### AN UPDATE ON THE WINDING RIDGE DEMONSTRATION PROJECT FOR THE BENEFICIAL USE OF CCBS TO REDUCE ACID FORMATION IN AN ABANDONED UNDERGROUND MINE<sup>1</sup>

by

### Leonard Rafalko and Paul Petzrick<sup>2</sup>

Abstract. The Maryland Department of Natural Resources Power Plant Research Program (PPRP) and the Maryland Department of the Environment Bureau of Mines (MDE) have undertaken the Western Maryland Coal Combustion By-Products (CCB)/Acid Mine Drainage (AMD) Initiative. The Initiative is a joint effort with private industry to demonstrate the beneficial application of CCBs to create flowable grouts for injection into underground mines to reduce the formation of acidity (i.e., AMD). The Initiative commenced in 1995 with the Winding Ridge Project, which is its first demonstration project of this technology. For this project, 5,600 cubic yards of CCB grout were injected into the Frazee mine in 1996. The grout consisted of 60% FBC product, and 20% Class F fly ash and FGD product, mixed with mine water. Over the course of the project, an extensive set of water quality data has been generated. Water quality monitoring started prior to grout injection in 1995, and continues through the current time. The purpose of this paper is to present the key findings of post-injection monitoring of the mine discharge water quality. Postinjection monitoring shows that there have not been any significant increases in AMD-related parameters or trace elements in the mine water other than short-term or transient water quality changes immediately after injection. During this transient period, mine discharge showed elevated levels of iron, aluminum, total acidity and lower pH, as well as certain trace elements. These changes are attributed in part to flushing acid waters from the mine during injection. About 1 year after grout injection, iron, aluminum, total acidity and trace element concentrations and loadings dropped to levels comparable to or below pre-injection conditions. pH has also trended subtly upward over this time. Calcium and sulfate levels have been elevated since injection indicating some grout dissolution. Since grout cores recovered from the mine show that the hardened grout is intact and competent, and has retained its strength and low permeability, any dissolution appears to be limited to grout surfaces exposed to or in contact with acid mine water.

Additional Key Words: Maryland Department of Natural Resources Power Plant Research Program, Maryland Department of the Environment Bureau of Mines, Winding Ridge Project, Acid Mine Drainage, Fluidized Bed Combustion, Flue Gas Desulfurization.

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### Introduction and Purpose

The Maryland Department of Natural Resources Power Plant Research Program (PPRP) and the Maryland Department of the Environment (MDE) Bureau of Mines (BOM) have undertaken the Western Maryland Coal Combustion By-products/Acid Mine Drainage (AMD) Initiative. The Initiative is a joint effort with private industry to demonstrate the beneficial application of coal combustion by-products (CCBs) to create flowable grouts for placement in underground coal mines to reduce the formation of acid. The Initiative is a key component of Maryland's overall ash utilization program to promote and expand the beneficial use of all CCBs. Ultimately, the Initiative is targeting significant acid reduction at large AMD sources in Maryland, such as the Kempton Mine Complex.

The Initiative is a multi-year project that started in April 1995 with the Winding Ridge Project. The Winding Ridge Project involved the injection of a 100 percent CCB-based grout into the Frazee Mine, which is a small 10-acre, underground coal mine in Garrett County, Maryland.

In 1998, the authors reported on the means and methods of the grout injection phase of the Winding Ridge Project, and presented post-injection water quality data for the first year following injection (Rafalko and Petzrick, 1998). Since that time, an extensive set of water quality monitoring data has been generated for the project, and continues through the current time. The purpose of this paper is to present the key findings to date of the post-injection monitoring of the mine discharge water quality.

### Review of the Physiographic Setting and Mine Hydrology of the Frazee Mine

The Frazee Mine is located atop of Winding Ridge in Garrett County, Maryland (Figure 1). The Frazee 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 ranges from 1.0% to 3.5%. Acid-base accounting performed on overburden samples indicates that a small (15 to 46 centimeters 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. Ground water monitoring wells installed at upgradient and downgradient locations showed that the Frazee Mine occurs in unsaturated bedrock, and that the regional ground water table is approximately 15 meters below the mine pavement.

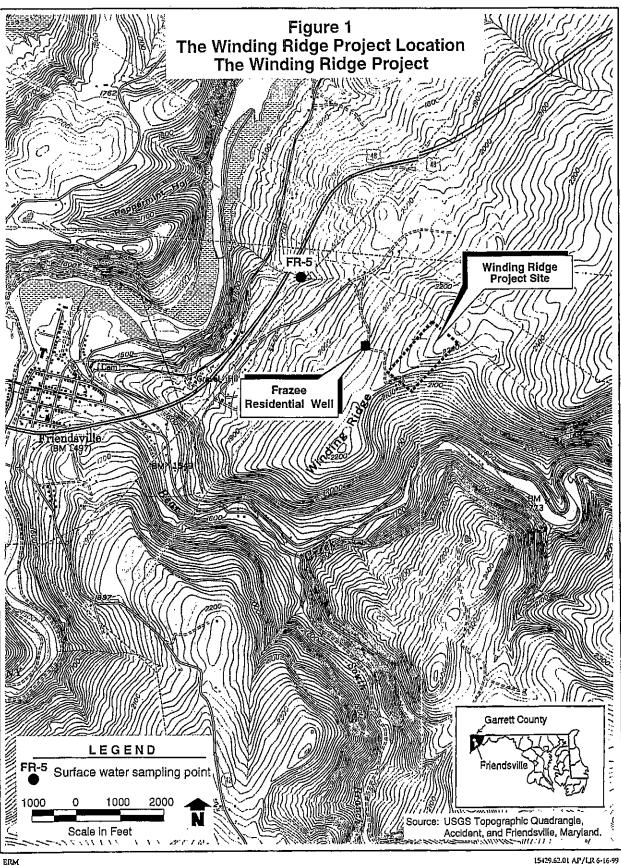
Infiltrating precipitation impounded within the Frazee Mine created a pre-injection mine pool of at least 550,000 gallons. This mine pool resided in the lower tunnel, while the upper tunnel was predominantly dry. Although there are four known mine entries, the only mine discharge is from Mine Opening No. 2 (MO2). At MO2, discharge occurs from a lower and upper seep. The elevation of the lower seep is about 3 meters below the mine pool elevation, and flow is continuous at about 2 gallons per minute. The elevation of the upper seep coincides with the mine pool elevation. Consequently, flow from the upper seep is intermittent depending on the mine pool elevation. When the mine pool elevation is above the upper mine seep, flow occurs, generally at about 3 to 5 gpm. Otherwise, the upper seep is dry.

The pre-injection water quality from MO2 is typical of AMD-quality water. The pH values ranged from 2.50 - 3.45 standard units, and sulfate concentrations ranged from 80 to 1,800 milligrams per liter (mg/L). TDS ranged from about 160 to 2,900 mg/L, and total acidity ranged from 50 to 2,400 mg/L. The upper range of iron concentrations was 250 to 300 mg/L.

### CCB Grout Formulation and Mine Injection Phase

The CCBs used for the Project were FGD byproduct (forced oxidation system) and Class F fly ash from Virginia Power Company's Mt. Storm power plant, and FBC by-product from the Morgantown Energy Associates 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 by-product, 20% FGD by-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 moisture content was about 57% on a dry weight basis. Grout samples collected during injection showed a spread of about 20 centimeters, and a 28-day unconfined compressive strength of 520 pounds per square inch (psi).



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Full-scale injection began on 7 October 1996 and ended on 8 November 1996. More than 5,600 cy of grout were injected into the Frazee Mine, consisting of 3,800 tons of FBC ash, and 1,200 tons each of fly ash and FGD by-product. The project used 520,000 gallons of water, consisting of 449,000 gallons of untreated mine water (pH of about 3) and 71,000 gallons of river water.

### Post-Injection Monitoring Results

### In-Situ Grout Sampling and Results

In September 1997, nearly one year after grout injection was completed, nine coreholes were drilled at the Frazee Mine. The objective was to collect grout core samples from the mine to evaluate weathering processes that had occurred to the grout in the mine environment. The corehole locations targeted injection boreholes in both the wet and dry parts of the mine.

In general, the grout cores 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. In some cores, it was evident that shale from the collapsed mine roof was entrained by the grout flow during grout injection. The permeability ranged from  $6.02 \times 10^{-8}$  to  $1.89 \times 10^{-6}$  cm/sec. The unconfined compressive strengths ranged from about 560 psi to 1,400 psi. Grout cores collected in 1998 and 1999 were also in good shape, and generally showed little evidence of in situ weathering.

### Post-Injection Mine Hydrology

AMD continues to flow from the mine from ungrouted areas and other unknown voids. Postinjection water level measurements from piezometers in the lower mine tunnel show that the mine pool elevation is essentially the same as its elevation prior to injection. This information indicates that the grout in the mine has not created new sub-pools within the lower tunnel or raised the water level such that the pool is contacting new pyritic materials.

AMD seepage from the Frazee Mine has been measured at the lower and upper seep at MO2 since 1995. The flow data from MO2 show that the Frazee Mine hydrologic conditions have not changed since grout injection, which is consistent with the hydrologic conditions indicated by the water level data from the piezometers. At the lower seep, mine seepage has been continuous, at flow rates of about 1 to 2 gpm. Conversely, the discharge from the upper seep is intermittent, and dependent on the mine pool elevation.

### Post-Injection Monitoring Results of Mine Discharge

The analytical parameters for mine discharge, mine water, ground water and surface water included those indicative of AMD, such as pH, total acidity, iron, sulfate, and aluminum. The water samples were also analyzed for trace elements such as arsenic, copper and chromium.

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 ribs as the mine pool elevation fluctuates.

### AMD-Related Parameters and Other Major Ions

Table 1 summarizes the pre and post-injection water quality results for AMD-related parameters and other major ions for the lower and upper seeps at MO2, and piezometers constructed in the lower mine tunnel. The results show that there have been no significant increases (or decreases in the case of pH) in AMDrelated parameters in the mine water.

The pH data for the lower seep and upper seeps are presented in the temporal plots in Figure 2. At the lower seep, pH fluctuated within the historically observed range of values during and immediately after gront injection. Since injection, however, pH has exhibited an upward trend at the lower seep. Conversely, the upper seep has not shown any appreciable change in pH since injection. This observation is attributed to the recharge of hydrogen ions to the mine water as the mine pool rises and falls to expose pyritic strata to repeated wetting and drying cycles.

Figures 3 and 4 show temporal plots of concentrations and loadings for acidity and sulfate for the lower and upper seeps. The results show that the water quality for the mine discharge exhibited a transient condition during the first year after grout injection. This transient condition is illustrated by Figure 5, which clearly shows the differences in concentration ranges and averages for acidity, iron and sulfate from pre-injection through post-injection

# Table 1Summary of Frazee Mine Water QualityThe Winding Ridge Project

Parameter	Range of Concentration Values for Lower Seep				Range of Concentration Values for Upper Seep				Mine Piezometers
	Pre-Injection 1/95 - 9/96	Injection	Post-In	jection	Pre-Injection	Injection	Post-Injection		Post-Injection <sup>(5)</sup>
		10/96 - 11/96	11/96 - 9/97	10/97 - 3/99	1/95 - 9/96	10/96 - 11/96	11/96 - 9/97	10/97 - 3/99	10/97 - 3/99
рН	2.50 - 3.04	2.50 - 3.01	2.68 - 3.37	2.92 - 3.32	2.77 - 3.45	2.50 - 3.20	2.86 - 3.3	2.84 - 3.34	3.49 - 6.12
Acidity, mg/L	227 - 2,361	1,218 - 1,910	204 - 2,902	304 - 1,002	50 - 957	128 - 515	344 - 2,519	167 - 630	91 - 439
Major Ions, mg/L									
Iron	35 - 329	152 - 320	42 - 328	6 - 156	3 - 151	8 - 50	11 - 320	13 - 95	28 - 92
Calcium	<1 - 68	3 - 242	3 - <b>49</b> 0	70 - 418	1 - 36	31 - 520	7 - 354	112 - 309	183 - 489
Magnesium	13 - 97	45 - 64	21 - 69	23 - 52	3 - 47	12 - 22	19 - 76	14 - 44	17 - 48
Potassium	<1 - 3	<1-3	<1 - 22	11 - 27	<1 - 3	1.5 - 2	2.4 - 17	8 - 15	17- 74
Sodium	<1-3	1-5	4 - 22	5 - 15	<1 - 3	<1-1	4 - 12	4 - 11	10 - 18
Sulfate	140 - 1,769	821 - 4,201	496 - 5,840	870 - 1,858	87 - 761	209 - 2,948	472 - 2608	500 - 1,513	620 - 1,600
Chloride	<1 - 37	<1 - 2	ND - 27	ND - 17	<1 - 14 <sup>(4)</sup>	1.5	1 - 18	3 - 9	5 - 19
Trace Elements <sup>(1)</sup> , mg/L									
Aluminum	20 - 110	55 - 175	28 - 250	10 - 78	5 - 48	12 - 35	22 - 175	18 - 62	5 - 28
Cobalt	0.62 - 0.93 <sup>(2)</sup>	0.76 - 0.89	0.58 - 2	0.31 - 0.69	0.04 - 0.39 <sup>(3)</sup>	0.08 - 0.11	0.30 - 1	0.18 - 0.56	0.02 - 0.341
Copper	0.02 - 0.32	0.29 - 1.76	0.14 - 2	0.03 - 0.17	0.02 - 0.24	0.03 - 0.04	0.09 - 1.09	0.08 - 0.12	ND - 0.08
Manganese	3 - 16	1 - 12	2 - 13	2 - 17	0.48 - 5.7	1.6 - 2.8	1.4 - 6	1.2 - 4.3	2 - 5.5
Nickel	<1 - 2	2 - 3	1-5	0.20 - 2	0.08 - 1.78	0.23 - 0.24	0.67 - 2.74	0.38 - 1.15	0.57 - 1
Zinc	3 - 4	4 - 5	3 - 11	2 - 12	0.26 - 1.75	0.56 - 0.64	1.35 - 6	0.89 - 2.3	0.5 - 3

Notes:

ND - Not Detected

(1) - Antimony, Arsenic, Barium, Beryllium, Cadmium, Chromium, Lead, Mercury, Selenium, Silver, Thallium, and Vanadium were sporadically

detected, in generally less than 25% of the mine discharge samples.

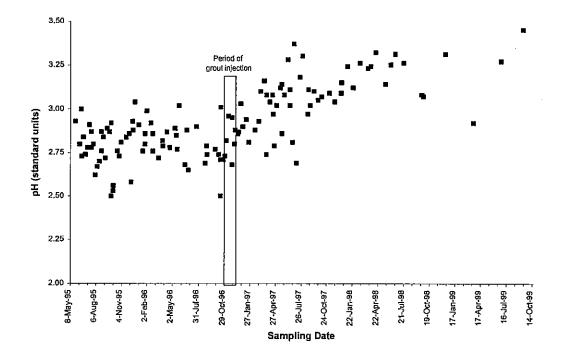
(2) - Does not include anomalous result of 42 mg/L on 10/6/95.

(3) - Does not include anomalous result of 6.3 mg/L on 11/20/95.

<sup>(4)</sup> - Does not include anomalous result of 42 mg/L on 1/4/96.

<sup>(5)</sup> - Range of concentration values.

Figure 2 pH Results for the Upper and Lower Seeps at Mine Opening 2



A) Lower Seep (continuous flow)

B) Upper Seep (intermittent flow)

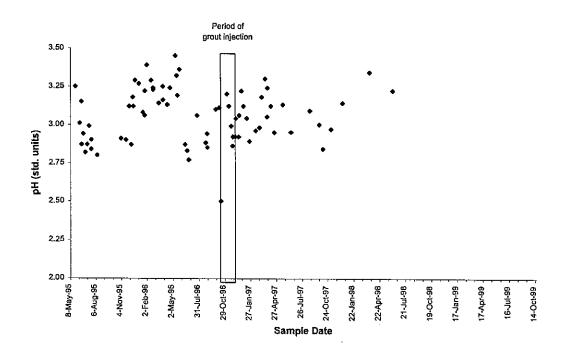
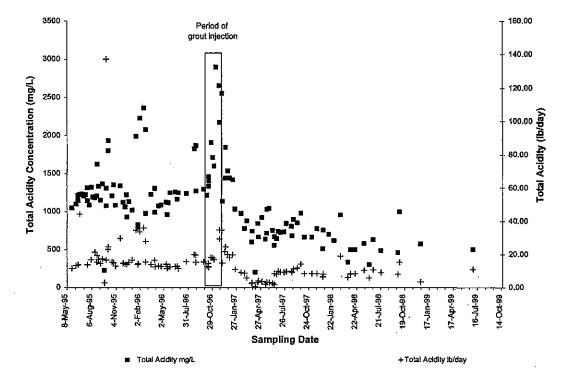
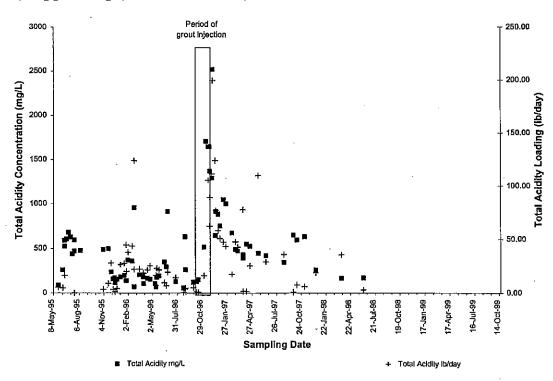


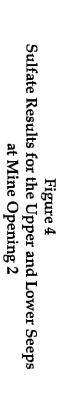
Figure 3 Total Acidity Results for the Upper and Lower Seeps at Mine Opening 2

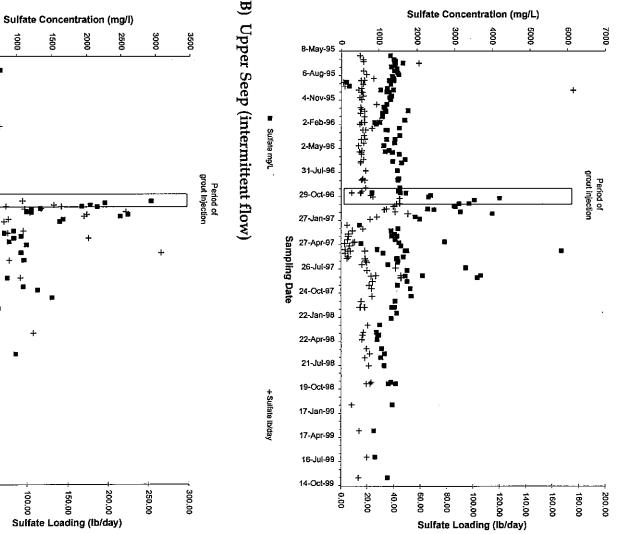
## A) Lower Seep (continuous flow)



## **B)** Upper Seep (intermittent flow)







A) Lower Seep (continuous flow)

300

+ Sulfate Ib/day 1000

500

C 8-May-95

6-Aug-95

4-Nov-95

2-Feb-96

2-May-96

31-Jul-96

29-Oct-96

27-Jan-97

27-Apr-97

26-Jul-97

24-Oct-97

22-Jan-98

22-Apr-98 21-Jul-98

19-Oct-98

17-Jan-99

17-Apr-99

16-Jul-99

14-Oct-99

0.00

50.00

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Sample Date

Sulfate mg/L

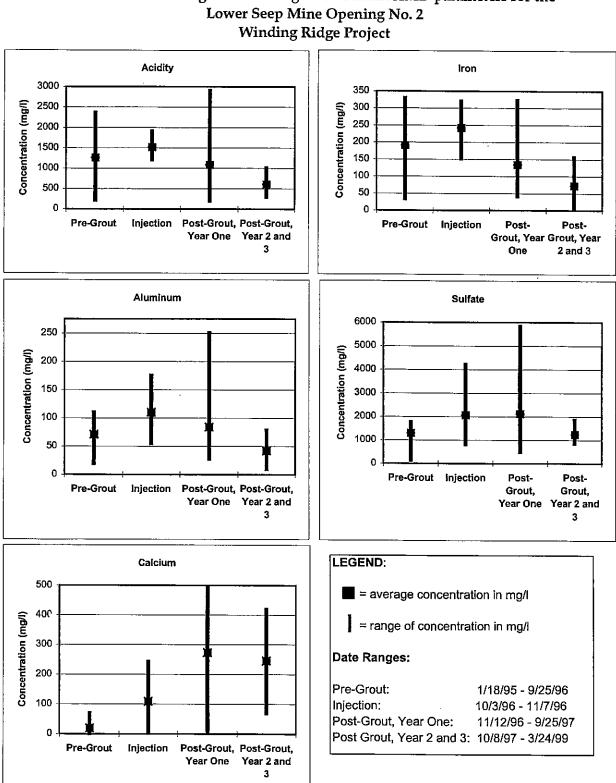


Figure 5 Concentration Ranges and Averages for Certain AMD parameters for the

monitoring data from March 1999. During the first year (November 1996 to September 1997) after grout injection, the concentrations and loadings for AMDrelated parameters increased significantly compared to the pre-injection conditions. Concentrations and loadings have since leveled off during the second and third years (October 1997 to March 1999) after grout injection.

The transient condition is probably due to a combination of factors. One contributing factor is that the grout injection phase could have indirectly caused an 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, which would have oxidized and created acid weathering products available for mobilization once the mine pool rose to preinjection levels. Another contributing factor to the transient condition 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 occurrence.

To assess the water quality data from the lower and upper seep further, the difference between the pre-injection and post-injection water quality for AMD-related parameters was evaluated by co-plotting pre and post-injection concentrations for mine discharges of similar magnitude. This method was selected to allow a direct comparison of pre and postconcentration data under normalized flow conditions. Accordingly, Figures 6 and 7 were prepared by plotting pre and post-injection concentrations for total acidity and sulfate, respectively, for mine discharges of similar magnitude from MO2. Note that the data during the transient period were not included in these analyses since they are not considered to be representative of the water quality that would discharge from the Frazee Mine over the long-term.

The analyses show that the post-injection concentrations for total acidity, iron and sulfate at the lower seep all fall within or below the pre-injection concentrations. The results for the upper seep show some post-injection concentrations above per-injection concentrations for similar flows. This is not considered significant as the upper seep has been dry for the majority of monitoring events after grout injection, and therefore contributes little to the total discharge emanating from MO2.

Other major ions, such as calcium, potassium and sodium, which are non-toxic, do not exhibit the same pattern as the AMD-related parameters. Calcium levels, for example, were negligible prior to injection but have remained elevated since grout injection, ranging from about 150 to 500 mg/L. The persistent calcium as well as sulfate concentrations suggest, to some extent, that some grout is dissolving. As mentioned previously, however, the grout cores from the mine show that the grout is strong, intact and competent, with a low permeability. Therefore, any dissolution is most likely localized to grout surfaces that are exposed to or in contact with acidic mine waters.

### Trace Elements

Table 1 also summarizes the results of the trace element analyses for mine water samples collected from the lower and upper seeps at MO2, and the piezometers. The only trace elements that were routinely detected during pre and post-injection monitoring were aluminum, cobalt, copper, manganese, nickel, and zinc.

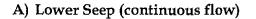
Collectively, the water quality data to date show that there have not been any significant increases in trace elements in the discharge from the Frazee Mine. In fact, the water quality monitoring data show that all trace elements detected during post-injection monitoring were also detected during pre-injection monitoring. There was no single trace element present in the mine discharge after injection that was not present in the pre-injection mine discharge.

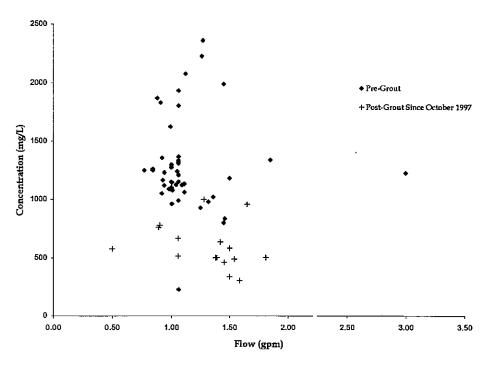
Figures 8 and 9 show temporal plots for aluminum and copper (the plots are similar for cobalt, nickel, manganese, and zinc). As with the AMDrelated parameters, the plots show a period of transition for the first year following grout injection. By the second year after grout injection, however, the trace elements have consistently been within or lower than their observed ranges during pre-injection.

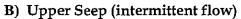
The difference between the pre-injection and post-injection water quality for the trace elements was evaluated in the same manner described above for the AMD-related parameters. Figures 10 and 11 were prepared by co-plotting pre and post-injection concentrations for aluminum and copper (the results were similar for cobalt, manganese, nickel, and zinc), respectively, for mine discharges of similar magnitude from MO2.

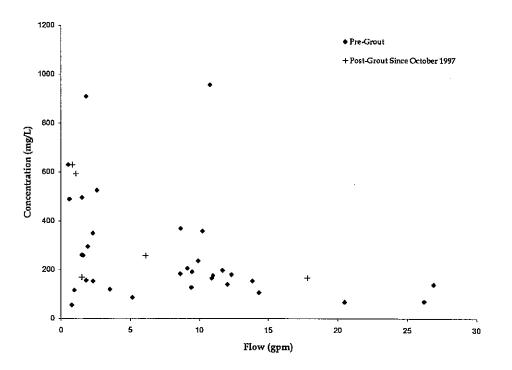
For the lower seep, the analyses show that the post-injection concentrations for aluminum and copper all fall within or below the pre-injection concentrations.

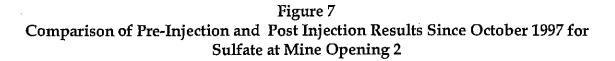
## Figure 6 Comparison of Pre-Injection and Post Injection Results Since October 1997 for Total Acidity at Mine Opening 2

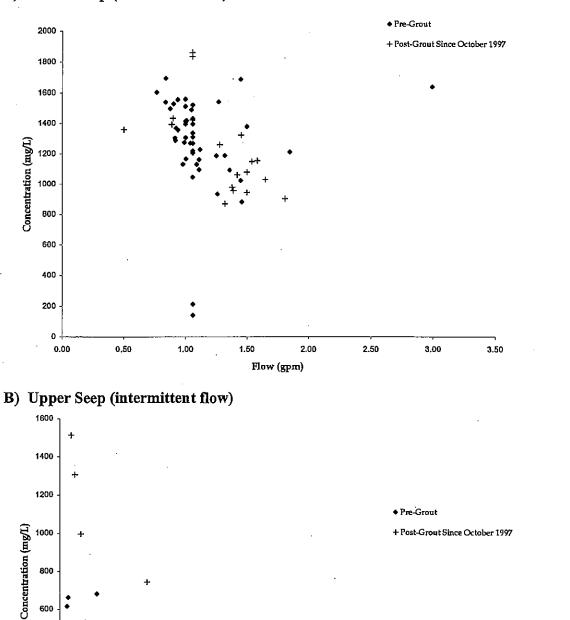












A) Lower Seep (continuous flow)

400

200

0 -0,00

5.00

10.00

304

20.00

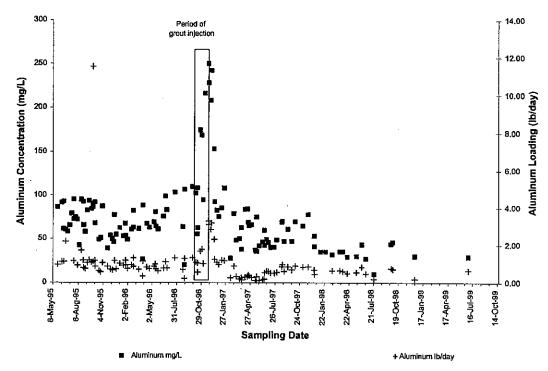
25.00

30.00

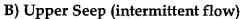
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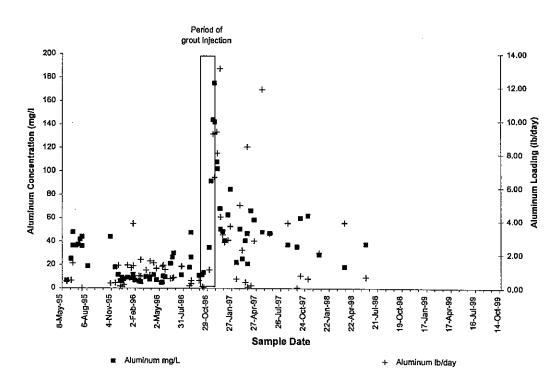
Flow (gpm)

Figure 8 Aluminum Results for the Upper and Lower Seeps at Mine Opening 2



## A)Lower Seep (continuous flow)





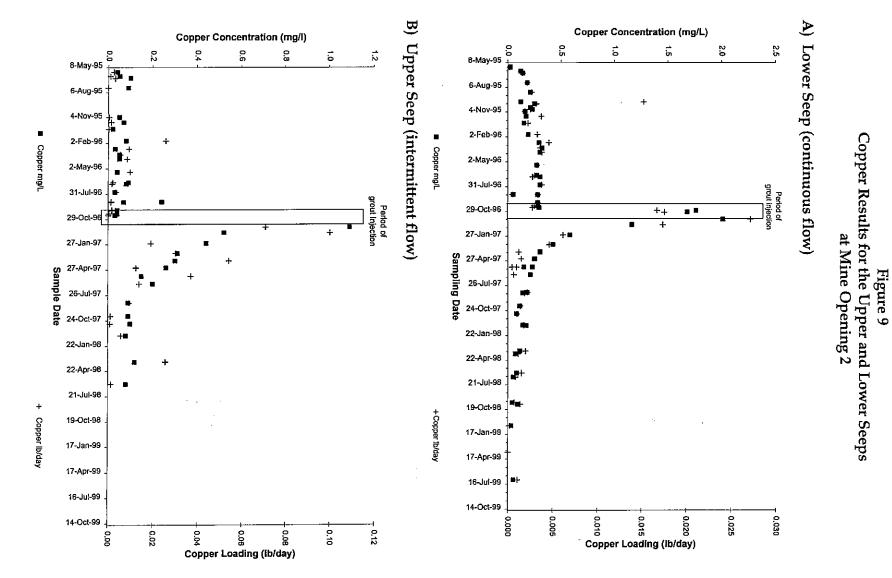
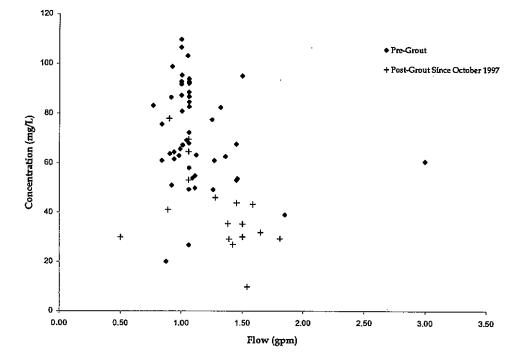
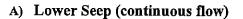
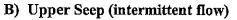


Figure 10 Comparison Pre-Injection and Post Injection Results Since October 1997 for Aluminum at Mine Opening 2







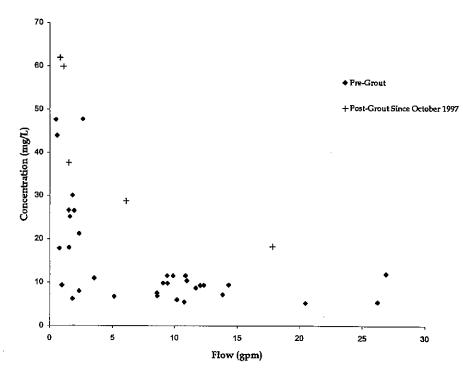
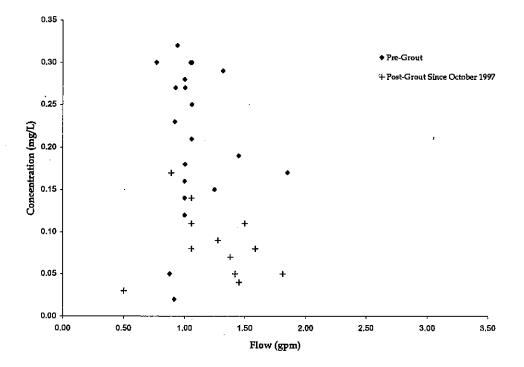
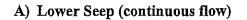
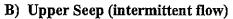
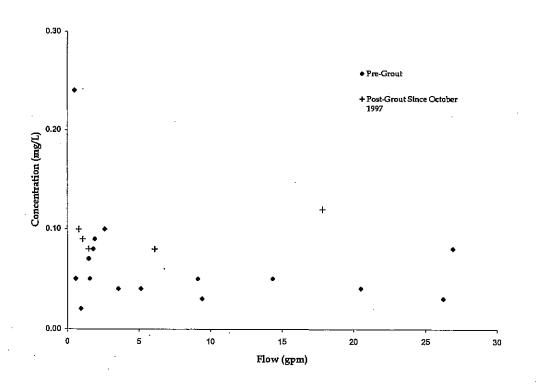


Figure 11 Comparison of Pre-Injection and Post Injection Results Since October 1997 for Copper at Mine Opening 2









The results for the upper seep show some post-injection concentrations above per-injection concentrations for similar flows. As mentioned earlier, this is not considered significant as the upper seep has been dry for the majority of monitoring events after grout injection, and therefore contributes little to the total discharge emanating from MO2.

### Ground Water and Surface Water

The water quality data from ground water monitoring wells and a surface water sample location show no adverse impacts from grouting the mine. Essentially, there is no evidence of AMD at these monitoring locations, and therefore, there could not be any impacts from grouting.

### Conclusions

The Winding Ridge Project has demonstrated that CCBs can be used beneficially to form a grout that can be injected into an abandoned, underground coal mine. The fact that the grout's strength and low hydraulic conductivity were retained as the injected grout cured in the mine indicates that the grout formulation used for this project would be an acceptable material to control mine subsidence.

Collectively, the water quality data from the lower and upper seeps, and the grout cores provide

evidence that the grout has entombed pyritic mine debris, and covered pyritic surfaces in the mine, which has reduced the volume of pyrite that would have otherwise been available for acid formation. This is most evident in the water quality data from the lower seep, which show that the concentrations and loadings of total acidity and iron have leveled off to values lower than pre-injection conditions.

Since total acidity and iron levels have decreased to levels below pre-injection conditions, the persistent levels of sulfate after grout injection must be attributable in part to a source other than pyrite oxidation. The most likely source is the dissolution of calcium sulfate and sulfite species from the grout surfaces exposed to the acidic mine water. The fact that calcium levels have been elevated since grout injection is consistent with the idea that the grout is a contributing source of sulfate.

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