ARCADIS
Infrastructure, environment, buildings

ARCADIS G&M, Inc.
6 Terry Drive
Suite 300
Newtown
Pennsylvania 18940
Tel 267 685 1800
Fax 267 685 1801

ENVIRONMENT

TRANSMITTAL LETTER

To:
Bill Dadamo, P.E.
Mining Engineer Supervisor
Bureau of Abandoned Mine Reclamation
Cambria Office
286 Industrial Park Road
Ebensburg, PA 15931-4119

Copies:
Dr. Robert Eppley, BCWA

From:
Peter Milionis

Date:
02 May 2005

Subject:
DRAFT Final Report, Figures 1 and 2
Tide Mine Project, Center Township,
Indiana County, Pennsylvania

ARCADIS Project No.:
NP000601.0001

We are sending you:
☒ **Attached** ☐ **Under Separate Cover Via ________ the Following Items:**

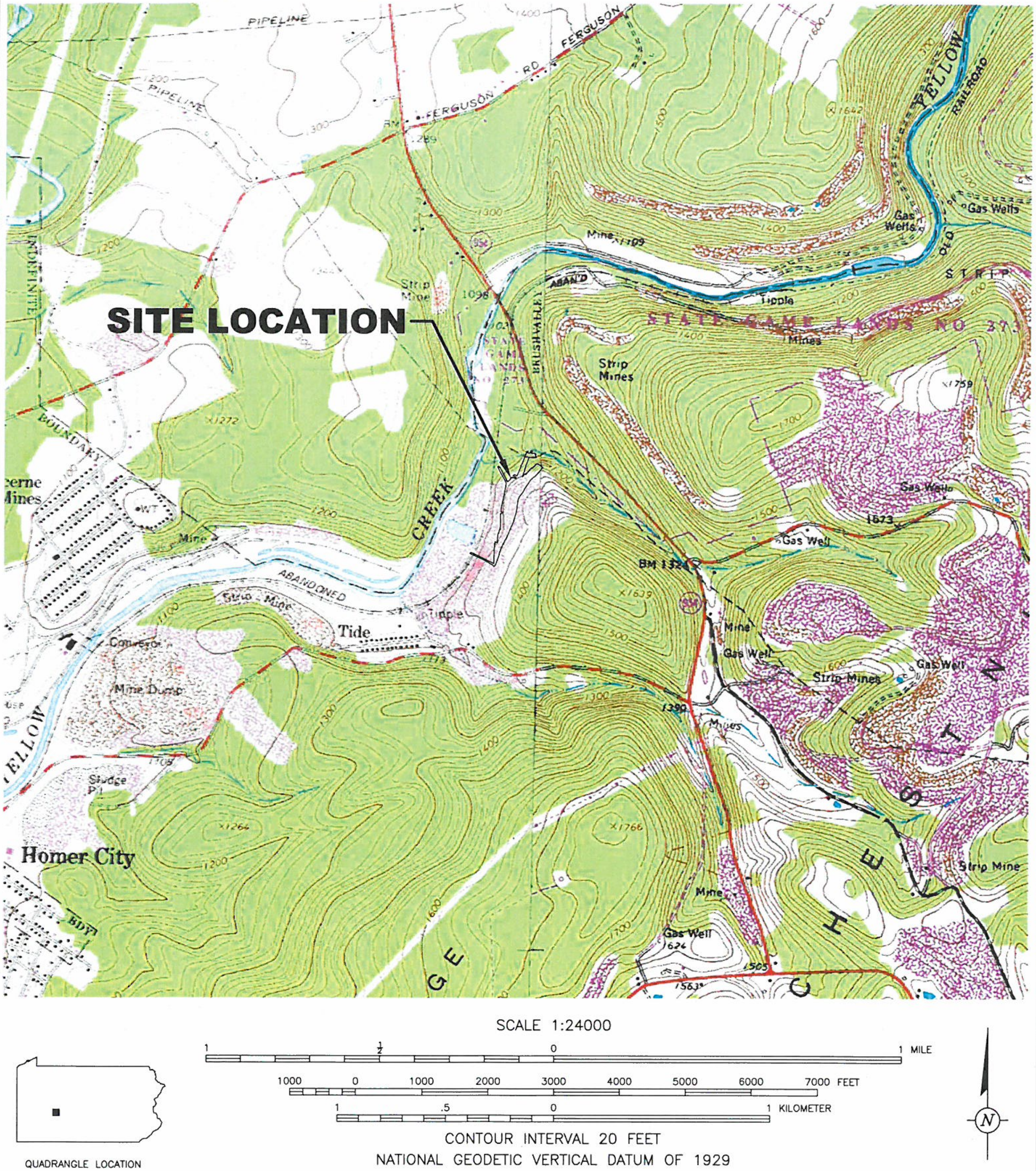
☐ Shop Drawings
☒ Figures
☐ Other: ____________________
☐ Plans
☐ Samples
☐ Specifications
☐ Copy of Letter
☐ Change Order
☐ Reports

Copies	Date	Drawing No.	Rev.	Description	Action*
4	5/2/2005	1	-	Site Location Map	FA
4	5/2/2005	2	-	Well Location and Equipment Set-Up	FA

Action*
☐ A Approved
☐ AN Approved As Noted
☐ AS As Requested
☐ Other: ____________________
☐ CR Correct and Resubmit
☐ F File
☒ FA For Approval
☐ Resubmit _____ Copies
☐ Return _____ Copies
☐ Review and Comment

Mailing Method
☐ U.S. Postal Service 1st Class
☐ Certified/Registered Mail
☐ Other: ____________________
☐ Courier/Hand Delivery
☐ United Parcel Service (UPS)
☐ FedEx Priority Overnight
☒ FedEx Standard Overnight
☐ FedEx 2-Day Delivery
☐ FedEx Economy

Comments: Figures 1 and 2 to accompany the DRAFT Final Report sent via electronic mail on 1 May 2005.



SOURCE: USGS 7.5 MIN. TOPOGRAPHICAL QUADRANGLE INDIANA, BRUSH VALLEY, PA.

ARCADIS
GERAGHTY & MILLER

DRAWN
M. WASILEWSKI

DATE
7/8/04

PROJECT MANAGER
P. MILIONIS

DEPARTMENT MANAGER
A. HANNUM

SITE LOCATION MAP

LEAD DESIGN PROF.
F. LENZO

CHECKED
P. MILIONIS

TIDE MINE
INDIANA COUNTY, PENNSYLVANIA

PROJECT NUMBER
NP000XXX.0001

DRAWING NUMBER
1

G:\APROJECT\PADEP_MINE RECLAMATION\TIDE MINE\WORKPLAN\HASP\CADD\FIG-1 SITE LOCATION MAP.DWG, 07/09/04 03:23pm, LAYOUT: 8.5x11 v

DRAFT REPORT

IN-SITU BIOREMEDIATION DEMONSTRATION PROJECT

ABANDONED TIDE MINE

CENTER TOWNSHIP, INDIANA
COUNTY, PENNSYLVANIA

Kelly S. Houston
Staff Engineer

Peter N. Milionis, P.G.
Project Manager

Joseph G. Harrington
Business Practice Director

James M. Harrington
Project Director

DRAFT REPORT

IN-SITU BIOREMEDIATION DEMONSTRATION PROJECT FINAL REPORT

ABANDONED TIDE MINE

CENTER TOWNSHIP, INDIANA COUNTY, PENNSYLVANIA

AMD 32 (2404) 101.1

Prepared for:
Blacklick Creek Watershed Association/
Pennsylvania Department of
Environmental Protection

Prepared by:
ARCADIS
6 Terry Drive
Suite 300
Newtown
Pennsylvania 18940
Tel 267 685 1800
Fax 267 685 1801

Our Ref.:
NP000601.0001

Date:
29 APRIL 2005

Table of Contents

Tables

Figures

Appendix – Well Boring Logs

DRAFT REPORT

IN-SITU BIOREMEDIATION DEMONSTRATION PROJECT

Abandoned Tide Mine
PADEP Ref. # AMD 32(2404) 101.1

1. Introduction

Under contract with the Blacklick Creek Watershed Association (BCWA) with funding from the Pennsylvania Department of Environmental Protection (PADEP), Bureau of Abandoned Mine Reclamation (BAMR), ARCADIS G&M, Inc. (ARCADIS) performed a demonstration study of in-situ bioremediation of acid mine drainage (AMD). A site location map is provided as Figure 1. A summary of the six month Tide Mine in-situ demonstration project is provided below under the following sections:

- Site Background Information;
- Overview of the In-Situ Passive Bioremediation Technology Demonstration;
- In-Situ Bioremediation Demonstration Project Chronology;
- Stated Demonstration Study Objectives;
- Preliminary In-Situ AMD Treatment Results and Discussion;
- Preliminary In-Situ AMD Treatment Conclusions; and,
- Cost Benefit Analysis Associated with In-Situ Treatment.

2. Site Background Information

The Tide Mine, also known as the Waterman #3 Mine, is located in Center Township, Indiana County, Pennsylvania. The mine was operated in the 1910's through 1930's. 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 crop to allow for dewatering of the mine. Currently, much of the site is covered with stockpiled coal waste debris. Access is available to the top of the debris pile, however, road improvements were necessary to enable access (Figure 2).

The BCWA completed the Yellow Creek Restoration Project 2C Passive Treatment System in July 2003 to treat the water from the drainage shaft, which is currently in operation. Geochemical data has been collected between September 1997 and May 2002 along with some outflow data.

Based on topographic maps provided by L. Robert Kimball and Associates (Kimball) (26 November 2003), ARCADIS estimated the mine pool volume based on a surface water elevation of 1,092 feet above mean sea level. Using this elevation, the volume was determined as follows:

- The total aerial extent of the mine is approximately 335,000 square feet (7.7 acres), assuming the mine is flat.
- The height of the mine is 4.5 feet.
- The range of void space for the mine is approximately 50% to 60%.
- Total mine volume is approximately 5.6 to 6.8 million gallons.
- Estimated "beach Area" length of the mine pool is approximately 1,650 feet.

3. Overview of the In-situ Passive Bioremediation Technology Demonstration

The objective of the in-situ passive bioremediation process was to transform the environment in the mine workings from a sulfide oxidation environment to a sulfate reduction environment on the host rock and in the mine pool. In addition, the capillary and water-level fluctuation zone immediately above and adjacent to the mine pool was transformed temporarily from an oxygen-rich to a carbon dioxide-rich environment.

To achieve sulfate reducing conditions in the mine pool, growth of sulfate reducing bacteria was initiated. Growth of sulfate-reducing bacteria is optimal at near-neutral pH, under anaerobic conditions, and in the presence of excess organic electron donors.

The ARCADIS patented technology implemented at Tide Mine creates a physical infrastructure system to manipulate the mine workings, provides for the injection of chemicals to directly affect the mine pool biogeochemistry, and provides for the injection of organic carbon sources to support native microbes for further biogeochemical changes in the mine pool. Specifically, the ARCADIS approach involves the integration and application of the following three processes:

1. Chemical neutralization of the mine pool through addition of sodium hydroxide to raise the pH above 5.0 and allow sulfate-reducing bacteria to flourish;

2. Displacement of oxygen in the environment above the mine pool through direct introduction of carbon dioxide gas and off-gassing of biologically produced carbon dioxide gas from the mine pool to mitigate the oxidation cycle that fuels and perpetuates acid formation; and,

3. Development of an anaerobic, sulfate reducing environment within the mine pool by providing excess organic carbon in the form of readily degradable sugars and alcohols.

The activity and populations of bacteria present in the mine pool increased as the excess carbon injected into the minepool was metabolized; consuming dissolved oxygen for respiration at a rate greater than it can be recharged, thus creating an anaerobic environment. Following the depletion of dissolved oxygen, bacteria began utilizing alternative electron acceptors such as manganese, iron, and sulfate, to support respiration.

The establishment of a reducing environment was supported by the microbial consumption of the excess organic carbon substrates maintained in the mine pool. Alkalinity was formed by biologically produced carbon dioxide dissolving in the mine pool water, which provided continued buffering capacity. As a direct result of the applied technology, not only was the pH of the water in the mine pool neutralized, but also dissolved metal concentrations exhibited decreasing concentration trends through the formation of sulfide, hydroxide and carbonate-based precipitates.

3. In-Situ Demonstration Project Chronology

The first phase of field work associated with the demonstration project included site grading and well drilling activities. Three liquid injection wells (i.e., IW-1, IW-2, and IW-3) and one gas injection well (i.e., IW-4) were installed during the period 1 through 24 June 2004. Site grading work was performed by Maudie Excavating and Hauling, Homer City, Pennsylvania and L. Robert Kimball and Associates (Kimball), Ebensburg, Pennsylvania provided drilling and well installation services. Boring logs for Injection Wells IW-1 through IW-4 are provided as Appendix A.

Godwin Pumps, Leetsdale, Pennsylvania was retained to provide the recirculation system rental pump, fuel tank, and piping. Fusion welded six-inch diameter high density polyethylene (HDPE) and process controls and instrumentation were installed during the period 15 through 24 June, 2004. A 70 horsepower, diesel powered pump was mobilized to the site on 18 June 2004 and set on a gravel pad adjacent to the mine discharge pond. Well and equipment locations are shown on Figure 2.

Three 4,000-gallon polyethylene tanks were rented from Baker Tanks, Inc., Pittsburg, Pennsylvania and mobilized to the site during 12 through 13 July 2004. The three tanks were equipped with piping and instrumentation and used as follows:

- One tank was staged adjacent to the recirculation pump and was loaded with 25% caustic (i.e., sodium hydroxide) solution, which was fed into the recirculated water stream during pump operation to elevate the mine pool pH;
- One tank was staged adjacent to the IW-1 well head and was loaded with 40% alcohol (i.e., methanol) to passively drip organic carbon into the mine pool during the later stages of the demonstration project; and,
- One tank was staged adjacent to the IW-2 well head and loaded with 40% alcohol to passively drip organic carbon through both IW-2 and IW-3 well heads into the mine pool during the later stages of the demonstration project.

Mine pool water was conveyed from the discharge pond and to Injection Wells IW-1 through IW-3 by the six-inch diameter HDPE piping. Piping and instrumentation details are provided on Figure 3 for the recirculation piping, caustic feed, pump suction, and methanol feed.

Significant activities that were conducted during the demonstration project following recirculation system installation and startup and shakedown procedure are summarized in Table 1.

At the completion of the demonstration project, the following quantities of water were recirculated and reagents injected:

- Approximately 15,000,000 gallons of water were recirculated during the demonstration project;
- Approximately 6,100 gallons of 25% caustic solution were added to the mine pool over the three months of recirculation system operation;
- Approximately 51,000 gallons of 20% molasses solution were added to the mine pool over the three months of recirculation system operation; and,

- Approximately 15,000 gallons of 40% methanol solution were added to the mine pool over the entire six-month demonstration study. During the last three months, alcohol was the sole source of organic carbon in the mine pool.

4. Stated Demonstration Study Objectives

The objectives of the Tide project were to document that an underground coal mine pool can be biogeochemically modified using the injection of alkaline and organic carbon reagents and carbon dioxide gas, to reduce the toxicity of the mine water, and achieve specific water quality improvements. The original demonstration project proposal prepared by ARCADIS set forth the following:

> Demonstrate that ARCADIS' in-situ passive technology can effectively change key physical, chemical, and microbiological parameters in the mine workings including:
>
> 1. No dissolved oxygen in the mine pool
> 2. No ferric iron in the mine pool
> 3. Reduced iron concentrations in the mine pool discharge
> 4. Increased pH and alkalinity in the mine pool
> 5. Carbon dioxide production from the saturated zone into the unsaturated zone
> 6. Reduced manganese concentrations in the mine pool discharge
> 7. Reduced aluminum concentrations in the mine pool discharge

5. Preliminary In-Situ AMD Treatment Results and Discussion

The preliminary in-situ AMD treatment results are discussed below with respect to the specific project objectives stated in the ARCADIS proposal and Work Plan, and summarized in Section 4 of this report. The results obtained during the demonstration project are then used to develop a conceptual model of the mine workings and to predict iron and sulfate concentrations under steady-state sulfate-reducing conditions in the mine pool. It should be noted that the predictions stated in Section 5.2 of this report only account for liquid phase amendment of the mine workings (i.e., organic carbon addition to the mine pool) and do not consider future gas phase amendment of the mine workings (i.e., maintaining a carbon dioxide-rich anaerobic gas blanket throughout the unsaturated portions of the working). Gas-phase control of the mine workings would significantly reduce the acid loading to the mine pool and would yield higher quality water as a result of in-situ prevention and treatment of AMD.

5.1 Results and Discussion

Table 2 presents a comprehensive summary of analytical data associated with the In-Situ Bioremediation Demonstration Study conducted at Tide Mine. As a basis for further discussion ARCADIS offers the following preliminary conclusions about the Tide Mine pool data during the demonstration study:

5.1.1 Bromide Tracer

The Tide mine pool has a smaller active volume and shorter residence time than anticipated, which reduced the potential reaction time in the pool.

a. The hydraulic residence time of reagents and tracers was approximately in the range of two weeks from the time of injection to the time reagent/tracer peak concentrations were measured in the mine pool discharge pond. Figure 4 shows the results of the bromide injection study performed in IW-3, and from this information a residence time distribution curve can be inferred. Bromide was injected on 25 September 2005, and by 28 September bromide measured 4.7 mg/L, and a peak concentration of 7.2 mg/L bromide was observed on 5 October, 10 days after injection. The first moment of the bromide residence time distribution curve centroid was evaluated to estimate an average hydraulic residence time of the mine pool at 18 days. The relationship between retention time and flow rate was used to estimate a reactive volume of 2.0 to 2.5 million gallons and an average residence time under non-pumping conditions between 2 and 3 weeks, depending on discharge rates. Approximately 86% of the bromide mass that was injected into the mine pool was accounted for in the discharge pond.

b. There was a two to three week lag between when organic carbon concentrations should have reached peak concentrations and when peak concentrations were observed; specifically, maximum concentrations should have been achieved the week of 12 to 19 October, while maximum concentrations were observed 2 November. On Figure 5, the difference between the "short residence time" and "long residence time" is 2 million gallons at a 100 gpm discharge rate, and 3 million gallons at a 70 gpm discharge rate, respectively. Based on the bromide results and the measured flows, these calculations should bracket the range of average hydraulic residence times and reactive pool volumes during the test.

c. The first molasses injection conducted on 20 July 2005 also shows a very rapid appearance at the discharge point (one day) and also a rapid washout to background levels (34 days to complete washout on 24 August), as shown on Figure 6.

The observed mine pool response to the bromide and molasses injection show that the mine pool does not have an optimal reaction time (closer to two months would be considered optimal) to achieve complete sulfate reduction in the mine pool. The observed mine pool residence time was insufficient to achieve improvements in water chemistry through more complete sulfate reduction (i.e., greater iron removal by sulfide precipitation) during the demonstration study; however, as discussed in Conclusion #5 below, additional time to establish larger populations of sulfate reducing bacteria will result in a higher relative sulfate reduction reaction rate per unit of mine pool volume.

5.1.2 Dissolved Oxygen

Based on system performance, the first objective of eliminating dissolved oxygen in the mine pool was achieved and is being maintained. The ability of a field instrument to reliably measure dissolved oxygen below 1 mg/L is questionable, particularly in the presence of reactive sulfide. Sulfhydryl ions (HS-) are known to interfere with the reference electrode materials, which are otherwise inert to most ions in oxygenated waters. For this reason we consider the very low levels of dissolved oxygen observed in the pool to be essentially zero. The most significant support of essentially zero dissolved oxygen is that from September through January, dissolved sulfide has been measured in the pool discharge. The reaction rate between dissolved oxygen and dissolved sulfide is extremely rapid (on the order of minutes for complete reaction), making the presence of sulfide in the pool discharge the most reliable measurement documenting that there is no dissolved oxygen in the Tide mine pool. Figure 7 shows dissolved sulfide concentrations in the Tide pool discharge.

5.1.3 Ferric Iron

The second objective of eliminating ferric iron in the mine pool was also achieved and is being maintained. Ferric iron concentrations are shown along with total organic carbon on Figure 8. Since the first injection of organic carbon in July 2004, ferric iron measurements have decreased to non-detect for all measurements except 9 and 24 August, when organic carbon from the first molasses injection was being depleted in the mine pool, and on 22 November and 7 December, during the transition from recirculation conditions to the more passive methanol drip. From these data, it can be concluded that as long as organic carbon is sufficiently supplied to the mine pool, ferric iron can be eliminated.

It is important to emphasize that as long as ferric iron and dissolved oxygen are eliminated from the mine pool, continued leaching of metal-sulfide minerals in the fractured rock matrix of the mine pool cannot continue. As detailed in the following chemical Equations (Singer and Stumm, 1970), AMD is generated by either oxygen reacting with pyrite (catalyzed by bacteria) or ferric iron reacting with pyrite:

Initiation Reaction:

$$FeS_{2(s)} + H_2O + 3.5\ O_2 \rightarrow Fe^{2+} + 2\ SO_4^{2-} + 2\ H^+ \qquad (1)$$

Propagation Reactions:

$$Fe^{2+} + 0.25\ O_2 + H^+ \rightarrow 0.5\ H_2O + Fe^{3+} \qquad (2)$$

$$14\ Fe^{3+} + FeS_{2(s)} + 8\ H_2O \rightarrow 15\ Fe^{2+} + 2\ SO_4^{2-} + 16\ H^+ \qquad (3)$$

Through the Tide Mine demonstration, ARCADIS has shown that the addition of organic carbon to the mine pool can eliminate these causative agents of AMD within the mine pool.

5.1.4 Dissolved Iron

The third objective of reducing iron concentrations is only now being achieved. There was clearly a large amount of ferric iron solid phase compounds stored in the mine, and, upon dissolution of the solid phase, the ferric iron was reduced to ferrous iron, which is soluble under the reducing conditions that existed in the mine pool after organic carbon was injected. Figure 9 shows the increase of dissolved iron concentrations during the early phase of the formation of reducing conditions. It should be noted that the iron measured in the mine discharge was entirely comprised of ferrous iron. Since 26 October 2005, there has been a consistent decrease in iron concentrations. After 26 October, with the pH in the 5-6 range (Figure 10), without any dissolved oxygen, and with low ORP conditions (Figure 11), the major phase that accounts for iron removal is iron sulfide. As noted above, the extent of the iron sulfide formation is being limited by the extent of sulfate reduction and the short residence time of water containing carbon sources in the mine pool.

In addition to reductive dissolution of solid ferric iron compounds, which is a transient condition which peaked on 5 October 2005, the recirculation system was clearly exposing previously dry underground mine workings to recirculation water. Examination of conductivity trends on Figure 10 shows that even without substantial reductive dissolution of iron there was a very sharp rise in conductivity measured on 21 July that corresponds to the onset of the recirculation system. During the operation of the recirculation system, the conductivity has remained higher than baseline, and with the recirculation system shut off, the conductivity has decreased. While this is a surrogate parameter that measures many dissolved compounds together, there is an indication that the recirculation of water in the mine workings contributed to the increase in overall dissolved constituents in the mine waters.

5.1.5 pH

Increased pH has been achieved (Figure 10) and is being maintained far in excess of the time that could be affected by the sodium hydroxide addition to the mine pool. During recirculation system operation, sodium hydroxide was metered at a rate that resulted in a pH of approximately 6.5 to 7.5 standard units in the recirculation stream; thus, the caustic solution became fully dissolved in the mine pool and density effects of the caustic solution within the mine pool are considered negligible. As discussed in Conclusion #1 above, all dissolved parameters are washed out of the mine pool within the conservative range of 30-40 days. The last time an alkaline reagent was added to the mine pool was 14 October, which indicates, at a minimum, all of the alkalinity measured beyond 1 December has been generated from microbial consumption of the organic carbon reagent during iron and sulfate reduction. Figure 9 shows that alkalinity has continued to be generated in the mine pool, ranging from 18 to 40 mg/L since December 1. Both the pH and alkalinity in the mine pool have decreased since the recirculation system and alkaline reagent addition have ceased. The system does show some resilience in that the pH has not returned to baseline conditions, ORP remains low, ferric iron has not returned to baseline conditions, and some alkalinity remains.

The continued, but low levels, of alkalinity in the mine pool discharge is consistent with the continued oxidation of the organic carbon added to the top of the mine pool. The low residence time, as noted in Conclusion #1 above, is currently preventing the full conversion of TOC into carbon dioxide and bicarbonate, and thus the alkalinity being produced is limited. As the abundance of microbes, particularly sulfate reducing bacteria (SRB), increases with additional growth time, the relative reaction rate per unit volume of mine pool will increase, and the efficiency of the mineralization of the added organic carbon to form alkalinity will also increase. The combination of alkalinity production by sulfate reduction, and the consumption of oxygen and ferric iron in the mine pool and mine atmosphere will in time lead to a stable anaerobic environment being created in the Tide mine, with the consequent avoidance of AMD generation.

5.1.6 Carbon Dioxide Gas Injection

The relative contribution of liquid and gas phase oxidants, specifically oxygen, to the AMD chemistry shown in Equations 1 through 3 above can be determined through an analysis of oxygen sources and sinks within the mine workings. A mass balance on oxygen within the mine workings (i.e., dissolved oxygen, gaseous oxygen, and sulfate, the dominant end product of oxygen in sulfide mineral oxidation) clearly shows that gaseous oxygen is the dominant source of oxygen (i.e., conservatively greater than 98%) that participates in AMD reactions. Oxygen is depleted from the mine atmosphere through thin film diffusion into the aqueous phase and near 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 addition of carbon dioxide to the zone above the mine pool has led to an exclusion of oxygen and substantially lowered oxygen concentrations in the mine void. This lowered oxygen condition was maintained for approximately 3 months from this single injection of carbon dioxide (Figure 12). Based on ARCADIS's understanding of atmospheric transfer into mine voids and, as demonstrated at Tide Mine, maintenance of approximately 5% carbon dioxide within the mine workings results in a non-buoyant atmosphere in the mine, substantially limiting gas exchange. The ratio of oxygen to carbon dioxide to stop gas exchange is 4:1, that is, 4 moles of oxygen are compensated for, or prevented from transferring into the mine by the addition of 1 mole of carbon dioxide. Another way of stating the same thing is that a 5% carbon dioxide atmosphere in a mine void space is a "dead zone" where gas transfer is slowed and becomes diffusion-limited. Figure 13 shows that this theoretical ratio based on gas density is consistent with what was empirically observed in the Tide mine (i.e., a 4:1 molar ratio of oxygen to carbon dioxide).

It is estimated that ambient air gas flow into and out of the mine workings must occur at approximately 20 standard cubic feet per minute (SCFM) to supply the amount of oxygen discharged from the mine workings as sulfate. At an average gas flow rate of 20 SCFM, the mine workings would exchange one unsaturated mine volume in one to two years. This relatively low gas flow is likely diffusion or barometrically-controlled and occurs over the entire 125 acres of unsaturated mine workings. Since it appears that the Tide Mine workings are not convectively controlled, gas-phase control would likely require a continuous source of carbon-dioxide gas. Deep, mostly saturated mine pools are expected to require significantly less maintenance in gas-phase control of the mine workings. Because of the high degree of subsidence, fine grained debris pile overlying the mine workings, no known unsaturated portals or tunnels, relatively small volume percentage of the mine workings exchanged on a daily basis, and the relatively low sulfate levels discharged from the mine pool (i.e., advectively-controlled mine workings systems are expected to discharge sulfate at concentrations on the order of 1,000 to 10,000 mg/L at much higher flow rates), it is not likely that the Tide Mine workings gas phase are advectively controlled.

The less than optimal construction of IW-4 affects our certainty that all of the carbon dioxide added to the mine went to the desired zone, and consequently, it is possible that the construction of gas Injection Well IW-4 may have limited carbon dioxide delivery to the mine zone. Thus, the longevity of the carbon dioxide injection would have been greater than the observed 3 month duration with a direct injection into the mine void. However, even at the loss rate that can be inferred from this test, it would only take a small amount of carbon dioxide to maintain a 5% carbon dioxide atmosphere in the zone immediately above the mine pool. If this carbon dioxide could be supplied by a combustion process offgas, the cost for this carbon dioxide would be relatively inexpensive.

5.1.7 Manganese

No significant effect was observed on manganese concentrations during the test (Figure 14). Manganese carbonates precipitate at very slow rates, and require pH control. Therefore we cannot expect sulfate reducing pool conditions alone to achieve reductions in manganese, without some source prevention; disrupting either oxygen supply or sulfide availability, or water transport, around the gangue leaching interface.

5.1.8 Aluminum

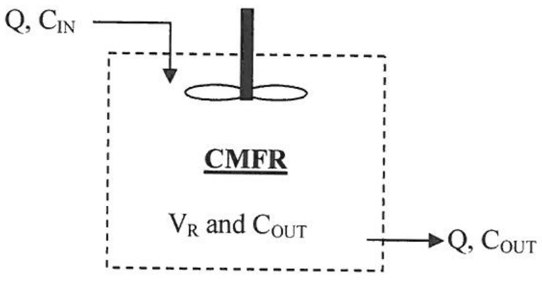
Aluminum concentrations were substantially lowered as a result of the pH increase during alkaline reagent addition (Figure 14). Aluminum hydroxides are insoluble in the pH 6 range, and as pH decreases, aluminum hydroxide can be expected to re-dissolve, and hence act as a solid phase buffer in the mine pool. While ARCADIS has demonstrated that aluminum precipitation can be effectively accomplished by injection wells in a mine pool, as has been previously demonstrated, ARCADIS does not propose to keep maintaining alkaline reagent addition to the mine pool to accomplish aluminum removal. Rather, ARCADIS believes that maintenance of reducing conditions, an anoxic environment, and no ferric iron in the mine pool, will in time lead to reduced leaching of aluminum from the primary minerals in the mine rocks, and that aluminum production will decrease. The fact that aluminum concentrations have not returned back to baseline concentrations more than 3 months after alkaline reagents have stopped being added to the mine, supports the contention that in-situ microbially-generated reducing conditions slows the production of dissolved-phase aluminum.

5.2 Development of Tide Mine Workings Conceptual Model

As discussed under Section 5.1.6 above, greater than 98% of the oxygen participating in the AMD-generating chemistry (Equations 1 through 3) is a result of gas-phase contributions, which likely occur within the unsaturated mine workings. Therefore, at a minimum, approximately 95% (i.e., unsaturated) of the mine workings contribute most, if not all, of the AMD to the mine pool. The mine pool has been saturated since the 1930's and it is probable that the pyritic rock within the mine pool participates marginally in the generation of AMD. With the above assumptions, it can be concluded that the unsaturated mine workings are the dominant source of AMD at Tide Mine. Therefore, by conversion of the mine pool to an anaerobic state, it can be conceptualized that the mine pool served as a Completely Mixed Flow Reactor (CMFR) with near constant influent concentrations (i.e., iron and sulfate fed into the mine pool from the unsaturated portion of the mine workings) and flow (100 gallons per minute [gpm]).

A mass balance on a reactive species in a CMFR can be expressed conceptually, graphically, and mathematically as follows (Weber and Digiano, 1996):

Net Rate of Transport Through Reactor	+ -	Net Rate of Transformation Within Reactor	=	Net Rate of Change Within Control Volume



$$QC_{IN} - QC_{OUT} + r\,V_R = V_R \frac{\Delta C_{OUT}}{\Delta t} \qquad (4)$$

Where,

$Q =$ Steady-state flow rate from unsaturated mine working into mine pool and out the discharge (volume per time)

$C_{IN} =$ Concentration of species entering the mine pool from the unsaturated portions of the mine workings (moles per volume)

$C_{OUT} =$ Concentration of species in the CMFR and observed in the discharge pond (moles per volume)

$r =$ Reaction rate (moles per time)

$V_R =$ Reactor volume (volume)

$\frac{\Delta C_{OUT}}{\Delta t} =$ Change in concentration versus time (moles per time)

For purposes of evaluating performance of in-situ liquid-phase treatment at Tide Mine, the assumption is made that baseline and long-term conditions (i.e., species concentrations) are at steady state. Therefore, the net rate of changed within the mine pool term on the right hand side of Equation 4 is set to zero. The term V_R/Q is referred to as the average hydraulic retention time (τ) and has been determined to be approximately 18 days, as discussed in Section 5.1.1 above.

Equation 4 can be solved at discrete time steps to estimate the reaction rate term. For purposes of this analysis, the reaction rate term will be treated as a lumped parameter, although reaction rates typically follow a concentration dependence in first and second order systems. The steady-state solution to the partial differential Equation 4 solved for the effluent concentration yields the following equation:

$$C_{OUT} = C_{IN}\,(1 + r\,\tau) \qquad (5)$$

In summary, Equation 4 has been used to estimate the average sulfate reduction rate and the average sulfide generation rate in the mine pool during the later part of the demonstration study. As the only other significant sulfide sink in the system, the difference between sulfate reduction and sulfide generation can be attributed to iron sulfide precipitation. It is assumed that sulfide loss due to oxygen scavenging through oxygen diffusion into the mine pool and hydrogen sulfide volatilization loss occur at an insignificant rate compared to iron sulfide precipitation.

Ferrous sulfide precipitates on a one-to-one iron-to-sulfide molar basis and the rate of sulfide depletion is equal to that of iron depletion (i.e., precipitation) in the mine pool in an anaerobic system. Using an average baseline total iron concentration of approximately 38 mg/L, the median iron depletion rate (equal to sulfide depletion rate on a molar basis) observed during the latter part of the demonstration study of 315 mol Fe/(L day), and accounting for the mass transfer and mixing effects as derived in Equation 5, the projected total iron concentration in the mine pool under steady state conditions (C_{OUT}) will be approximately 6 mg/L, if the system is maintained anaerobic and sulfate-reducing within the treatable extents of the pool. The calculations summarized above are presented in Table 3 and the sulfate, sulfide, and total iron mine pool discharge data are shown on Figure 15.

6. Preliminary In-Situ AMD Treatment Conclusions

The following types of reactions that form the basis for in-situ treatment in a mine pool and the atmosphere above the mine pool have been demonstrated in the Tide Mine project:

- It has been shown that a chemically reducing condition with no dissolved oxygen, no ferric iron, and low concentrations of dissolved sulfide, can be created in a mine pool by adding alkaline reagents and organic carbon to the mine pool;

- It has been shown that carbon dioxide excludes oxygen in the atmosphere within mine voids far more effectively than we would expect from a lighter inert gas, and that this exclusion is at a molar ratio of close to the projected 4:1 O_2 to CO_2; and,

- It has been shown that sulfate reduction can be stimulated in a mine pool, which forms the basis for long-term iron precipitation as an iron sulfide and alkalinity generation for pH buffering and aluminum precipitation.

7. Cost Benefit Analysis Associated with In-Situ Treatment

As stated in the proposal to conduct the demonstration study, stabilized reductions in sulfate and dissolved metals concentrations are longer term goals (i.e., greater than six months) of the project and the reduced metals loading benefit of the anaerobic system has only recently been seen in the performance monitoring data. Therefore, the costs incurred to-date are not representative of the long-term maintenance costs and should not be limited to the results observed during the six-month demonstration study; system efficiency may increase with an increasing population of sulfate-reducing bacteria. However, ARCADIS believes that formation and maintenance of sulfate-reducing pool conditions alone at the Tide Mine site will not achieve discharge goals particularly for gangue minerals (Al, Mn). Because of this, it is only possible to draw the conclusion that utilization of sulfate reducing conditions in mine pools should only be conducted after source reactions have been addressed to the extent possible. At Tide Mine, the source of more than 90% of the contaminants soluble in the mine pool is from oxidation reactions occurring above the mine pool and not from ferric ion leaching of minerals in the mine pool.

The results from the gas-phase amendment in the source areas indicated that a small addition of carbon dioxide gas resulted in a large benefit; oxygen concentrations dropped far more than would be predicted from inert gas displacement only. The reason for this drop is derived from the molecular weight balance between oxygen combustion and carbon dioxide addition. Five percent carbon dioxide addition into the mine gas mixture can effectively reverse and overcome the buoyancy effects of combustion of 20% oxygen in air. The demonstration study gas-phase observations at the Tide Mine allow us to predict cost-benefit relationships for larger mines from the results.

Acid generation equations can be approximated using air from Equation 1:

$$FeS_{2(s)} + H_2O + 18(N_2/O_2) \rightarrow Fe^{2+} + 2\ SO_4^{2-} + 2\ H^+ + 14N_2 \qquad (6)$$

Because of the large volume of buoyant, oxygen-depleted nitrogen that is formed and exits the Tide Mine daily, new oxygen-rich air is drawn into the mine. At 600 mg/L sulfate in about 90 GPM waters leaving the mine, we calculate the volume of air drafting into the mine at a minimum of 19 CFM. In fact, it is greater than this because of the additional heat given off from the oxidation processes, so this is a minimum rate for buoyancy reasons alone. By maintaining 5% carbon dioxide in the mine workings, we project that acid production will be cut by more than 80%. Once the capital installation costs are incurred for the gas capture and delivery system, the incremental maintenance costs are very small, and are primarily related to those costs necessary to monitor the gas concentrations and to ensure that the gas injection rate is adjusted as the oxidation processes slow down. The impediment to creating this system at the Tide Mine has been the uncertainty about the allowable beneficial re-use of compressor off-gases from the natural gas wells in the vicinity of the Tide Mine. Assuming permitting concerns could be addressed, the actual cost to maintain the injection of these waste gases is insignificant to the benefit of reducing acid production by approximately 80%.

ARCADIS estimates the annual O&M program costs to maintain an anaerobic mine pool at Tide Mine to be approximately $59,520 and the gas phase maintenance costs to reduce gangue mineral leaching to be about $23,000. This is likely not cost-competitive with passive treatment system costs supplied by BAMR. However, for larger systems, and particularly for mines where pumping must be maintained for control of the contaminants due to a limited area for passive treatment, then these costs and the expected source prevention costs, become much more cost competitive.

7.1 Iron Treatment Benefits Analysis

Liquid-phase amendment of the mine pool to cause formation and maintenance of sulfate reducing conditions, such as we have created herein, can confidently be projected to provide benefits for reduction of total iron and particularly ferric iron from the mine pool discharges. This is particularly expected if the pool residence time is greater than about 50 days, although the kinetic precipitation rate is strongly controlled by the pH of the system with decreased precipitation rates expected with lower pH. If the pool was initially at a lower starting pH, or was ineffectively neutralized initially, then removal of iron by FeS precipitation would require that the pool residence time be much longer to achieve the projected iron removal efficiency (Miller & Tsukomoto 2003).

7.2 Gangue Mineral (Al, Mn) Treatment Benefits Analysis

Observations of the aluminum and manganese chemistry allow us to draw the conclusion that the primary zone of leaching of soluble gangue minerals is above the saturated zone of the mine pool. As these metals are directly unaffected in a sulfate-reducing environment once leached, the need to further evaluate the benefits of inundation of the vadose zone with an inert gas is underlined.

7.3 Mine Works: Relationship of Saturation to Treatment Benefits

If the ratio of the vadose zone of the mine workings to the saturated pool volume is low (i.e. pool is large in ratio to the unsaturated zone volume), then we expect that mine pool treatment processes alone will be relatively more cost-effective. Our projection of cost effectiveness in this configuration is because the zone of oxidation where excess acid is formed will not be the dominant source of total contaminants. The pool will provide a zone where ferric ions, formed in the vadose zone, are reduced on mineral sulfide surfaces to release additional ferrous ions and cause leaching of gangue minerals, perpetuating the further release of contaminants. If the pool is dominated by a sulfate-reducing geochemical environment, then the ferric ions will be first reduced by the soluble carbon circulating in the pool volume and will not have the exposure to the lower reactivity rock minerals within the pool. The rate and extent of total primary sulfide dissolution will therefore be lowered through maintenance of the sulfate-reducing pool conditions and treatment of the iron dissolved in the vadose zone will have sufficient reaction time to be substantially complete before exiting the mine pool through the discharge.

7.4 Conceptual Mine Demonstrating Cost Effectiveness of In-Situ Treatment

To demonstrate the cost effectiveness of the ARCADIS in-situ treatment technology, a conceptual mine is considered which must utilize 5,000 tons per year of lime to neutralize acidity. The following analysis only accounts for reagent costs associated with lime and in-situ treatment.

The addition of molasses to the mine pool to reduce the iron would require reversal of ferric ion formation, as detailed in the following equations:

$$24Fe^{3+} + 24e^{-} \rightarrow 24Fe^{2+} \qquad (7)$$

$$C_6H_{12}O_6 \text{ (sugar in molasses)} + 6H_2O \rightarrow 6CO_2 + 24H^{+} + 24e^{-} \qquad (8)$$

Based on the stoichiometry shown in Equation 7 and 8, approximately 195 tons per year of molasses would convert ferric ion back to ferrous ions and also prevent the additional release of another 220 tons of contaminants. Addition of more than this amount of molasses would not be cost effective.

Subsequent or previous addition of carbon dioxide to the gas stream entering this hypothetical mine would require about 2,000 tons of carbon dioxide delivered at 5% concentration, which would prevent the oxidative release of at least 4,500 tons of the contaminants. The avoided costs would therefore be (220 tons from molasses + 4500 tons from carbon dioxide). If the carbon dioxide is a waste product, its capture cost will be about $15/ton and the molasses costs will be about $200/ton. For comparison, the lime cost would be about $100/ton. Annual reagent costs are summarized below:

- Lime treatment, 5,000 tons x $100/ton = $500,000

- In-situ treatment
    - Molasses, 195 tons x $200/ton = $39,000
    - Carbon dioxide, 2,000 tons x $15/ton = $30,000
    - Total estimated in-situ treatment reagent cost = $69,000

It should be noted that at a nominal acid concentration of 500 mg/L, the required discharge flow would be on the order of 4,000 gallons per minute. At such a flow, the capital cost and/or land requirement for construction of passive or active treatment systems would be substantial. With in-situ treatment, the residence time of the mine working is utilized to carry out the necessary biogeochemical reactions and significantly less capital and operational costs are incurred with the increased reagent tankage costs associated with higher flows.

Net savings for a very large mine pool such as this hypothetical example could be more than 70% of the reagent costs. This example will only be achievable where CO_2 sources are local and where the pool residence time is long enough to allow complete precipitation of reduced contaminants in the pool to be achieved.

8. References

Miller, G. and Tsukomoto, T., Leviathan Mine passive treatment study; presented in the proceedings of the Mine Design Closure Conference at Polson Montana. Montana Tech 2003

Singer P.C. and Stumm W. Acid Mine Drainage: The Rate-Determining Step. *Science*. 1970, 167, 1121-1123.

Weber, W.J. and DiGiano, F.A. *Process Dynamics in Environmental Systems.* John Wiley and Sons, Inc., New York, 1996.

Tables

Figures

Table 1. Demonstration Project Chronology.
Tide Mine Demonstration Project, Center Township, Indiana County, Pennsylvania

Date	Task	Description
7/20/2004	Startup/shakedown	Start system and leak check. Confirm proper operation of caustic and molasses injection system.
	Caustic delivery	Approximately 3,900 gallons of 25% caustic solution was delivered to the tank adjacent to the recirculation pump.
	Molasses injection	Test run of molasses injection performed concurrently with initial week long system operation with caustic injection.
8/9/2004	Full-time operation	Full-time operation of the recirculation system began with caustic addition to initially elevate pH.
8/11/2004	O&M begins	Kimball begins performing recirculation system operation and maintenance activities three times per week.
	Methanol delivery	Approximately 4,000 gallons of 40% methanol was delivered to the two tanks adjacent to IW-1 and IW-2.
9/1/2004	Molasses injection	Second molasses delivery unloaded to suction side of pump for distribution to the mine workings through the recirculation system. Total mass of molasses injected is approximately 18,000 pounds. Breakthrough of the injected molasses is observed in the mine pool between 12 and 24 hours following injection.
	Caustic flow	Litmus paper with an approximate accuracy of 1 pH unit is used to meter the flow rate of caustic solution into the recirculated water stream. Target pH of the recirculated water stream is 7 standard units.
9/8/2004	Molasses injection	Third molasses delivery unloaded to suction side of pump for distribution to the mine workings through the recirculation system. Total mass of molasses injected is approximately 27,000 pounds.
9/13/2004	Methanol feed	Methanol solution feed initiated to Injection Wells IW-1 through IW-3. Low flow rate targeted to slowly introduce alcohol as a molasses alternative organic carbon source. Target flow is approximately 20 gallons per day (gpd) of alcohol solution.
9/15/2004	Molasses injection	Fourth molasses delivery unloaded to suction side of pump for distribution to the mine workings through the recirculation system. Total mass of molasses injected is approximately 36,000 pounds.
9/22/2004	Molasses injection	Fifth molasses delivery unloaded to suction side of pump for distribution to the mine workings through the recirculation system. Total mass of molasses injected is approximately 45,000 pounds.
	Caustic delivery	Approximately 2,200 gallons of 25% caustic solution was delivered to the tank adjacent to the recirculation pump.
9/24/2004	Carbon dioxide gas injection	The carbon dioxide gas injection event was conducted 22 through 24 September 2004. Approximately 40,000 pounds of carbon dioxide gas was injected into the mine workings over the three day period.
9/25/2004	Bromide tracer injection	Approximately 330 pounds of sodium bromide was mixed as a slurry and injected into the IW-3 well head.
9/29/2004	Molasses injection	Sixth molasses delivery unloaded to suction side of pump for distribution to the mine workings through the recirculation system. Total mass of molasses injected is approximately 54,000 pounds.

Table 1. Demonstration Project Chronology.
Tide Mine Demonstration Project, Center Township, Indiana County, Pennsylvania

Date	Task	Description
9/30/2004	Emergency pump service	Godwin technician performs emergency pump service because of overheating. Low water flow and pump overheating resulted from the intake assembly settling in discharge sediment.
10/1/2004	Gas sample tubing	Drop gas sample tubing was installed with end shrouds to prevent water uptake during gas sampling in well IW-1A and IW-4.
10/6/2004	Molasses injection	Seventh molasses delivery unloaded to suction side of pump for distribution to the mine workings through the recirculation system. Total mass of molasses injected is approximately 63,000 pounds.
10/11/2004	Caustic flow	Caustic flow increased to purge minimal remaining solution from tank.
10/15/2004	Molasses injection	Eighth molasses delivery received at site. Approximately 4,000 gallons are unloaded to the tank that formerly held caustic solution and the remaining approximate 1,000 gallons are fed into the pump suction manifold. Molasses flow rate from the tank is metered to empty tank over a one week period. Higher TOC results in the mine pool are observed coincident with slow addition of molasses solution to the recirculated water stream. Following complete processing of the eighth molasses delivery, approximately 72,000 pounds of molasses have been injected into the mine workings.
10/22/2004	Molasses injection	Ninth molasses delivery received at site. Approximately 4,000 gallons are unloaded to the tank that formerly held caustic solution and the remaining approximate 1,000 gallons are fed into the pump suction manifold. Following complete processing of the eighth molasses delivery, approximately 81,000 pounds of molasses have been injected into the mine workings.
10/25/2004	Methanol delivery	Approximately 3,700 gallons of 40% alcohol solution is delivered to the tank feeding IW-2 and IW-3.
10/29/2004	Molasses injection	Tenth and final molasses delivery received at site. Approximately 4,000 gallons are unloaded to the tank that formerly held caustic solution and the remaining approximate 1,000 gallons are fed into the pump suction manifold. Following complete processing of the eighth molasses delivery, approximately 90,000 pounds of molasses have been injected into the mine workings.
11/3/2004	Recirculation system offline	The recirculation system is offline; system decommissioning and demobilization conducted between 15 and 17 November 2004. One tank remains onsite adjacent to IW-2 to feed the well heads of IW-1 through IW-3.
	Methanol flow rate	Methanol drip flow rate increased. Alcohol is now the sole source of organic carbon in the mine pool.
12/13/2004	Methanol delivery	Approximately 3,800 gallons of 40% alcohol solution is delivered to the tank feeding IW-1 through IW-3.
1/5/2005	Methanol delivery	Approximately 3,700 gallons of 40% alcohol solution is delivered to the tank feeding IW-1 through IW-3.
2/9/2005	End	End of demonstration project. All alcohol solution has been injected into the mine pool.

TABLE 2.

Mine Pool Water Quality Data Summary
Tide Mine Demonstration Project, Center Township, Indiana County, Pennsylvania

SAMPLE DATE	EH	ORP (mv)	TEMP °C	Dissolved Oxygen (mg/l)	pH (field)	pH (lab)	Specific Conduct. (umhos/cm)	Total Acidity		Net Acidity (calculated) (mg/l)	Total Alkalinity (mg/l)	Total Iron (mg/l)	Dissolved Iron (mg/l)	Ferrous Iron (mg/l)	Ferric Iron (mg/l)	Total Aluminum (mg/l)	Dissolved Aluminum (mg/l)	Total Manganese (mg/l)	Dissolved Manganese (mg/l)	Total Sulfates (mg/l)	Total Sulfide (mg/l)	BOD 5 Day (mg/l)	Total Organic C (mg/l)	Total Chloride (mg/l)	Total Bromide (mg/l)
								(calculated) (mg/l)	(lab "Hot") (mg/l)																
03/30/2004	597.0	211.0	11.2	0.9	3.4	3.2	na	199.2	174	174	0.00	33.50	33.30	26.36	7.14	17.10	17.00	3.55	3.56	589.40	0.10	2.80	0.50		
04/14/2004	na	na	11.1	2.6	na	3.2	na	202.5	209.8	210	0.00	36.70	36.30	28.81	7.89	16.60	16.10	3.36	3.22	538.40	0.10	3.60	cancelled		
05/12/2004			13.6	1.9	3.3	3.2	na	195.7	210.2	210	0.00	37.50	35.60	31.39	6.11	15.40	15.30	3.39	3.37	564.70	0.10	4.00	2.20		
05/25/2004	591.3	206.0	13.3	2.2	3.4	3.4	na	196.2	224.8	225	0.00	42.70	42.20	40.80	1.90	16.70	16.60	3.07	3.02	582.30	0.10	6.20	0.90		
06/03/2004	587.3	203.5	13.1	1.5	3.4	3.3	na	187.3	224.0	224	0.00	38.40	37.70	39.16	0.00	15.50	15.10	3.42	3.33	588.70	0.10	5.60	1.30		
06/17/2004	590.3	205.6	13.1	1.08	3.4	3.3	950	212.4	224.4	224	0.00	48.90	49.10	42.67	6.23	15.80	14.80	3.68	3.49	557.80	0.10	6.10	0.80		
06/23/2004	592.1	207.6	13.0	1.7	3.3	3.3	974	198.0	197	197	0.00	38.90	38.70	34.92	3.98	16.80	16.10	3.61	3.52	584.00	0.10	4.40	0.70	5.20	0.20
06/30/2004	593.0	208.4	13.1	1.61	3.3	3.3	969	163.9	185	185	0.00	31.70	30.70	28.04	3.66	13.20	13.00	3.10	3.04	575.50	0.10	3.50	0.70	5.80	0.20
07/09/2004	589.5	204.3	13	1.5	3.4	3.3	961	182.5	187.6	188	0.00	36.60	36.90	31.24	5.36	14.70	15.00	3.11	3.04	505.40	0.10	0.20	0.70	6.30	0.20
07/15/2004	590.0	204.7	12.3	0.9	3.4	3.2	888	186.6	178.2	178	0.00	31.80	30.20	18.30	13.50	14.50	14.00	3.13	3.25	517.10	0.10	1.70	0.70		
07/21/2004	592.4	206.7	13.5	1.28	3.37	3.3	1188	174.2	208.2	208	0.00	31.50	30.30	25.49	6.01	14.60	14.30	3.53	3.49	545.60	0.10	16.00	14.80	6.30	0.20
07/26/2004	593.2	208.2	12.6	1.05	3.35	3.3	1000	186.3	246.8	247	0.00	35.00	33.30	27.54	7.46	15.40	15.00	3.60	3.58	617.10	0.10	*	38.77	8.10	0.20
08/02/2004	583.9	200.2	13.4	0.72	3.52	3.5	950	189.0	223.4	223	0.00	49.10	48.60	51.75	0.00	13.50	13.50	3.19	3.29	605.00	0.10	23.00	18.20	6.50	0.20
08/09/2004	571.3	186.9	13.2	0.65	3.82	3.7	884	182.4	216.8	217	0.00	54.20	53.40	53.71	0.49	12.20	12.00	4.10	4.04	647.90	0.13	30.00	24.00	7.80	0.20
08/16/2004	587.1	200.7	13	0.6	3.5	4.0	885	163.2	179.4	178	1.80	52.40	48.90	54.23	0.00	9.76	8.74	3.91	3.65	589.80	0.10	14.50	9.60	6.30	0.20
08/24/2004	432.0	175.6	13.6	1.12	3.93	3.9	935	163.5	173.4	173	0.00	53.30	53.20	51.07	2.23	9.63	9.37	3.60	3.62	600.10	0.10	6.80	3.10	7.30	0.20
08/31/2004	352.2	91.0	13.2	1.1	5.56	5.6	1230	51.5	57.2	34	23.40	19.20	17.70	20.00	0.00	2.31	0.82	1.56	1.50	668.30	0.10	10.00	3.20	10.50	0.20
09/07/2004	351.3	89.2	13.3	0.56	5.46	5.4	1098	118.2	118	79	38.60	54.70	50.90	55.91	0.00	2.38	1.59	2.69	2.60	747.30	0.10	69.90	43.00	10.90	0.30
09/14/2004	327.2	65.4	13.2	0.51	5.88	5.8	1193	236.4	187.2	102	85.20	116.00	116.00	120.77	0.00	2.60	2.60	3.40	3.40	729.30	0.10	119.00	59.00	12.00	0.70
09/21/2004	338.0	76.1	12.6	0.57	5.7	5.7	989	216.5	178.6	118	60.20	95.60	96.90	106.62	0.00	3.63	1.86	3.23	3.22	722.80	0.29	84.90	46.00	8.70	0.20
09/28/2004	325.8	64.2	12.8	0.54	5.91	6.1	1077	297.6	182.6	10	172.80	153.00	144.00	152.90	0.10	3.30	1.15	3.28	3.17	630.20	0.26	155.00	44.00		4.70
10/05/2004	321.5	60.1	13.0	0.43	5.97	6.2	1087	359.1	192.6	24	168.20	175.00	175.00	189.45	0.00	2.58	1.28	3.55	3.56	622.40	0.55	>59.0	78.00		7.20
10/12/2004	304.8	44.1	12.6	0.34	6.27	6.3	1229	312.1	33.6	-206	239.40	138.00	144.00	168.50	0.00	1.57	0.63	3.31	3.37	590.60	0.28	147.00	85.00		4.60
10/19/2004	312.8	50.9	12.7	0.58	6.13	6.1	1292	304.7	82.6	-165	247.20	137.00	145.00	156.28	0.00	3.39	1.63	3.71	3.85	581.20	0.45	246.00	160.00		2.50
10/26/2004	317.4	56.4	12.8	0.41	6.03	6.0	1244	343.0	234	-7	241.00	156.00	160.00	170.00	0.00	5.83	2.69	3.84	3.71	565.00	0.57	348.00	189.00		2.20
11/02/2004	333.6	71.7	12.9	0.44	5.74	5.7	1272	318.6	239	37	202.40	129.00	132.00	149.78	0.00	7.98	5.36	3.68	3.71	425.60	0.52	604.00	261.00		1.30
11/16/2004	339.4	77.2	12.6	0.55	5.6	5.6	956	294.7	222.6	141	81.60	131.00	120.00	144.01	0.00	5.55	3.74	3.60	3.46	616.70	0.16	115.00	61.60		0.70
11/22/2004	347.3	86.9	12.5	0.69	5.47	5.4	912	269.8	220.6	167	53.80	124.00	113.00	122.53	1.47	7.26	5.10	3.61	3.44	527.60	0.72	*	44.10		0.50
12/7/2004	344.7	81.7	12.8	0.99	5.58	5.6	924	263.1	263.1	221	41.80	118.00	104.00	111.90	6.10	7.21	6.74	3.73	3.57	509.80	0.52	>90	47.40		
12/22/2004	516.6	78.4	11.6	0.87	5.49	5.5	740	209.2	181.2	152	29.40	84.00	84.80	88.60	0.00	8.05	4.31	3.36	3.39	556.10	0.45	47.10	41.60		
01/05/2005	517.6	78.6	12.0	1.23	5.63	5.3	737	210.5	271.2	237	34.20	83.00	80.90	88.19	0.00	8.36	4.32	3.49	3.43	510.40	0.31	106.80	54.60		
01/18/2005	566.9	128.7	11.8	1.27	4.62	4.6	818	183.4	225.0	207	18.20	58.80	55.10	61.36	0.00	12.10	11.10	2.96	2.81	520.20	0.23	133.00	55.60		
02/01/2005	525.9	89.3	11.4	1.17	5.27	5.0	881	188.6	191.2	164	26.80	73.40	69.10	77.04	0.00	8.06	5.77	3.15	3.00	482.50	1.36	91.00			
02/15/2005	539.6	101.5	12.2	0.91	5.12	4.8	856	197.2	196.8	179	18.20	71.30	69.50	76.38	0.00	9.81	7.16	3.01	2.95	438.00	1.69	143.00	42.10		
03/01/2005	555.0	116.8	11.7	1.78	4.93		809																		

Table 3. Demonstration Study Rate Determination

Tide Mine Demonstration Project, Center Township, Indiana County, Pennsylvania

SAMPLE DATE	Elapsed Time (days)	Total Fe (mg/l)	Fe D (mg/l)	Ferrous Fe+2 (mg/l)	Ferric Fe+3 (mg/l)	Total Sulfates (mg/l)	Total Sulfide (mg/l)	Sulfate Decay Rate (umol S/L day)	Sulfide Gen Rate (umol S/L day)	Repeaat Analysis Sorted Sulfate Decay Rate (umol S/L day)	Repeaat Analysis Sorted Sulfide Gen Rate (umol S/L day)
03/30/2004		33.50	33.30	26.36	7.14	589.40	< 0.1				
04/14/2004		36.70	36.30	28.81	7.89	538.40	< 0.1				
05/12/2004		37.50	35.60	31.39	6.11	564.70	< 0.1				
05/25/2004		42.70	42.20	40.80	1.90	582.30	< 0.1				
06/03/2004		38.40	37.70	39.16	0.00	588.70	< 0.1				
06/17/2004		48.90	49.10	42.67	6.23	557.80	< 0.1				
06/23/2004		38.90	38.70	34.92	3.98	584.00	< 0.1				
06/30/2004		31.70	30.70	28.04	3.66	575.50	< 0.1				
07/09/2004		36.60	36.90	31.24	5.36	505.40	< 0.1				
07/15/2004		31.80	30.20	18.30	13.50	517.10	< 0.1				
07/21/2004		31.50	30.30	25.49	6.01	545.60	< 0.1				
07/26/2004		35.00	33.30	27.54	7.46	617.10	< 0.1				
08/02/2004	0	49.10	48.60	51.75	0.00	605.00	< 0.1				
08/09/2004	7	54.20	53.40	53.71	0.49	647.90	0.13				
08/16/2004	14	52.40	48.90	54.23	0.00	589.80	0.10				
08/24/2004	22	53.30	53.20	51.07	2.23	600.10	< 0.1				
08/31/2004	29	19.20	17.70	20.00	0.00	668.30	< 0.1				
09/07/2004	36	54.70	50.90	55.91	0.00	747.30	0.10				
09/14/2004	43	116.00	116.00	120.77	0.00	729.30	0.05				
09/21/2004	50	95.60	96.90	106.62	0.00	722.80	0.29				-0.16
09/28/2004	57	153.00	144.00	152.90	0.10	630.20	0.26	-74	0.11	-249	-0.07
10/05/2004	64	175.00	175.00	189.45	0.00	622.40	0.55	23	0.67	-152	0.09
10/12/2004	71	138.00	144.00	166.50	0.00	590.60	0.28	-24	-0.16	-95	0.11
10/19/2004	78	137.00	145.00	156.28	0.00	581.20	0.45	-3	0.46	-74	0.12
10/26/2004	85	156.00	160.00	170.00	0.00	565.00	0.57	-21	0.47	-66	0.22
11/02/2004	92	129.00	132.00	149.78	0.00	425.60	0.52	-249	0.24	-54	0.23
11/16/2004	106	131.00	120.00	144.01	0.00	616.70	0.16	116	-0.07	-40	0.24
11/22/2004	112	124.00	113.00	122.53	1.47	527.60	0.72	-152	1.23	-24	0.40
12/7/2004	127	118.00	104.00	111.90	6.10	509.80	0.52	-40	0.22	-22	0.46
12/22/2004	142	84.00	84.80	88.60	0.00	556.10	0.45	12	0.23	-21	0.47
01/05/2005	156	83.00	80.90	88.19	0.00	510.40	0.31	-54	0.12	-3	0.67
01/18/2005	169	58.80	55.10	61.36	0.00	520.20	0.23	-22	0.09	12	1.13
02/01/2005	183	73.40	69.10	77.04	0.00	482.50	1.36	-66	1.30	23	1.23
02/15/2005	197	71.30	69.50	76.38	0.00	438.00	1.69	-95	1.13	115.7	1.30
mean over study (umol S/L day):								-46	0.43		
median over study (umol S/L day):										-32.4	0.241
net rate of sulfide loss (mol S/day):								451		315	
net rate of iron loss, as ferrous sulfide (mol Fe/day):								-451		-315	
net rate of iron loss, as ferrous sulfide (lb Fe/day):								55		39	
Predicted steady-state Fe concentration, mg/L (<0 = 0, rate of precipitation greater than rate input):								-8.3		5.6	

Concentrations averaged to determine baseline concentrations

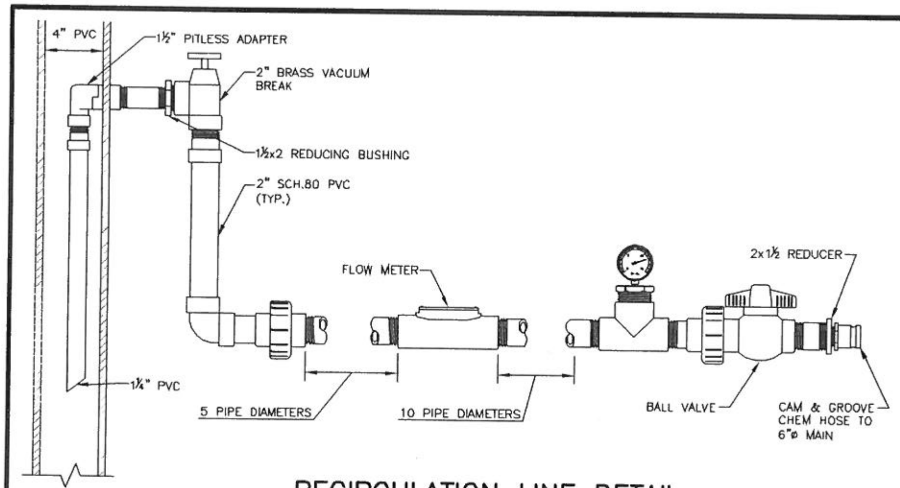
Constants Used in Calculations:

Q	τ	V_R	C_{IN} (Fe)	C_{IN} (SO_4)	C_{IN} (S)
(gpm)	(days)	(gal)	(mg/L)	(mg/L)	(mg/L)
100	18	2.6E+06	38	567	0
		(L)			
		9.8E+06			

Equations Used in Calculations:

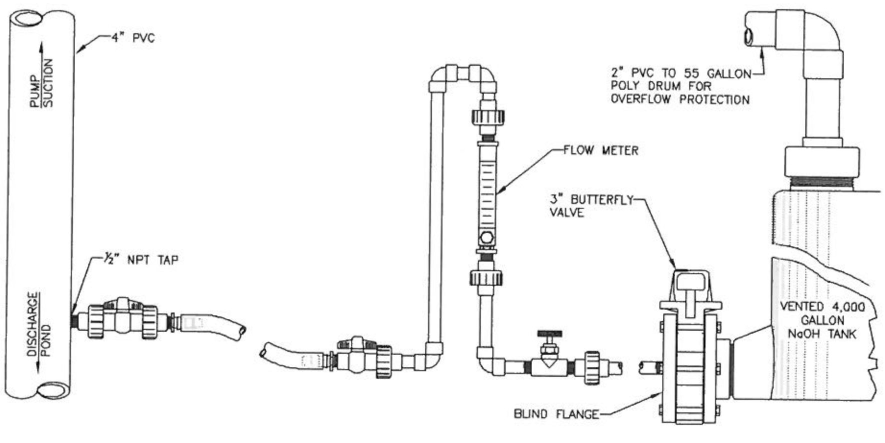
$$\text{Reaction Rate} = r = \frac{\Delta C_{OUT}}{\Delta t} + \frac{\overline{C}_{OUT}}{\tau} - \frac{C_{IN}}{\tau}$$

$$\text{Average Hydraulic Retention Time} = \tau = \frac{V_R}{Q}$$



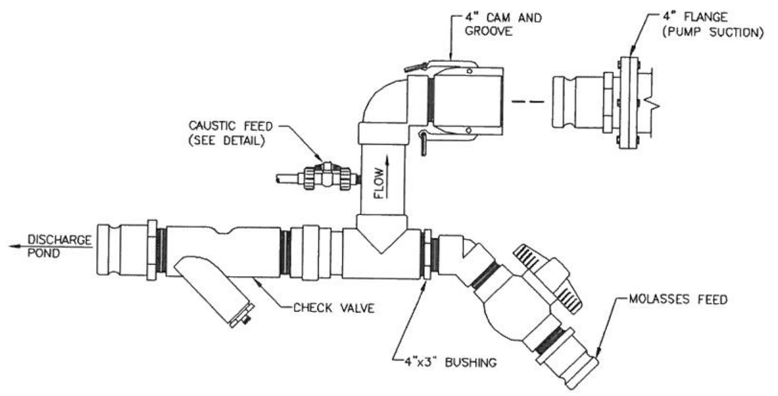
RECIRCULATION LINE DETAIL

NOT TO SCALE



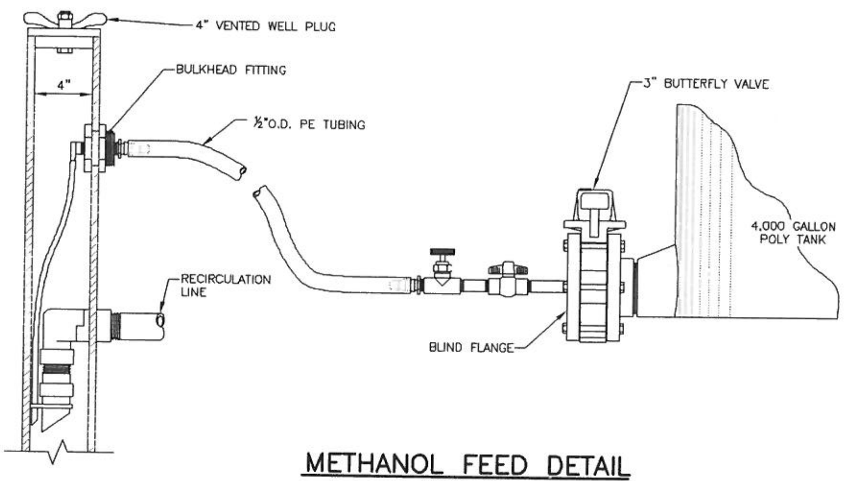
CAUSTIC FEED DETAIL

NOT TO SCALE



PUMP SUCTION DETAIL

NOT TO SCALE



METHANOL FEED DETAIL

NOT TO SCALE

NO.	DATE	REVISION DESCRIPTION	BY / CKD

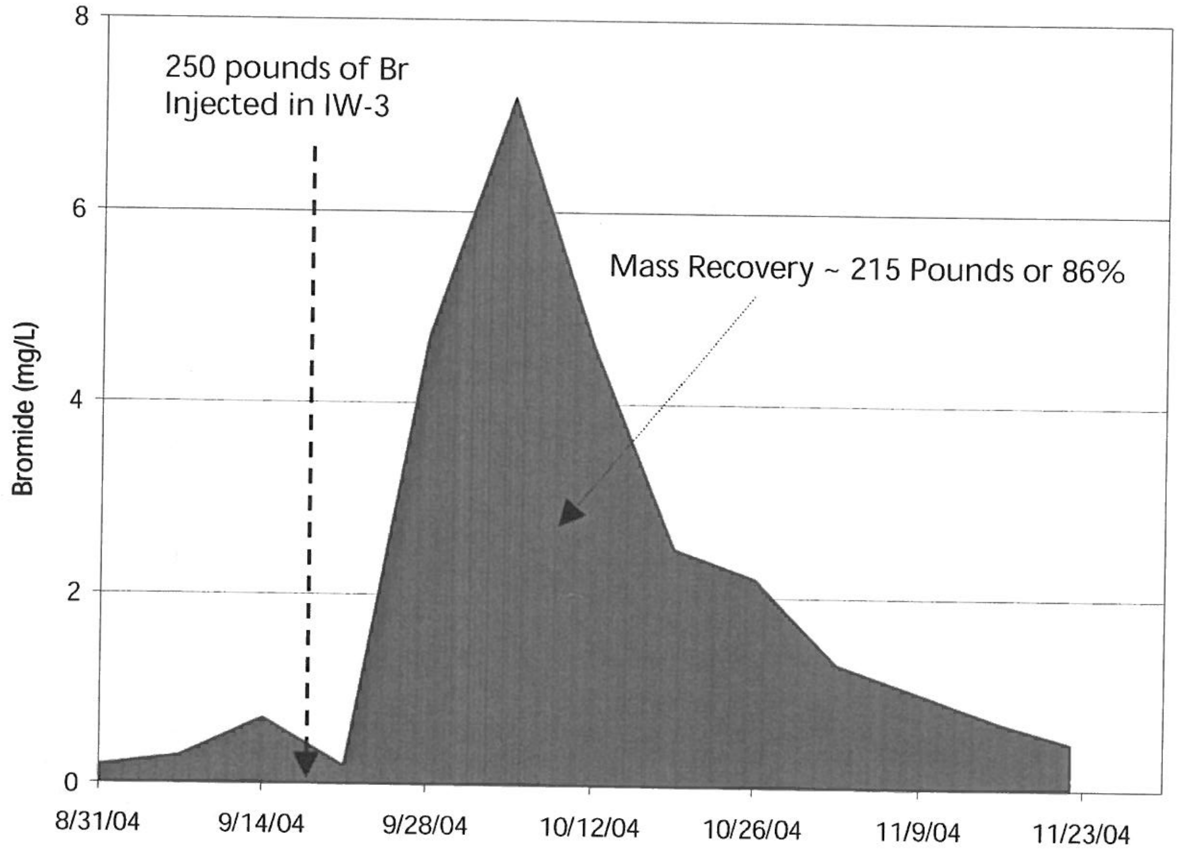
ARCADIS

6 Terry Drive
Suite 300, Newtown, Pa 18940
Tel: 267/685-1800 Fax: 267/685-1801

TIDE MINE
INDIANA COUNTY, PENNSYLVANIA

DRAWN M. WASILEWSKI	DATE 6/24/04	PROJECT MANAGER P. MILIONIS	DEPARTMENT MANAGER A. HANNUM
PIPING AND INSTRUMENTATION DETAILS		LEAD DESIGN PROF. K. BEIL	CHECKED K. HOUSTON
		PROJECT NUMBER NP000xxx.0001	DRAWING NUMBER 3

Figure 4. Bromide Concentrations in the Tide Mine Pool Discharge August to November 2004


250 pounds of Br Injected in IW-3

Mass Recovery ~ 215 Pounds or 86%

Figure 5. Observed vs. Predicted TOC Concentrations in the Tide Mine Pool Discharge.

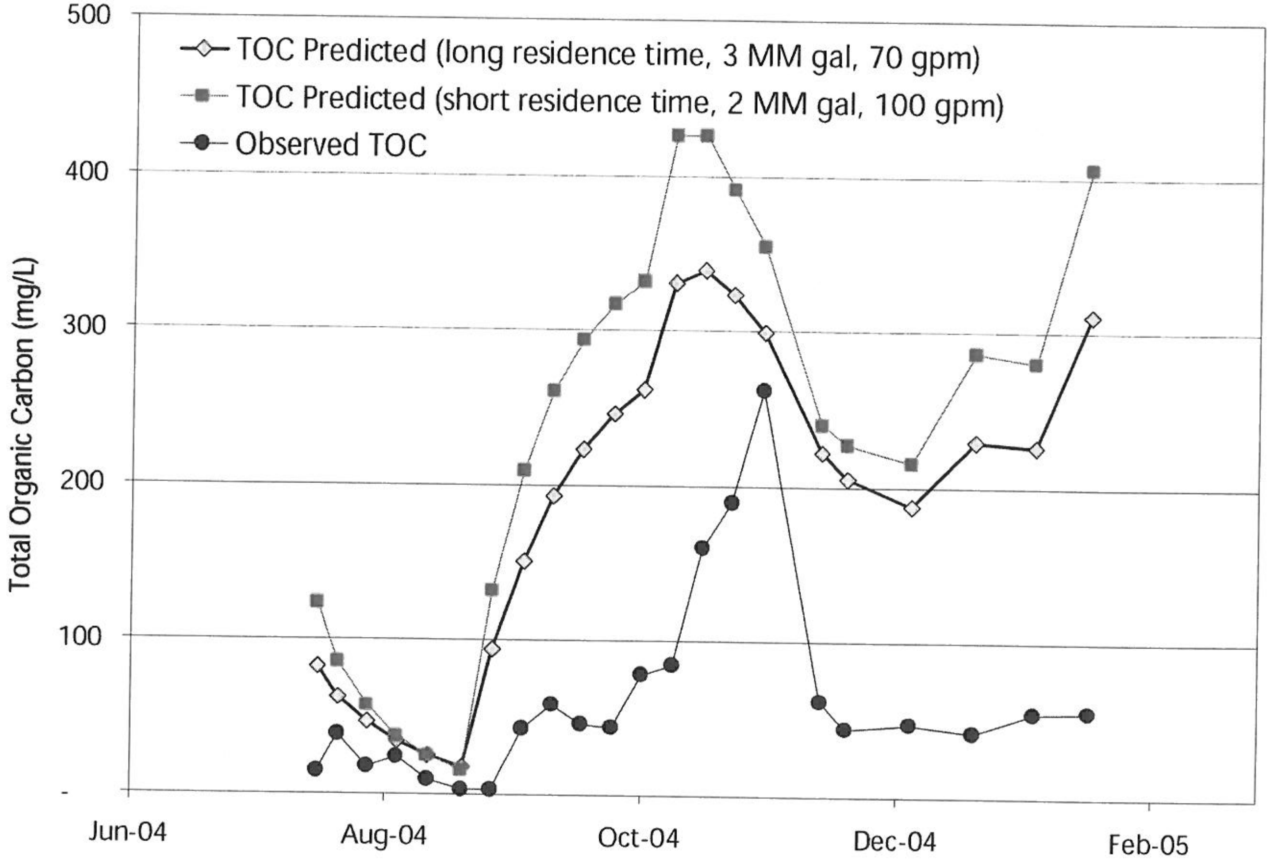


Figure 6. TOC Short-Term Trends in the Tide Mine Pool Discharge After Trial (i.e., First) Organic Carbon Injection

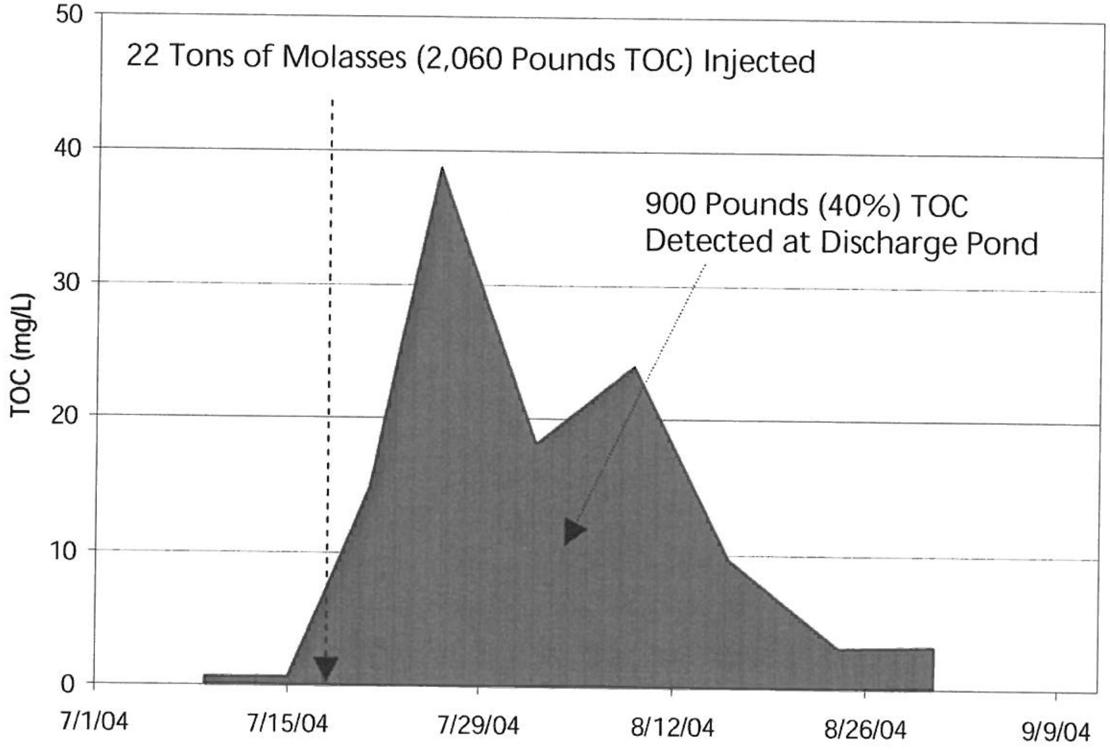


Figure 7. Aqueous Sulfide Measured in the Tide Mine Pool Discharge, August 2004 through January 2005.

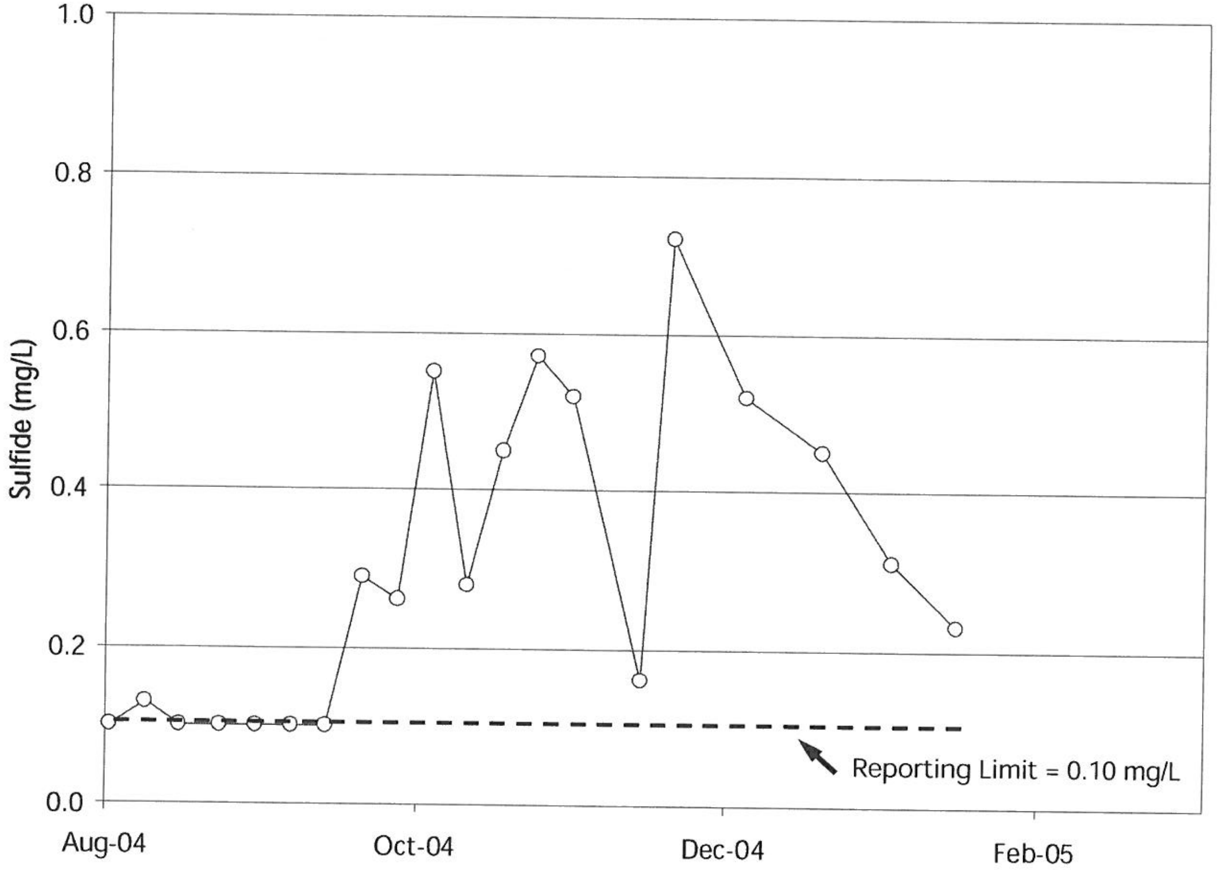


Figure 8. Ferric Iron and TOC Concentrations in the Tide Mine Pool Discharge Over Time.

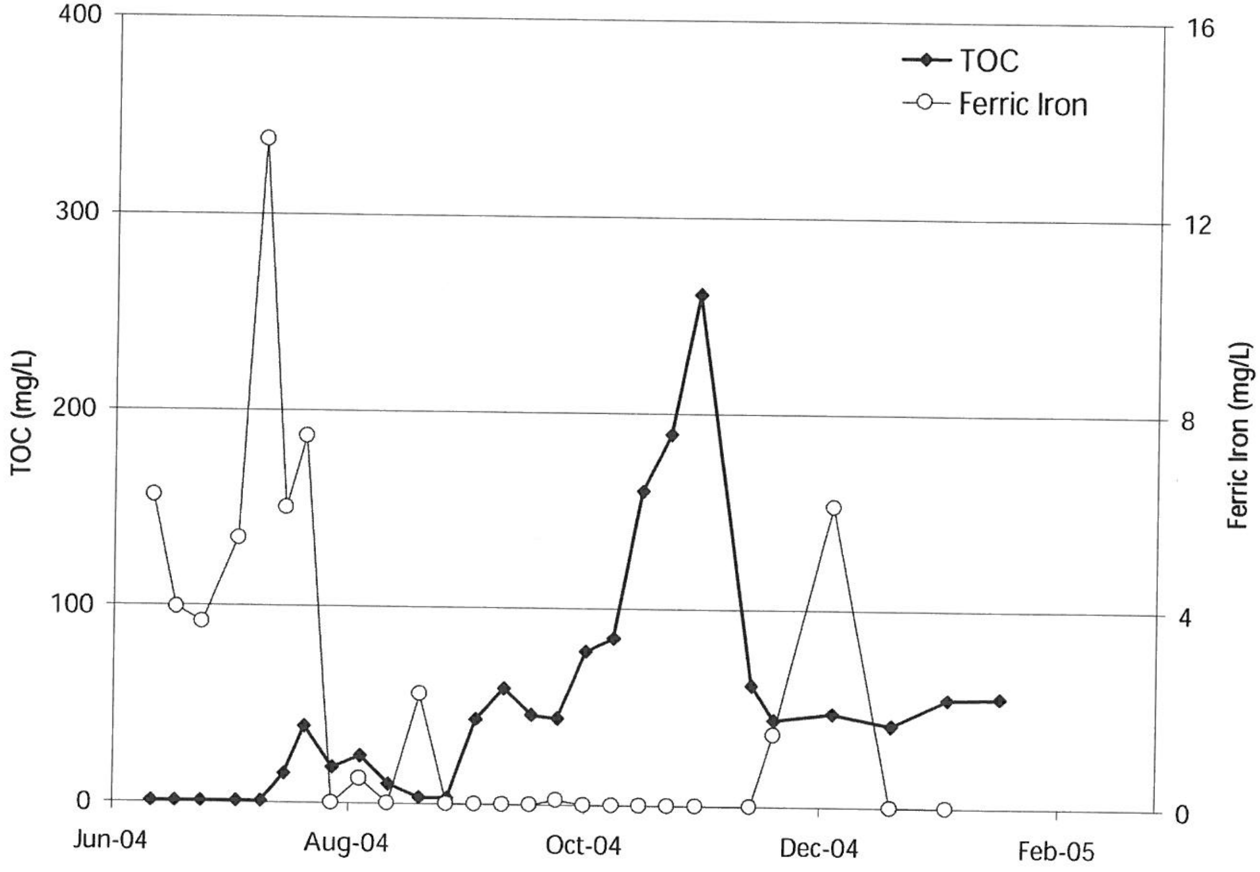


Figure 9. Dissolved Iron and Alkalinity Concentrations in the Tide Mine Pool Discharge Over Time.

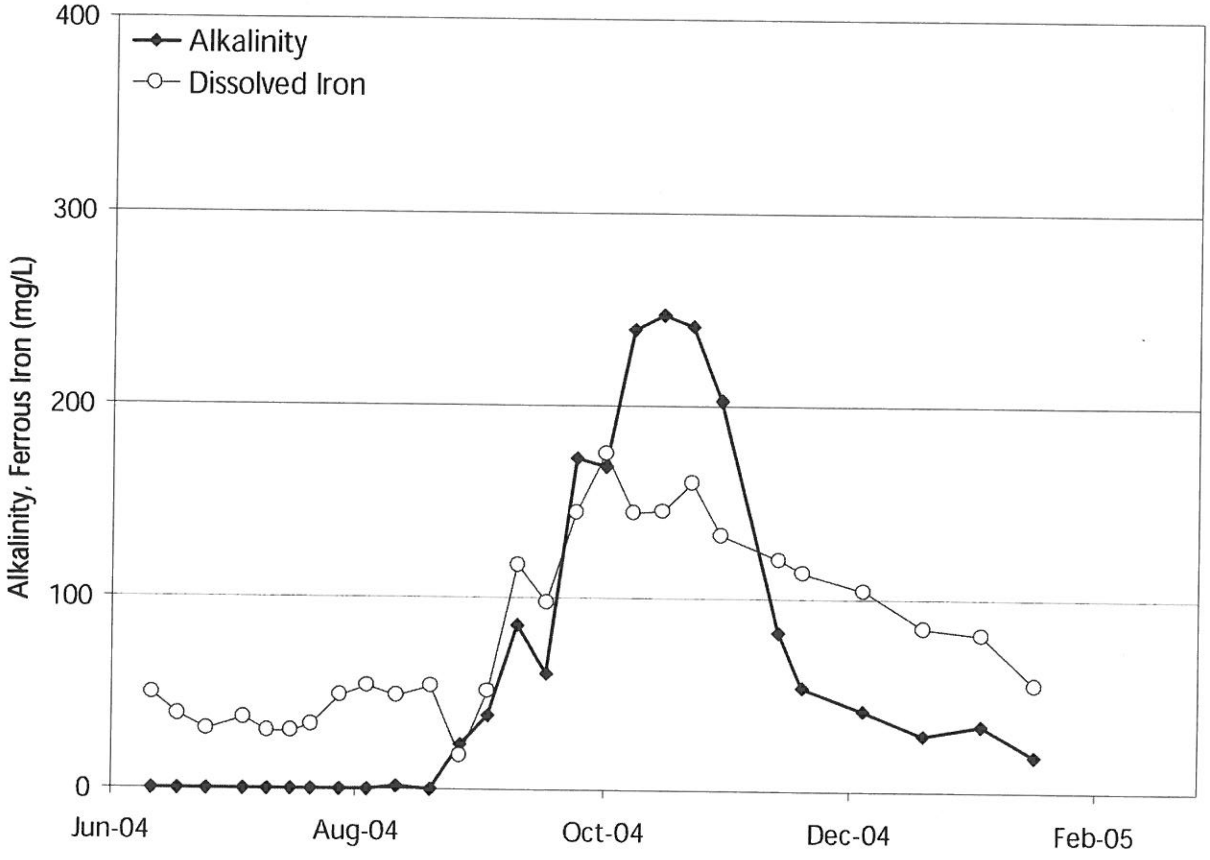


Figure 10. Conductivity and pH Trends in the Tide Mine Pool Discharge Over Time.

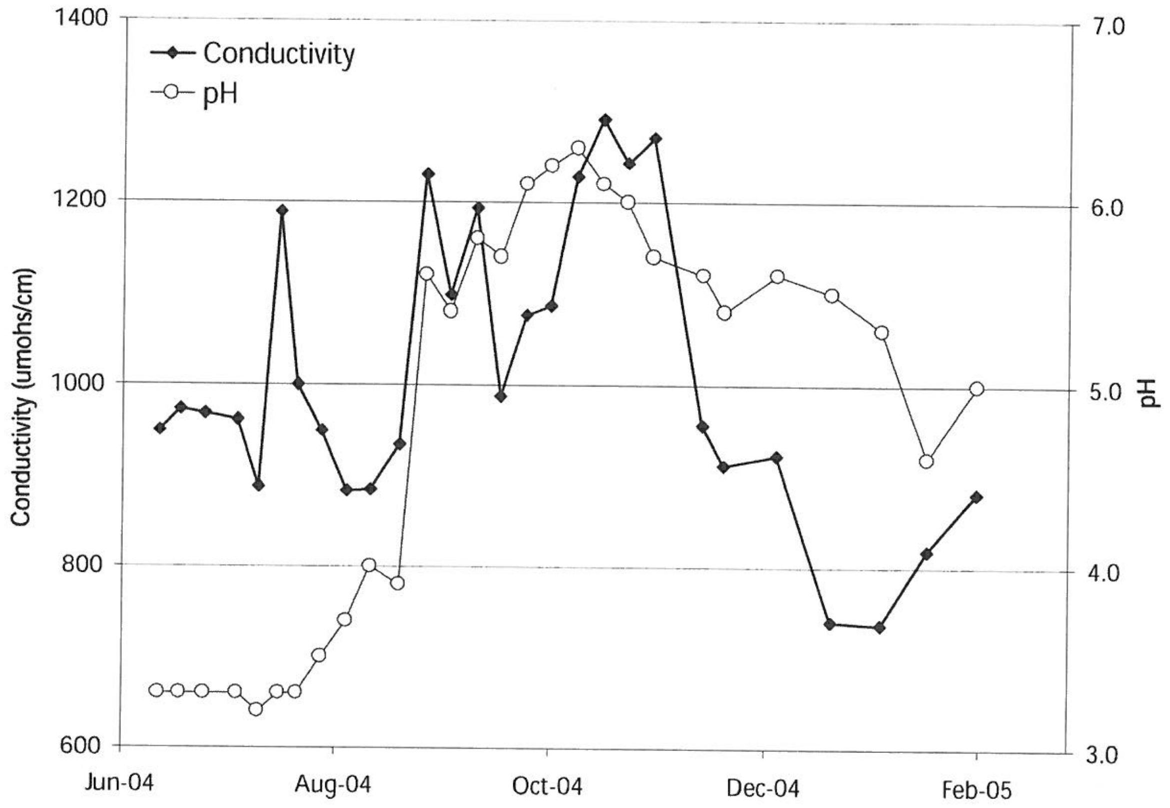


Figure 11. Oxidation-Reduction Potential (ORP) Trends in the Tide Mine Pool Discharge Over Time.

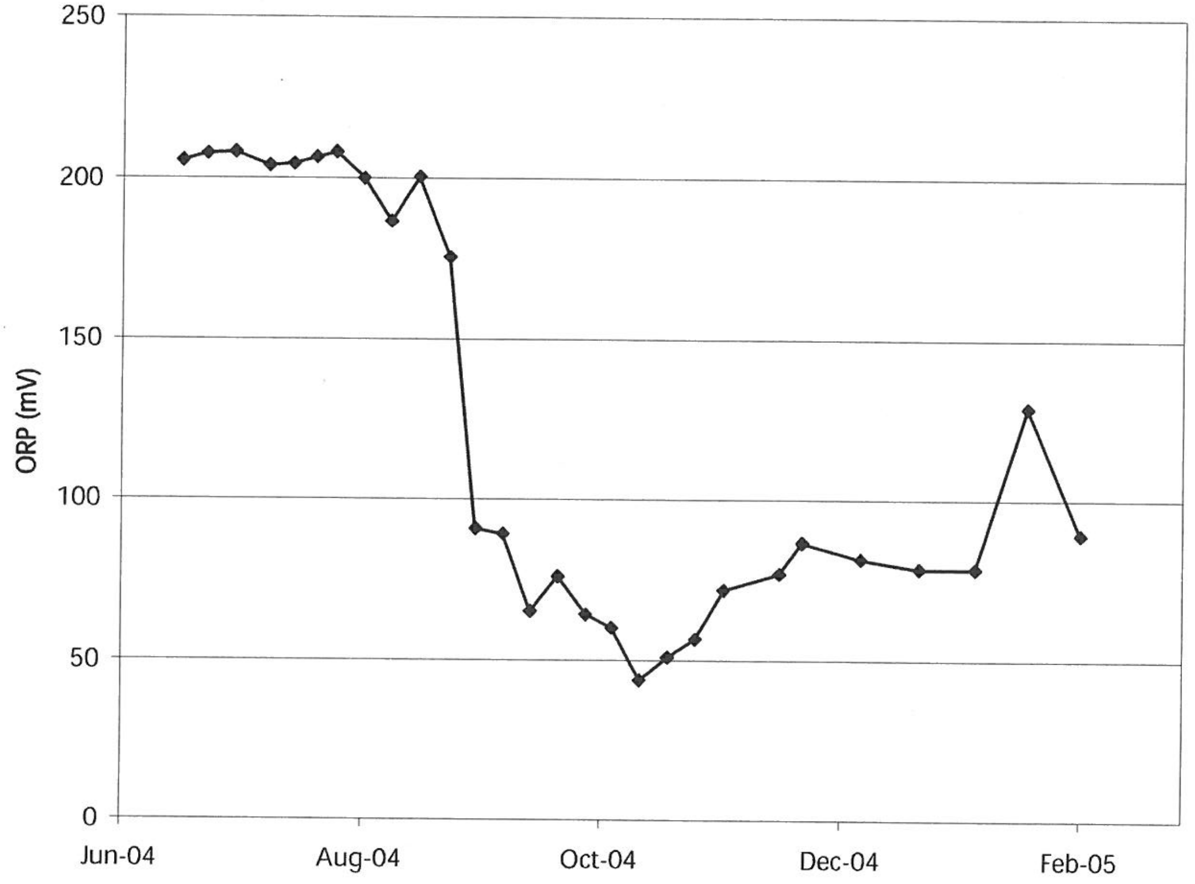


Figure 12. Temporal Trends of Oxygen and Carbon Dioxide Measured in Injection Well IW-4.

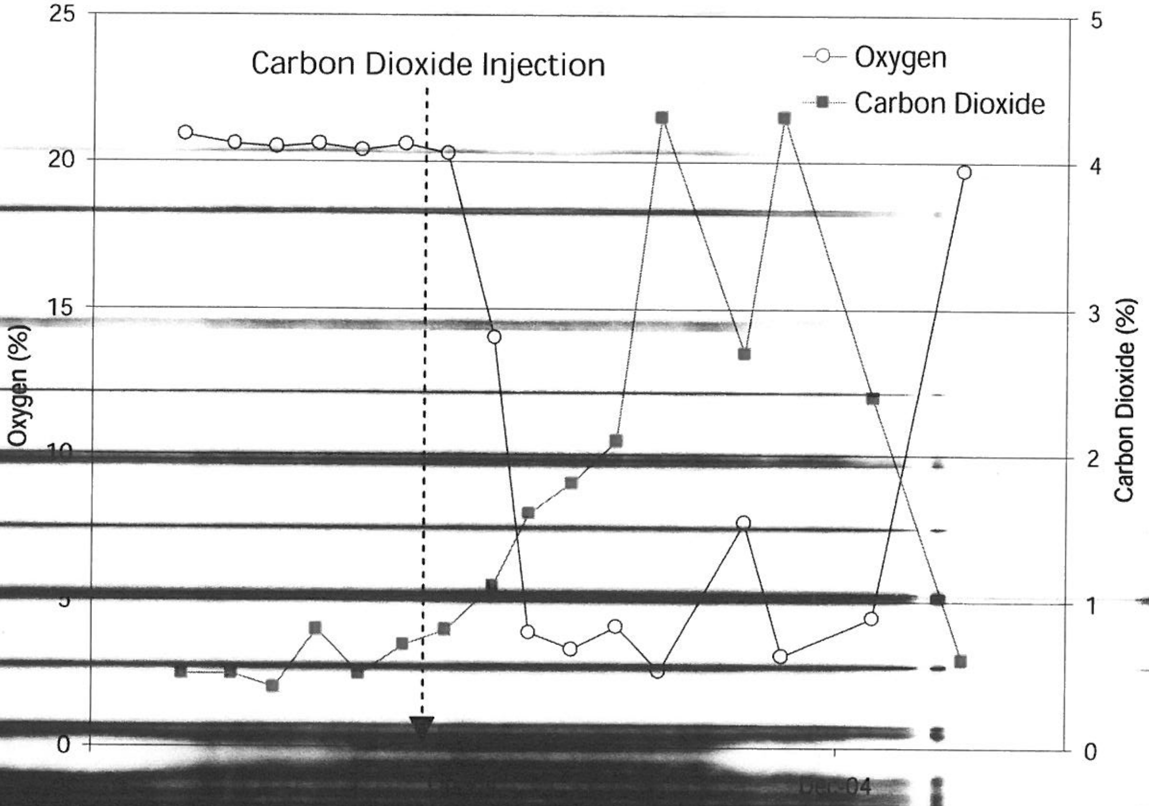
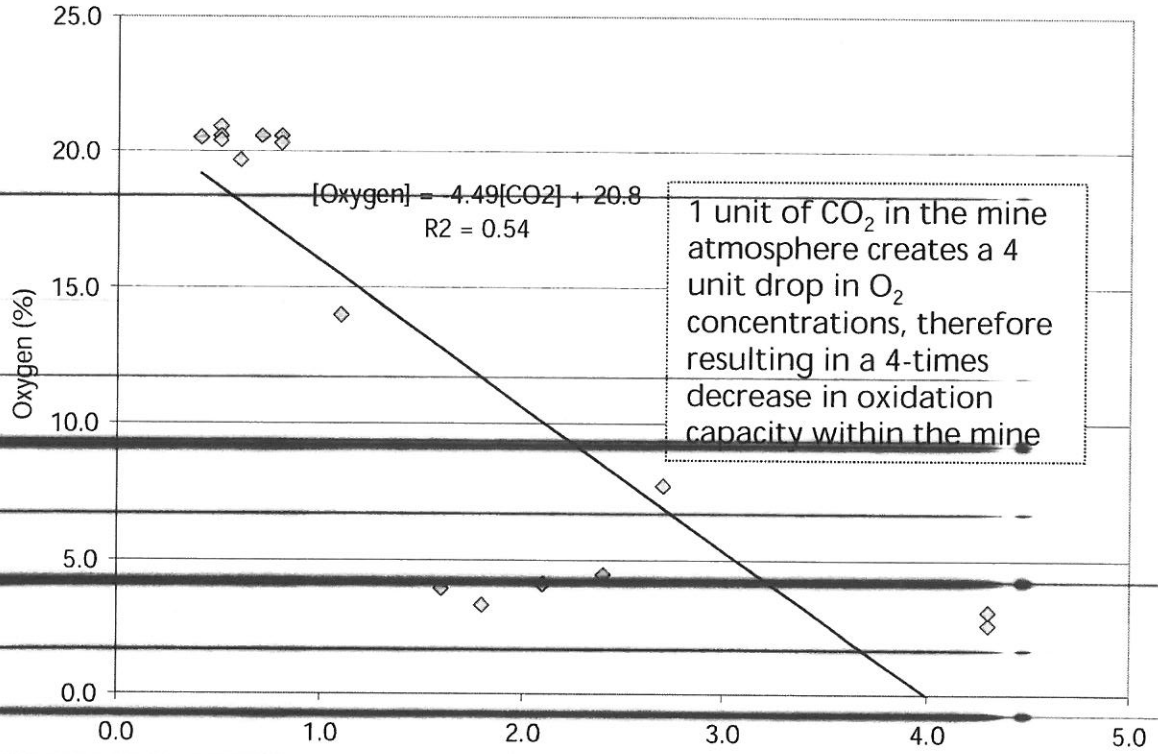


Figure 13. Correlation of Oxygen and Carbon Dioxide Readings in IW-4.



1 unit of CO_2 in the mine atmosphere creates a 4 unit drop in O_2 concentrations, therefore resulting in a 4-times decrease in oxidation capacity within the mine

Figure 14. Dissolved Manganese and Aluminum Concentrations in the Tide Mine Pool Discharge Over Time.

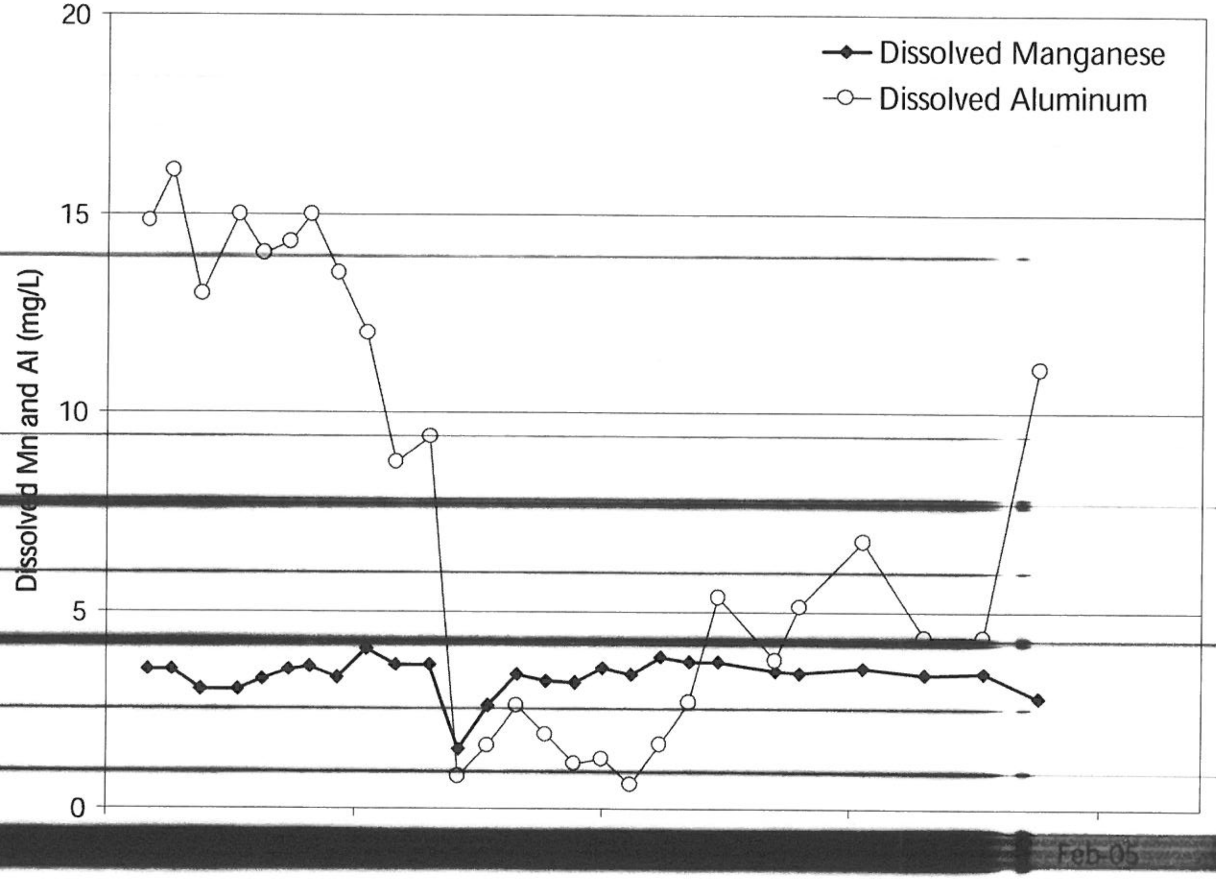
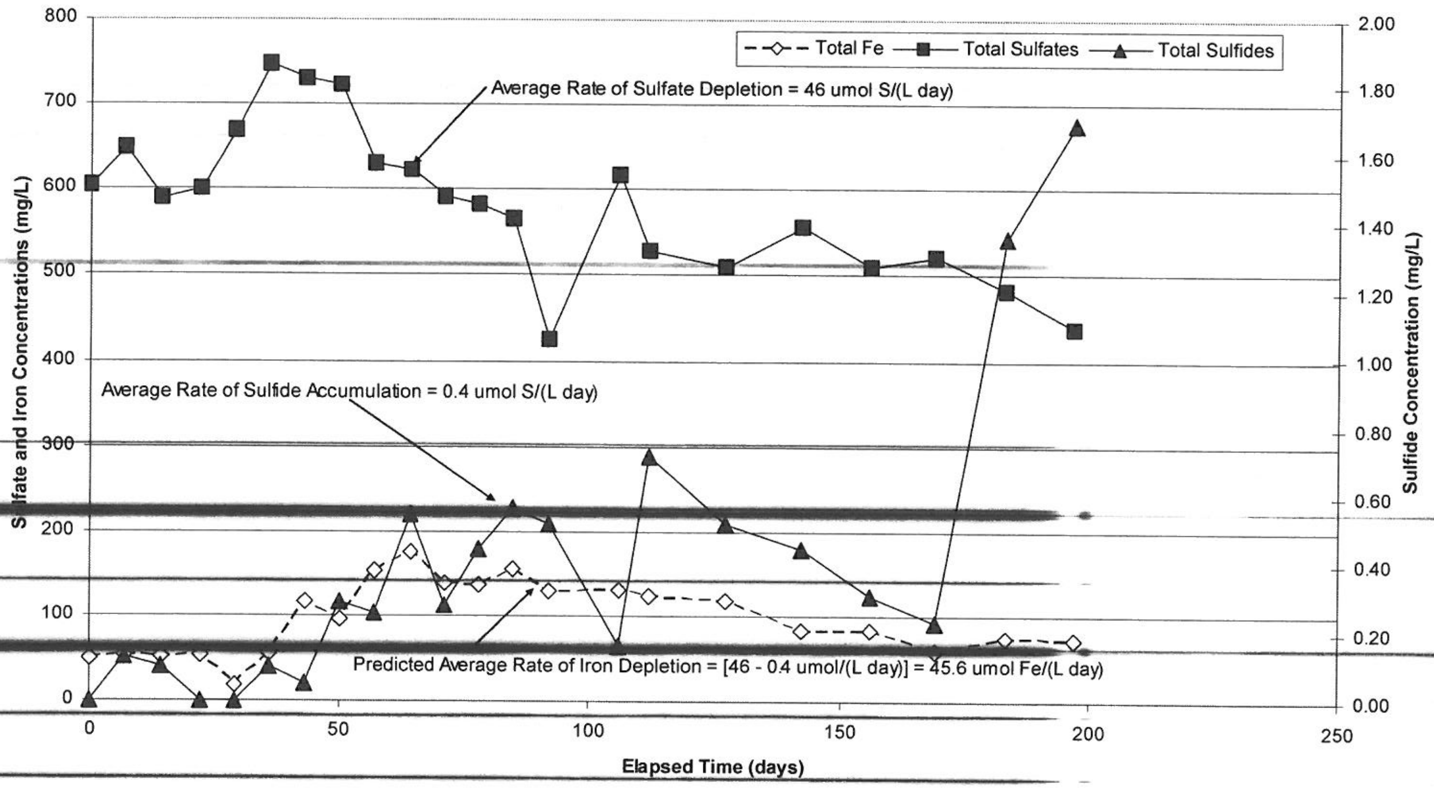
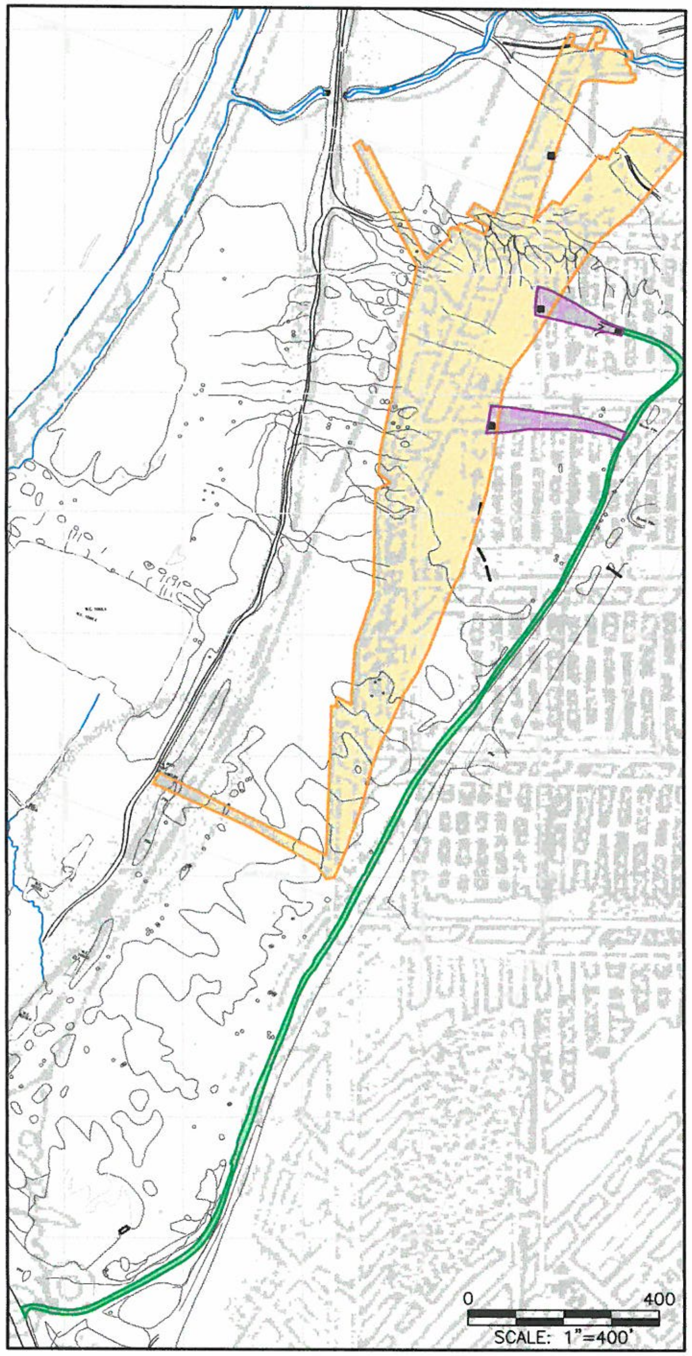


Figure 15. Demonstration Study Rate Determination Data



G:\APROJECT\PADEP_Mine Reclamation\CADD\FIG-2 LAYOUT-FINAL REPORT.DWG 5/02/2005 - 10:33:19 AM Layout: PROPOSED WELLS



OVERALL SITE PLAN

SCALE: 1"=400'