

Effects of Acid Mine Drainage on CCP Grout: A Bench-Scale Weathering Experiment

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KEYWORDS: CCP grout weathering, CCP buffering, beneficial use, CCP grout, acid mine drainage, AMD

ABSTRACT

Measuring 10 cm thick and 20 cm by 48 cm on a side, four blocks composed of 100 percent stabilized Coal Combustion Product (CCP) grout were created to document the effects of acid mine discharge (AMD) flowing over cured CCP grout. Maryland Environmental Restoration Group created blocks from varying mix ratios of R. Paul Smith pulverized fly ash and Warrior Run fluidized bed combustion ash as part of ongoing Maryland Power Plant Research Program (PPRP) research to demonstrate the beneficial use of CCPs.

Initiated in June 2005, the experiment documents the physical and chemical degradation of CCP grout that could occur if placed as cover on abandoned underground mine pavement and exposed to AMD. To simulate abandoned mine conditions and determine environmental impacts; blocks of varying composition were placed in flowing water ranging from pH 7 to pH 3.0. Western Maryland Resource Conservation & Development collected samples of the circulating water monthly, (now quarterly), analyzing for trace metals and selected contaminants of concern. Due to the inherent buffering capabilities of the CCP grout when exposed to AMD, water samples are analyzed daily for pH and must be adjusted weekly to the specified pH level through the addition of a 5 percent sulfuric acid solution.

To date, the monitoring has shown an increase in standard water quality parameters (i.e., calcium, potassium, sulfate, TDS), expected from CCP grout weathering under acidic conditions. No water quality constituents show increased concentration trends that would indicate increasing weathering and/or chemical dissolution of the blocks over time.

Introduction

Through a cooperative effort of public and private sectors, the Maryland Power Plant Research Project (PPRP) has developed a program to evaluate the beneficial use of coal combustion products (CCPs) in an environmentally safe and effective manner. As a part of program, PPRP developed a bench-scale study to examine long-term weathering effects associated with a cured 100 percent CCP grout. The PPRP has demonstrated previous successes in the beneficial use of CCPs to mitigate subsidence and Acid Mine Drainage (AMD) from abandoned underground coal mines. These demonstration projects are a key component to promote and expand the beneficial use of all CCPs on a massive scale. The ultimate goal of these efforts is to utilize CCP-based grouts to significantly reduce acid production at AMD sources, such as the Coketon/Kempton Mine Complex, (Maryland's largest source of AMD), and to mitigate subsidence problems associated with lands adversely affected by coal mining.

Successful PPRP demonstration projects using CCP grout include Winding Ridge¹ and the Kempton Man Shaft² demonstration projects, both of which utilized a grout consisting of 100 percent CCPs. This paper builds upon the previous PPRP success demonstrating the beneficial use of CCPs to mitigate subsidence and AMD. This bench-scale study examines the application of CCP grout as an environmentally benign option to mitigate AMD formation in abandoned underground mine lands in Western Maryland and the surrounding Mid-Atlantic Highlands.

AMD Background

AMD is created from drainage flowing over sulfide-rich minerals that often emanates from surface or deep coal mines. Usually highly acidic with elevated levels of dissolved metals, AMD is formed by a series of chemical reactions (often facilitated by microbial activity⁴) that occur when oxygenated water comes in contact with pyrite (FeS_2) exposed during mining operations. The result of the reactions is a solution of sulfuric acid (H_2SO_4) and iron hydroxide [$\text{Fe}(\text{OH})_3$].

AMD formation typically occurs in deep mines where oxygenated water comes into contact with pyrite-bearing coal seams, high-sulfur mine pavement, or collapsed mine debris. The low pH of AMD degrades stream water quality to levels that may be toxic to aquatic flora and fauna.

Coal production from subsurface mining in the Western Maryland region has left a legacy of acid mine drainage affecting large areas of the Potomac River headwaters. Currently, the abandoned 60 square kilometer (km) Coketon/Kempton Mine Complex continually produces 13,000 cubic meters of AMD each day that drains to surface water features².

CCP Background

Left unstabilized, CCPs are known to leach soluble metals to the environment and may significantly contaminate ground and surface water. However, properly engineered and stabilized CCP mixtures have been demonstrated to be an environmentally benign material useful for roadbase, highway embankments, and mine fill³.

A significant component of CCPs, fly ash consists primarily of silicon dioxide, aluminum oxide and iron oxide which, in the presence of water, will chemically combine with cement and/or free lime to produce a cementitious material with excellent structural and engineering properties. Under PPRP direction, Hemmings & Associates, LLC of Atlanta, GA has developed various CCP mix designs (e.g., Hemmings & Associates, 2005) for grout and mine backfill which maintain long term strength and cohesion suitable for a variety of surface and underground mine reclamation and restoration requirements. Because of the complexity of abandoned mine workings, CCP-based grout needs to adapt to a variety of anticipated underground conditions constrained by the following generalized performance criteria:

- Sufficient fluidity to ensure easy pumping, and optimum fissure and/or mine shaft penetration;
- Adequate strength to abate surface ground subsidence; and
- Cured material characteristics that permanently reduce acid formation.

An additional consideration is that the CCP grouts be stable and compatible with the mine water present in the flooded underground mine workings which often receive acidified water. This is particularly important with respect to strength retention for subsidence control while also retaining the physical and chemical integrity necessary to resist dissolution and the release of soluble metals. Optimizing the balance between a viscosity suitable for injection and cementing properties is a key technical component in the design of a CCP grout.

While this paper documents the environmentally benign results of leaching experiments from a 100 percent CCP grout, the application, feasibility and effectiveness of mine void grouting with CCP-based material has been demonstrated by the PPRP in numerous projects including Winding Ridge¹ and the Kempton Man Shaft².

Siege of Acre

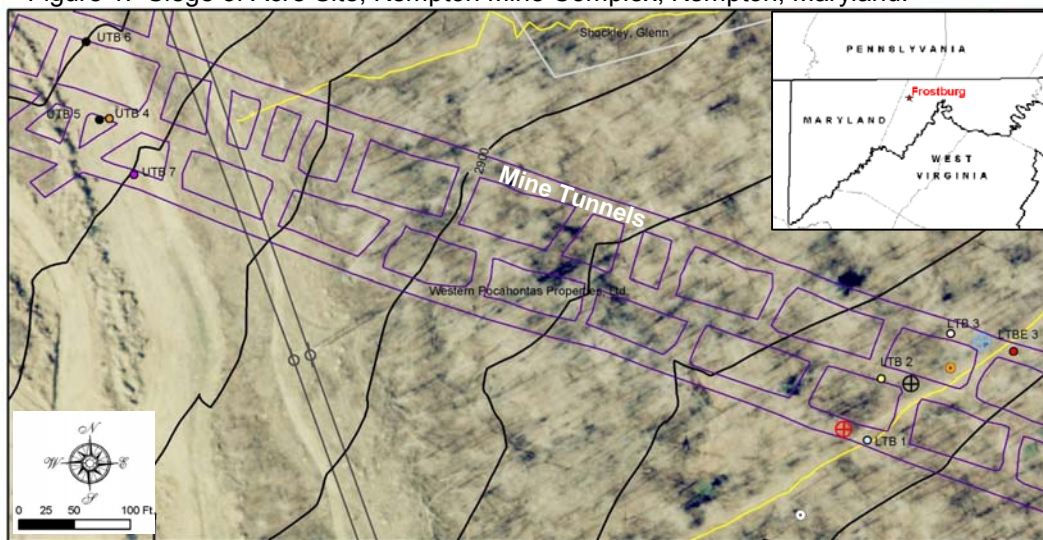
The weather block experiment was undertaken based on observations at the Siege of Acre portion of the Coketon/Kempton Complex. The Coketon/Kempton Mine Complex consists of nine interconnected abandoned underground mines. Seven percent of the 60 square km mine complex is in Garrett County Maryland, and the remaining portion of the complex is in Tucker County, West Virginia. During mining activities, ground water was pumped to the surface to keep mine

tunnels from flooding. When the mines were closed in the 1950s, pumping stopped and portions of the mine tunnel network gradually filled with ground water.

Acid mine water currently exists in two underground mine pools – the Kempton Pool and Coketon Pool. The Kempton Pool is the larger of the two, containing about 4.2 million cubic meters (m) of water. Although the majority of the Kempton mine pool lies in West Virginia, all of the surface discharge (i.e., an average of 13,000 cubic m per day) of AMD flows into Maryland’s Laurel Run, a tributary of the North Branch of the Potomac River.

The Siege of Acre segment of the Coketon/Kempton Complex is in the northern extremity of the mine workings in Maryland (Figure 1). The proposed Siege of Acre project focuses on three isolated, parallel tunnels, each 16 feet wide, that run “up dip” from the northern edge of the Kempton Mine Pool for approximately 230 m.

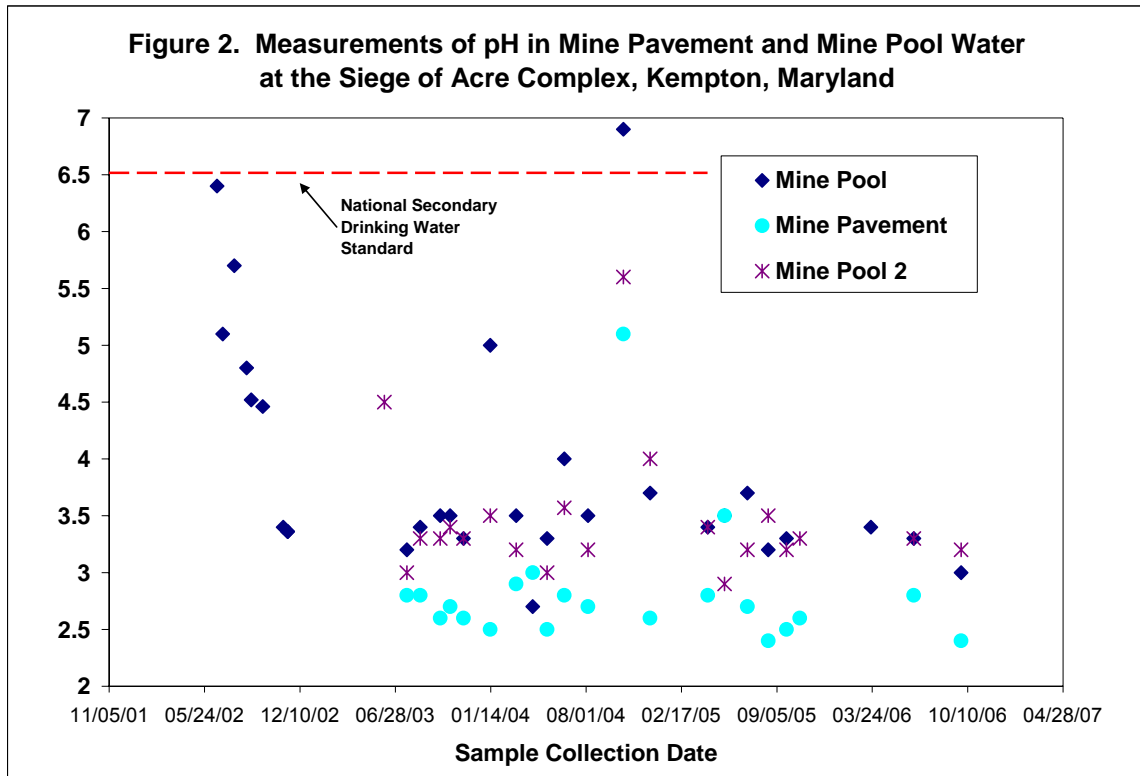
Figure 1. Siege of Acre Site, Kempton Mine Complex, Kempton, Maryland.



As an experimental site, the Siege of Acre tunnels are representative of several kilometers of other air and water-filled tunnels along the western edge of the Kempton mine pool as well as other underground mines in Maryland and the Mid-Atlantic Highlands.

The proposed Siege of Acre Project is a field-scale experiment to demonstrate how CCP grout can be economically used to reduce acid formation by coating the mine floor and associated debris to prevent exposure to air and water. The high-sulfur pyritic mine material and debris have been shown to be encapsulated and isolated from ground water by a hydraulically-placed grout fluid comprised of mine water and locally available CCPs. This method of mixing and placement was successfully used by PPRP for mine filling at Winding Ridge².

There is evidence that water is entering the Siege of Acre tunnel network at a fairly constant rate, steadily flowing along the mine pavement floor and occasional debris piles, at a slope of 15 to 30 degrees. Baseline water-quality monitoring of the water flowing on the existing tunnel pavement indicates that water flowing to the mine pool is highly acidic with a pH range of 2.3 to 2.7 (Figure 2).



The proposed project includes the injection of approximately 500 cubic meters of CCP-based grout into the mine. This highly flowable grout would form an approximate 0.5 meter thick barrier effectively shielding the exposed pyritic material on the mine floor from ground water entering the mine tunnels.

Objective of the Weathering Block Experiment

The objective of the experiment is to evaluate the long-term leaching, weathering, and erosional affects of acidic and non-acidic water flowing over the CCP grout. The flowing water is intended to simulate both acidic mine water and more pH neutral water encountered in fresh ground and stream water.

The application of CCP grout to underground abandoned mines is intended as a permanent solution to significantly mitigate or eliminate the aforementioned AMD¹. Many studies⁴ have conducted standard Toxicity Characteristic Leaching Tests (TCLP) and Synthetic Precipitation Leaching Procedure (SPLP) tests on

CCPs (stabilized and unstabilized); however, few studies have subjected CCP grout to simulated field conditions in underground mines. These bench-scale CCP grout weathering experiments are designed to subject the CCP grout blocks to flowing water that simulates subsurface mine conditions. The simulations will aid in both a long-term evaluation of CCP grout weathering and in the evaluation of current projects planning to utilize CCPs.

Desired CCP Mix Design Properties

CCP grouts can be engineered to fit a range of circumstances³. The general requirements for CCP grouting in underground mine applications include:

- Fluidity to insure optimum placement in voids;
- Sufficient strength that is consistent with the surrounding geology;
- Low permeability; and
- Long-term durability, free of deterioration or decomposition, and substantial weathering.

In order to ensure the long-term durability of cured CCP grout, the physical and chemical weathering processes must be understood. Although the blocks were created to simulate the conditions over deep mine pavements, this CCP weathering block experiment is pertinent to a variety of mine void stabilization and grouting applications that would otherwise use conventional Portland-based cement grout.

To that end, four blocks composed of 100 percent CCPs blocks were mixed, allowed to cure for 28 days, and then subjected to flowing water at pH levels of 3, 4, and 7. The pH levels were chosen to simulate AMD, acidic landfill leachate, and/or AMD impacted stream water, respectively. The experiments were initiated in June 2005 and are continuing to the present day.

CCP Weathering Block Properties

Initially, two inch grout cube samples were prepared during scoping tests based on grouts prepared for PPRP³ and were allowed to cure at ambient temp in their molds for 28 days before testing for strength development. A total of twelve cubes were created at four different dry weight CCP mix ratios of 70:30:0, 63:27:10, 52:5:22.5:25, and 35:15:50 of Warrior Run Fluidized Bed Combustion Bag-house ash (WRBH), Warrior Run Fluidized Bed Combustion Bed-drain Ash (WRBD), and R. Paul Smith Pulverized Fly Ash (PFA) material, respectively.

Each dry CCP mix ratio was then combined with tap water to create a 55 percent and 65 percent solids content mix. These blocks were then allowed to cure/harden for 3, 7, and 28 days before strength testing (Table 1).

Table 1. Strength Development Data for FA-FBC Fluid Grouts

Mix Design (BH:BD:PFA)	Constituents, Adjusted to Percent				Density (Cw%)	Fluidity	water to FBC ratio	Compressive Strength (psi)		
	Warrior Run FBC- Baghouse	Warrior Run FBC-Bed Drain	RPSmith PFA	Water				3	7	28
	70-30-0	38.5	16.5	0.0				45.0	55.0	High
70-30-0	40.3	17.3	0.0	42.5	57.5	Target	0.74	34	236	593
70-30-0	42.0	18.0	0.0	40.0	60.0	Low	0.67	30	388	792
63-27-10	39.4	16.9	6.3	37.5	62.5	Low	0.67	71	669	1113
63-27-10	41.0	17.6	6.5	35.0	65.0	Low	0.60	116	989	1366
63-27-10	42.5	18.2	6.8	32.5	67.5	V. Low	0.53	253	1107	
52.5-22.5-25	31.5	13.5	15.0	40.0	60.0	High	0.89	73	334	579
52.5-22.5-25	32.8	14.1	15.6	37.5	62.5	Target	0.80	68	410	689
52.5-22.5-25	34.1	14.6	16.3	35.0	65.0	Low	0.72	88	509	967
35-15-50	20.1	8.6	28.8	42.5	57.5	V. High	1.48	24	76	219
35-15-50	21.0	9.0	30.0	40.0	60.0	High	1.33	32	194	253
35-15-50	21.9	9.4	31.3	37.5	62.5	Target	1.20	54	253	312

NOTES:

FBC = Fluidized Bed Combustion Ash

PFA = Pulverized Fly Ash

CCP Weathering Block Experimental Setup

After creation of the initial blocks for strength testing, four blocks of 100 percent stabilized CCP grout were created in June 2005. These blocks, measuring 10 cm thick and 20 cm by 48 cm on a side from varying mix ratios of R. Paul Smith pulverized fly ash (PFA), Warrior Run fluidized bed drain bed combustion ash (WRBD-FBC), Warrior Run Bag House Fluidized Bag House (WRBH-FBC), and water were created for the actual weathering experiment.

The blocks included in the experiment are summarized in Table 2. This included one block composed of 70 percent WRBH and 30 percent WRBD, (i.e., no PFA in the mix) prepared at a total water content (Cw) = 57.5 percent that produced an 8" spread using ASTM Method C143 (i.e., standard slump test). This block is currently exposed to flowing water at pH 3. Three blocks were composed of 52.5 percent WRBH, 22.5 percent WRBD, and 25 percent PFA prepared at Cw = 60 percent. Each grout mix prior to curing produced an 8" spread.

Table 2. Weathering Block Composition

Block Number	Dry Weight Percent		Dry Weight Percent		Cw	pH
	Warrior Run Baghouse	Warrior Run FBC ¹	Warrior Run FBC ¹	Bed Drain Dry Weight Percent R. Paul Smith PFA ²		
1	52.5		22.5	25	60	7
2	70		30	0	57.5	3
3	52.5		22.5	25	60	3
4	52.5		22.5	25	60	4

NOTES:

¹ Fluidized Bed Combustion Ash

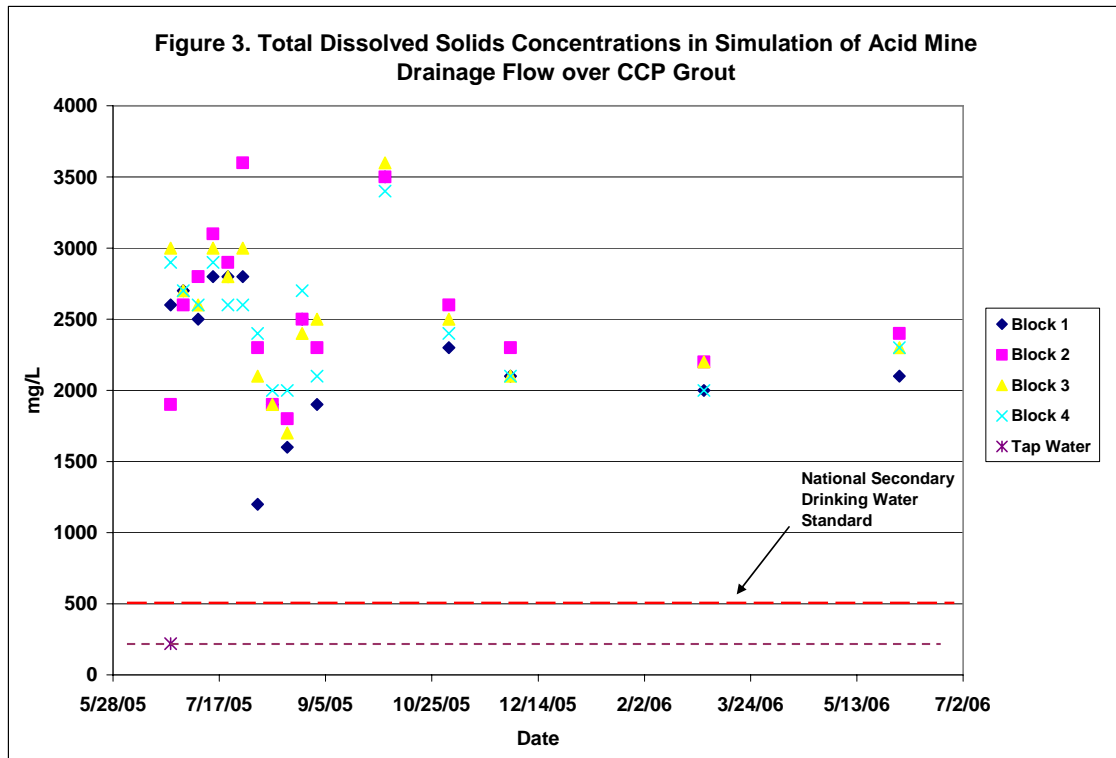
² Pulverized Fly Ash

Cw = Total Water Content

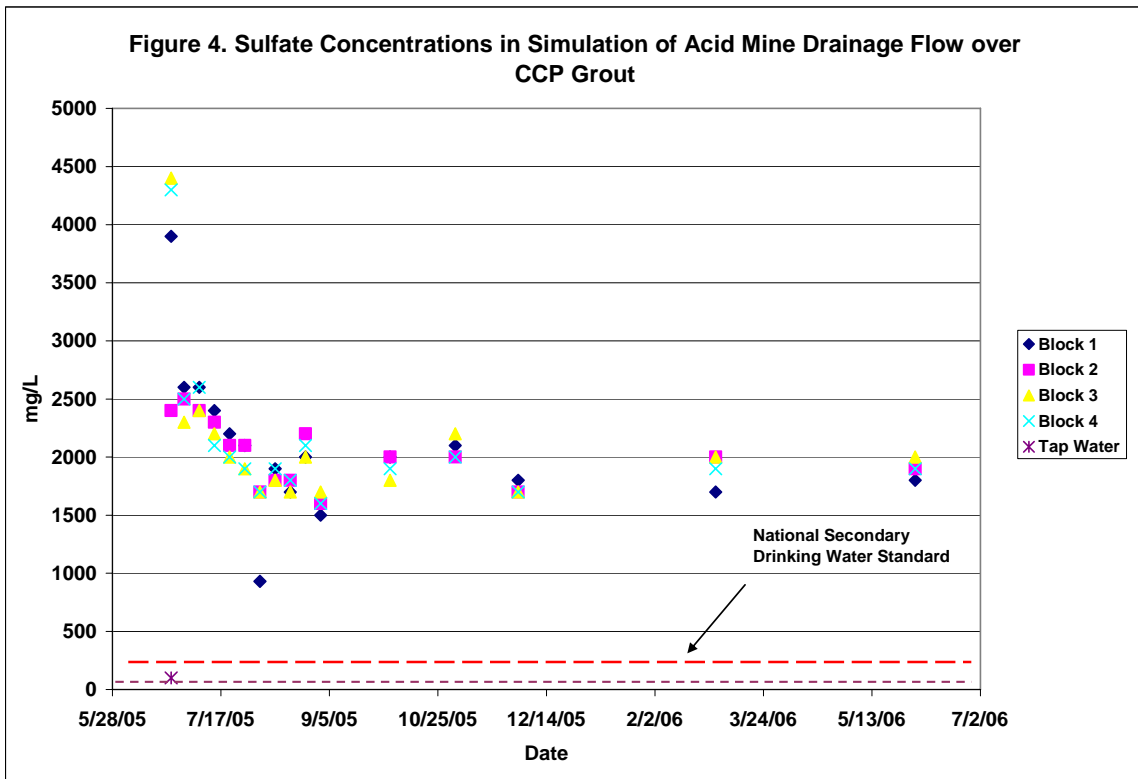
The four test blocks were allowed to cure in their molds at ambient temperature and 100 percent relative humidity in a sealed plastic container for 28 days before initiating the exposure testing. To determine any environmental impacts, blocks of varying composition were formed with a 2-cm deep groove in which running water, ranging from a neutral pH 7 to pH 3, would continually flow. The blocks are tilted at a 30 degree angle in order to simulate the flowing water conditions that would be encountered on sloped mine pavement. The water is recycled through the system using typical fish pond pumps and occasionally water is added to compensate for water loss due to evaporation. Also, due to the inherent buffering capabilities of the CCP grout when exposed to mine acid, these samples are analyzed daily for pH and must be adjusted back to the desired pH level through the addition of a solution of 5 percent sulfuric acid.

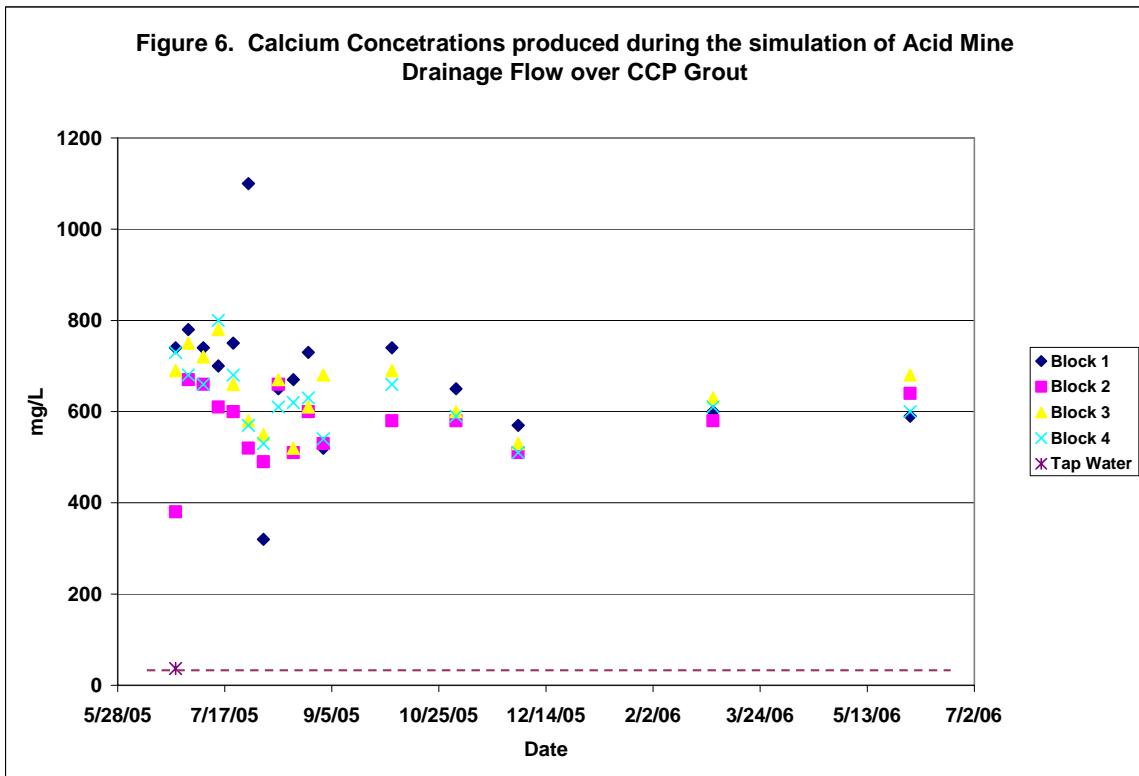
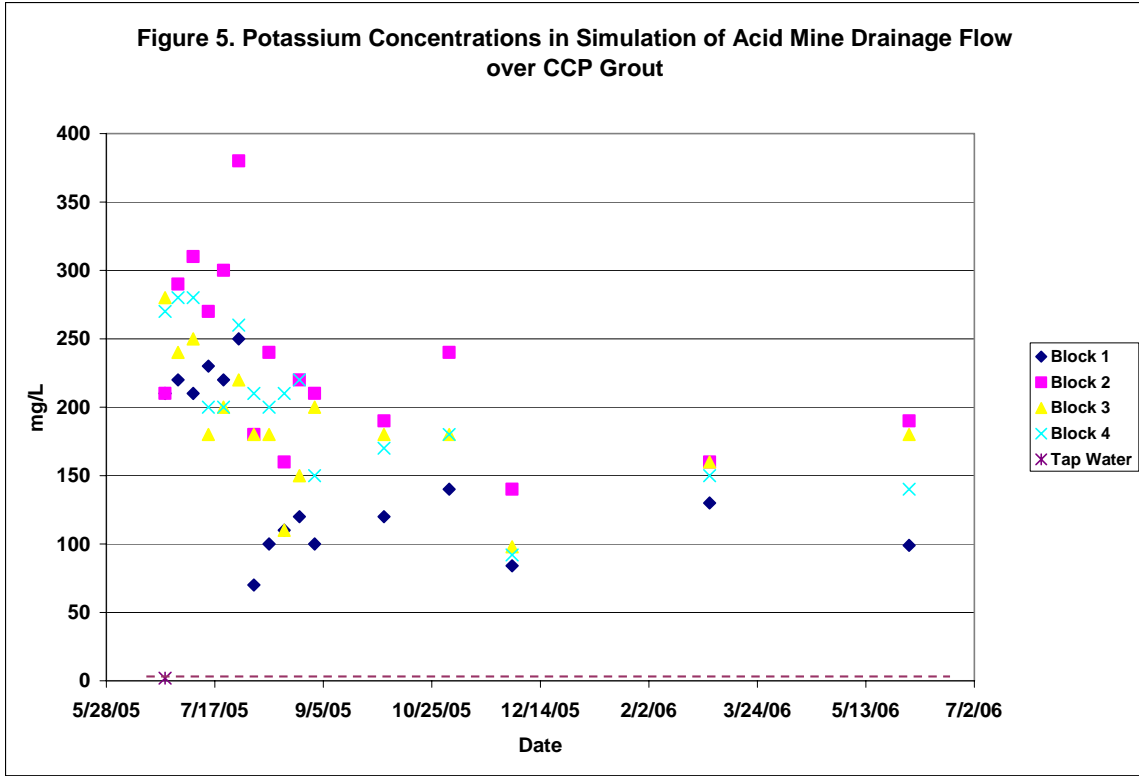
Water Quality Results

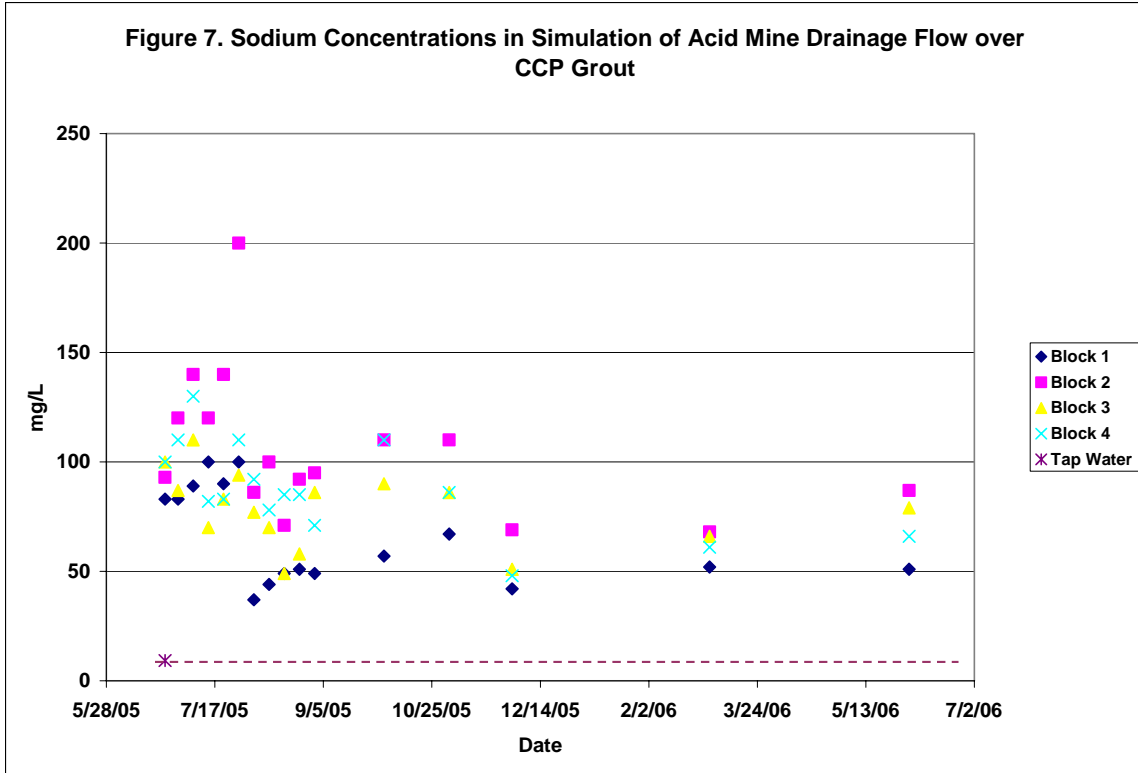
Samples of the circulating water were collected and analyzed for contaminants of concern such as sulfate and aluminum. Over a year of water quality monitoring has been conducted on the water flowing over the CCP weathering blocks. Over the first 8 weeks of the experiment, the water flowing over the blocks was sampled weekly, followed by monthly sampling for 3 months. Currently the sampling has been reduced to quarterly events. The results of the sampling are presented below in Figures 3 through 10. For a baseline comparison, the concentrations of each constituent are also shown for the tap water that was used to form the solutions. Initially, total dissolved solids (TDS) concentrations increased over an order of magnitude above the original tap water before stabilizing (Figure 3).



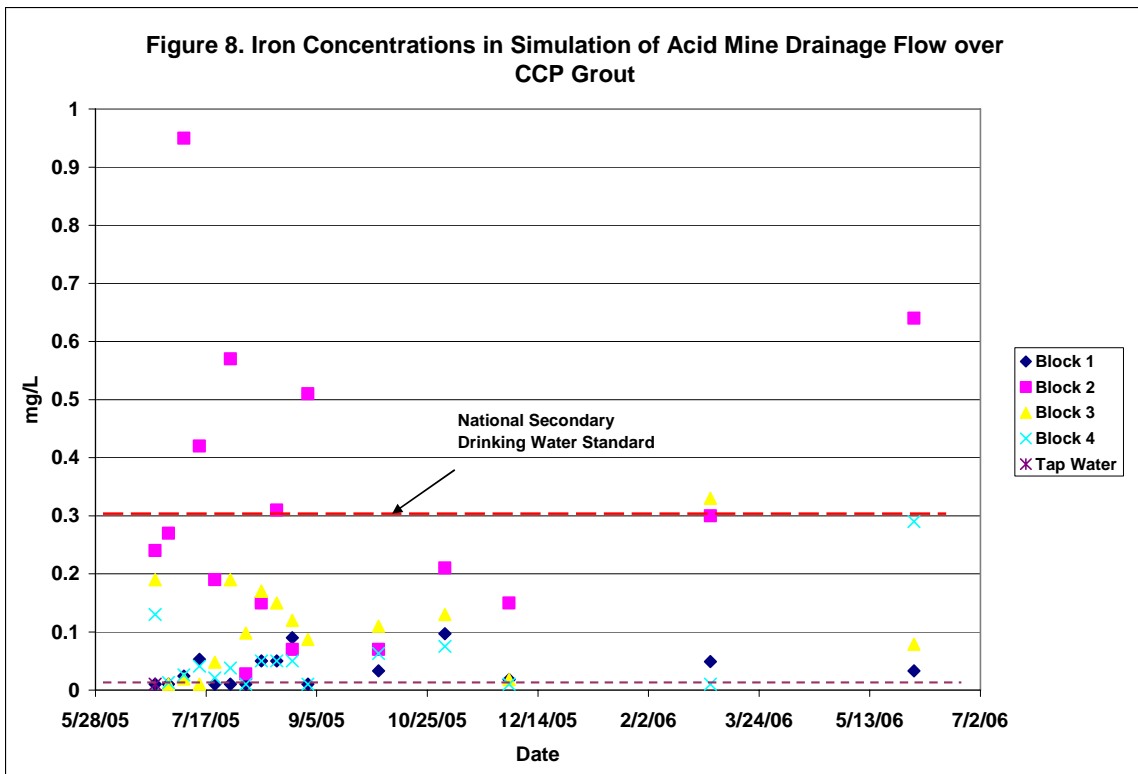
The majority of the TDS (approximately 2,300 mg/L) appears to be composed of sulfate (approximately 2,000 mg/L) shown in Figure 4 and much smaller proportions of potassium (100-200 mg/L) shown in Figure 5, calcium (600-800 mg/L) shown in Figure 6, and sodium (50-100 mg/L) shown in Figure 7. As with TDS, these constituents initially increase significantly over the background concentrations in tap water and then gradually stabilize suggesting that the system is approaching steady-state conditions. Similar results have been observed for the Winding Ridge Project¹. Concentrations of sulfate, calcium, and potassium increased significantly after injection of the grout, but have gradually decrease (over the past 10 years) suggesting that the grout dissolution slows over time and will approach some steady state.

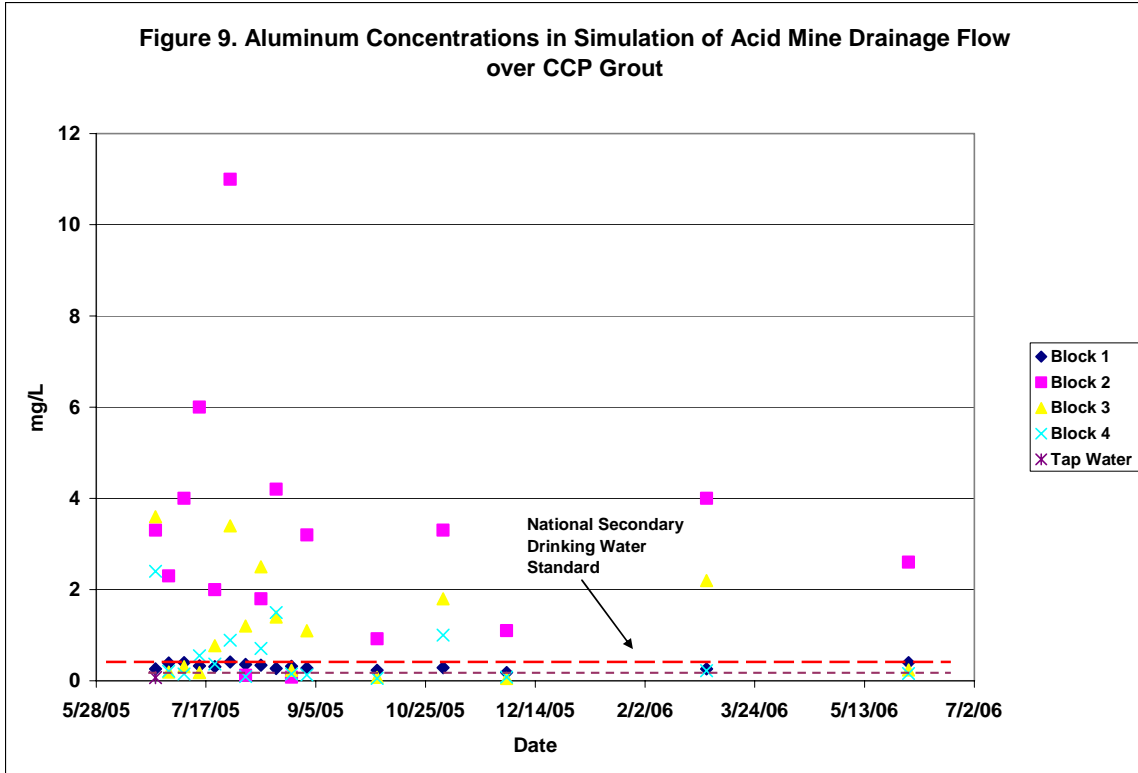




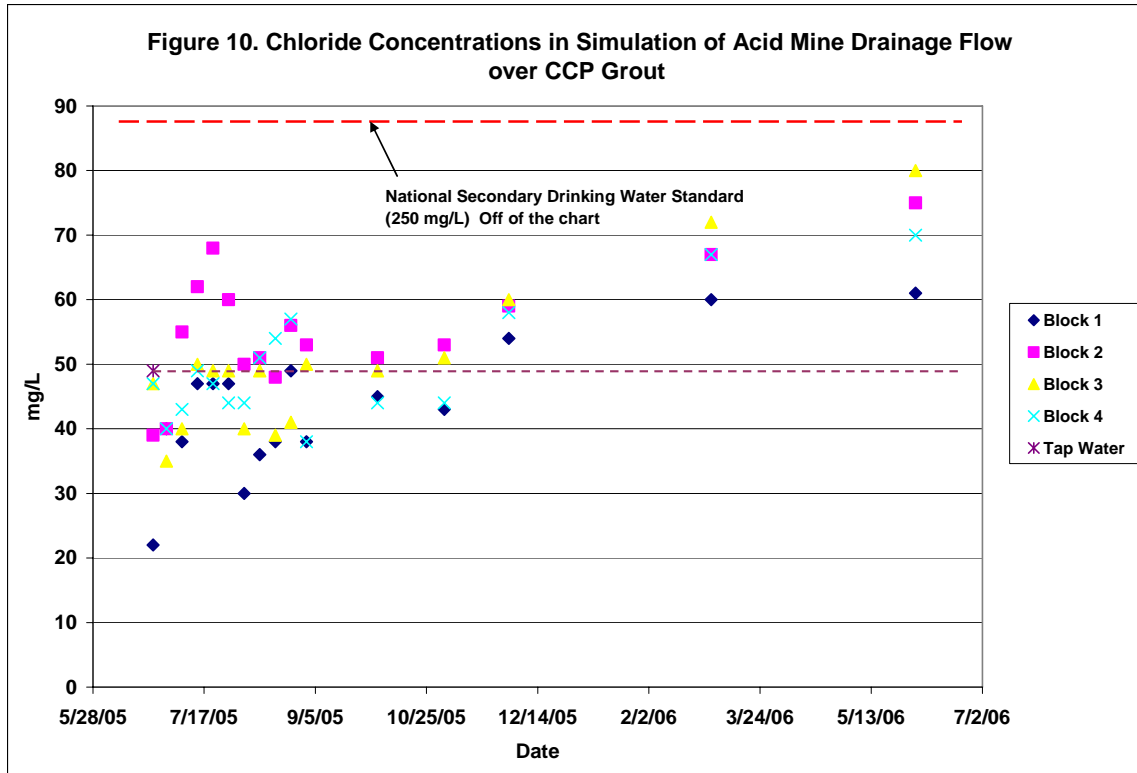


Low concentrations of iron (Figure 8) and aluminum (Figure 9) are also present in the water samples, although at concentrations that are not considered to be significant.





The lone exception to the decrease in constituents is chloride (Figure 10). After an initial decrease in dissolved concentration (from 50 to 20 mg/L), concentrations increased to 60 to 80 mg/L in all of the samples. While an initial increase in chloride was observed at Winding Ridge¹ chloride concentrations eventually decreased in the same manner as sulfate, potassium, sodium, etc. The steady increase of chloride concentrations observed in the weathering blocks was not observed elsewhere and may be an artifact of evaporation.



Thus far, the water monitoring has shown an increase in standard water quality parameters that might be expected from weathering CCP grout (i.e., calcium, potassium, sulfate, TDS). While each of these constituents has shown an increased concentration compared to the initial sample of tap water, no constituents show any upward trends that might indicate that there has been an increase in weathering and/or chemical dissolution over time.

Summary

For over one year now, an on-going PRRP weathering experiment subjected cured blocks of 100 percent CCP grout to a constant flow of water ranging from pH 7.0 to pH 3.0 with the lower pH ranges simulating the flow of acidic mine water over and/or through any grout fractures. To date, results from initial weathering experiments indicate that no hazardous constituents leach at any detectable level from the cured CCP grouts and that there is only limited weathering of the grout which produces an increase in TDS whose main constituent is sulfate.

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