems. It should be noted again that high concentrations of aluminum, such as those observed at the Winding Ridge site are problematic for ALD systems due to armoring. The grouting approach used at Winding Ridge is not susceptible to this type of failure.

Figure 13
Comparison of Winding Ridge Grout Injection to ALDs



Note: Anoxic Limestone Drains data from Cravotta and Waltzlaf, 2002.

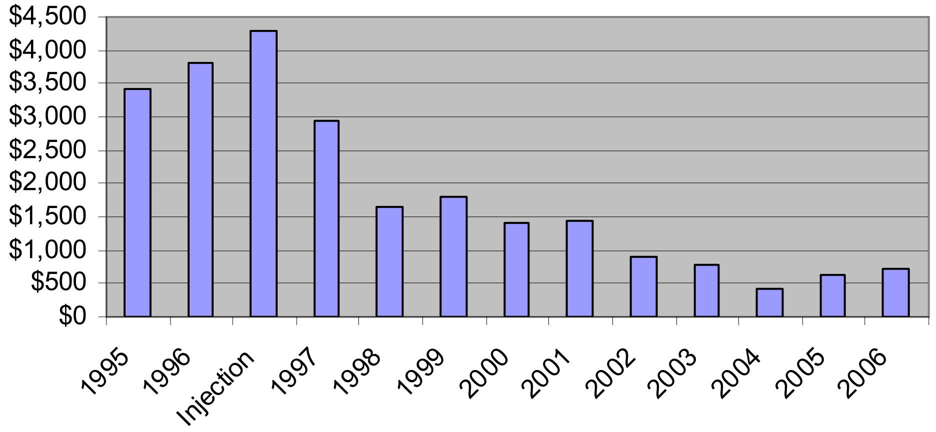
Chemical Neutralization

A common active treatment method for AMD is to add acid-neutralizing chemicals in powder or liquid form to the mine discharge water via a doser or similar delivery mechanism. Commonly used chemicals include crushed limestone, hydrated lime, caustic soda, and anhydrous ammonia. Like ALDs, these active treatment systems can be expected to raise the pH of acidic discharges very effectively due to the nature of the chemicals used. However, these systems can also generate large quantities of iron and aluminum hydroxide sediment downstream of the chemical delivery point. Unlike the aluminum hydroxides that can precipitate within ALDs, this material does not directly hinder the functionality of the treatment system. It can, however, significantly increase the sediment load in any stream receiving the treated discharge. Increased sediment loading of this type can choke stream vegetation, negatively impact overall stream health, and in some cases, is aesthetically very unappealing.

Grout injections, like the one performed at Winding Ridge could be used as pre-treatment approaches to reduce the load of acidity or other dissolved constituents that must be addressed by treatment systems. This would reduce the amount of chemical required to treat the AMD and consequently lower the annual maintenance costs for the system. Lowering the load of metals like iron and aluminum that reach the treatment point could also reduce the amount of hydroxide precipitate (sediment) generated downstream of the treatment point as well.

As an example, the computer program AMDTreat[6] was used to calculate the chemical costs to actively treat pre and post-injection discharge at Winding Ridge. The average flow rate from both the upper and lower seeps was used to calculate the annual volume of water discharging from the mine. The annual cost of chemicals needed to treat this volume of water with hydrated lime was calculated (only the annual cost of chemicals required for treatment was calculated as it was assumed that the costs to construct the treatment system would not change for pre-injection vs. post-injection conditions). The cost of hydrated lime was assumed to be $0.022 per kilogram. Transportation costs, which can be a significant cost component, are not included in the analysis. Based upon these assumptions, the annual cost to treat the pre-injection discharge using hydrated lime was estimated at $3,500 per year, while the annual cost to treat the 2006 post-injection discharge using the same treatment method was estimated at $720 per year (Figure 14). Therefore, mine grouting represents a significant reduction in long-term maintenance costs if an active treatment system were to be installed at this site.

Figure 14
Estimated Annual Costs to Treat Frazee Mine AMD Using Hydrated Lime After Grout Injection*



*Material Transportation costs not included.

CONCLUSIONS

The CCP grout placed in the Frazee Mine remains stable ten years after injection. Although the acid discharge from the mine has not been eliminated, significant improvements in the water quality of the mine discharge have been achieved. The average pH of the discharge has increased by approximately 1 pH unit and the average acidity of the mine discharge has decreased by as much as 80%. The concentrations and loadings of other AMD-related parameters (Fe, Al, and sulfate) and various trace metals have also decreased relative to their pre-injection levels.

Some dissolution of the grout has occurred, as indicated by the concentrations and loadings of nontoxic major ions (Ca, K, Na, and Cl) that increased during injection and remain at or above pre-injection levels. The concentrations and loadings of these parameters in the mine discharge have decreased steadily over the past ten years since injection, indicating that dissolution of the grout is slowing. Trace metals do not appear to be leaching from the grout into the mine water. No trace metals have been detected in the mine discharge that were not detected prior to injection (in other words, no new trace metals have been detected since injection) and the concentrations of trace metals that were detected prior to injection are currently below their pre-injection levels, and in some cases, are found to be below detection levels reported by the laboratory.

Analysis of samples from shallow ground water monitoring wells at the site show that shallow ground water outside of the mine has not been impacted by the grout. Analysis of deep ground water samples indicates that there may have been some impacts to deeper ground water due to AMD and to grout injection. These impacts, however, appear to be minor.

The results of the Winding Ridge Project show that CCPs can be used successfully to create a grout for mine backfilling, which both reduces the volume of CCPs that must be placed in landfills and mitigates the environmental impacts associated with AMD. The technique of grouting mines to prevent the formation of AMD offers several benefits over traditional AMD treatment methods. Alternatively, mine grouting could be used in conjunction with traditional AMD treatment methods to reduce the costs of annual maintenance for these systems.

Building upon the success of the Winding Ridge Project, PPRP is proposing to implement CCP-grout injection projects at the Coketon/Kempton Mine Complex (Coketon/Kempton Complex). The Coketon/Kempton Complex is Maryland's largest source of AMD as it discharges thousands of pounds (thousands of kilograms) of acidity per day into Laurel Run. PPRP is working jointly with the Kempton Work Group, which includes MDE and private industry, to fund, design and implement AMD abatement projects at this site. The Coketon/Kempton Complex consists of nine interconnected mines, and covers twelve square miles (thirty one square kilometers). As such, it provides an enormous opportunity to beneficially use millions of tons of CCPs for the betterment of Maryland's terrestrial and aquatic resources, and to demonstrate CCP use under various conditions.

In 2003, a CCP grout was used to construct a seepage barrier at the Kempton Manshaft, a former mine shaft, which acts as a conduit directing good quality ground water into the Kempton mine pool. In addition, PPRP is planning another demonstration project in a small, isolated section of the Coketon/Kempton Complex known as Siege of

Acre. The Siege of Acre project would involve the injection of a CCP grout to coat acid-producing mine pavement with the goal of preventing contact between water and pyritic materials without completely filling the mine.

In addition, the PPRP has completed a cost optimization study to evaluate the use of CCPs for deep mine restoration. Specifically, the Cost Optimization Study is considering the means, methods, and associated costs to use CCPs from the AES Warrior Run power plant for deep mine restoration in the nearby Georges Creek Basin[7].

Because leaching of trace metals and other elements from CCPs and CCP-based grouts used to mitigate AMD continues to be of concern to many citizens and government entities, PPRP has continued to research the effect of acidic waters on CCP-based grouts as they would be emplaced into mine environments. Specifically, PPRP in conjunction with other research partners is conducting block weathering experiments in which cured blocks of CCP-based grout material were subjected to continuously running low pH-adjusted water over long periods of time[4].

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