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REALITY CHECK: PASSIVE TREATMENT OF MINE DRAINAGE AN EMERGING TECHNOLOGY OR PROVEN METHODOLOGY?

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ABSTRACT

Passive treatment of mine drainage using constructed wetlands has been employed on coal and metal mine sites since about 1985. The technology has advanced significantly since then; there are currently over 600 of these systems treating coal mine drainage in the Eastern U.S. at flow rates of hundreds of liters per minute. Passive treatment performance at three metal mines discussed in this paper has been positive for a wide variety of flows, water chemistry, and climates. The sites include a high-altitude underground copper mine, acidic seepage from a gold heap leach pad, and pumped effluent from an active underground lead mine in Missouri.

INTRODUCTION AND BACKGROUND

Natural systems have been removing metals from water for eons; examples include pyrite fixed into coal beds and bog iron ore deposits. For the past dozen years, wetlands and bogs have been the natural method of choice for improving water quality. Contaminant reductions are being seen through the precipitation of hydroxides, precipitation of sulfides, and pH adjustments. Local conditions, oxidation state, and water and soil chemistries dictate whether such natural reactions occur under oxidizing (aerobic) or reducing (anaerobic) conditions. Man-made or constructed wetlands/bioreactors employ the same principles as natural wetlands but are designed to optimize processes occurring naturally in wetland ecosystems. The key goal of bioreactors/wetlands is the long-term immobilization of metals in the substrate materials. Metals are precipitated as carbonates or sulfides in the bioreactor substrate (anaerobic cells) and as oxides and hydroxides in aerobic (rock filter) cells.

Anaerobic bioreactors have been successful at substantially reducing metal concentrations and favorably adjusting pH on metal mine drainages. It

is generally recognized that the bacteria commonly found in cattle and other domestic animal intestinal tracts include sulfate reducers and a consortium of other bacteria. Hence, cow or other animal manures have been frequently used as bacterial inoculum for anaerobic biotreatment cells. These same bacteria are found in many natural wetlands and bogs and in lakes and ocean water. Aerobic biotreatment systems are similar to "natural" wetlands in that they typically have shallow depths and support vegetation in the form of algae and emergent plant species.

Since 1988, there have been rapid advancements in understanding the functioning of wetland/bioreactor systems. The first large-scale aerobic system (7.6 cu m per min or 2,000 gpm capacity) was built in 1992 by TVA in Alabama; the West Fork Unit system (4.5 cu m per min or 1,200 gpm capacity) was constructed in Missouri in 1996 and is the first large-scale anaerobic biotreatment system. At West Fork, an aerobic "rock filter" cell provides polishing treatment for manganese and other parameters.

The passive treatment technique holds promise over typical chemical treatment methods because large volumes of treatment residuals are not generated; in fact, residual disposal may be delayed for decades or longer. One volunteer passive treatment system outside an abandoned metal mine that has operated unattended since about 1889, over a century (Beining and Otte, 1997), has been identified in Ireland. This volunteer passive treatment system reportedly has 70 percent of its total metal removal capacity remaining.

Metals Removal Mechanisms in Passive Treatment Systems

Many physical, chemical, and biological mechanisms are known to occur within passive treatment systems to reduce the metal concentrations and

neutralize the acidity of the incoming flow streams. Notable mechanisms include:

- Sulfide and carbonate precipitation catalyzed by sulfate-reducing bacteria (SRB) in anaerobic zones
- Hydroxide and oxide precipitation catalyzed by bacteria in aerobic zones
- Filtering of suspended material
- Metal uptake into live roots and leaves
- Ammonia-generated neutralization and precipitation
- Adsorption and exchange with plant, soil, and other biological materials.

Remarkably, some studies have shown that plant uptake does not contribute significantly to water quality improvements in passive treatment systems (Wildeman, et al., 1993). However, plants can replenish systems with organic material and add aesthetic appeal. In aerobic systems, plant-assisted reactions appear to aid overall metal-removal performance, perhaps by increasing oxygen and hydroxide concentrations in the surrounding water through photosynthesis-related reactions and respiration in the plant root zone. Plants also appear to provide attachment sites for oxidizing bacteria/algae. Research has shown that microbial processes are a dominant removal mechanism in passive treatment systems (Wildeman, et al., 1993). One anonymous researcher considered a passive treatment system as a "bioreactor with a green toupee," referring to the substrate where most of the bioreactions occur and the collection of plants that grow on top of the treatment cells.

Typical Conditions for Using Aerobic Systems

For slightly acidic (pH greater than 5.5) acid rock drainage (ARD) without excessive dissolved iron concentrations, hydroxide and oxide precipitation catalyzed by bacteria may be utilized as the dominant removal mechanism. Aerobic systems are similar to "natural" wetlands in that they typically have shallow depths. For the same level of treatment capacity, aerobic systems typically require larger areas than anaerobic systems. This can be an important design consideration if land availability is an operational constraint. Aerobic systems have been used to treat coal mine drainages at 17 of TVA's mine and coal washing plant sites in Alabama and Tennessee (Wildeman, et al., 1993). When the pH of the drainage is greater than 5 and iron is less than 50 mg/L, effluent quality consistently meets off-site discharge criteria. While some metal mine drainage can also have pH values above 5.5, aro-

bic reactions typically cannot raise the pH high enough to efficiently remove heavy metals such as copper, lead, zinc, nickel, and cadmium. However, aerobic systems are effective at removing iron and manganese.

Typical Conditions for Using Anaerobic Systems

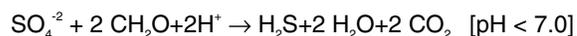
Anaerobic systems, sometimes referred to as "compost" systems, can raise pH and reduce dissolved metals concentrations in an anaerobic geochemical environment developed by the controlled decay of organic matter. The "compost" name is somewhat a misnomer, for experience has shown that *composted* organic matter is a relatively poor long-term SRB nutrient source for anaerobic systems. The composting process consumes much of the beneficial organic material needed for the process to work over the long term.

For very acidic waters (pH less than 5.5), sulfide precipitation assisted by SRB thriving in anaerobic zones in the wetland substrate has been demonstrated to be the most significant metal removal mechanism. The SRB reactions involve the generation of:

- *Sulfide ion* (S^{2-}), which combines with dissolved metals to precipitate sulfides
- *Bicarbonate* (HCO_3^-) which has been shown to raise the pH of the effluent.

The SRB, which appear to function best above pH 5.0, are believed to produce hydrogen sulfide gas (H_2S) and bicarbonate (HCO_3^-) in accordance with the following reactions (Wildeman, Brodie, and Gusek, 1993):

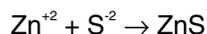
Hydrogen sulfide/carbon dioxide:



Sulfide ion/bicarbonate:



The hydrogen sulfide gas, bubbling up through the wetland substrate or occurring as the dissolved sulfide ion, precipitates metals as sulfides, essentially reversing the reactions that occurred to produce ARD. For example, the following reaction occurs for dissolved zinc, forming amorphous zinc sulfide (ZnS):



The key conditions for SRB health are a pH of 5.0 (maintained by the SRB itself through the bicarbonate reaction), the presence of a source of sulfate (typically from the ARD), and organic matter ($[CH_2O]$ from the substrate). Anaerobic wetlands and bioreactors have been successful at substantially

reducing metal concentrations and favorably adjusting pH of metal mine drainages.

WORKING SYSTEM CASE HISTORIES

Knight Piésold has been involved with about two dozen ARD and mine water remediation projects, some of which have resulted in the construction of large-scale systems. Discussion of selected results from three of these sites follows.

Brewer Gold Mine, South Carolina

This open pit gold mine (which has since been closed) had two ARD sites, a flooded open pit and a spent cyanide heap leach pad. Two anaerobic pilot cells were built. The cells were filled with a mixture of composted turkey manure, sawdust, phosphate rock reject (limestone), and cow manure SRB inoculum. The cells treated 3.8 and 2.8 L per min (1.0 and 0.75 gpm) (pit and pad flows, respectively) for approximately 18 months. This discussion focuses on the treatment of spent heap leach pad (Pad 5) effluent. The pad had been rinsed to reduce cyanide concentrations, but its effluent had turned acidic.

A 0.73 m (2.4 ft) deep, 372 sq m (4,000 sf) anaerobic cell was commissioned in early September 1993 and operated by mine personnel who were instructed to minimize ponding on the cell surface to preclude iron hydroxide formation. As discussed below, Pad 5 effluent water chemistry varied considerably during the experiment, showing the resilience of passive treatment in this respect. In fact, the Pad 5 Cell was originally designed for a flow of 19 L per min (5 gpm), but by the time the system was commissioned, influent water chemistry had deteriorated so that the flow was reduced to 50 percent of the design value to prevent overwhelming the cell's biochemistry. Cell dimensions were determined by balancing the estimated volumetric sulfate-reducing capacity (about 0.3 moles of sulfate reduced per day per cubic meter of substrate) with the molar loading of dissolved metals. The surface area was based on positive experience at other sites (20 sq m per L per min or 800 sf per gpm) with similar water chemistry.

Throughout the testing program, Pad 5 influent concentrations fluctuated in response to rainfall events on the heap and the presumed rise of pyrite oxidation activity as buffering leach solutions were rinsed out. Iron concentration varied from 8 mg/L after a leach solution flush to about 3,950 mg/L at decommissioning. Key metals concentration, metals removal efficiency, and field data gathered during the Pad 5 Cell operation are graphically shown in Figures 1 and 2 which detail:

- Metal removal performance on a percent-age-of-influent basis

- Influent and effluent pH field measurements and flow rate into the cell
- Redox/Eh field observations
- Total iron removal performance
- Total aluminum removal performance
- Total copper removal performance.

Right after start-up, volunteer vegetation invaded the cell surface, marking the "vegetation flourishes" period of the cell history. The cell vegetation was intentionally suppressed in two subsequent events and the cell refitted with a fresh source of native hay before the system was decommissioned in February 1995 to accommodate ongoing reclamation/closure activities.

As shown on Figure 1, after the start-up period until June 1994 (the "vegetation flourishes" period), the Pad 5 Cell had erratic metal removal performance. The redox/Eh during this time was erratic, which was in concert with the metals removal with the exception of iron, which was nearly 99 percent removed. Copper removal was particularly erratic; at times, copper in the effluent exceeded influent values, that is, copper was being remobilized. Aluminum removal paralleled copper values but never exceeded influent concentrations. Remarkably, effluent pH remained around the 6.5 value during this time despite large variations in influent pH due to leach solution being flushed from the heap after storm events or earthmoving activities.

The high redox/Eh values and other observations (e.g., effluent temperatures higher than 10°C) prompted the intentional elimination of the Pad 5 surface vegetation in June 1994, beginning the post-vegetation I period. Immediately thereafter and until the vegetation was again intentionally eliminated on October 27, 1994 (beginning of the post-vegetation II period), the percentage of aluminum, copper, and iron removed became steadier and more consistently in the range between 95 percent and 100 percent.

As shown on Figure 2, influent metal concentrations began to increase at the beginning of the post-vegetation I period and increased steadily until decommissioning. Iron in particular increased to about 3,950 mg/L, over an order of magnitude higher than the design concentration or the initial influent concentration. Remarkably, metals removal in the cell kept pace, especially during the post-vegetation II period as shown on Figure 2 for aluminum, iron, and copper. Flow was maintained at about 2.8 L per min (0.75 gpm) because it was difficult to adjust it any lower. As shown on Figure 1, pH in the effluent decreased from 6.5 to 6.0 during

the post-vegetation I period, which prompted the second intentional defoliation event. Toward the last month of the post vegetation I period, the removal percentage of aluminum began to drop below 50 percent, corresponding to a drop in iron removal. This change prompted another vegetation elimination.

The vegetation was again eliminated on October 27, 1994. From this time to the decommissioning of the Pad 5 Cell, copper, iron, and aluminum removal were consistently very near 100 percent. The effluent pH was observed to maintain a value of around 6.5. Sulfate influent and effluent differences increased even more markedly than in the post-vegetation I period. Remarkably, permeability of the organic substrate appeared to be unaffected by the elevated aluminum concentrations in the influent; aluminum tends to form a gel-like hydroxide precipitate which plugs limestone-dominated SAPS units used to treat coal mine drainage after a few months of operation (Kepler, et al., 1997).

Brewer Pad 5 Conclusions: After start-up, this cell removed metals using oxidation reactions promoted by the plants on the cell surface; the limestone in the substrate probably assisted by buffering the iron hydrolysis reactions. This is supported by the excellent iron removal efficiency and the poor-to-negative removal efficiency for copper.

Once the vegetation was removed the first time, anaerobic SRB-fostered reactions returned as the dominant removal mechanism. This is supported by the low redox/Eh, the marked improvement in metals removal, and observed increases in sulfate reduction.

After the second defoliation, sulfate reduction exceeded design expectations which allowed the cell to continue to function despite the order of magnitude increase in metal loading, most notably iron. The sulfate reduction peaked at a rate of over 2.0 moles/day/cubic meter; it is suspected that this phenomena would not have continued had the cell been operated for a few more months. The higher than expected rate was likely related to the readily digestible source of carbon provided by the recently killed vegetation. The root and stem tissues of the dead plants appeared to provide a superior nutrient carbon source compared to the hard wood cellulose (sawdust) tissues already present in the substrate. The hay that had been added to the cell during retrofit probably functioned in the same manner. This is consistent with reports of others (Tsukamoto, et al., 1997) using ethanol as an organic source.

A carbon mass balance analysis was conducted with the available data. During the period when vegetation flourished, the carbon necessary for cell

operation was low because of the predominance of aerobic reactions. After the successive defoliations and as sulfate reduction became the predominant bio-geochemical reaction in the cell, carbon utilization by metal precipitation reactions and sulfate reduction tracked each other remarkably well. That is, all carbon needed for metals removal appeared to be derived from the hard wood substrate and the recently killed plants.

If live, green plants were not so detrimental to cell performance, say with a deeper cell, it appears that sulfate reduction rates could be maintained at the design rate of 0.3 moles/day/cubic meter. The organic matter from the plants might provide a "balanced" diet for sulfate reducers, allowing both easily digestible plant tissues to compliment the "roughage" provided by the hard wood substrate component. With a deeper cell, surface vegetation may provide a small component to prolong cell life although total long term self-sufficiency may not be feasible, i.e., the cell would have a finite life governed by initial SRB-available carbon levels.

Ferris-Haggarty Mine/Osceola Tunnel, Sierra Madre Mountains, Wyoming

This high-elevation 2,900 m (9,500 ft) abandoned underground copper mine has neutral pH discharge with 3 to 20 mg/L dissolved copper and low sulfate (typically less than 100 mg/L SO₄); water temperature is close to freezing ($\pm 4^{\circ}\text{C}$), and the mine is accessible only by a 32-km (20-mile) snowmobile trek for nine months out of the year. Flow from the portal varies from 57 to 114 L per min (15 to 30 gpm) in the winter months to 1.7 cu m per min (450 gpm) or more during the spring runoff. Copper concentration initially observed at the portal was fairly constant all year long, somewhat independent of flow rate. However, since the completion of tunnel rehabilitation activities, a spike of elevated copper concentration and low pH (3.8) was observed coincident with the spring freshette.

The first of two pilot-scale passive treatment cells was composed of a single gravity-fed anaerobic SRB-cell configured in a downflow mode. In the summer of 1997, a 4.6-m (15-ft) diameter and 1.2-m (4-ft) deep cell was filled with a mixture of softwood sawdust, hay, limestone, cow manure, and gypsum. The proportions in the recipe were selected based on a six-week-long bench-scale (trashcan-size) test conducted in the summer of 1996. Results of a second pilot-scale cell constructed in the summer of 1999 are not available. The discussions that follow deal solely with the *first* pilot cell.

Due to the low mine water temperature, the initial slug of water used in incubation was heated to about

15°C. The cell was incubated for about a week before it received full design flow of 19 L per min (5 gpm) at about 3EC. The cell had been fully operational since early September 1997. Snow depths on site can reach 3 m (10 ft) over a typical winter season. The pilot cell was enclosed in a shed to allow winter access for sampling, inspection, and data retrieval.

Geochemical activity in the underground mine itself provides some metals remediation; not all the metal loading observed underground is accounted for at the tunnel portal. Seasonal flow from underground ore chutes exhibits low pH (3.8), elevated copper (30 to 50 mg/L), and some ferric iron. The principal ore involved in this ARD generation is suspected to be chalcopyrite. The ARD from the ore chutes (chute/shaft water) appears to mix with relatively pristine groundwater entering the furthest in-by portions of the mine and other fresh water infiltration sources closer to the portal. Under certain conditions, copper carbonates and silicates precipitate as a green or blue-green sludge on the floor of the tunnel. This geochemical phenomenon acts to remediate copper loading at the portal during a portion of the year. However, the accumulated sludge acts both as a sink and a source for copper loading at the portal; at other times of the year, copper loading at the portal was greater than that observed at the ore chutes. It is suspected that the sludge was redissolving in response to shifts in geochemical equilibrium of the mine water. Since the tunnel was reopened and the floor of the tunnel was mucked out, this source/sink phenomena has been somewhat suppressed.

The pilot cell was designed based on an estimated sulfate reduction rate of 0.15 moles/day/cubic meter of substrate, the value that was observed in the best cell in the 1996 bench-scale study. This results in a retention time in the cell of less than 12 hours.

The pilot cell was outfitted with an ISCO 6700 automatic sampler and a YSI probe to monitor pH, conductivity, redox potential, and water temperature in late October 1997, just prior to a blizzard that effectively ended the short field season. No heat-trace equipment was installed; all pipes carrying water were buried and/or fitted to maintain flow to prevent freezing.

Bi-monthly site visits via snowmobile were conducted during the winters of 1997/98 and 1998/99 to collect data and samples. Monthly sampling was conducted during the summers of 1998 and 1999. During the winters, sub-freezing air temperatures resulted in an ice covering over about 40 percent of the cell surface. Flow through the cell decreased from an initial value of 19 L per min (5 gpm) in

October 1997 to about 11.4 (3 gpm) in the subsequent months.

A number of physical and chemical parameters were evaluated for the pilot-scale cell from start-up in August 1997 through June 1999 in order to evaluate the efficiency of the pilot-scale cell. Parameters discussed in this paper include copper removal, pH, sulfate reduction, redox potential, temperature, and saturated hydraulic conductivity.

Figure 3 (Reisinger, et al.) shows total copper removal for the pilot-scale cell. Copper removal during the first nine months of operation (that is, from August 1997 through May 1998) ranged from 95 to 100 percent. Once more highly contaminated chute/shaft water (from deeper in the mine) was introduced in June 1998, copper removal efficiencies decreased to generally between 89 to 97 percent. The removal efficiencies noted during December 1998 (84 percent) and May 1999 (63 percent) were likely due to system upsets caused by contaminated water not being fed to the cell.

As shown in Figure 3, the pH of the processed water remained relatively neutral even with a change in feed waters from relatively neutral pH (Osceola Tunnel portal water) to a pH ranging from about 3.5 to 4.0 (chute/shaft water). Both the SRB and limestone incorporated into the substrate recipe likely contributed to the ability of the cell to maintain a relatively neutral pH.

Sulfate reduction is an indication of the level of SRB activity. The greater the sulfate reduction, the more the SRB activity. During the first several months of cell operation, sulfate reduction was not apparent and was likely masked by the addition of gypsum into the substrate recipe. Gypsum addition was done to enhance the cell environment for the SRB during system start-up. After the first several months, the cell generally exhibited sulfate reduction, especially during the period when higher sulfate-containing chute/shaft water was being processed.

Figure 3 also shows Ev measurements for pilot cell inflow and discharge. Ev is a measure of redox potential. The more positive the Ev value, the more oxygen-enriched the water. The more negative the Ev value, the more oxygen-deprived the water. Ev values for processed water in the range of -200 millivolts (mv) or lower suggest an anaerobic environment. As can be seen in Figure 3, Ev values are generally below -200 mv with the exception of the positive value observed during June 1999. This value is likely due to the cell not processing water at the time of the site visit.

One of the challenges of the project was the near-freezing temperature of the water requiring treatment. Temperatures of processed water ranged from about 1° to 8°C (34° to 46°F). Previous researchers (Kuyucak, 1991) suggested that sulfate-reducing reactions are not efficient enough at low temperatures (less than 10°C) to make passive treatment practical in winter conditions. However, others (Postgate, 1979) observed SRB in sub-freezing situations (from +4° to -40°C) in sea water in Antarctica. Pilot-scale data suggest that the SRB can function at the design activity rate at water temperatures approaching less than 1°C as recorded by an automated temperature probe at the pilot-scale cell discharge.

Conclusions: A pilot-scale passive treatment test conducted at the Ferris-Haggarty site over two years suggests the viability of removing copper using passive treatment techniques at near-freezing temperatures. Pilot-scale passive treatment testing will continue at the site into summer 2000; a full-scale system is planned for construction in the future. In August 1999, a second pilot-scale cell was constructed with a slightly different substrate mixture and buried to more closely mimic the planned full-scale system. The advantage of low maintenance requirements for passive treatment make passive treatment attractive compared to other more active technologies, especially at remote sites such as Ferris-Haggarty.

Doe Run Company, West Fork Unit, Missouri

This operating underground lead mine has a neutral pH discharge with 0.4 to 0.6 mg/L lead and 0.36 mg/L zinc; flow is about 4.5 cu m per min (1,200 gpm). The large-scale system was designed based on the performance of a pilot-scale system and interim bench-scale studies. Including engineering and permitting, the large-scale system cost approximately \$US700,000 (Gusek, et al., 1998) and required about four months to construct. System operational costs included water quality monitoring as mandated by law. No additional costs for reagents were incurred; since the system uses gravity flow, moving parts are few and include valves, minor flow controls, and monitoring devices. Based on carbon depletion rates observed in a pilot system, the anaerobic cell substrate life was projected to be greater than 30 years; the full-scale biotreatment system should be virtually maintenance-free. Should mine water quality deteriorate, the full-scale design included a 50 percent safety factor. The pilot-scale system of 95 L per min (25 gpm) was tested by operating for about 90 days at double the design capacity; compliance effluent with respect to total

lead concentration and other key performance parameters resulted from this test.

The biotreatment system is composed of five major parts: a settling pond, two anaerobic cells, a rock filter, and an aeration pond (Gusek, et al., 1998). The system is fully-lined. The design was also integrated into the mine's pre-existing fluid management system. A rectangular-shaped, 40-mil HDPE-lined settling pond has a top surface area of 3,030 sq m (32,626 sf) and a bottom surface area of 1,930 sq m (20,762 sf). The sides have slopes of 2 horizontal to 1 vertical (2H:1V). The settling pond is nominally 3 m (9.8 ft) deep. It discharges through valves and parshall flumes into the two anaerobic cells.

Two anaerobic cells were used, each with a total bottom area of about 1,390 sq m (14,935 sf) and a top area of about 1,930 sq m (20,600 sf). Each cell was lined with 40-mil HDPE and was fitted with four sets of fluid distribution pipes and three sets of fluid collection pipes. The distribution/collection pipes were connected to commonly shared layers of perforated HDPE pipe and geonet materials sandwiched between layers of geofabric (which were subsequently removed). This feature of the design was intended to allow control of sulfide production in hot weather by decreasing the retention time in the cell through intentional short-circuiting.

The spaces between the fluid distribution layers were filled with a mixture of composted cow manure, sawdust, inert limestone, and alfalfa, referred to hereafter as "substrate." The total thickness of substrate, piping, geonet, and geofabric was about 2 m (6 ft). The surface of the anaerobic cells was covered with a layer of crushed limestone. Water treated in the anaerobic cells flowed by gravity to a compartmentalized concrete mixing vault and thereafter to a rock filter cell. The gravity-driven flows can be directed upward or downward.

The rock filter is an internally-bermed, clay-lined shallow cell with a bottom area of about 5,900 sq m (63,000 sf) and a nominal depth of 30 cm (1 ft). It is constructed on compacted fill that was systematically placed on the west side of a pre-existing mine water settling pond. Limestone cobbles line the bottom of the cell, and the cell is compartmentalized by limestone cobble berms. The discharge from the rock filter flows through a drop pipe spillway and buried pipe into a 40-mil HDPE-lined aeration pond. The aeration pond surface covers approximately 8,000 sq m (85,920 sf). The aeration pond discharges through twin 30-cm (1-ft) diameter HDPE pipes into a short channel that leads to monitoring outfall 001 and thence into West Fork.

After the water pumped from the underground mine enters the settling pond, all flows are by gravity.

Wildeman, et al. (1998) theorized from sulfate-reducing stoichiometry that carbon depletion would be the most likely factor limiting the operational longevity of an anaerobic substrate. Simultaneous alkalinity and sulfate reduction values were used to independently estimate carbon consumption rates (and cell life span) in West Fork Unit substrate. A carbon balance analysis revealed a projected cell longevity (about 80 years) consistent with early estimates by Wildeman, et al.

West Fork Operations Results: Since start-up, the system discharge has met permit requirements. Discharge levels of lead and other metals were reduced substantially from average influent levels. For lead, the level was reduced from a typical average of 0.50 mg/L to between 0.027 and 0.050 mg/L; zinc, cadmium and copper effluent concentrations were also reduced. The following conclusions were reached as a result of completing this landmark project:

1. A practical large-scale anaerobic design has been developed to bring lead values down to stringent water quality standards.
2. Bacterial sulfate reduction is the major lead removal process.
3. An aeration step is needed to polish for manganese, biological oxygen demand, fecal coliform removal, and re-oxygenation.
4. Pilot testing should include as many features of the final design as possible to minimize start-up difficulties.
5. Education of regulators on innovative water treatment techniques can facilitate permit approvals.

SUMMARY

The three case studies provide a broad spectrum of water flow rates, metal mine drainage chemistry, and environmental conditions where passive treatment systems can work. In conclusion, the passive treatment of ARD holds much promise, especially for the chronic, low flows or loadings associated with mine and mill site drainages that nag the closure and reclamation processes. Hurdles still remain in completely understanding and designing for the biochemical and geochemical reactions that occur in passive treatment systems. However, the performance data available from the three sites considered in this paper appear to be consistent among the group and with the results of previous work collectively support the author's assertion that the technology has progressed toward becoming a "proven methodology" for treating ARD.

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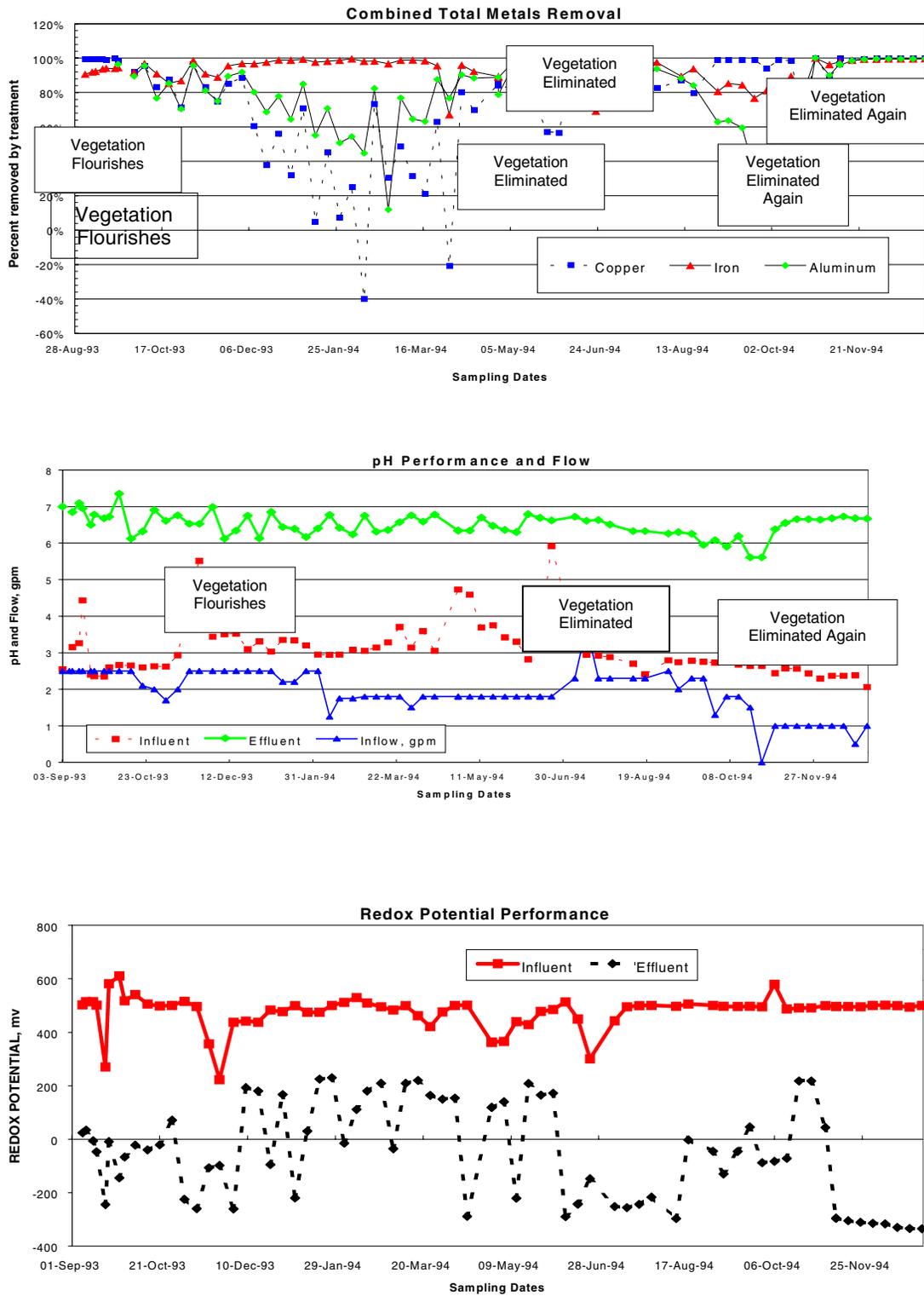


Figure 1. Brewer Pilot Passive Treatment Results.

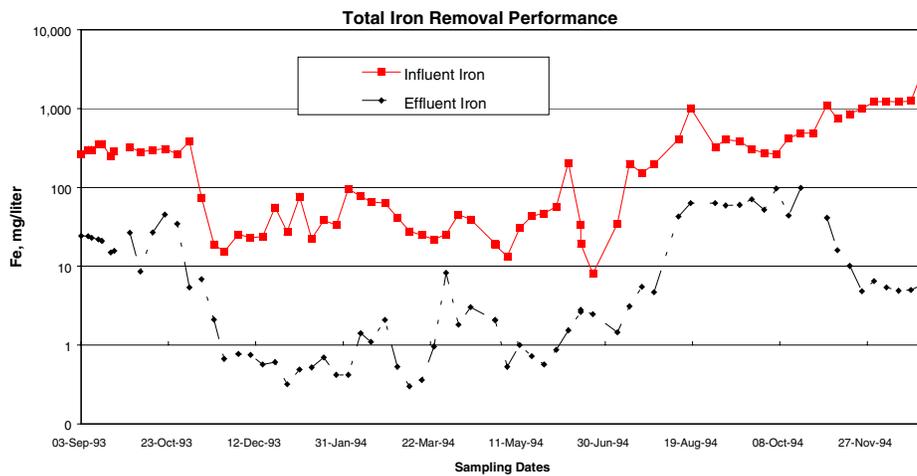
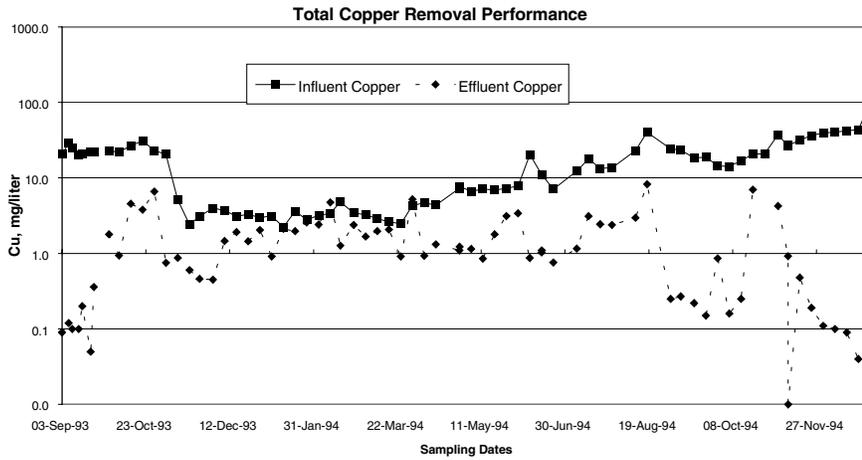
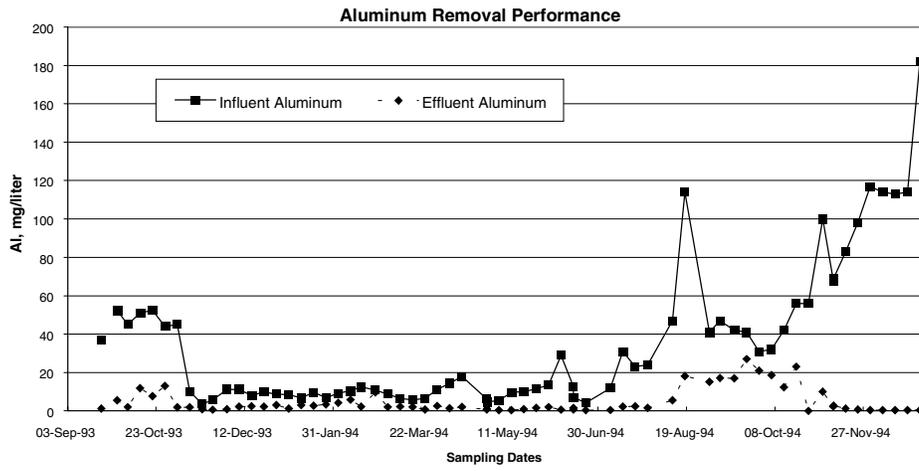


Figure 2. Brewer Pilot Passive Treatment Results.

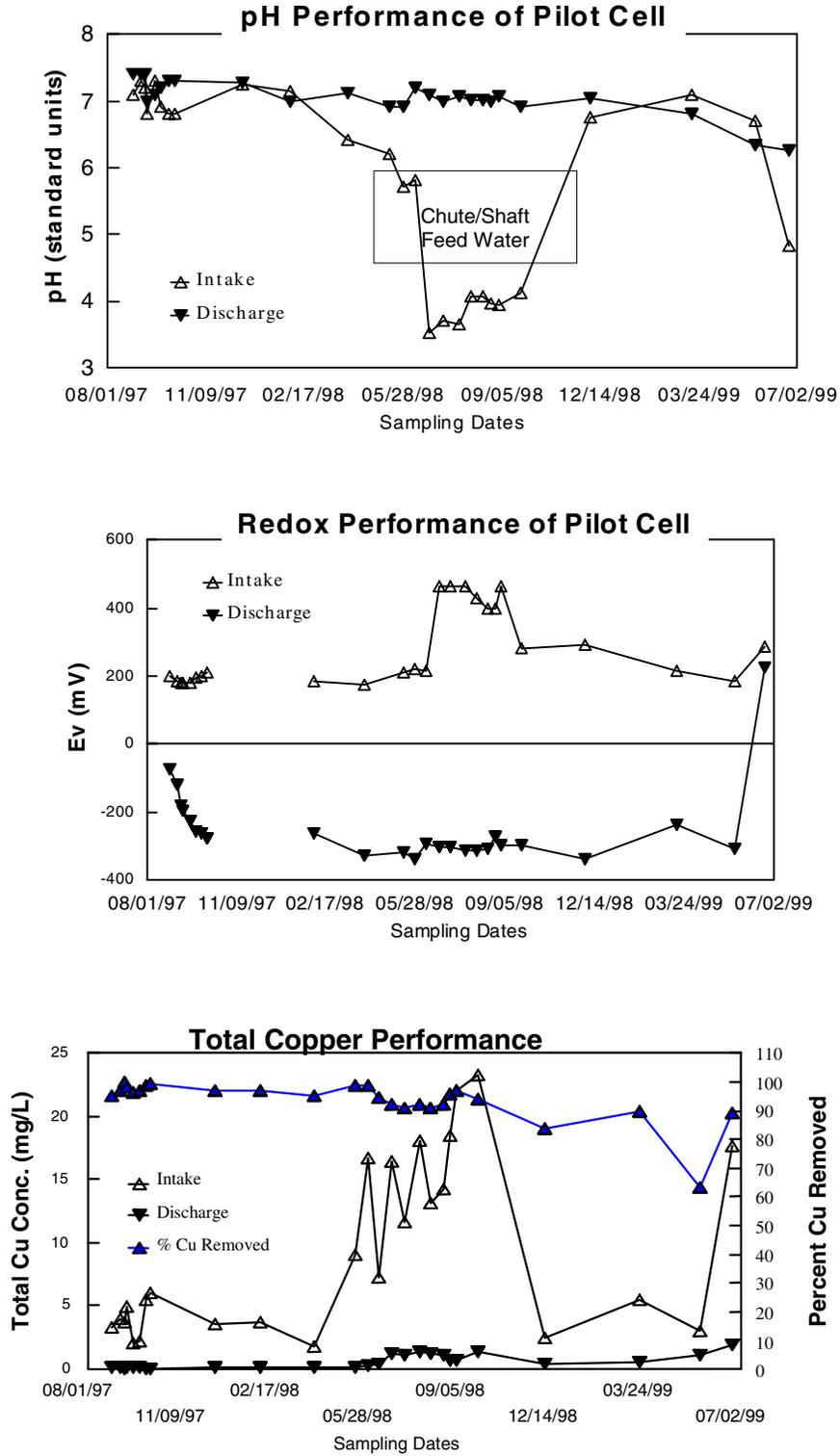


Figure 3. Ferris Haggarty Mine, WY Pilot Cell Data.

Passive Treatment of Aluminum-Bearing Acid Rock Drainage ⁽¹⁾

James J. Gusek, P.E. ⁽²⁾ , Thomas R. Wildeman, Ph.D. ⁽³⁾

Abstract: When acid rock drainage attacks clay-bearing formations at hard rock mining sites, significant amounts of dissolved aluminum can be created. The geochemistry of aluminum is complex and this can cause problems in passive treatment systems. The formation of the mineral gibbsite [Al (OH)₃] is especially problematic as it is a gelatinous solid. Gibbsite tends to form in limestone-dominated passive treatment cells and the sludge tends to plug the void spaces between the limestone rock, becoming a major maintenance problem. While the precise mechanisms have not been completely identified, the precipitation of gibbsite is avoided in sulfate reducing bacteria (SRB) cells. It is suspected that unidentified alternative aluminum compounds form in the SRB cells instead of gibbsite, and these compounds are less prone to plugging. This paper will present several case histories of SRB passive treatment projects that involved treating acid rock drainage with high aluminum concentrations.

Additional keywords: sulfate reduction, acid mine drainage, aluminosilicates, aluminosulfates.

Introduction

It is ironic that many domestic drinking water treatment plants add aluminum in the form of alum as a coagulant while the mining industry works diligently to remove it from acid mine drainage/acid rock drainage (AMD/ARD). When found in a mine effluent that is actively treated using lime dosing, aluminum probably assists in the settling of iron hydroxide flocs. Conversely, the presence of aluminum in mine effluents that are passively treated typically causes maintenance headaches.

Neutralization processes that raise the pH dominate many passive treatment system components. Anoxic limestone drains (ALD's) and Successive Alkalinity Producing Systems (SAPS) are typical examples of neutralizing cell types; their ultimate goal is to add alkalinity so that iron-laden AMD/ARD is buffered against pH drops when the iron is ultimately hydrolyzed and precipitated as a hydroxide. The presence of aluminum in the AMD/ARD is problematic for SAPS and ALD's (Sterner, et al., 1997) because the geochemical conditions found in them favor the formation of the mineral gibbsite [Al (OH)₃], which is a gelatinous solid. The gibbsite sludge tends to fill the void spaces between the limestone rock used in a typical SAPS or ALD and becomes a major maintenance problem. Small amounts of aluminum in the AMD/ARD thus preclude the use of an ALD; aluminum can be tolerated in minor amounts by SAPS units, but periodic flushing of sludge from the unit (about once every several months) is required to maintain cell effectiveness.

Geochemistry of Aluminum

The dissolution of aluminosilicates such as clay minerals by the oxidizers (hydrogen ion and ferric ion) in AMD/ARD is the primary source of dissolved aluminum in typical AMD/ARD solutions. Coincidentally, it is also the source of any dissolved silica (SiO₂) or (H₄SiO₄ [aq]). The precipitation of solid-phase aluminum from AMD/ARD can be complex. The primary reaction most familiar to workers in AMD/ARD mitigation is the precipitation of gibbsite, as shown below.



This is the favored reaction when limestone dissolution or other alkalinity source abruptly raises the pH of the ARD/AMD. As previously discussed, this reaction is problematic due to sludge buildup in limestone-dominated passive treatment structures.

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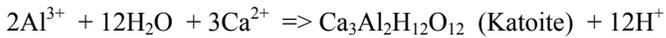
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There are many other aluminum-related reactions possible, complicated by:

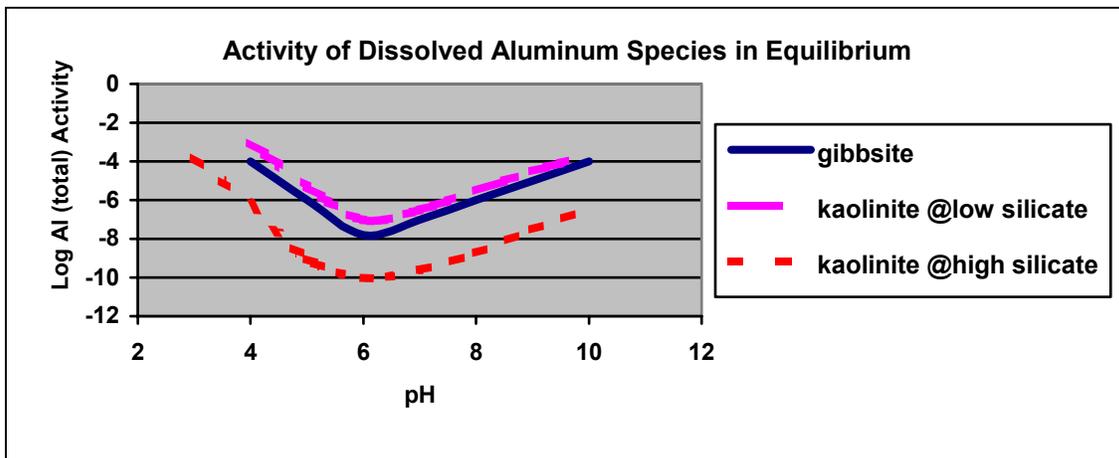
- organic matter in the form of ligands (Drever, 1988), which may tend to keep aluminum in solution through a complexation process called chelation, and
- the presence of other anions and cations.

Drever (1988) noted that the activities (or relative concentrations) of other ionic species can affect the solubility of gibbsite, particularly silica and other anions like sulfate, magnesium and potassium. The following chemical equations are offered as a sample of the over 100 potential reactions that may be possible for precipitating aluminum from the dissolved condition:



The presence of organic molecules such as humic acid, fulvic acid, formic acid or other organic and inorganic ligands have been shown to complex with aluminum and form aqueous compounds that may be mildly resistant to chemical precipitation or encourage the formation of non-gibbsite complexes (Sposito, 1996). The fluoride ion is especially notorious in creating strong ionic complexes with aluminum that are difficult to disrupt. (Drever, 1988).

To illustrate the complexity of aluminum solubility in the presence of a particular anion, the following solubility diagram for total aluminum with two dissolved silicate activities is presented. At low silicate concentrations, the formation of gibbsite is favored over kaolinite; in this instance, silicate activity was 1×10^{-5} . At a higher silicate activity (1×10^{-2}), the reverse is true and the formation of kaolinite is favored over gibbsite in the entire range of pH values. Similar trends are found in other silicate species such as pyrophyllite $[\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2]$.



Ref: After Drever, 1988

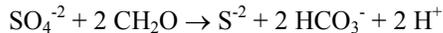
In summary, it is well established that the solubility of various aluminum species can be controlled by factors other than pH.

Sulfate Reducing Bioreactors

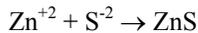
Sulfate reduction has been shown to effectively treat AMD/ARD containing dissolved heavy metals, including aluminum, in a variety of situations. The chemical reactions are facilitated by the bacteria *Desulfovibrio* in sulfate reducing bioreactors as shown in cross section below. The sulfate reducing bacterial reactions involve the generation of:

- Sulfide ion (S^{2-}), which combines with dissolved metals to precipitate sulfides, and
- Bicarbonate (HCO_3^-), which has been shown to raise the pH of the effluent.

The sulfate reducing bacteria, which appear to function best above pH 5.0, produce sulfide ion (S^{2-}) and bicarbonate (HCO_3^-) in accordance with the following reactions (Wildeman, et al., 1993):



The dissolved sulfide ion precipitates metals as sulfides, essentially reversing the reactions that occurred to produce ARD. For example, the following reaction occurs for dissolved zinc, forming amorphous zinc sulfide (ZnS):



The geochemical behavior of aluminum in sulfate reducing bioreactors has not been documented beyond preliminary evidence as discussed below in three case histories. Suspected reasons for the observed behavior are offered subsequently in the paper.

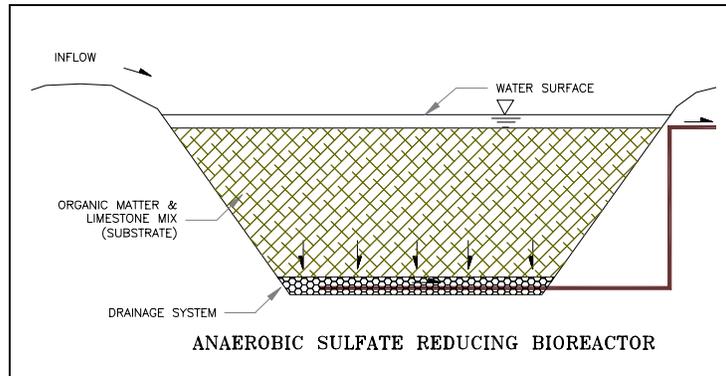
Case Histories

Knight Piésold has been involved with about two dozen AMD/ARD and mine water remediation projects, some of which have resulted in the construction of large-scale systems. Discussion of selected results from three of these sites that involved aluminum follows.

Underground Coal Mine, Pennsylvania

An underground coal mine in western Pennsylvania, closed in 1985, had mined coal from the Lower Kittanning Seam. The mine pool that developed is relatively small and its level is controlled by mine pumps that currently feed a lime dosing treatment system. The pumping rate varies with local precipitation from about 11 to over 220 gpm. The acidic drainage has a pH of about 2.8, iron of 130 mg/L, aluminum of about 30 mg/L, manganese of about 2 mg/L and acidity of 450 mg/L.

In August 2000, six bench-scale test cells were operated for 12 weeks to evaluate the application of SRB anaerobic bioreactors at the site. Bench test cell volumes were about 180 liters (32 gallons); treatment flow was about 6.5 ml/min (9.4 liters per day). The cells were filled with a mixture of chipped wood, sawdust, crushed limestone, cow manure, mushroom compost and hay in varying amounts. The results of the bench test showed similar treatment efficiencies among the test cells; typically, 99 percent of the iron and aluminum were



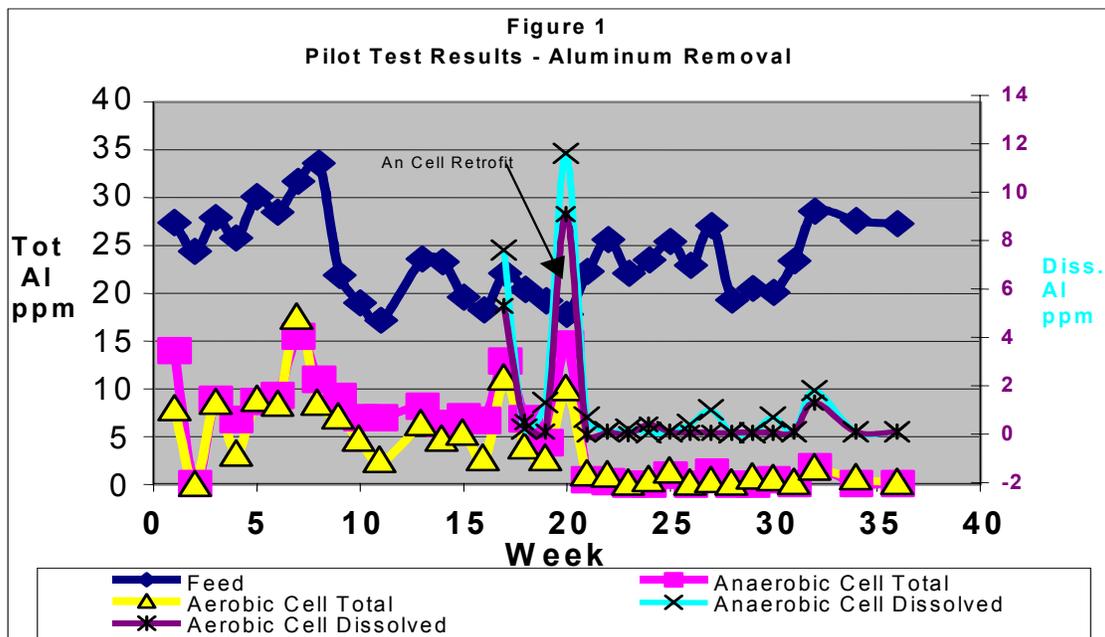
removed. Aluminum plugging was a concern, however, and one cell was sliced in half at the conclusion of the test period and no evidence of gibbsite formation was observed.

This encouraging finding supported the design of a 1.7 gpm pilot scale system (shown to the right) that was constructed in late November 2000 and operated for 14 months as of the date of this writing, March 2002. The pilot cell is about three feet deep and has a surface area of about 4,000 square feet. It feeds an aerobic polishing wetland about 120 square feet in size that discharges into a holding pond that is within the mine water management/treatment system. Data available for the first 36 weeks of operation are shown on Figure 1.



As stated earlier, the cell was commissioned in late November 2000, just as the winter season began. Incubation water temperatures were far below the ideal 10 degrees centigrade and the cell “limped” through the first 19 weeks of depressed temperature conditions. Redox and pH data suggested that conditions were favorable for sulfate reduction at anticipated design rates by Week 20. However, actual sulfate reduction rates were erratic, indicating that the cell was under stress. In early March 2001, field observations confirmed a short circuit had formed in the feed end of the cell and corrective measures were taken, which hopefully will be the topic of future paper.

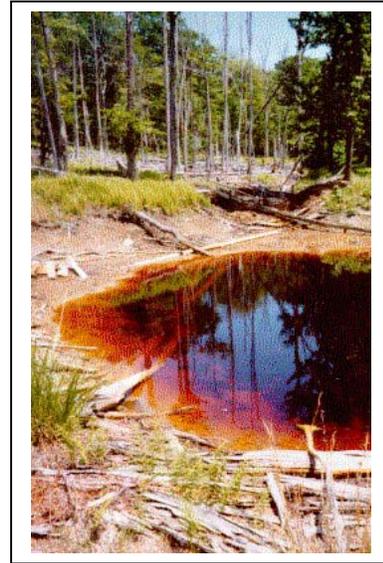
As shown on Figure 1, the aluminum removal rates improved after the retrofit and remain acceptable (less than 0.1 mg/L) despite a late-2001 increase in the feed concentration of aluminum up to 40 mg/L (Week 51) due to drought conditions.



During the operation of this SRB cell, some plugging of the effluent piping (one-inch diameter clear plastic tubing) was observed due to biological oxygen demand sludge accumulation. With the exception of the short circuiting event that required the repair, there was no other evidence of gibbsite sludge plugging during the 14 months of operation of this pilot cell.

Fran Mine, Pennsylvania

Fran Contracting mined a 37-acre surface coal mine in East Keating Township, Clinton County, Pennsylvania in Sproul State Forest. Mining of the site from 1974 to 1977 resulted in post-mining discharges of AMD that destroyed aquatic life in 2.8 miles of Camp Run, 1.3 miles of Rock Run and 2.1 miles of Cooks Run, all tributaries of the Susquehanna River. This impact occurred despite the in-situ remediation efforts that the Pennsylvania Bureau of Abandoned Mine Reclamation (BAMR) conducted in 1993. BAMR personnel have characterized the quality of discharge from this site as the “worst AMD/ARD in the entire State of Pennsylvania from a surface coal mine”. The AMD/ARD averages 2,900 mg/L of sulfate, 2,800 mg/L of acidity, 407 mg/L of iron, **237 mg/L of aluminum**, and 42 mg/L of manganese. It has a pH of about 2.3 or less and also contains heavy metals including copper, zinc, cadmium, chromium and arsenic. While the source of the AMD is a coal mine, it is comparable to AMD/ARD from an abandoned metal mine. Peak flow rate from this site is only 30 gpm, but this loading is enough to impact five miles of potential fishery downstream.

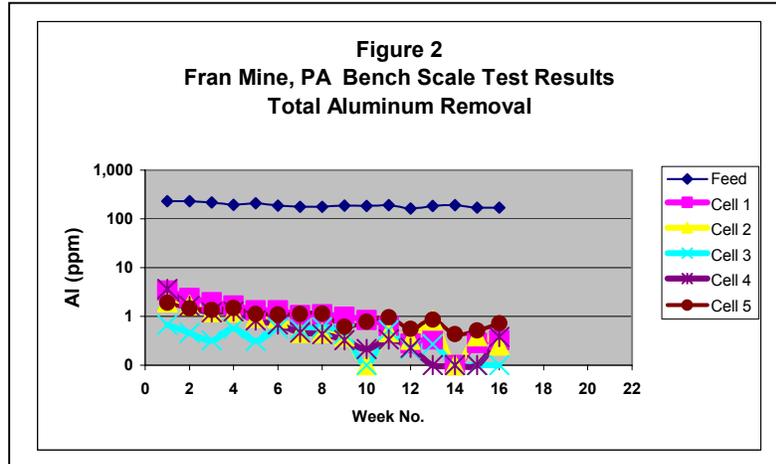


In early August 2001, Knight Piésold, supported by funding secured by the Allegheny Mountain Chapter of Trout Unlimited, constructed five bench-scale SRB bioreactors with the assistance of BAMR personnel. The five cells, built using various organic substrate mixtures, were operated for about 20 weeks. Figure 2 is a plot of the results for aluminum removal for the first 18 weeks.

Figure 2 below shows that with the exception of Cell 5, which was a cell with a high limestone content (50 percent by weight), the cells behaved similarly in removing metals and improving the pH of the Fran Mine feed water. While all the cells showed similar results, the iron removal efficiency of Cell 4 showed the best performance compared to the other four cells. In the final six weeks of sampling data, the total iron concentration in the influent to all cells averaged about 370 mg/L. Effluent from Cell 4 averaged 3.7 mg/L; Cells 1 and 2, the next best with regards to iron, averaged 20.1 and 47.5 mg/L, respectively, over the same period. Aluminum removal was excellent for all cells. The last six week average feed concentration was 178 mg/L. Effluent concentration for the cells ranged from 0.21 mg/L (Cell 4) to 0.67 mg/L (Cell 5) during this time period.

In mid-January 2002, all cells were subjected to an “autopsy” to evaluate how much, if any, plugging occurred due to the precipitation of metal sulfides and other metallic compounds during the test period. The autopsies of the cells did not reveal any visible accumulations of aluminum precipitate, even in Cell 5. The effluent pipe and limestone drainage layers were typically clean. Unfortunately, the cells were frozen, so it was not possible to closely examine the substrate for traces of aluminum deposits. Regardless, all cells operated from early August to late December without any need for “flushing” to maintain the flows.

This is encouraging from a maintenance standpoint; the full-scale sulfate reducing cells may be able to operate unattended for years, perhaps decades, without requiring flushing, major maintenance, or retrofitting. This needs to be confirmed at a pilot scale; a pilot cell is planned for construction in the spring of 2002.



Prior to the start of dissecting the bench cells, sample aliquots were recovered from the feed water holding tank, and the discharge pipes of Cells 2, 4 and 5. These samples were submitted to the Colorado School of Mines for total metals analysis using an induction coupled plasma spectrometer or ICP unit. The results of the analysis are shown on Table 1. This analysis confirms that there are other heavy metals present in the Fran Mine AMD that might impact Cook's Run, including trace amounts of cadmium, cobalt, copper, chromium nickel, and zinc. The results in Table 1 suggest that the sulfate reduction in the bench cells, especially Cell 4, was very efficient at lowering the concentration of these other heavy metals in addition to the iron and aluminum that were analyzed weekly.

Table 1
Fran Mine Bench Scale Final Samples
ICP Analysis by Colorado School of Mines Chemistry Department

Parameter	Duplicates		Bench 2	Bench 4	Duplicates		Det. Limits
	Feed Sample 1	Feed Sample 2			Bench 5A	Bench 5B	
Aluminum	382	305	0.11	BDL	0.09	0.17	0.02
Cadmium	0.12	0.10	0.01	0.00	0.03	0.03	0.00
Cobalt	2.96	2.40	0.06	0.02	0.26	0.22	0.01
Chromium	0.20	0.16	BDL	BDL	0.01	0.01	0.00
Copper	1.99	1.61	BDL	0.01	BDL	BDL	0.00
Iron	876	709.16	38.10	0.66	94.21	107.22	0.00
Manganese	97.95	79.28	21.77	2.86	38.34	38.80	0.00
Nickel	3.60	2.93	0.03	0.04	0.28	0.24	0.00
Sulfur	1,846	1,463	466	69	417	446	0.06
Sulfate (calc'd)	5,538	4,389	1,398	207	1,251	1,338	n/a
Silicon	85.22	66.96	11.36	6.83	41.70	45.67	0.01
Tin	0.22	0.17	0.04	BDL	BDL	BDL	0.02
Zinc	7.05	5.75	0.02	0.05	0.10	0.06	0.00

It is curious to note the marked decrease in silicon, from about 77 mg/L in the feed water (average of 68 and 85 mg/L) and about 7 mg/L in the Cell 4 effluent. This reduction suggests that silicate-based metal compounds, perhaps higher density aluminosilicates, might be forming in the substrate in lieu of the typical gibbsite which is so problematic in many SAPS and other limestone-based passive treatment systems.

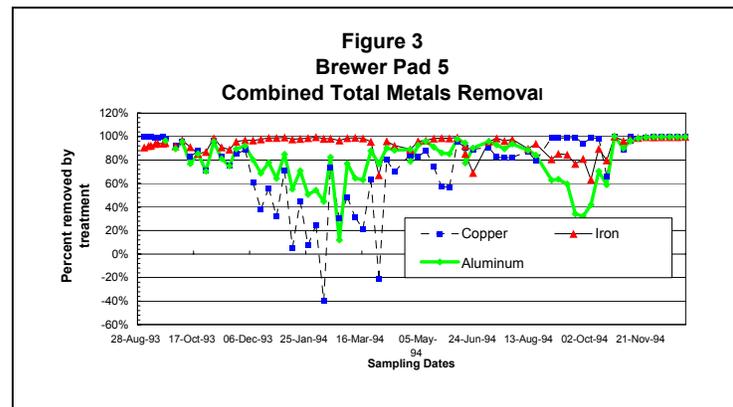
Brewer Gold Mine, South Carolina

This open pit gold mine (which has since been closed) had two AMD/ARD sites, a flooded open pit and a spent cyanide heap leach pad. Two pilot scale sulfate-reducing cells were built, one of which is shown in the photo on the right. The cells were filled with a mixture of composted turkey manure, sawdust, phosphate rock reject (limestone), and cow manure SRB inoculum. The cells treated 3.8 and 2.8 L per min (1.0 and 0.75 gpm) (pit and pad flows, respectively) for approximately 18 months. This discussion focuses on the treatment of spent heap leach pad (Pad 5) effluent. The pad had been rinsed to reduce cyanide concentrations, but its effluent had turned acidic.



This sulfate reducing cell was described in more detail elsewhere (Gusek, 2000). Throughout the testing program, Pad 5 influent concentrations fluctuated in response to rainfall events on the heap and the presumed rise of pyrite oxidation activity as buffering leach solutions were rinsed out. Iron concentration varied from 8 mg/L after a leach solution flush to about 3,950 mg/L at cell decommissioning; pH values varied from 4.7 down to 2.0 at decommissioning. Aluminum concentration in the raw feed to the Pad 5 cell averaged about 60 mg/L with a range of 4 to 220 mg/L. At the time of the pilot testing (1994-1995), there was more concern about the iron concentrations than the aluminum values.

Typical cell effluent values included a pH of 6.5, iron of 44 mg/L and aluminum of 6 mg/L. As shown in Figure 3 below, the removal of aluminum in the cell was erratic. This occurred in response to changing redox conditions that were traced to the effects of plant growth on the cell surface. Regardless, there were no indications of gibbsite formation during the 18-month pilot test.



Suspected Aluminum Behavior in Sulfate Reducing Conditions

Visual observations of organic substrates during sulfate reducing bench cell autopsies at the Fran Site failed to detect gibbsite despite being exposed to aluminum concentrations over 200 mg/L. The operation of pilot scale cells for over year at the Dixon Run No. 3 Site in Pennsylvania and the 18 month test at the Brewer Mine in South Carolina did not exhibit plugging conditions that might be attributed to gibbsite formation. It is suspected that aluminum species that are physically denser than gibbsite are being preferentially precipitated in the reduced conditions found in a typical sulfate reducing bioreactor.

Geochemical modeling may reveal likely mineral phase candidates that may be forming. These may include silicates like kaolinite or pyrophyllite or aluminum sulfates like jurbanite, diaspore, boehmite or basaluminite. Even with modeling results, however, the precise mechanisms that occur in different sulfate reducing bioreactors might be site-specific and generalizations on the phenomenon may prove to be elusive.

Mitchell and Wildeman (1996) compared the behavior of aluminum predicted by a geochemical model (MINTEQA2) with laboratory test results. Most of the mineral phases considered were either aluminum hydroxides or aluminosulfate species. They found that modeling results required some adjustments to better match their laboratory test data. In particular, it was difficult to account for all the aluminum precipitation assuming just one species; jurbanite and diaspore caused the precipitation of too much aluminum and boehmite and basaluminite caused the precipitation of too little.

The results of rudimentary stoichiometric calculations using the Fran Mine silica values presented in Table 1 suggest that there was an insufficient amount of silica present to account for all the aluminum precipitated as an aluminosilicate species. Thus, other non-silicate species such as aluminosulfates may be forming as well. Which species forms first (i.e., aluminosilicates or aluminosulfates) will be dictated by the solubility products of the respective compounds in the conditions unique to each AMD/ARD source and the local redox conditions in the sulfate reducing bioreactor.

Summary

The three case studies provide some insight into the potential for sulfate reducing bioreactors to accept and effectively treat dissolved aluminum. The mechanisms are not well understood because of the complexity of aluminum geochemistry. Future work may involve geochemical modeling and laboratory work to further understand the phenomenon. This situation should provide many future research topics. But from a practical perspective, as long as the plugging problem is solved, AMD/ARD abatement design professionals may be provided with yet another powerful tool in the passive treatment arsenal.

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Operational results of a 1,200-gpm passive bioreactor for metal mine drainage, West Fork, Missouri

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ABSTRACT: An active underground lead mine produces water having a pH of 8.0 with 0.4 to 0.6 mg/L of Pb and 0.36 mg/L of Zn. This water is pumped at the rate of 1,200 gpm (0.076 m³/s) into a five-cell, bioreactor system covering about 5 acres (2 hectares). The gravity flow system is composed of a settling basin followed by two anaerobic bioreactors arranged in parallel which discharge into a rock filter polishing cell that is followed by a final aeration polishing pond. The primary lead removal mechanism is sulfate reduction/sulfide precipitation. The discharge has met stringent in-stream water quality requirements since its commissioning in 1996. However, there have been startup and operational difficulties. The system was designed to last about 12 years, but estimates suggest a much longer life based on anticipated carbon consumption in the anaerobic cells.

1 INTRODUCTION

The West Fork Unit is an underground lead-zinc mine purchased by the Doe Run Company from Asarco in 1998 that discharges water from mine drainage to the West Fork of the Black River (West Fork) under an existing NPDES permit. The West Fork Unit is located in Reynolds County in central Missouri, in the New Missouri Lead Belt, about three hours from St. Louis.

Flow rates in West Fork vary from about 20 cubic feet per second (cfs) to more than 40 cfs (0.56 to 1.13 m³/s). Water quality is relatively good, despite being located in an area with naturally high background levels of lead due to the bedrock geology. The mine discharges about 1,200 gpm (2.7 cfs or 0.076 m³/s) on the average or about 10 percent of the total flow in West Fork.

The adoption of water quality-based discharge limits, in its NPDES permit issued in October 1991, prompted Asarco to evaluate treatment methods for metal removal. Evaluations of alternative treatment processes determined that biotreatment methods were feasible and cost less than half as much as active sulfide precipitation. The goal of the water treatment project was to ensure that the stringent water quality-based limits in the permit would be consistently met.

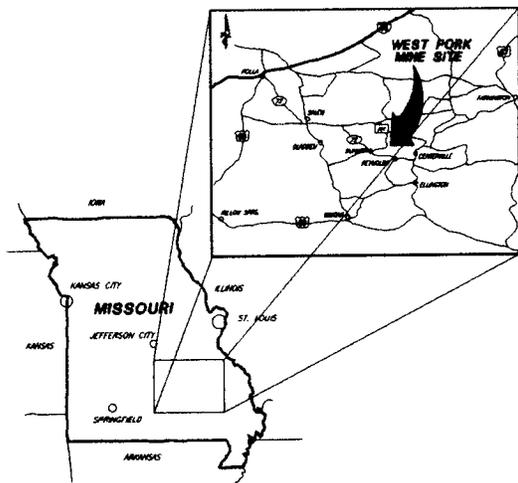


Figure 1 - Site Location

Since 1987, a group from Knight Piésold and Co. and the Colorado School of Mines has been active in developing passive treatment methods for metal-mine drainages. The primary treatment method is through the generation of hydroxides and sulfides through microbial metabolism. The biogeochemical principles are summarized in Wildeman, et al. (1995), and Wildeman and Updegraff (1998). The design principles are explained in Wildeman, Brodie, and Gusek (1993). In the case of the West Fork Unit, biotreatment consists of two stages:

1. An anaerobic unit that generates sulfide through sulfate reduction and is responsible for the lead removal.
2. An aerobic unit that is a rock filter/wetland. This unit is responsible for removing dissolved organic matter and excess sulfide from the effluent from the anaerobic cell. The aerobic unit also reoxygenates and polishes the water before it enters the river.

Extensive laboratory, bench-scale, and pilot scale tests were made on the anaerobic unit. These are described in Wildeman, et al. (1997), and Gusek, et al. (1998). The design and permitting of the system are also discussed in Gusek, et al. (1998), and Wildeman, et al. (1999). This paper concentrates on the operation of the full-scale system since its start in 1996.

2 SYSTEM DESCRIPTION

The system was designed based on the performance of the pilot-scale reactor and the interim bench scale studies. The large-scale system was estimated to cost approximately \$500,000 and required about three months of construction time. Operational costs include water quality monitoring as mandated by law. No additional costs for reagents are incurred; since the system uses gravity flow, moving parts are few and include valves, minor flow controls, and monitoring devices. Based on carbon depletion rates observed in the pilot system, the anaerobic cell substrate life was projected to be greater than 30 years; the full-scale biotreatment system should be virtually maintenance-free. Should mine water quality deteriorate, the full-scale design included a 50-percent safety factor.

The biotreatment system is composed of five major parts: a settling pond, two anaerobic cells, a rock filter, and an aeration pond (Knight Piésold, 1997). The system is fully lined. The design was also integrated into the mine's pre-existing fluid management system.

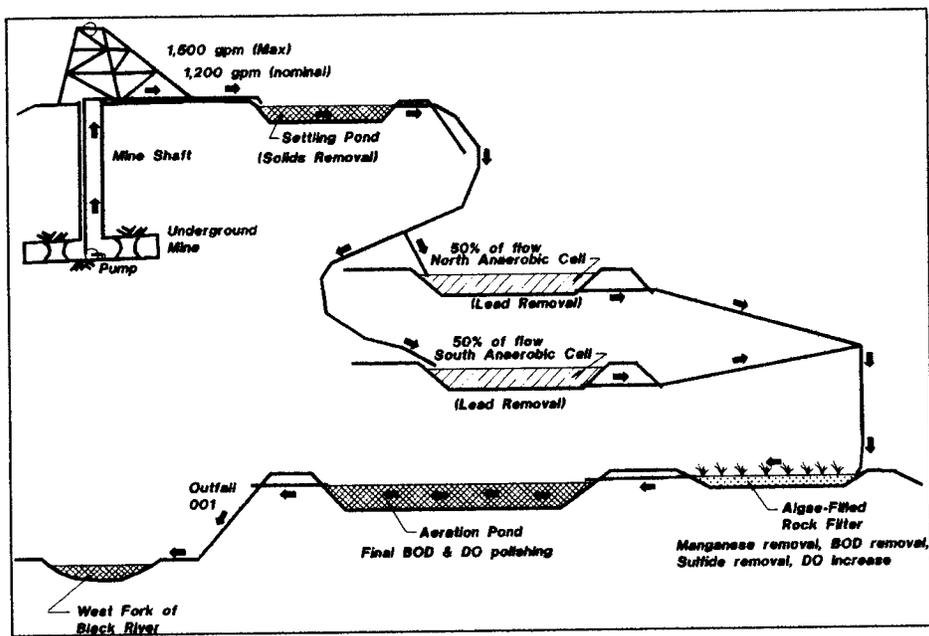


Figure 2 - System Configuration

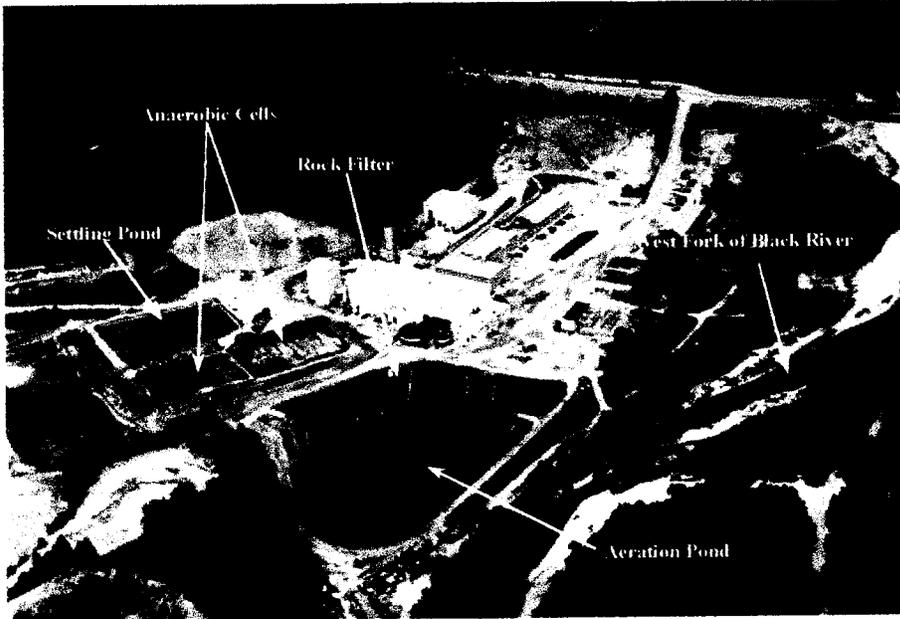


Figure 3 - Aerial View

A rectangular-shaped, 40-mil HDPE-lined settling pond has a top surface area of 32,626 ft² (3,030 m²) and a bottom surface area of 20,762 ft² (1,930 m²). The sides have slopes of 2 horizontal to 1 vertical (2H:1V). The settling pond is nominally 9.8 ft (3 m) deep. It discharges through valves and parshall flumes into the two anaerobic cells.

Two anaerobic cells are used, each with a total bottom area of about 14,935 ft² (1,390 m²) and a top area of about 20,600 ft² (1,930 m²). Each cell is lined with 40-mil HDPE and was fitted with four sets of fluid distribution pipes and three sets of fluid collection pipes, which were subsequently modified (see Start Up discussion). The distribution/collection pipes were connected to commonly shared layers of perforated HDPE pipe and geonet materials sandwiched between layers of geofabric. This feature of the design was intended to allow control of sulfide production in hot weather by decreasing the retention time in the cell through intentional short circuiting.

The spaces between the fluid distribution layers were filled with a mixture of composted cow manure, sawdust, inert limestone, and alfalfa, referred to hereafter as “substrate.” The total thickness of substrate, piping, geonet, and geofabric was about 6 feet (2 m). The surface of the anaerobic cells was covered with a layer of crushed limestone. Water treated in the anaerobic cells flows by gravity to a compartmentalized concrete mixing vault and thereafter to a rock filter cell. The gravity-driven flows can be directed upward or downward.

The rock filter is an internally bermed, clay-lined shallow cell with a bottom area of about 63,000 ft² (5,900 m²) and a nominal depth of one foot (30 cm). It is constructed on compacted fill that was systematically placed on the west side of a pre-existing mine water settling pond. Limestone cobbles line the bottom of the cell, and the cell is compartmentalized by limestone cobble berms. The discharge from the rock filter flows through a drop pipe spillway and buried pipe into a 40-mil HDPE-lined aeration pond. The aeration pond surface covers approximately 85,920 ft² (8,000 m²). The aeration pond discharges through twin 12-inch (30-cm) HDPE pipes into a short channel that leads to monitoring outfall 001 and thence into West Fork.

After the water pumped from the underground mine enters the settling pond, all flows are by gravity.

3 START-UP EXPERIENCE

Bench-scale test results suggested that the anaerobic cells be incubated with settled mine water for about 36 hours or less before fresh mine water was introduced at full flow to minimize initial levels of BOD, fecal coliform, color, and manganese. For about two weeks, pumps recycled the water within the two anaerobic cells. Based on data collected in field, and subsequent laboratory confirmation, the water from the anaerobic cells was routed to the tailings pond for temporary storage and later treatment and release. At that point, the rock filter and aeration ponds were brought on-line. In the meantime, the mine discharged according to plan through an overflow pipe from the settling pond as it had during construction of the other components.

After about six weeks of full-scale operation, the apparent permeability of the substrate was found to be lower than expected and the system was operating nearly at capacity. The system had been designed so that either of the two anaerobic cells could accept the full flow amount on a temporary basis in case maintenance work required a complete cell shutdown.

Research found that H_2S gas, generated by the sulfate-reducing bacteria, was being retained in the substrate in the anaerobic cells; this created a gas-lock situation that prevented full design flow. A temporary solution was obtained by periodic "burping" of the cells using the control valves. However, the "burping" had to be performed at 24-hour intervals, and it was determined that this solution was too labor-intensive.

The sulfide gas lock problem was investigated in December 1996 by installing vent wells in the substrate and measuring the gas pressures. Observations indicated that the gas was a factor in apparent short circuiting of the water passing through the cell. The layered geotextiles (geonet and geofabric), originally intended to promote horizontal flow, appeared to be trapping the sulfide gas beneath them and vertical flow was being restricted. The permeability of the substrate itself was for the most part unaffected. However, construction practices in the south anaerobic cell could have contributed to the situation. Here, a low ground bearing bulldozer was used to place substrate in nominal 6-inch (15-cm) lifts. This could have created a layering effect that may have trapped gas as well. Substrate layers in the north anaerobic cell were placed in a single lift, and no layering effect was observed during subsequent excavation. It is noteworthy that the mid-cell geotextiles had not been a feature of the pilot test cell design.

The first phase of a permanent solution was implemented with a trenching machine that ripped through the geonet/geofabric layers in the south anaerobic cell. This disrupted the gas-trapping situation. Subsequently, the substrate from the entire south anaerobic cell was excavated and the cell refilled without the geotextiles in June 1997. Identical action was taken on the north anaerobic cell in September 1997. These actions have solved the gas lock problem.

4 MAINTENANCE EXPERIENCE

Although this is technically a passive treatment system, when one considers trying to direct the flow of 1,200 gpm (0.076 m³/s) through approximately 3,930 yd³ (3,000 m³) of material there is certain to be some hydraulic problems. In addition, the design of the anaerobic cells made provisions for the water to bypass portions of the cells during the summer to eliminate excess buildup of sulfide in the cell effluent. In the summer of 1997 and 1998, operation of the system included by-passing some portions of the cell to maintain lower sulfide concentrations. However, when this was tried, short-circuiting within the cells and plugging of the substrate made maintenance during the summer more extensive than during the winter.

Perhaps the most troublesome maintenance issue was that a combination of sediment in the mine water along with algae buildup on the cell surfaces would block the infiltration of water into the cells.

This would necessitate periodically draining the cells and rototilling the top of the substrate so as to break up the accumulation cake. Often at the same time as a cell was tilled, water would be back-flushed through the discharge pipes to dislodge precipitate accumulation. When such maintenance was done, the rock filter would still receive discharge. It has proved to be an effective buffer between the cells and the discharge pond. This maintenance cycle of tilling and back-flushing had to be done almost once a month during the summer of 1998. During the winter, buildup was not as extensive and maintenance of the cell surfaces was less frequent. Currently, schemes are being investigated to try a drastic reconditioning of the cells to permanently increase the hydraulic conductivity of the anaerobic cells.

Other than repairing a bubble that appeared under the liner of the aeration pond, there has been no maintenance needed on the rock filter and the aeration pond.

5 OPERATIONAL RESULTS

5.1 The Anaerobic Cells

The average influent water quality can be compared with discharge water quality (Table 1) during the June through November 1997 period. Discharge levels of Pb and other metals were reduced substantially from average influent levels. For Pb, the level was reduced from a typical average of 0.40 mg/L to between 0.027 and 0.050 mg/L. Zn, Cd, and Cu effluent concentrations were also reduced.

Table 1 - West Fork Mine Water Quality Data

Parameter	Typical Average Influent Water Quality in mg/L	Range of Water Quality Discharge in mg/L (June - November 1997)
Pb	0.4	0.027 - 0.050
Zn	0.36	0.055 - 0.088
Cd	0.003	<0.002
Cu	0.037	<0.008
Oil and Grease	--	<5.0
H ₂ S	--	0.011 - 0.025
Total Phosphorus	--	<0.05 - 0.058
Ammonia as N	0.52	<0.050 - 0.37
Nitrate and Nitrite	2	<0.050 - 1.7
True Color	--	10 - 15
BOD	1.7	<1 - 3
Fecal Coliform	—	<1 - 2
pH	7.94	6.63 - 7.77
TSS	—	<1 - 4.2

More extensive analysis of the operational data from June 1997 through June 1999 has shown some interesting results. The plumbing system in the anaerobic cells was designed to run the cells upflow or downflow, to use a portion of the cell when sulfide production became too high, and to be back-flushed in case precipitation occurred in the discharge line. All three features have been used. The cells have been run in the upflow direction during the first winter so that the substrate compaction that occurred during the summer could be relieved. The three levels of discharge pipes are routinely monitored for

sulfide production, and the valves are adjusted accordingly to eliminate excess sulfide. In the summer, these adjustments become more difficult as attempts are made to only use portions of the cells. In addition, the cells are routinely back-flushed to maintain good circulation of mine water through the cells.

By operating the anaerobic cells in this fashion, over four seasons from July 1997 to July 1998, the average concentration of 40 analyses of total Pb in the water entering the cells is 0.45 and the average concentration of Pb in the water exiting the cells is 0.085. Results for zinc are not as extensive. From March 1998 to November 1998, the average concentration of 10 analyses of total Zn in the water entering the cells is 0.44 and the average concentration of Zn in the water exiting the cells is 0.102.

Within the anaerobic cells, production of enough sulfide has never been a problem. During the summers of 1997 and 1998, sulfide concentration in discharges from some portions of the cells routinely exceeded 12.0 mg/L, the upper quantitation limit of the analytical procedure. This correlates with the pilot cell results where, during the two summers in which it operated, sulfide concentrations reached 20 mg/L. According to Wildeman, et al. (1997), at this level of sulfide concentration, the production of sulfide in the anaerobic cells is about 2 moles sulfide per cubic meter per day. As expected, during the winter, concentrations of sulfide in the cell effluent are lower. However, even during the months of December, January, and February, sulfide concentrations in the discharge from some portions of the cell were between 2.0 and 7.7 mg/L. These concentrations have been higher than the average of 0.3 mg/L of sulfide that was found during the winter the pilot cell operated (Wildeman, et al., 1997).

5.2 The Rock Filter

Of the five parts of the system, the operation of the rock filter has been the most interesting. It operates as a natural wetland where water of a depth of 1 to 2 feet (30 to 60 cm) meanders through the limestone cobbles. Flora and fauna have thrived in this ecosystem. It has served the important function of cleansing the excess sulfide in the water that is leaving the anaerobic cells. From July 1997 to September 1998, the average of 55 analyses of sulfide concentration in the water entering the rock filter is 3.3 mg/L. In 55 analyses of sulfide in the rock filter effluent, sulfide was detected in the water 20 times and none of these were above 0.25 mg/L.

Because the water entering the rock filter contains a significant concentration of sulfide, a unique ecosystem of algae and bacteria have developed in this area. In the summer of 1997, red algae/bacteria started to develop in this influent area and have persisted. In addition, a white scum has developed in this area. Indeed, the rock-filter influent area looks like a pool of the primordial soup. During the summer of 1997, when high levels of sulfide were entering the rock filter, the water would develop a milky white colloidal suspension that would persist throughout the wetland system. This milky suspension had diurnal characteristics. It would be more persistent in the morning and sometimes clear up during the day. In the summer of 1998, this milky suspension was not as evident even though the concentrations of sulfide entering the rock filter were sometimes higher. Vegetation in the rock filter was much more lush in the second summer. The speculation is that this milky suspension is colloidal sulfur. If it is, then this form of wetland ecosystem removes it.

Besides removing sulfide from the water, the rock filter also plays a significant role in further reducing the concentration of lead in the water. Over four seasons from July 1997 to July 1998, the average concentration of 40 analyses of total Pb in the water entering the rock filter is 0.085 and the average concentration of Pb in the water exiting the rock filter is 0.050. The mechanism for lead removal in the rock filter is not known.

6 CONCLUSIONS

In the introduction to this paper it was stated that the biotreatment system should be virtually maintenance free. That has not been the case with the anaerobic cells. Keeping these cells from clogging has required periodic rototilling and back-flushing. Because attempts were made during the summer to use only a portion of the two cells, maintenance has been more extensive at this time than during the winter. Nevertheless, these cells have performed according to design and have been effective at removing lead from the mine water. Because of this necessary maintenance, the design of the plumbing system to include back-flushing, upflow and downflow, and use of only a portion of the cell has been particularly advantageous.

The need for the rock filter has been found to be essential. Its operation has shown some surprises. The presence of sulfide in the water has caused a unique ecosystem that effectively removes this constituent from the water. The removal of sulfide is more important in the summer. The rock filter also removes a significant amount of lead. The removal mechanism is unknown.

7 ACKNOWLEDGMENTS

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