

Field Demonstration of In-Situ Treatment and Prevention of Acid Mine Drainage in the Abandoned Tide Mine, Indiana County, Pennsylvania

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Abstract

The Blacklick Creek Watershed Association (BCWA) and ARCADIS G&M, Inc. (ARCADIS), in association with the Pennsylvania Department of Environmental Protection (PADEP)-Bureau of Abandoned Mine Reclamation (BAMR), have completed a demonstration study of the ARCADIS-patented process for in-situ treatment and prevention of acid mine drainage (AMD) within the workings of an abandoned bituminous coal mine located in western Pennsylvania. In conjunction with the characterization of mine pool hydraulics through injection of a bromide tracer, the in-situ treatments implemented at Tide Mine include the initial addition of alkalinity to create an environment suitable for biological activity, injection of organic carbon into the mine pool to facilitate microbially-mediated metals reduction and precipitation, and injection of carbon dioxide gas into the atmosphere above the mine pool to control the dominant source of oxygen that perpetuates the AMD process. Collectively, these treatments raised the pH from a baseline of approximately 2.5 to over 6 during the study period and the mine pool is currently maintaining a pH above 5 through microbially-produced (i.e., bicarbonate) alkalinity. Ferric iron has been reduced to non-detect concentrations within the anaerobic mine pool and aluminum concentrations have been decreased by approximately 30%, with additional metals removal expected as the system becomes controlled by ferrous sulfide precipitation. The injection of carbon dioxide gas into the mine workings decreased oxygen concentrations above the mine pool from over 20% (ambient air conditions) to less than 5% for a duration of approximately three months, thus mitigating the source of AMD within the mine.

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Introduction

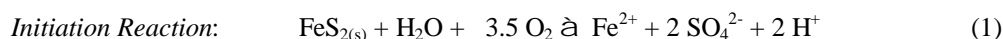
A field demonstration of the Green World Science® patented process technology [1] was performed at the abandoned Tide Mine located in Center Township, Indiana County, Pennsylvania. ARCADIS owns an exclusive patent license of the Green World Science® process, which consists of transitioning a previous aerobic, acid mine drainage (AMD)-producing mine pool to a biologically-mediated sulfate reducing state in-situ. Through this process, the entire mine pool undergoes treatment and the source of AMD is addressed in-situ. The project was conducted through a grant agreement between the Blacklick Creek Watershed Association (BCWA), the Pennsylvania Department of Environmental Protection (PADEP) – Bureau of Abandoned Mine Reclamation (BAMR), and ARCADIS.

Pennsylvania has a rich coal mining history as a result of the vast deposits of anthracite and bituminous coal found in the eastern and western portions of the Commonwealth, respectively. These coal deposits have been mined extensively from the 1800s through to the present day. As a result of past mining practices, Pennsylvania is home to over 250,000 acres of abandoned mines and approximately 2,400 miles of rivers and streams that are impacted with AMD and do not meet water quality standards [2]. Many other

states in the coal-rich regions of Appalachia (e.g., Ohio, West Virginia, Kentucky, etc.) and the rocky mountain states of the western United States have similar issues related to AMD.

Mining activities typically provide for direct exposure of sulfide minerals to molecular oxygen, either through staging of mining wastes on ground surface or through the advancement of tunnels and shafts that provide a direct conduit for oxygen-rich ambient air to penetrate deep below the earth's surface. In each case, sulfide minerals that existed previously in a mostly anaerobic environment are brought in direct contact with molecular oxygen. Pyrite (FeS_2) is the dominant sulfide mineral that participates in AMD reactions. AMD-impacted water is characterized as having low pH, high sulfate concentrations, and high dissolved metals (e.g., iron, aluminum, and manganese) concentrations.

The series of reactions associated with AMD occur in the aqueous phase. The vast volume of most underground mine workings, with unsaturated fractures, mine shafts, or tunnels receiving water from seeps, springs, and direct infiltration, provide sufficient surface area for transfer of gaseous oxygen into the aqueous phase. As a result, ambient air with an oxygen concentration of approximately 21% provides a continuous source of oxygen to facilitate the AMD reactions. The dominant AMD initiation and propagation aqueous phase reactions are summarized below [3]:



In the initiation reaction (Equation 1), molecular oxygen directly oxidizes pyrite to form ferrous iron and sulfuric acid. During the propagation reactions shown in Equations (2) and (3), ferrous iron is further oxidized to ferric iron by molecular oxygen, and ferric iron in turn acts as an electron shuttle further oxidizing additional solid phase pyrite. As seen in the products of Equations (2) and (3), the resulting AMD water has elevated levels of protons (high pH), ferric and ferrous iron, and sulfate. As a result of solubility limitations, the concentration of ferrous iron is typically greater than ferric iron in AMD-impacted waters.

The Green World Science® in-situ biological AMD treatment, a technology process patent owned exclusively by ARCADIS, effectively removes oxygen and ferric iron from the mine pool through conversion of the previously aerobic system to an anaerobic, strongly reducing state. As seen in Equations (1) through (3) above, oxygen and ferric iron are the causative agents of AMD and serve as the sole electron donors in the oxidation of sulfide minerals. Elimination of the causative agents of AMD effectively halts the reactions responsible for perpetuating the AMD process.

Field Demonstration Site Initial Conditions

The abandoned Tide Mine, also known as the Waterman #3 Mine, is located in Center Township, Indiana County, Pennsylvania. The mine was operated in the 1910s through 1930s. Mining was conducted from the down-dip side and progressed up dip to allow for free drainage. Two drainage tunnels were advanced to the lowest portion of the coal seam to allow for passive dewatering of the mine. Currently, much of the site is covered with stockpiled coal waste debris. The location of Discharge Tunnel A has been identified and water flowing from Discharge Tunnel A has been the subject of a number of treatment technology studies. The second Discharge Tunnel B has currently not been mapped. Figure 1 provides a conceptual model of the workings of Tide Mine.

Baseline geochemical and flow data are characterized by the following:

- Discharge flow is approximately 90 to 100 gallons per minute (gpm);
- pH is between 2.5 to 3 standard units;
- 300 parts per million (ppm) acidity; and,
- Non-detect alkalinity.

Utilizing topographic maps and historical mine maps provided by L. Robert Kimball and Associates (Kimball), the mine pool volume was estimated based on mine layout and the water surface elevation of the Discharge Tunnel A pond. The mine pool volume was initially determined as follows:

- The total areal extent of the mine is approximately 335,000 square feet (7.7 acres), assuming the mine is flat;
- The height of the mined coal seam and mine workings, prior to substantial subsidence, was approximately 4.5 feet;
- The range of void space for the mine following subsidence is estimated at approximately 50% to 60%;
- The initial estimate of total mine pool volume is estimated in the range of 5.6 to 6.8 million gallons; and,
- The estimated length of the “beach” associated with the mine pool is approximately 1,650 feet.

Technology Description

The Green World Science® technology process patent is predicated on mitigating the sources that propagate the AMD chemical reactions by converting a previously aerobic mine workings system to a biologically-mediated sulfate-reducing system in-situ. Sulfate-reducing conditions are maintained within the mine pool through the addition of an electron donor (i.e., organic carbon source). Sulfide is formed in-situ through the sulfate-reduction process, which then facilitates the precipitation of metal sulfides within the mine workings. The in-situ biological treatment of AMD is facilitated by the large residence times typically offered by vast underground coal mine networks.

It is well known that microorganisms will participate in a preferential series of biogeochemical reactions to carry out catabolic respiration [4]. In the presence of excess organic carbon, which serves as an electron donor, a succession of microbial processes are stimulated that first consume dissolved oxygen and then progress to consume additional naturally-occurring electron acceptors. As microbial populations and respiration rates increase, electron acceptors are depleted from the mine pool at a rate greater than they can be recharged naturally, resulting in a more reducing environment with lower oxidation-reduction potential (ORP). The general sequence of alternate electron acceptor utilization and respiration byproduct formation is as follows, from the most thermodynamically favorable to the least:

<u>Reactants</u> <u>(Alternate Electron Acceptors)</u>		<u>Intermediates</u>		<u>Products</u>
Nitrate (NO_3^-)	→	Nitrite (NO_2^-)	→	Nitrogen (N_2)
Ferric Iron (Fe^{3+})		→		Ferrous Iron (Fe^{2+})
Manganic Manganese (Mn^{4+})		→		Manganous Manganese (Mn^{2+})
Sulfate (SO_4^{2-})		→		Sulfide/Hydrogen Sulfide (H_2S)
Carbon Dioxide (CO_2)		→		Methane (CH_4)

In addition to the products listed above, carbon dioxide is produced as the carbon end product of the nitrate, ferric iron, manganic manganese, and sulfate reduction respiration processes. With enhanced biological populations, sufficient amounts of carbon dioxide are produced for the dissolution of carbon dioxide into the aqueous phase, resulting in carbonate alkalinity, and evolution of carbon dioxide gas from the mine pool into the unsaturated portions of the mine workings.

In the mine workings of a typical aerobic system free to exchange with ambient air, buoyant gases (i.e., less dense than air) result from AMD reactions consuming oxygen from the gas phase and producing heat. This warmed, oxygen-depleted air has a density less than the incoming air and exits the mine through chimney

effects, thus pulling in new, oxygen-rich ambient air. This convective cycle provides a perpetual source of oxygen to supply the AMD reactions depicted in Equations (1) and (2) above.

When carbon dioxide gas can be maintained in the mine workings atmosphere at a minimum concentration of five percent (5%), the resulting gas has a density greater than ambient air and an anaerobic dense gas blanket is formed over the mine pool, effectively halting the chimney effects that result from AMD chemistry oxygen removal. The ability to maintain a dense anaerobic blanket within the mine workings is determined by the level of gas phase advection occurring within the mine workings. The anaerobic blanket is easily maintained when carbon dioxide losses are minor (i.e., due to diffusion and small amounts of advection); however, the anaerobic blanket may require external sources of carbon dioxide gas to maintain the dense blanket if gas losses are major, including gross advective and barometric pumping losses. Cost effective sources of external carbon dioxide gas are available for most mine sites through the reuse of existing waste streams, including as examples, combustion products (natural gas combustion results in approximately ten percent carbon dioxide) and wastewater treatment plant offgas.

Demonstration Project Plan

Three separate phases of redox-modifying activities occurred at the demonstration site. Phase I of the project was initiated in July 2004 and included recirculation of mine pool water and the additions of sodium hydroxide (to raise the pH), a bromide tracer (to characterize mine pool hydraulics), and an organic carbon source (to stimulate sulfate-reducing bacteria). In Phase II (completed in September 2004), carbon dioxide gas was injected into the void space above the mine pool to eliminate the dominant source of oxygen that propagates the AMD process. Phase III (initiated in October 2004 and completed in February 2005) consisted of passive alcohol addition to the mine pool to sustain microbial sulfate reduction processes.

The BCWA retained Kimball to provide injection well drilling services. Four injection wells were installed in June through July 2004 to provide access to the mine workings at the locations shown on Figure 1. Injection Wells IW-1, IW-2, and IW-3 were constructed just above the beach zone to facilitate recirculation of mine pool water and reagent injection. Injection Well IW-4 was constructed upgradient of the beach zone in the unsaturated portion of the mine workings to facilitate carbon dioxide gas injection.

A 70 horsepower (hp) pump was staged adjacent to the Discharge Tunnel A pond to recirculate water from the pond to Injection Wells IW-1, IW-2, and IW-3. Caustic solution was staged in a temporary tank adjacent to the pump and was continuously fed into the recirculated water stream to initially increase pH of the mine pool.

Recirculation of mine pool water was conducted for a three month period, during which time molasses was periodically injected at the pump suction intake and distributed throughout the mine pool. Molasses provides readily degradable sugars and nutrients able to support the diverse microbial populations necessary to transition the mine pool from the original aerobic state to a state where sulfate reduction is the dominant biogeochemical process. Concurrent with the later part of recirculation system operation, alcohol was passively added to the mine pool through the wellheads of Injection Wells IW-1, IW-2, and IW-3. Alcohol was passively dripped into the mine pool as the sole source of organic carbon during the last three months of the demonstration study.

Results and Discussion

Tracer study

Approximately 256 pounds of bromide were injected into the mine pool through Injection Well IW-3 on 25 September 2004. Bromide concentrations were measured throughout the course of the demonstration study to first identify background levels of bromide and to measure the response of the mine pool to the pulse input of bromide tracer following injection. Bromide concentrations measured in the Discharge Tunnel A pond over time are shown on Figure 2.

Baseline levels of bromide measured in the discharge pond were below the detection limit of 0.2 milligrams per liter (mg/L). An elevated bromide concentration was first observed three days following injection and the maximum detected bromide concentration was measured 12 days following injection.

The average hydraulic residence time within the mine pool has been estimated by two independent methods including analysis of the first moment of the residence time distribution curve centroid and through the continuously-stirred tank reactor (CSTR) model [5]. As shown on Figure 2, both evaluations yield an average hydraulic retention time of 18 days. Thus, two independent evaluations yield comparable average hydraulic retention times for the tracer study conducted in the Tide Mine pool.

Combining the average hydraulic retention time of 18 days with flow rates measured at the discharge pond that ranged between 40 and 100 gallons per minute (gpm) during the demonstration study, results in an estimate of active mine pool volume of approximately 2 to 2.5 million gallons. The calculated active mine pool volume is approximately 2.8 times less than the volume first assumed based on the geometry of the mine and water level within the mine. It can thus be concluded that the mine workings have stagnant portions of standing water that contribute minimally to mine pool flow and overall pool hydraulics.

Changes in Biogeochemistry

Alkalinity, ORP, and pH data are summarized on Figure 3. Caustic solution and dilute molasses solution were added to the recirculating mine pool water during the first three months of the demonstration study. The addition of caustic solution to the mine pool resulted in elevated levels of alkalinity measured in the discharge pond during the first three months of the study. As seen on Figure 3, the addition of caustic solution raised the pH from approximately 3.2 to over 6 standard units. Elevated pH and the delivery of excess organic carbon resulted in biological consumption of electron acceptors and transitioned the mine pool system from an aerobic to strongly reducing, anaerobic state, as indicated by the sharp decrease in ORP.

Figure 4 shows total organic carbon (TOC), sulfate, and sulfide concentrations measured in the Tide Mine discharge pond as a function of time. As seen on Figure 4, baseline TOC concentrations were typically less than 1 mg/L and a noticeable increase in TOC concentration was observed following the first injection of molasses. As expected, TOC concentrations within the mine pool responded similarly to the bromide tracer and near complete washout of the initial molasses injection occurred within one month. Subsequent molasses injections performed on a weekly basis elevated the TOC concentration in the mine pool to over 250 mg/L.

In addition to readily degradable sugars, molasses contains sulfate. As seen on Figure 4, sulfate concentrations within the mine pool are shown to increase following the initiation of molasses injection. Following a lag time of approximately 50 days after the first molasses injection, sulfate-reducing conditions were achieved within the mine pool. Contemporaneous with a downward trend in sulfate concentrations, sulfide begins to be detected above the analytical detection limit of 0.10 mg/L. Sulfide is one of the sulfur end products of sulfate reduction and provides conclusive proof that in-situ sulfate reduction is occurring. Since the initial detection of sulfide within the mine pool, sulfide concentrations have been detected continuously, with the maximum concentration observed in early February 2005, indicating that the sulfate-reduction process is being maintained through passive addition of alcohol. As expected, field-measured dissolved oxygen (DO) has been less than 2 mg/L throughout the duration of the study with maintenance of the reducing system and the production of sulfide, which acts as an aggressive oxygen scavenger in aqueous systems.

The recirculation system was decommissioned in early December in conjunction with startup of passive alcohol addition, which served as the sole source of TOC within the mine pool. As seen with the TOC, sulfate, and sulfide data shown on Figure 4, sulfate-reducing conditions are maintained with passive application of alcohol to the mine pool.

Dissolved metals (i.e., ferrous iron, ferric iron, manganese, and aluminum) concentrations over time are presented on Figure 5. As seen on Figure 5, baseline mine pool metals concentrations are characterized by approximately 7 mg/L ferric iron, 40 to 50 mg/L ferrous iron, 15 mg/L aluminum, and 3 mg/L manganese.

Following an increase in pH and a conversion to anaerobic conditions, significant changes are observed in the mine pool chemistry. Aluminum concentrations decrease by approximately 87% as a result of pH increasing from 3.1 to approximately 6. As expected, no significant changes in manganese concentrations are observed with the change in mine pool pH and ORP.

With the addition of excess organic carbon to the mine pool, ferric iron is depleted from the mine pool because it is a thermodynamically favored electron acceptor compared to sulfate. Intermittent detections of ferric iron were observed during the transition of the mine pool from an aerobic to an anaerobic state and during the shift from molasses to alcohol as an organic carbon source. As ferric iron and dissolved oxygen are the causative agents of AMD, the mitigation of ferric iron in the system will decrease the relative rates of the AMD reactions and the rates at which acid and dissolved metals are produced within the mine workings.

Shortly following the observed depletion of ferric iron from the mine pool, ferrous iron concentrations show a steady increasing trend into the third month of the demonstration study. Prior to transitioning the mine pool to a reducing state, ferric iron concentrations were maintained at approximately 7 mg/L through ferric iron solubility limitations. Decades of AMD reactions and subsequent precipitation of ferric hydroxide within the mine workings have generated a large mass of solid phase ferric iron. Prior to the demonstration study, ferric hydroxide was in mineral dissolution equilibrium with the mine pool water. Following conversion to a reducing environment and the subsequent removal of aqueous phase ferric iron, the dissolution chemical reaction was shifted to promote the reductive dissolution of ferric hydroxide. Upon entering the aqueous phase under reducing conditions, ferric iron is immediately consumed biologically as an electron acceptor and ferrous iron is generated.

As shown on Figures 4 and 5, ferrous iron concentrations continue to increase in excess of 175 mg/L through the reductive dissolution process; however, ferrous iron concentrations begin to decrease in early October 2005, which coincides with the detection of elevated sulfide concentrations within the mine pool. Coincident with the early October ferrous iron peak, a predominant black ferrous iron precipitate was observed in the mine pool. Thus, it can be concluded that the peak and subsequent decline in ferrous iron concentration were caused by the rate of ferrous iron sulfide precipitation exceeding the rate that dissolved ferrous iron was generated through solid phase ferric hydroxide reductive dissolution and subsequent biological conversion to ferrous iron. Since the early October peak, ferrous iron concentrations have been decreasing through passive addition of alcohol. The decreasing dissolved metals trends are expected to continue as the population of sulfate-reducing bacteria increase and ferrous sulfide precipitates coat the mine workings, effectively blanketing and removing reactive pyrite and other sulfide minerals from participating in AMD reactions.

As seen on Figure 3, elevated pH and alkalinity are observed well beyond the timeframe expected through caustic solution delivery to the mine pool, which ceased in early October 2004. Enhanced biological activity within the mine pool through addition of excess organic carbon has resulted in the generation of carbonate alkalinity. This alkalinity is serving as a buffer to maintain pH around 5 standard units. The generation of alkalinity and subsequent buffering of pH has provided an environment capable of supporting enhanced biological activity through the passive addition of a carbon substrate.

Carbon Dioxide Injection

Carbon dioxide gas was injected into the unsaturated portion of the mine pool over a three day period at an approximate flow rate of 100 to 500 standard cubic feet per minute (SCFM). Baseline mine atmosphere measurements indicate near ambient concentrations of oxygen (21%) and carbon dioxide (< 1%). Once injected, the pure carbon dioxide gas mixed with existing gases within the mine and resulted in a dense blanket over the mine pool with depleted oxygen concentrations (less than 5%) and elevated carbon dioxide concentrations (approximately 5%). The dense anaerobic blanket was self-sustaining with depleted oxygen concentrations for approximately three months following carbon dioxide injection.

Figure 6 presents a regression curve between oxygen and carbon dioxide gas concentrations in volume percent, including both baseline and post-injection data. Figure 6 shows that one unit of carbon dioxide in the mine atmosphere creates a four unit drop in oxygen concentration. Thus, the depletion of 21% oxygen

through pyrite oxidation and the maintenance of 5% carbon dioxide results in a four-fold decrease in the oxidation capacity within the mine workings.

A mass balance on oxygen within the mine workings (i.e., dissolved oxygen, gaseous oxygen, and sulfate, the end product of oxygen in sulfide mineral oxidation) clearly shows that gaseous oxygen is the dominant source of oxygen (i.e., greater than 98%) that participates in AMD reactions. Oxygen is depleted from the mine atmosphere through thin film diffusion into the aqueous phase and immediate consumption through the AMD reactions presented in Equations (1) and (2) above. The removal of oxygen results in a less dense, buoyant gas compared to ambient air and chimney effects pull fresh, oxygen-rich ambient air into the mine workings to perpetuate the AMD cycle. With the addition of only 5% carbon dioxide gas, which is much heavier than ambient air, a dense anaerobic blanket is maintained above the mine pool. Oxygen ingress into the reactive portions of the mine workings is then limited to diffusion through the dense anaerobic blanket and is much slower than the buoyant driven advection previously carrying oxygen to the mine workings.

The benefit of carbon dioxide gas injection was seen for approximately three months as determined by depleted oxygen concentrations in the mine atmosphere. Throughout the three month period, the loss rate of the dense gas was greater than could be maintained through biologically-produced carbon dioxide. Therefore, a long-term sustainable source of carbon dioxide gas is necessary to maintain control of the gas phase at Tide Mine. Possible cost-effective gas phase controls within the mine include continuous injection of combustion offgases (typically five to 10 percent carbon dioxide gas) and a survey of the ground surface above the mine workings to identify the major conduits responsible for mine atmosphere exchange with ambient air.

Conclusions

The successful in-situ treatment in the mine pool and mine workings atmosphere has been demonstrated at Tide Mine. A chemically reducing environment with no dissolved oxygen, no ferric iron, and low concentrations of dissolved sulfide was created in the Tide Mine pool by adding alkaline reagents and organic carbon. Elevating carbon dioxide gas concentrations within the mine atmosphere excludes oxygen within the mine voids, and this exclusion is at a molar ratio close to 4:1 oxygen to carbon dioxide. Sulfate reduction was stimulated in the Tide Mine pool and forms the basis for long-term iron precipitation as an iron sulfide and alkalinity generation for pH buffering.

Acknowledgements

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Drainage

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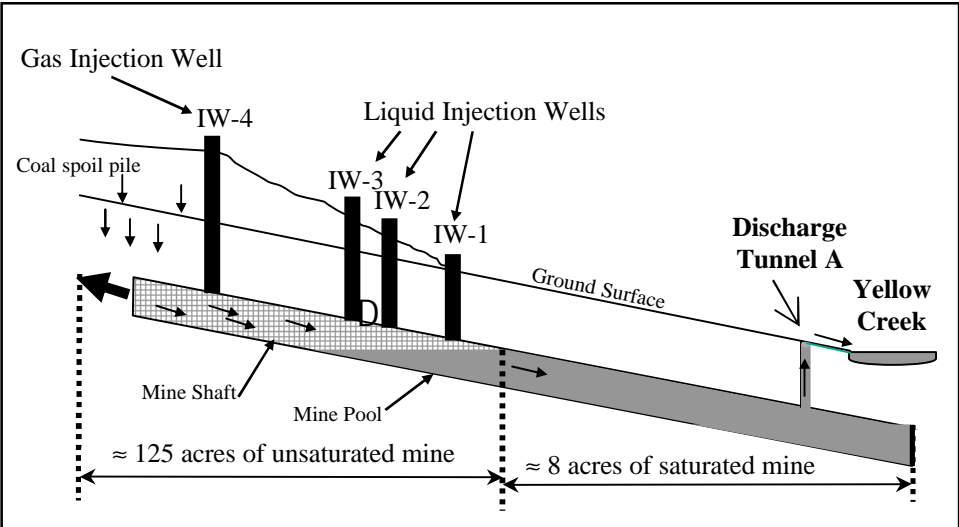


Figure 1. Tide Mine Workings
Conceptual Model.

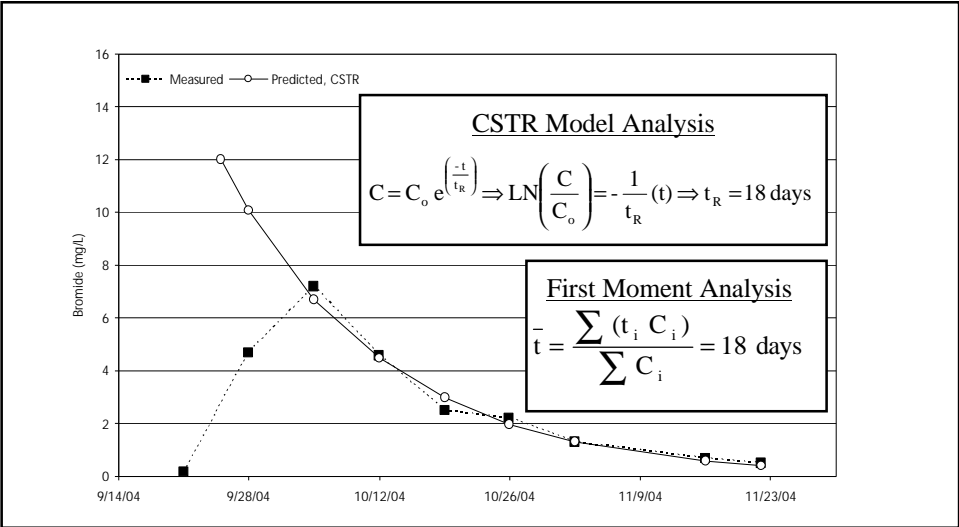


Figure 2. Bromide Concentration
Measured in the Discharge Pond
Following Pulse Input to Mine
Pool.

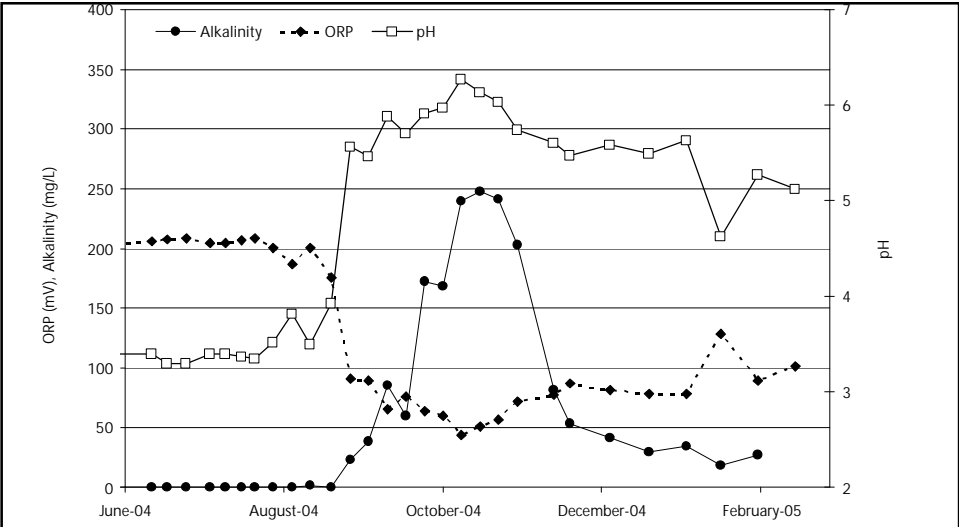


Figure 3. Alkalinity
Concentrations and ORP and pH
Measured in the Discharge Pond
Before and During In-Situ
Treatment.

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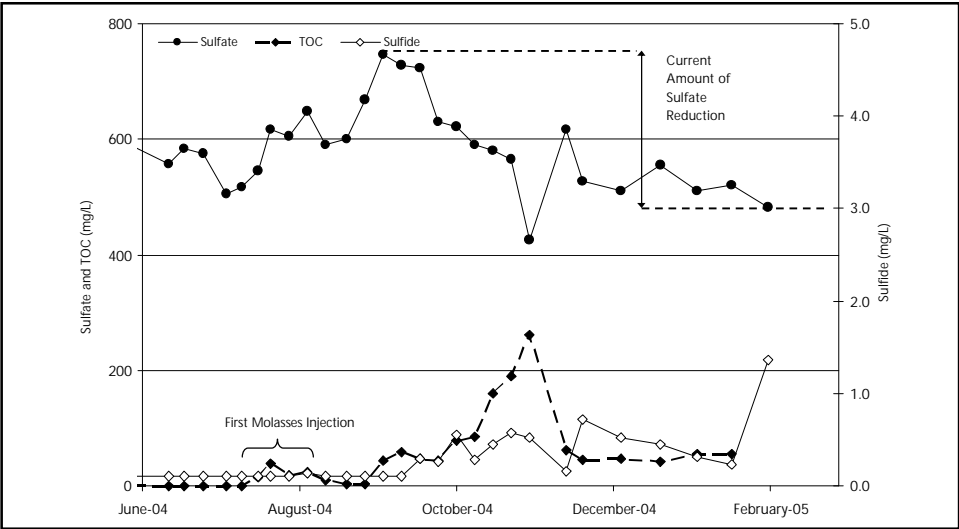


Figure 4. TOC, Sulfate, and Sulfide Concentrations in the Discharge Pond Before and During In-Situ Treatment.

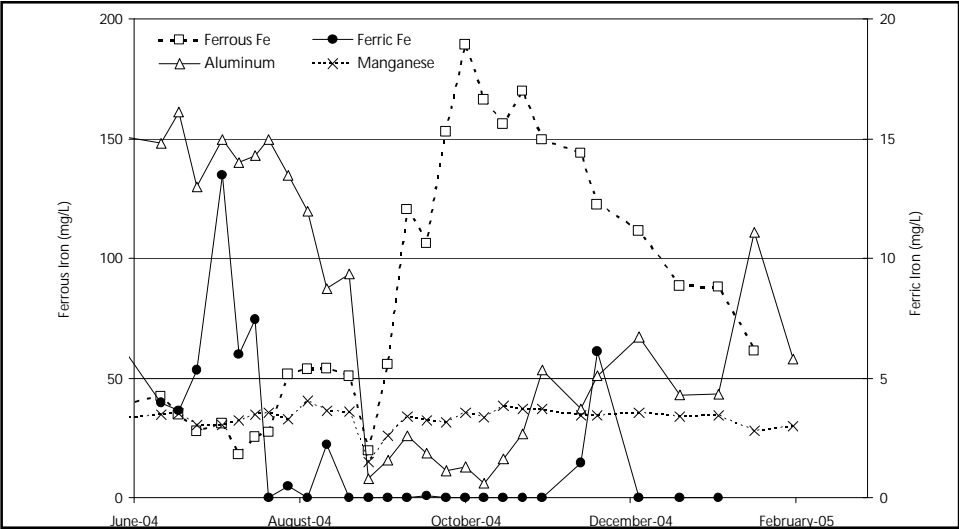


Figure 5. Ferrous and Ferric Iron, Aluminum, and Manganese Concentrations in the Discharge Pond Before and During In-Situ Treatment.

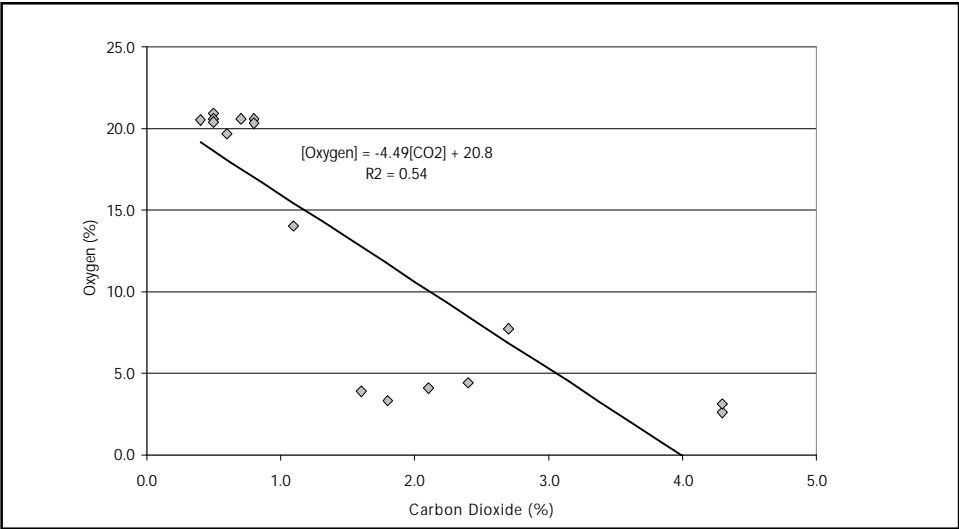


Figure 6. Oxygen and Carbon Dioxide Gas Concentrations Regression Analysis.