

ACTIVATED IRON SOLIDS TREATMENT FOR HIGH FLOW ACIDIC MINE DRAINAGE: RESULTS OF PILOT STUDIES¹

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Abstract. Historic coal mining in the eastern United States coal regions has created numerous large underground reservoirs of iron-laden acidic mine drainage (AMD) that can discharge at very high volumes (> 50 L/s) and cause aesthetic and water quality degradation to the receiving surface waters. This degradation can all but eliminate aquatic life in receiving waters through the accumulation of iron solids, also known as “yellowboy”. Conventional active treatment (e.g., lime) is costly and produces low-density (1-4% solids) and impure sludge. The high treatment cost generally limits its application to regulatory AMD discharges. The size of passive treatment (80 to 800 hectares for high flow discharges) typically limits this approach to lower flow AMD discharges. Activated Iron Solids (AIS) treatment of AMD is a new treatment process that uses heterogeneous ferrous iron oxidation, a catalytic process associated with the surfaces of insoluble ferric hydroxides. In this process, dissolved ferrous iron is adsorbed to the ferric hydroxides where rapid oxidation to ferric iron forms new iron hydroxides. AIS treatment uses engineered systems to maintain high ferric hydroxide concentrations in suspension, thereby creating rapid oxidation environments. Testing of this new treatment approach was conducted in a portable two-stage, flow-through AIS system at four high flow AMD discharges in Pennsylvania that included a range of iron-containing AMD chemistries; pH 5.6 to 6.4; alkalinity 30 to 250 mg/L (net alkaline and net acidic waters included); dissolved iron concentrations ranging from 15 to 70 mg/l; and flows ranging from 40 to 650 L/s. The 20,000 liter portable system is fully equipped with aeration, mixers, chemical feed, pumps, and controllers, and permits testing of a full range of operational conditions. The pilot study results indicate AIS treatment operates at slightly acidic pH (6.5 to 6.8) oxidizing ferrous iron to less than 0.05 mg/L and with effluent iron less than 2 mg/l for a variety of AMD chemistries, while producing a high density (>20%) and pure (>95% iron oxide/hydroxide) sludge. No alkaline agent was needed for alkaline waters and an inexpensive agricultural limestone powder was found to produce required alkalinities at dissolution efficiencies greater than 80% for net acidic waters. AIS treatment costs for full-scale systems would be less than \$0.10 per 1,000 liters of treated water when including operating and capital costs.

Additional Keywords: Iron Oxidation, Iron Removal

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Introduction

The discharge of acid mine drainage (AMD) to surface waters in Pennsylvania and other eastern coal region U.S. states contaminates thousands of miles of waterways resulting in their non-compliance with numerous water quality standards including, but not limited to pH, total iron, suspended solids, and aesthetics. The AMD is a result of past (and unregulated) surface and underground coal mining that exposed pyritic minerals to atmospheric oxygen, resulting in the oxidation of the pyrite and the production of AMD.

Of particular concern is AMD produced in the vast historic and abandoned deep mine workings found throughout the coal region. The pyrite oxidizes to create AMD that collects and is stored in the mine voids forming large underground reservoirs of contaminated AMD. These large underground AMD reservoirs discharge at one or more points, typically from air portals (for air circulation during active operations), water portals/drains (to maintain a minimal water level in the mine during active operations), from the mine entry, or from boreholes drilled to relieve mine pool pressures. The later was a post-mining activity performed by various agencies to prevent mine pools from infiltrating into basements and underground structures.

Because of the size of the deep mines, this type of AMD discharge tends to be very high flow with elevated ferrous iron but may contain adequate alkalinity for iron removal. In addition, the deep mine discharges are typically the largest contributor of AMD pollution (iron loading) in the watershed and/or subbasin. Treatment of the high flow AMD discharges is mandatory to achieve water quality goals in the receiving stream. Input of high flow and high iron AMD to surface waters causes: 1) in-stream iron concentrations to levels exceeding water quality standards; 2) the deposition of iron oxides/hydroxides, known as “yellowboy”, onto stream bottoms smothering aquatic life and causing aesthetic and sediment problems; and 3) pH to decrease to less than 6, a water quality standard, in streams where acidity exceeds alkalinity. These types of impacts lead to degradation of the receiving waters to conditions that do not meet the waters designated aquatic life, recreational, and water supply uses.

The treatment of the high flow deep mine AMD discharges requires iron removal, and this iron removal is a multi-step process involving:

1. Oxidation of dissolved ferrous iron (Fe^{2+}) to ferric iron (Fe^{3+});
2. Hydrolysis of Fe^{3+} to form insoluble ferric hydroxide ($\text{Fe}(\text{OH})_3$);

3. Flocculation of tiny (sub micrometer) $\text{Fe}(\text{OH})_3$ particles to form larger (micrometer) particles;
4. Settling of suspended $\text{Fe}(\text{OH})_3$ particles from solution.

Depending on the type of treatment, one or more of the above processes will control the removal of iron. In passive treatment the oxidation (Step 1) of Fe^{2+} iron is very slow and determines iron removal and the size of the passive treatment system. In conventional chemical treatment (e.g., lime) typically performed at pH greater than 8, the settling (Step 4) typically controls iron removal. The new and innovative process, AIS treatment, provides an alternative to passive treatment and chemical treatment that may offer both rapid oxidation and rapid settling, but at slightly acidic pH (6-7) typically found in this type of discharge.

The AIS process can involve the use of recirculated $\text{Fe}(\text{OH})_3$ solids to enhance the oxidation of Fe^{2+} iron. Recirculation of solids has been used in a number of lime-based active treatment systems collectively known as high-density sludge (HDS) processes (Evans 1965, Herman and Korb 1989, and Pfeifer 1990). The HDS process involves the precipitation of ferrous hydroxide solids at high pH (typically greater than 12) through the use lime (hydrated or quick) on recycled and pre-treated sludge. The precipitated ferrous hydroxides are then directly oxidized to ferric hydroxides in subsequent processing. The AIS process is substantially different because the process involves the oxidation of adsorbed Fe^{2+} iron, not precipitation of $\text{Fe}(\text{OH})_3$, on the surface of iron hydroxides at slightly acidic pH (6-7). Nor does the AIS process require lime to raise the pH (>8) in order to achieve ferrous hydroxide precipitation.

The purpose of this proposed study was to conduct treatment studies using a flow-through pilot-scale AIS treatment process at a number of high flow (> 50 L/s, 4.3 MLD) AMD discharges. The study included pilot-scale treatment (1 to 5 L/s) at four (4) locations across Pennsylvania with different AMD chemistries to demonstrate the wide-spread application of AIS treatment. AIS treatment has been investigated in bench-scale studies and a demonstration SBR system. The purpose of this field pilot-scale study is the next step to demonstrate the technology and develop design guidance for full-scale flow through systems. A portable (trailer-loaded) completely equipped (i.e., aeration, mixers, chemical feed, pumps, and controllers) steel tank pilot-scale system was used for the study.

A number of studies have been conducted to evaluate AIS treatment as a potential new and

innovative approach to removing iron from AMD (Dietz 2003, Dietz and Dempsey 2002, and Fish and Dietz 2005). The studies demonstrated the effectiveness of the heterogeneous iron oxidation to remove iron from AMD on bench-scale to small-scale basis. This study was conducted to test a modified AIS treatment process, employing a portable two-stage flow through pilot scale system, at four different AMD discharges located in both the bituminous and anthracite coal regions of Pennsylvania.

Iron Oxidation

The oxidation of Fe²⁺ iron is the first and most crucial step in the removal of iron. Without the oxidation step, Fe²⁺ iron would remain in solution (except at very high pH) and removal of iron from AMD would not be possible. There are two types of Fe²⁺ iron oxidation in aqueous solutions:

1. ***Homogeneous Ferrous Iron Oxidation*** – is the long established oxidation process occurring in solution and involves the reaction of dissolved ferrous iron (Fe²⁺, Fe(OH)¹⁺ and Fe(OH)⁰) with dissolved oxygen (DO).
2. ***Heterogeneous Ferrous Iron Oxidation*** – is a newly identified oxidation process occurring on the surface of ferric oxide/hydroxide solids and involves the sorption of Fe²⁺ iron and DO followed by the rapid catalytic oxidation.

The first type, homogeneous Fe²⁺ iron oxidation occurs in solution and is most commonly associated with passive treatment and conventional (lime-based) chemical treatment of AMD. The homogeneous Fe²⁺ iron oxidation rate equation (Sung & Morgan 1980) is:

$$\text{Homogeneous Rate (M} \cdot \text{s}^{-1}) = -\delta[\text{Fe(II)}] / \delta t = k_{\text{Ho1}} \times [\text{Fe(II)}_{\text{diss}}] \times [\text{O}_2] / \{\text{H}^+\}^2 \quad (1)$$

Homogeneous iron oxidation is complex with the rate affected by the Fe²⁺ iron concentration [Fe(II)_{diss}], DO [O₂] and pH {H⁺}. Temperature is an integral part of the equation as it affects the reaction rate constant (*k_{Ho2}*); a decrease in temperature decreases the oxidation rate. The homogeneous rate equation is a reliable design tool that can be used to predict iron oxidation and removal for different AMD chemistry, and operating conditions (e.g., DO, pH and temperature).

Heterogeneous ferrous iron oxidation is an oxidation process that occurs on the ferric oxide/hydroxide surface and is the oxidation process utilized in AIS treatment. Heterogeneous iron oxidation is a two step processes that involves: 1) the sorption of Fe²⁺ iron to the surface of

the iron oxide/hydroxide; 2) rapid oxidation in the presence of DO to form new Fe³⁺ oxide/hydroxide. Equations and models for the reactions are contained in Dietz (2003). The equations are complex describing both sorption and oxidation process.

$$HeFIO \text{ rate (M} \cdot \text{s}^{-1}) = (-\delta[\text{Fe(II)}]/\delta t) = (k_{He1}[\text{O}_2]S_1) + (k_{He2}[\text{O}_2]S_2) \quad (2)$$

and

$$S_x = \frac{1 + ([\text{Fe(II)}]_{diss}) \times K_x^{app}}{[\equiv \text{Fe(III)}] \times \Gamma_x \times \{H^+\}^x} \quad (3)$$

where x is the reaction (either 1 or 2), k_{Hex} are the surface oxidation rate constants, K_x^{app} are the surface complexation constants, and $[\equiv \text{Fe(III)}]$ is the AIS concentration (in mg/L). Dietz (2003) determined the various thermodynamic constants for the equations including activation energies and enthalpies, which describe the effects of changing temperature. In current treatment systems (including passive treatment and lime treatment), heterogeneous iron oxidation is not very important (< 5% of the Fe²⁺ iron oxidation rate) due to the low Fe³⁺ oxide/hydroxide concentrations (typically less than 10 mg/L) that can be maintained in suspension without mechanical means. Iron Oxide Technologies, LLC has developed several treatment systems optimizing heterogeneous iron oxidation through concentrated suspensions of Fe³⁺ oxide/hydroxide solids in reactor systems. Using the above homogeneous and heterogeneous rate equations, and confirmed with bench-scale testing, the heterogeneous rate employed in AIS treatment (at iron oxide/hydroxide concentrations of approximately 2 g/L in suspension) is 75 to 150 times faster than pre-aeration/passive treatment in the pH range of 6 to 7. In addition, at the slightly acidic pH the heterogeneous rates would be comparable to iron oxidation and removal rates achieved in conventional lime-based treatment where pH is greater than 8.

Pilot AIS Treatment System Description

AMD Discharge Sites

The pilot studies were conducted at four locations where included locations in southwest, north-central and eastern Pennsylvania (Fig. 1). The locations were the:

1. Phillips AMD Discharge – a deep mine portal on the banks of Redstone Creek located to the south of Uniontown, Pennsylvania. *No current treatment.*

2. Monview-Mathies AMD Discharge – a deep mine entry discharge located on Little Mingo Creek near Monongahela, Pennsylvania. *Treated with sodium hydroxide and settling ponds.*
3. Blue Valley AMD Discharge – a deep mine portal in the Toby Creek watershed located near Brockway, Pennsylvania. *Treated using potassium permanganate as a chemical oxidant.*
4. Scotts Tunnel AMD Discharge – a deep mine drain located in the Shamokin Creek watershed to the west of Kulpmont, Pennsylvania. *No current treatment.*

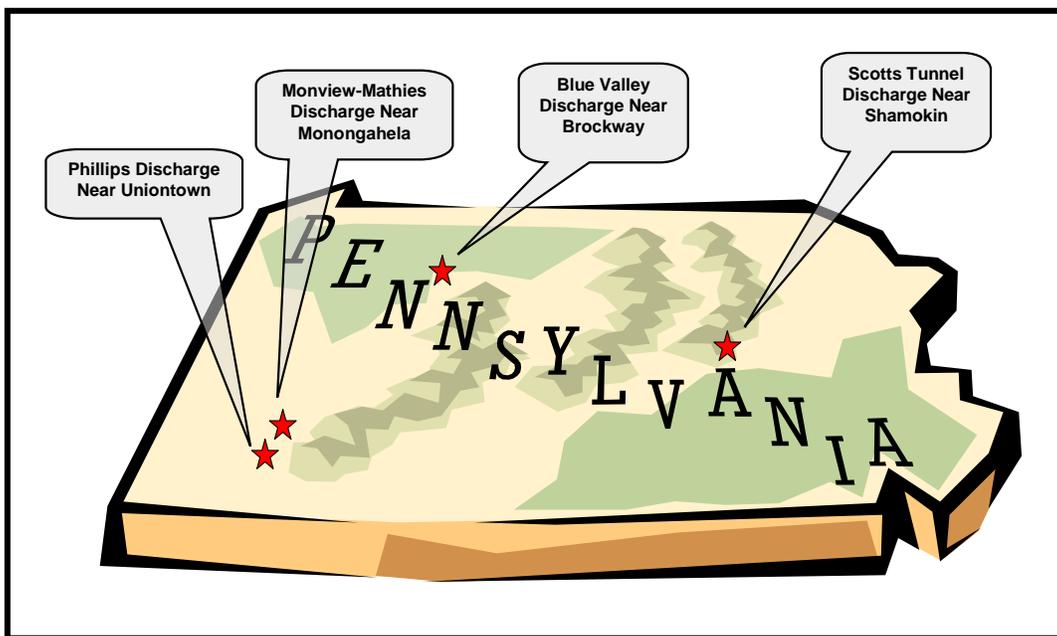


Figure 1. The four locations for the AIS Treatment Pilot-Scale Studies.

Three of the four locations were located in the bituminous coal region of Pennsylvania. The fourth, Scotts Tunnel AMD discharge, was located in the anthracite coal region. This permitted evaluation of the AIS treatment for differences in AMD chemistry associated with bituminous and anthracite regions. In addition, the AMD discharges were located over a range of latitudes and elevations that encompasses the differences expected in coal discharges of the region.

AMD Discharge Characteristics

The chemistry and flows for the discharges investigated in this study are summarized in Table 1. The discharge flows ranged from 4 million liters per day (MLD) Blue Valley to 55

MLD at the Scotts Tunnel Discharge. The discharge pH ranged from 5.8 at Scotts Tunnel to 6.8 at Monview-Mathies with alkalinity in the AMD discharges ranging from 36 mg/l to 325 mg/L, respectively. Total iron ranged from 14.0 mg/L at Blue Valley to 47.7 mg/L at Phillips. The total iron was comprised almost entirely of dissolved Fe²⁺ iron, except for the Monview-Mathies discharge, which had approximately 5 mg/L of particulate Fe³⁺ iron. All the discharges were low in Mn and Al, a common characteristic of deep mine coal discharges in Pennsylvania. The metal concentrations along with the alkalinity determined the total acidity of the discharges, which ranged from highly alkaline (-270 mg/L) at Monview-Mathies to slightly acidic (+20 mg/L) at Scotts Tunnel. Sulfate concentrations varied from a low of 230 mg/L at Scotts Tunnel to a high of 1,050 at Monview-Mathies. Temperature also varied across the discharges depending on the latitude and elevation with the lowest discharge temperature of 10.0°C measured at Blue Valley in northcentral Pennsylvania and the highest discharge temperature of 14.9 °C measured at Phillips in Southwestern Pennsylvania.

Table 1. Summary of the chemistry and flow for the deep mine discharges investigated in the AIS AMD pilot study.

Location	Flow MLD ¹	Temp. °C	pH	Total Fe (mg/L)	Fe(II) (mg/L)	Total Mn (mg/L)	Alkal. (mg/L)	Acid. (mg/L)	Sulfate (mg/L)
Phillips	35	14.9	6.1	47.7	47.6	3.0	235	-150	600
Monview-Mathies	16	13.8	6.8	26.0	21.1	1.5	325	-270	1,050
Blue Valley	4.0	10.0	6.3	14.0	13.5	3.5	200	-130	600
Scotts Tunnel	55	12.1	5.8	22.5	22.3	2.5	36	+20	230

¹ MLD is million liters per day

Carbon dioxide (CO₂) acidity was calculated to determine the amount of aeration needed to remove the CO₂ and maintain or raise the pH to levels needed for the effective oxidation of Fe²⁺ iron in the AIS treatment approach. In aqueous chemistry, CO₂ acidity is present in water as carbonic acid (H₂CO₃). The pH of water (controlled by the carbonate system) is determined by the concentrations of bicarbonate (HCO₃⁻), which is alkalinity, and H₂CO₃ according to the following relationship:



The pK_a of this equilibrium is 6.4, which would be the pH where the H_2CO_3 and HCO_3^- concentrations would be equal. This means an alkalinity (HCO_3^-) of 30 mg/L (as $CaCO_3$) would contain an equal CO_2 acidity (H_2CO_3) of 30 mg/L (as $CaCO_3$) to have a pH of 6.4. The CO_2 acidity was calculated for each of the discharges and ranged from 135 mg/L (as $CaCO_3$) for Scotts Tunnel to 475 mg/L for the Phillips discharge. The source of this CO_2 acidity is chemical neutralization reactions in the deep mine pool as well as decomposition reactions. The CO_2 acidity is about 100 to 300 times higher than is normally found in surface waters in equilibrium with the atmosphere.

The solubility of Ca and Mg in the AMD is an important aspect in various treatment methodologies. Adjustments of pH may create operation and maintenance issues by precipitating Ca and Mg. Figure 2 shows the calcium (calcite) solubility with respect to pH. Oversaturated conditions for Ca is only present at pH greater than 7.5 indicating calcium carbonate (calcite) precipitation is not a significant concern in AIS treatment as the operational pH is typically less than 7. Calcite precipitation will occur in lime (CaO) treatment which raises the pH to greater than 8. At pH greater than 8, Mg may also be removed as a hydroxide.

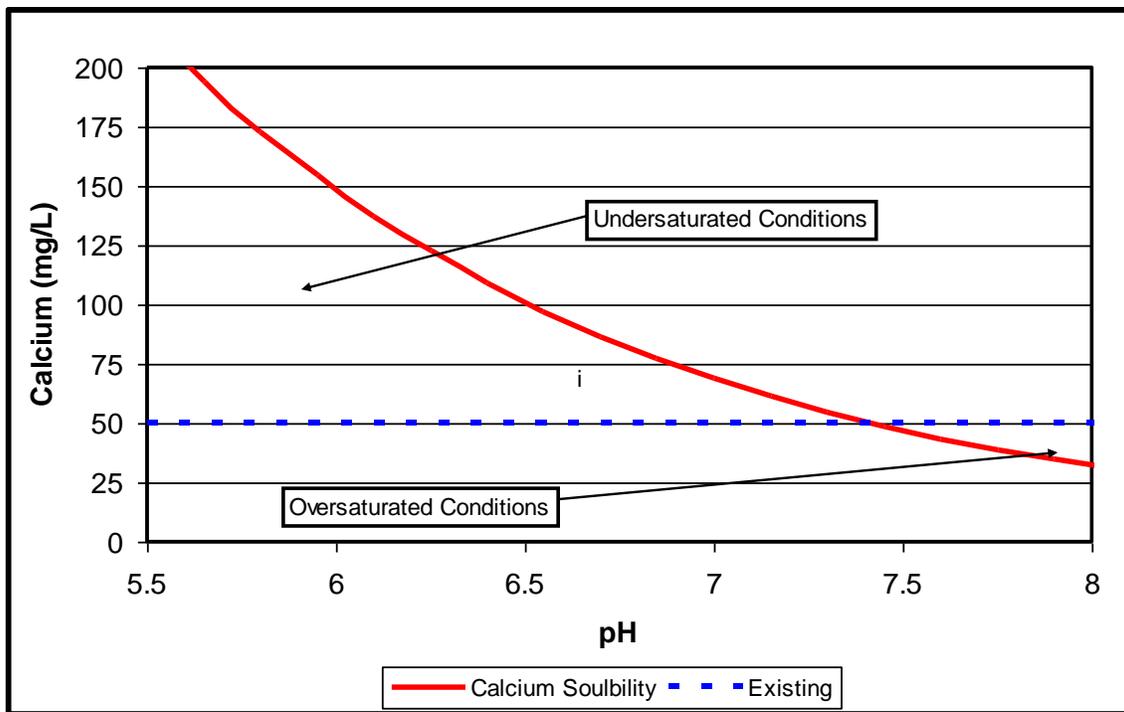


Figure 2. Calcium solubility in the AMD discharge with respect to pH.

AIS Pilot Treatment System

Iron Oxide Technologies, LLC has developed a new (patent pending) active treatment approach known as Activated Iron Solids (AIS) treatment of AMD. The innovative active AIS treatment process utilized for this pilot study is the two-stage AIS reactor system is schematically depicted in Fig. 3 and an example field setup is shown in Fig. 4. The pilot system consists of two 7,500 liter reactors in series equipped with mixers and bubble aeration. The reactors are followed by flocculation and clarification. In addition to the various treatment units, the system included the ability to add pulverized limestone and polymer, and re-circulate solids from the clarifier to the reactor.

The AIS treatment process has a high rate of ferrous oxidation at short detention times by artificially increasing suspended ferric oxide/hydroxide concentrations (AIS = 1.5 – 2.5 g/L). The high iron oxide concentrations produce a catalytic environment that promotes ferrous iron oxidation and removal while producing high-density and pure treatment solids (iron oxide solids). The pilot-scale flow through AIS system maintains high reactor AIS concentrations through recirculation of solids collected in the clarifier to the reactors and by mechanical mixing using the mixers and aeration.

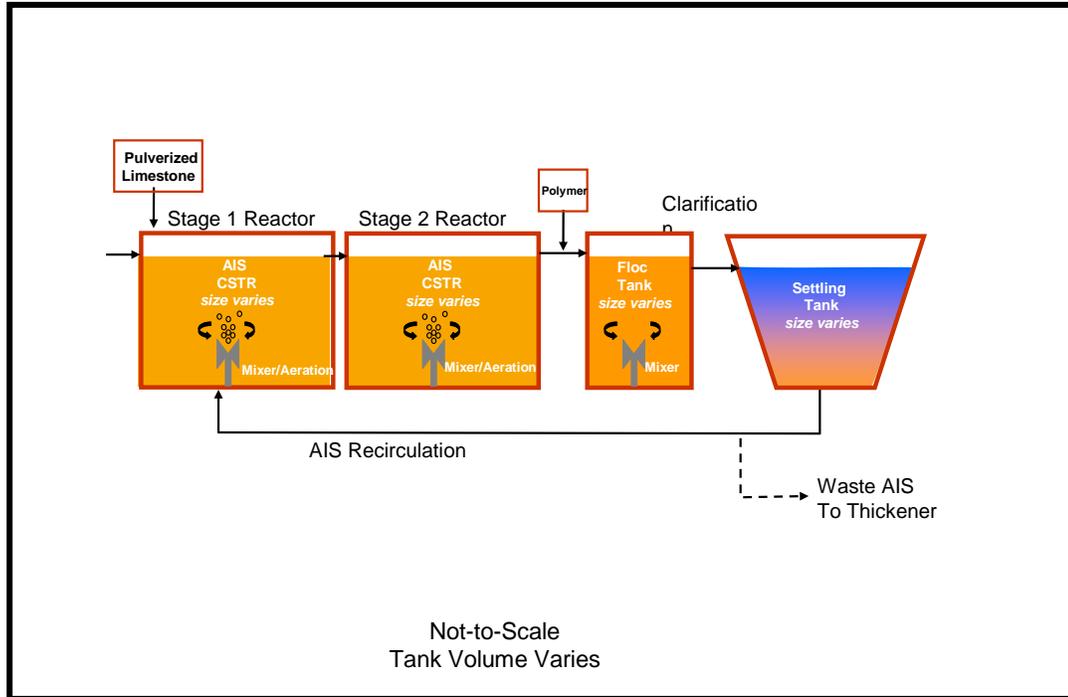


Figure 3. AMD Treatment in a two-stage flow-through AIS system showing reactors, pulverized limestone feed, polymer addition, flocculation, settling and return AIS.



Figure 4. AMD Treatment in a Two-Stage Flow-Through AIS System showing pilot system placed and operating at the Scotts Tunnel AMD Discharge Site.

Pilot Study Methods

Pilot studies were conducted at each of the four locations. The site specific placement of the pilot study at each location was identified based on proximity to the discharge, site characteristics, access to the location, and availability of electrical service. In only one case (the Phillips location) was a generator required. The locations for each pilot study were:

1. Blue Valley – located within the building of the Blue Valley AMD Treatment Facility and Fish Culture Station in the loading dock open area where the discharge could be pumped and electrical service provided from existing service.
2. Monview-Mathies – located between the mine shaft (and discharge) and a maintenance building where temporary electrical service was provided and the discharge was pumped from the mine shaft opening and returned to the existing underground pipe that directs the caustic soda treated discharge to a series of settling ponds.
3. Phillips – located adjacent to the AMD discharge in a flat area with the access road and pad installed by DEP-BAMR and electrical service provided by a diesel generator.
4. Scotts Tunnel - located adjacent to a discharge on an existing turn off along S.R 61 approximately ½ mile to the west of Kulpmont, PA and on Susquehanna Coal Company property where temporary electrical service was available.

Each site required various degrees of engineering services to develop the site for delivery and placement of the trailer pilot system, installation of electrical service, and installation and setup of the pilot unit.

Analytical Methods

Analysis for the pilot studies consisted of pH, DO, temperature, total iron, dissolved/ferrous iron, alkalinity, and conductivity. The pH was measured with a Fisher Scientific Accumet Portable Meter equipped with a Cole Parmer Accumet combination pH electrode. The pH electrode was calibrated daily prior to use with pH 4 and 7 buffers. DO and temperature were measured with an YSI Model 550A DO Meter. The DO Meter was calibrated prior to each use using the air saturation method. Total iron was measured using a Hach Iron Pocket Colorimeter Test Kit (0-3.00 mg/L) using Ferrover reagent after appropriate dilution. Dissolved iron was also measured with the Pocket Colorimeter but after filtration using a syringe and a 0.2 µm syringe

filter, and appropriate dilution. Ferrous iron was determined using Hach ferrous iron powder packets and the Hach Iron Pocket Colorimeter. Initial testing at each discharge indicated dissolved iron (filtered sample) equals ferrous iron. As a result, the dissolved iron test was used to determine ferrous iron. Alkalinity was measured on a 100 mL sample using a Hach Digital Titrator and a 1.600 N sulfuric acid cartridge. Conductivity was measured with an Oakton Conductivity Pen.

Aeration Only Testing

Aeration testing was conducted at three (Blue Valley, Monview-Mathies, and Scotts Tunnel) of the locations prior to the AIS testing to determine the required detention time and air flow to achieve adequate oxidation of the Fe^{2+} iron (dissolved) in the discharge. In the case of Scotts Tunnel, aeration testing was also conducted to determine if the addition of an alkaline material (i.e., powdered limestone) was needed. The results of the aeration could be compared directly to the AIS results to show the benefits of AIS treatment over aeration only treatment.

Aeration testing consisted of incrementally varying the AMD flow to the treatment system and providing aeration at various air flows. Flow was varied by adjusting weir plates on an inlet flow box that regulated the pumped water into the system. Flow was determined by water level measurement through a V-notch weir. Air flow was controlled by adjusting a gate valve to the desired air flow level, as measured at a Dwyer VISI-float flowmeter.

AIS Testing

The AIS testing at the four locations covered a broad range of AMD chemistries and operating conditions to determine optimal operating conditions for each of the discharges. The target AIS (as total iron) was between 1.5 and 2.5 mg/L in the reactors using re-circulated ferric oxide/hydroxide solids from the clarifier.

To start the pilot system, AIS solids were added to the pilot unit using solids retained from previous pilot studies. In the case of the Blue Valley pilot study, solids from the existing Blue Valley AMD treatment system were used for start-up. Ferrous iron is oxidized by potassium permanganate at the existing Blue Valley treatment facility. The added ferric oxide/hydroxide solids typically resulted in initial reactor AIS concentrations between 0.4 and 0.8 g/L. The addition of the solids simplified and shortened the start-up time required to accumulate AIS solids in the system (days versus weeks) to the target concentrations.

The initial AMD inflow was set based on calculated oxidation rates using the heterogeneous iron oxidation model. The AIS recirculation rate was set at a flow rate to maintain and increase the reactor AIS concentrations based on expected solids in the re-circulated flow and the AMD inflow rate. Air flow was set at an estimated rate based on the aeration only studies. The polymer used for the AIS testing was the Ciba Specialty Chemicals Magnafloc® 155, a medium molecular weight low charge anionic acrylamide polymer. This polymer was identified as the most suitable polymer for this application based on testing of multiple polymers at the pilot studies, based on bench testing of the AIS containing reactor water.

As AIS concentrations increased in the reactors, AMD flow to the system was gradually increased, by adjusting the inlet weir plates. Air flow was also adjusted to compensate for the increased flow. This startup method typically took between two and seven days depending on the AMD iron concentration at each site with longer startup durations required at lower influent iron concentrations. Monitoring was conducted during startup to monitor changing conditions. Once the startup procedure was complete, AIS testing and monitoring was conducted for a period of two to four weeks depending on the site conditions (i.e., electrical supply) with regular monitoring of the various operating conditions.

Results

Results of the pilot studies included aeration only testing, AIS testing and iron solids testing produced by the AIS system. The results are summarized in the following sections.

Aeration Only Testing

The results of the aeration only testing from the various pilot studies are summarized in Table 2. The detention times required to achieve substantial Fe^{2+} iron oxidation varied based on factors including pH, alkalinity, and temperature. The raw water pH and alkalinity determined the amount of CO_2 acidity in the water that must be removed to raise the pH to greater than 7, where the Fe^{2+} iron oxidation rate is faster. The alkalinity remaining after the iron acidity has been removed is also important in determining the pH of the water and the rates of oxidation. Temperature affects both the Fe^{2+} iron oxidation rate as well as the rate DO is added and CO_2 acidity is removed through aeration. As can be seen in the required detention times to lower than Fe^{2+} iron to less than 0.1 mg/L, the Monview-Mathies discharge has the lowest detention of the three discharges tested and this location had the highest raw water pH, alkalinity and

temperature. The Scotts Tunnel had the longest detention time to oxidize the ferrous iron, which was related to the lower pH resulting from the lower raw water alkalinity and the limited alkalinity remaining after removal of the iron acidity. Overall the detentions times required in aeration only tests to achieve low Fe²⁺ iron at the three locations ranged from approximately 6 hours at Monview-Mathies to greater than 20 hours at Blue Valley and Scotts Tunnel.

Table 2. Summary of pilot study effluent results where aeration only was used in the reactors (i.e., no AIS); all concentrations in mg/L.

Study Location	Det. Time (Hrs)	Air Flow (lpm)	pH	Diss. O ₂ (mg/L)	Temp. °C	Alk. (mg/L)	Fe(II) (mg/L)
Blue Valley	21.1	680	7.44	10.8	12.1	187	0.63
Blue Valley	9.5	680	7.02	11.0	11.2	195	2.55
Blue Valley	4.2	680	6.85	11.1	10.4	204	7.75
Monview-Mathies	18.1	510	8.33	9.6	19.1	350	0.03
Monview-Mathies	6.4	510	8.13	10.1	17.5	342	0.05
Monview-Mathies	2.6	510	7.54	10.7	14.8	340	0.25
Scotts Tunnel	28.2	510	6.35	9.50	18.8	2.9	0.70
Scotts Tunnel	14.8	510	6.40	10.1	17.2	2.9	1.50
Scotts Tunnel	3.6	510	6.47	11.0	16.3	25	16.7

The aeration only dissolved iron data was compared to the predictions using the homogeneous iron oxidation model (Equation 1) and reactor equations. The model results, summarized in Table 3, were consistent with the results from the Blue Valley and Monview-Mathies aeration only studies. The Scotts Tunnel aeration study had faster oxidation rates (approximately 2 times faster) than the homogeneous model predicted. The Scotts Tunnel AMD discharge has lower salinity than the other two discharges. Investigators have found lower salinity waters to have faster oxidation rates than higher salinity waters (Millero et al. 1987). This is related to the Fe²⁺ iron equilibrium reactions and the affect ionic strength has on the equilibriums.

Table 3. Comparison of measured versus modeled (homogeneous) effluent ferrous iron (Fe(II)) concentrations from the pilot study results where aeration only was used (i.e., no AIS); all concentrations in mg/L.

Study Location	Det. Time Hrs	Meas. Fe(II)	Calc. Fe(II)	Fe(II) Difference (Meas.- Calc.)
Blue Valley	21.1	0.51	0.12	+0.39
Blue Valley	9.5	3.74	3.45	+0.29
Blue Valley	4.2	8.0	8.0	0.00
Monview-Mathies	18.1	0.01	<0.001	0.00
Monview-Mathies	6.4	0.01	<0.001	0.00
Monview-Mathies	2.6	0.37	0.45	-0.08
Scotts Tunnel	28.2	0.70	0.94	-0.24
Scotts Tunnel	14.8	1.5	3.5	-2.0
Scotts Tunnel	3.6	16.3	16.7	-0.4

AIS Testing

The results of the AIS testing from the various pilot studies are summarized in Table 4 and can be compared to the influent AMD characteristics contained in Table 1. As can be seen in the two tables there are substantial differences in raw water chemistry and in the conditions observed from the treatment system. In the tests the reactor AIS concentration was substantial with concentrations ranging between 1.8 and 2.5 g/L in the pilot studies. This reactor AIS concentration was achieved by the recirculation of solids from the clarifier to the reactors and the suspension of the solids by mechanical mixers and aeration. It is this AIS concentration that caused the observed rapid oxidation of the ferrous iron in the AMD.

The detention times at each location to achieve near complete oxidation of the ferrous iron varied from 1 to 3 hours at the various sites. The detention times for a discharge were affected by a number of factors related to the AMD characteristics including Fe²⁺ iron concentration, pH, alkalinity, and temperature. The AMD pH and alkalinity determined the amount of CO₂ acidity in the water that must be removed to raise the pH; heterogeneous Fe²⁺ iron oxidation rate is also affected by pH. Temperature affects both the Fe²⁺ iron oxidation rate as well as the rate DO is added and CO₂ acidity is removed through aeration. The importance of temperature can be seen

in the required detention times to lower the ferrous iron to less than 0.05 mg/L. The Phillips discharge, which has the highest discharge temperature, has the lowest detention despite having the highest AMD Fe²⁺ iron of the four discharges tested.

Table 4. Summary of AIS pilot study effluent results from the various AMD locations.

Study Location	Det. Time Hrs	pH	Diss. O ₂ (mg/L)	Temp. °C	Reactor AIS (mg/L)	Fe(II) (mg/L)	Total Fe (mg/L)
Blue Valley	2.10	6.55	8.2	10.3	1,850	0.71	3.85
Blue Valley	2.10	6.81	9.5	10.3	1,980	0.04	5.40
Blue Valley	2.10	6.65	9.1	10.2	2,170	0.11	5.80
Monview-Mathies	2.60	7.15	8.6	15.0	1,830	0.07	8.15
Monview-Mathies	1.64	7.15	9.5	13.9	2,020	0.06	7.40
Monview-Mathies	1.08	7.07	9.3	14.4	2,120	0.14	5.20
Phillips	1.64	6.65	8.6	15.2	1,980	0.05	5.35
Phillips	1.08	6.41	8.2	15.2	2,200	0.00	6.25
Phillips	0.80	6.36	7.4	15.4	2,300	0.03	4.60
Scotts Tunnel ¹	2.50	6.61	10.6	13.4	2,340	0.15	2.15
Scotts Tunnel ¹	1.62	6.58	10.8	13.2	2,410	0.94	3.35
Scotts Tunnel ¹	3.25	6.90	10.5	13.6	2,370	0.06	1.95

¹ An inclined plate clarifier was used at this site in place of the flocculent clarifier used in previous pilot studies

Air flow in AIS testing was an important factor in the oxidation process by increasing both pH and DO. DO is increased through the transport of oxygen in the air to the water. pH is indirectly increased through the ex-solution of CO₂ in the water to the air. Based on the heterogeneous Fe²⁺ iron oxidation model, both the increase in DO and pH, substantially increased the Fe²⁺ iron oxidation rate. The heterogeneous model predicts that: 1) an increase in DO from 5 to 10 mg/L will double the heterogeneous Fe²⁺ iron oxidation rate; and 2) a pH increase of 0.3 will more than triple the heterogeneous Fe²⁺ iron oxidation rate.

The AMD chemistry for the Scotts Tunnel discharge tested in the pilot studies indicated the discharges was net acidic or contained insufficient alkalinity to maintain pH greater than 6.5 (i.e., net alkalinity less than 10 mg/L). In this pilot study pulverized limestone was tested as a source

of alkalinity. Pulverized limestone, also known as agricultural lime, is a fine powder produced by crushing limestone. It is calcium carbonate (CaCO_3) versus hydrated lime and quick lime which are calcium hydroxide (Ca(OH)_2) or calcium oxide (CaO), respectively. Pulverized limestone is lower in cost than hydrated lime or quick lime. In the pilot studies where pulverized limestone was used, it was added directly to the first reactor using a powder feed system. The pilot studies indicated that the pulverized limestone dissolved in the reactors due to the mixing provided and the acidic (pH ~ 6.5) reactor conditions, and provided the alkalinity needed to maintain reactor pH for AIS treatment. In the case of the Scotts Tunnel discharge, the alkalinity produced by the pulverized limestone was greater than 40 mg/L, which equated to between 85% and 95% of the measured dose to the pilot unit. This indicates the pulverized limestone, where needed, is an effective material to maintain pH and alkalinity in the AIS treatment process for low net alkalinity or slightly net acidic AMD. It should also be noted the amount of pulverized limestone in AIS treatment at the Scotts Tunnel discharge will be $\frac{1}{4}$ or less of the lime (hydrated or quick) dose required in conventional lime treatment.

The primary objective of the AIS pilot studies was to demonstrate the ability of AIS treatment to rapidly oxidize dissolved Fe^{2+} iron to Fe^{3+} iron at slightly acidic pH (6.6 to 7.0). The removal of the particulate iron was a secondary objective of the pilot studies. As can be seen in the first three pilot studies (Blue Valley, Monview-Mathies and Phillips) elevated effluent total iron occurred using inline polymer dosing and the integrated floc-blanket clarifier included in the pilot system. This floc-blanket clarifier was very sensitive to polymer dose and hydraulic loading and did not permit a great deal of operational flexibility. However, under optimal conditions effluent total iron of less than 2 mg/L was achieved. In order to overcome the floc-blanket limitations, an inclined-plate clarifier, preceded by a flocculation tank was employed at the Scotts Tunnel pilot study. Effluent total iron less than 2 mg/L was achieved in tests at the maximum recommended hydraulic loading to the clarifier with indications that an effluent total iron less than 1 mg/L can be achieved under optimal operating conditions (observed during polymer dose testing). The higher effluent total iron (> 3 mg/L) occurred during tests where the hydraulic loading was more than double the recommended loading to the inclined-plate clarifier. Based on this evaluation, AIS treatment can also achieve very low effluent total iron concentrations where adequate flocculation and clarification is provided.

Compared to aeration-only testing, the AIS pilot study results indicate AIS treatment can substantially decrease detention times. The required detention times at the Blue Valley and Scotts Tunnel locations were at least an order of magnitude less than the aeration only detention times, which also equates to a similar difference in overall system volume and size. The Monview-Mathies location AIS treatment detention time was slightly less than an order of magnitude, due to the higher pH that can be achieved with aeration only at this location, a direct affect of the AMD pH and alkalinity.

The results of the AIS pilot study were also used to evaluate the validity of the heterogeneous ferrous iron oxidation model for the sizing AIS reactor systems for the AMD discharge chemistry tested in the pilot studies. The heterogeneous Fe^{2+} iron oxidation model was used to predict the oxidation rate for the measured conditions in the reactors. The reactor Fe^{2+} iron concentration was then estimated using complete mix reactor equations. The results of the comparison are summarized in Table 5. Based on the measured versus modeled ferrous iron comparisons, the model provides reasonable predictions of the ferrous iron oxidation rates. In addition, because the model predictions are reasonable the use of the polymer in the pilot studies has no negative impact on the catalytic oxidation process. The results indicate the heterogeneous ferrous iron oxidation model is a valid tool to determine the reactor sizes in an AIS system to treat the range of AMD chemistries tested in the pilot study.

Iron Solids

Ferric oxide/hydroxide solids are continuously produced by the AIS treatment process. The wet solids produced during the pilot study were collected and characterized. AIS treatment solids were 2-4% in re-circulated flow and approximately 20-30% solids after 24 hours. Table 6 contains the analytical results from an AIS sample collected from the Phillips pilot study. The sample had a solids content of 21% after only 6 hours of settling. Additional settling time would increase solids content. Based on dry weight analysis, the AIS sample is nearly all iron (54%), which reflects greater than 95% iron oxides/hydroxides. Calcium is the second largest metal in the sample at 1.4% and equates to a CaCO_3 content of 3.5%. Additional metal analysis indicates the sample has very low trace metal concentrations, which should not limit the disposal or reuse options for the waste solids. The wet solids produced by the AIS treatment process are unique in characteristic, a result of the heterogeneous Fe^{2+} iron oxidation process.

Table 5. Comparison of measured versus modeled (heterogeneous) effluent ferrous iron (Fe(II)) during AIS pilot studies.

Study Location	Det. Time Hrs	Meas. Fe(II) mg/L	Calc. Fe(II) mg/L	Fe(II) Difference (Meas.- Calc.)
Blue Valley	2.10	0.71	0.48	+0.23
Blue Valley	2.10	0.04	0.06	-0.02
Blue Valley	2.10	0.11	0.07	+0.04
Monview-Mathies	2.60	0.07	0.01	+0.06
Monview-Mathies	1.64	0.06	0.01	+0.05
Monview-Mathies	1.08	0.14	0.01	+0.13
Phillips	1.64	0.05	0.01	+0.04
Phillips	1.08	0.00	0.48	-0.48
Phillips	0.80	0.03	2.3	-2.27
Scotts Tunnel	2.50	0.15	0.02	+0.13
Scotts Tunnel	1.62	0.94	0.27	+0.67
Scotts Tunnel	3.25	0.06	0.01	+0.05

Figure 5 compares iron oxides/hydroxides produced by AIS treatment with a commercially available synthetic iron-based pigment. As can be seen, there is minimal differences in physical characteristics between the two samples. The AIS treatment Fe^{3+} oxide/hydroxide solids are likely to be an acceptable material as a low-grade pigment without any additional processing.

The use of the AIS solids was also investigated for phosphorus sequestering in municipal wastewater treatment directly dosed and after conversion to a $FeCl_3$ solution using HCl acid (Fish & Dietz 2008). The study indicated the solids can be used directly but are 5 to 10 times more effective when applied as a $FeCl_3$ solution.

Table 6. Laboratory Analysis of AIS Sample from the Phillips Pilot Study.

	Unit	Detection Limit	Result	% Content
Solids Content (Wet)	%	0.01		20.8
----Dry Weight Basis----				
Iron	mg/kg	1	537,500	54
Manganese	mg/kg	1	348	0.03
Aluminum	mg/kg	5	3,580	0.35
Calcium	mg/kg	1	14,200	1.4
Magnesium	mg/kg	1	400	0.04
Sodium	mg/kg	1	160	0.02
Potassium	mg/kg	1	35	<0.01
Silica	mg/kg	1	97	<0.01
Arsenic	mg/kg	1	48	<0.01
Lead	mg/kg	0.25	0.9	<0.01
Selenium	mg/kg	0.25	<0.25	<0.01
Zinc	mg/kg	1	123	0.01

Discussion

The pilot studies indicated that AIS treatment is an effective treatment process for the oxidation and removal of iron from AMD where the discharges contain excess alkalinity and/or initial alkalinity. Comparing the results of AIS treatment with treatment by aeration alone indicates that this new treatment approach will decrease detention times by at least an order of magnitude versus non-chemical active treatment. Compared to passive treatment, AIS treatment will decrease treatment system size (based on area) by at least a factor of 50 and thereby provide an alternative approach where land area is limiting.



The AIS treatment approach was also compared to conventional lime-based treatment by comparing expected detention times using the homogeneous iron oxidation rate model and complete mix reactor equations for a pH 8, which represents the maximum homogeneous iron oxidation rate (Millero et al. 1987). Above pH 8, $\text{Fe}(\text{OH})_2$ forms and results in a system where both Fe^{2+} oxidation and ferrous hydrolysis (precipitation) occurs, and where the latter can control iron removal. After precipitation, the ferrous hydroxide solid is converted to ferric hydroxide through direct oxidation of the solid. According to the homogeneous iron oxidation rate model and the complete mix reactor equation the detention time to achieve a Fe^{2+} iron concentration less than 0.05 mg/L at pH 8 is approximately 1 hour. This detention time is similar to the detention times found for AIS treatment in the pilot studies, indicating that the treatment size of an AIS system would be similar to conventional lime-based treatment. However, AIS treatment would not require lime (hydrated or quick) for treatment or would use a lower dose of less expensive pulverized limestone.

Another important aspect of any AMD treatment is the overall expected costs, which are typically reported on a cost per 1,000 gallons of treated water. The treatment costs will vary depending on inclusion of the various AIS treatment system capital and operating costs. Table 7

Figure 5. Comparison of a Synthetic Iron Oxide Pigment to an AIS Treatment Produced Iron Hydroxide/Oxide.

summarizes the treatment costs per 1,000 gallons of treated water at the different pilot study locations for the various included costs and assuming average flow conditions. Table 7 treatment costs are a function of several factors including the discharge flow, discharge flow variability (i.e., difference between design flow and average flow), and the chemistry of the discharge (i.e., net alkaline versus net acidic). The treatment costs at the Blue Valley site are negative as they reflect a change in operating costs from current treatment using potassium permanganate as an oxidant. Based on the cost analysis AIS treatment costs can be as low as \$7 per 10^6 liters of treated water where there is a no cost disposal option of the treatment solids. When factoring all the costs of treatment (including 25-year annualized capital costs) the treatment costs remain under \$70 per 10^6 liters. As a comparison, the costs for lime (quick) at a conventional lime-based treatment system for the Phillips discharge would exceed \$40 per 10^6

liters treated; capital cost, electricity costs, maintenance, labor, and solids disposal would obviously increase treatment costs.

Table 7. Summary of estimated AIS treatment costs (per 10⁶ liters of treated water) for the AMD discharges evaluated in the pilot study.

Discharge Location	Ave. Flow MLD	Non-Personnel O&M Solids Reuse	Total O&M	Total O&M Annualized Capital Costs
Blue Valley ¹	2.6	-\$37	-\$32	-\$29
Monview-Mathies	9.8	\$10	\$45	\$63
Phillips	22.0	\$7	\$34	\$50
Scotts Tunnel	43.5	\$9	\$24	\$34

¹ negative costs reflect a change in costs compared to the current potassium permanganate oxidation system.

Summary

The AIS pilot study results indicate:

- AIS treatment effectively oxidizes Fe^{2+} iron to concentrations less than 0.1 mg/L, and requires short detention times to meet effluent objectives.
- AIS treatment solids can be rapidly settled with the addition of a polymer and effluent total iron is likely to be less than 1 mg/L.
- Observed oxidation rates by the AIS solids are consistent with the heterogeneous Fe^{2+} iron oxidation model.
- AIS Fe^{2+} iron oxidation rates are not affected by polymer dosing.
- Pulverized limestone can be used as an alkalinity source to address slightly net acidic discharges, such as the Scotts Tunnel AMD.
- Treatment areas are substantially less than passive treatment or aeration alone and are comparable to conventional lime-based treatment.
- Treatment costs are substantially less than conventional lime-based treatment.

Based on the results of the pilot studies full-scale systems will likely provide the needed cost effective and long term treatment of high flow net alkaline to slightly acidic mine water containing dissolved iron greater than 10 mg/L. The AIS treatment may also produce iron solids that are marketable and effluent water quality with beneficial use.

References

- American Water Works Association (AWWA). 2001. Water quality and treatment; A handbook of community water supplies, 5th edition. Technical Editor R.D. Letterman. McGraw-Hill, Inc., New York.
- Dempsey, B.A., H.C. Roscoe, R. Ames, R. Hedin, & B.-H. Jeon. 2001. "Ferrous oxidation chemistry in passive abiotic systems for treatment of mine drainage". *Geochemistry: Exploration, Environment, Analysis*, 1(1):81-88 <http://dx.doi.org/10.1144/geochem.1.1.81>
- Dietz, J.M. 2003. Abiotic heterogeneous ferrous iron oxidation in mine drainage: modeling and treatment processes. PhD Thesis in Environmental Engineering, Dept. of Civil & Environmental Engineering, the Pennsylvania State University, University Park, PA.

- Dietz, J.M. & B.A. Dempsey. 2002. Innovative treatment of alkaline mine drainage using recirculated iron oxides in a complete mix reactor. Proceedings America Society of Mining and Reclamation, 2002 pp 496-516. <http://dx.doi.org/10.21000/JASMR02010496>
- Evans, R.R. 1967. Precipitation of high density metallic hydroxides for recovery and disposal. p. 511-515 of Proc. 21st Purdue Industrial Water Conference, Lafayette, IN May 3-5, 1966.
- Fish, D.H. & J.M. Dietz. 2008. Use of iron oxides produced from the treatment of coal mine drainage as adsorbents to remove phosphorus from secondary wastewater effluent. Final Report for OSM PA (AMD-04) Grant. Submitted to the Pennsylvania Department of Environmental Protection, Harrisburg, PA. USA.
- Fish, D.H. & J.M. Dietz. 2005. AMD treatment using activated iron sludge. Detailed Technical Report for Growing Greener Grant ME # 3521119, submitted to the Pennsylvania Dept. of Environmental Protection, Harrisburg, PA. USA. Growing Greener Project No. 3521119.
- Hedin, R.S., R.W. Nairn, & R.L.P. Kleinmann. 1994. Passive treatment of coal mine drainage. 35 pp. U.S. Dept. of Interior, Bureau of Mines. Information Circular 9389.
- Herman, S.T. & M.C. Korb. 1989. The high-density sludge process – an improved technology to treat anthracite coal mine drainage. Bethlehem Steel Corporation.
- Millero, F.J., S. Sotolongo, & M. Izaguirre. 1987. The oxidation kinetics of Fe(II) in seawater. *Geochim. Cosmochim. Acta*, 51: 793-801. [http://dx.doi.org/10.1016/0016-7037\(87\)90093-7](http://dx.doi.org/10.1016/0016-7037(87)90093-7).
- Pfeiffer, J.B. 1990. High density solids from acid wastewater treatment. p. 625-629 of Proc. 44th Purdue Industrial Water Conference, Lafayette, IN May 9-11, 1989.
- Sung, W., & J.J. Morgan. 1980. Kinetics and product of ferrous iron oxygenation in aqueous systems. *Environ. Sci. Technol.*, 14: 561-68 <http://dx.doi.org/10.1021/es60165a006>