THREE CASE HISTORIES OF PASSIVE TREATMENT OF METAL MINE DRAINAGE

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ABSTRACT

Typical passive treatment systems for mitigating drainage from metal mines are similar to SAPS systems developed for coal mine drainage. Passive treatment performance at three metal mines has been positive for a wide variety of flows (from I to 1,200 gpm) and water chemistry (pH from 2.0 to 8.0; total metals from 0.4 mg/L to over 4,000 mg/L). The sites encompass a variety of mining situations and climatic conditions, including an abandoned underground copper mine site in Wyoming at 9,500 feet elevation that is virtually inaccessible for nine months out of the year. Another site in South Carolina involved the passive treatment of very acidic heap leach solution at a gold mine that has since been closed. The last site is an active underground lead mine in Missouri; the system here is currently treating 1,200 gpm to aquatic water quality standards in compliance with an approved NPDES permit. The longevity of this last system has been estimated to be on the order of decades before major maintenance is required.

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 10 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 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.

Since 1988, there have been rapid advancements in understanding the functioning of wetland/bioreactor systems. The first large scale aerobic system (2,000 gpm capacity) was built in 1992 by TVA in Alabama; the West Fork Unit system (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 anaerobic passive treatment technique holds promise over typical chemical treatment methods because large volumes of sludge are not generated; in fact, sludge disposal may be delayed until the end of the project life. In situ reclamation may also be feasible.

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 bacteria in anaerobic zones;
- Hydroxide precipitation catalyzed by bacteria in aerobic zones;
- Filtering of suspended material;
- Metal uptake into live roots and leaves;
- Ammonia-generated neutralization and precipitation; and
- 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(l). 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. Research has shown that microbial processes are a dominant removal mechanism in passive treatment systems (1). 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 ARD (pH greater than 5.5) without excessive dissolved iron concentrations, hydroxide 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 (1). When the pH of the drainage is greater than 5 and iron is less than 50 mg/L, effluent quality consistently meets offsite discharge criteria. While some metal mine drainage can also have pH values above 5.5, aerobic reactions typically can not raise the pH high enough to efficiently remove heavy metals like copper, lead, zinc, nickel and cadmium.

Typical Conditions for Using Anaerobic Systems

Anaerobic systems, sometimes referred to as "compost" systems, are similar to "Successive Alkalinity Producing Systems" or SAPS in that pH is raised and metals are reduced in an anaerobic geochernical 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 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 sulfate-reducing bacteria (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:

- hydrogen sulfide gas , which combines with dissolved metals to precipitate sulfides and
- bicarbonate, 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(1):

Hydrogen Sulfide: $SO_4^{-2} + 2\ CH_2O + 2H^+ \dashrightarrow H_2S + 2\ H_2O + 2\ CO_2$ [pH < 7.0]

Bicarbonate: $SO_4^{-2} + 2\ CH_2O \dashrightarrow HS^- + 2\ HCO_3^- + H^+$ [pH > 7.0]

The hydrogen sulfide gas, bubbling up through the wetland substrate or occurring as the dissolved sulfide ion (S^{-2}), 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):

$$Zn^{+2} + H_2S \dashrightarrow ZnS + 2\ H^+$$

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 (CHO, 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 Piesold LLC 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 inoculum. The cells treated 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 2.4 foot deep, 4,000 square foot 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 5 gpm but by the time the system was commissioned, influent water chemistry had deteriorated so that the flow was reduced to 50 % 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 (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 Figure 1 which details:

- metal removal performance on a percentage 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, and
- total copper removal performance.

Right after startup, 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 on-going reclamation/closure activities.

As shown on Figure 1 after the startup 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 % 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 continued around 6.5 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 10BC) 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 H period), the percent aluminum, copper and iron removed became steadier and more consistently in the range between 95 % and 100%.

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 11 period as shown on Figure 1 for aluminum, iron and copper. Flow was maintained at about 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. Towards the last month of the post vegetation I period, the percent removal of aluminum began to drop below 50%, 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 %. The effluent pH was observed to maintain a value of around 6.5. Sulfate influent and effluent differences increased even more markedly than the post vegetation I period.

Brewer Pad 5 Conclusions

After startup, 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 (2) 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 biogeochemical 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 come 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 (9,500 feet) abandoned underground copper mine has neutral pH discharge with 3 to 6 mg/L dissolved copper and low sulfate (less than 100 mg/L SO_4); water temperature is close to freezing (±4^0C) and the mine is accessible only by a 20-mile snowmobile trek for nine months out of the year. Flow from the portal varies from 15 to 30 gpm in the winter months to 450 gpm or more during the spring runoff. Copper concentration observed at the portal is fairly constant all year long, somewhat independent of flow rate.

The pilot scale passive treatment cell is composed of a single gravity-fed anaerobic cell configured in a downflow mode. In the summer of 1997, a 15 foot diameter and 4-foot 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 (trash-can-size) test conducted in the summer of 1996. Due to the low mine water temperature, the initial slug of water used in incubation was heated to about 15^0C. The cell was incubated for about a week before it received full design flow of 5 gpm at about 3^0C. The cell has been fully operational since early September, 1997. Snow depths on site can reach 10 feet 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 exhibit low pH (3.8), elevated copper (30-50 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 appears to mix with relatively pristine ground water 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 act's to remediate copper loading at the portal during a portion of the year. However, the accumulated sludge acts both as a sink and 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 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 per day per 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, 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.

Site visits via snowmobile were conducted in mid-December, 1997 and early February, 1998 to collect data and samples. The sub-freezing air temperatures resulted in an ice covering over about 40 % of the cell surface. Flow through the cell had decreased proportionately, down from 5 gpm in October to about 3 gpm in the winter months.

Performance data for the pilot system is shown on Figure 2 and it includes results for copper, pH, redox potential, conductivity, sulfate and temperature of the influent and effluent. The target copper concentration is about 0. 15 mg/L; since startup, the system has consistently met this criteria. It is suspected that the copper that is being discharged is a suspended solid, probably a colloidal sulfide. Speciation work planned for this winter will examine this issue. The redox potential of the cell has steadily decreased and has always maintained a consistent reducing level value (less than -100 mV). The sulfate concentration in the effluent was initially higher than the influent due to the presence of gypsum in the substrate. Winter - 98 readings indicate that influent sulfate has now matched the effluent value. As the initial gypsum is depleted, it is expected that the effluent sulfate concentration will drop below the influent. The temperature readings in the effluent have dropped steadily to a low of 0.17^0C. in response to the constant sub-freezing air temperature at the site. Total sulfide production has risen to about 0.24 moles per day per cubic meter of substrate, significantly higher than the design estimate of 0. 15 mole/d/m^3. Other workers (3) have suggested that sulfate reduction rates are poor at temperatures below 10^0C. Apparently the SRB bacterial suite at this site, combined with a tailored organic substrate mix, have adapted to the harsh temperature conditions and are performing beyond expectations at this time. Further sampling and analysis are planned on a bi-monthly schedule until 1999.

Ferris Haggarty Pilot Scale Preliminary Conclusions

The sulfate reducing bacteria appear to have adjusted/mutated in response to the subfreezing conditions at the site. Effluent copper concentration is about 0. 1 mg/L which meets the goal for discharge. The incubation of the cell at elevated water temperatures appears to have succeeded in establishing a viable SRB population.

Asarco, Incorporated West Fork Unit, Missouri

This operating underground lead mine has a neutral pH discharge with 0. 4 mg/L lead and 0. 18 mg/L zinc; flow is about 1,200 gpm. The large scale system was designed based on the performance of a pilot scale system and interim bench scale studies. The large scale system cost approximately $700,000 (4) (including engineering and permitting) and required about four months to construct. System 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 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 (25gpm) 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 (". The system is fully lined. The design was also integrated into the mine's pre-existing fluid management system. Specific design characteristics include:

- A rectangular-shaped, 40 mil HDPE-lined **settling pond** has a top surface area of 32,626 square feet (0.75 acres) and a bottom surface area of 20,762 square feet (0.48 acres). The sides have slopes of 2 horizontal to I vertical (2H: IV). The settling pond is nominally 10 feet 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 square feet (0.34 acres) and a top area of about 20,600 square feet (0.47 acres). 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. 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 management 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. The total thickness of substrate, piping, geonet and geofabric was about six feet. 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 square feet (1.4 acres) and a nominal depth of one foot. 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, It was planted with cattails (Typha lattifolia) and inoculated with local species of algae.

- 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 square feet (2.0 acres). The aeration pond discharges through twin 12-inch HDPE pipes into a short channel that leads to monitoring outfall 001 and thence into the West Fork of the Black River.

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

Wildeman, et al[1] 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[1].

West Fork Operational Results

Since startup, 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 0.40mg/L to between 0.027 and 0.050mg/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 remain in completely understanding and designing for the biochemical and geochemical reactions that occur in passive treatment systems. However, the performance data available from three sites considered in this paper appears to be consistent among the group and with the results of previous work.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the following persons or companies for contributing information or permission to publish this paper.

- Brewer Gold Company
- Asarco, Incorporated

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Figure 1, Brewer Mine Pad 5 Cell Pilot-Scale Performance Data

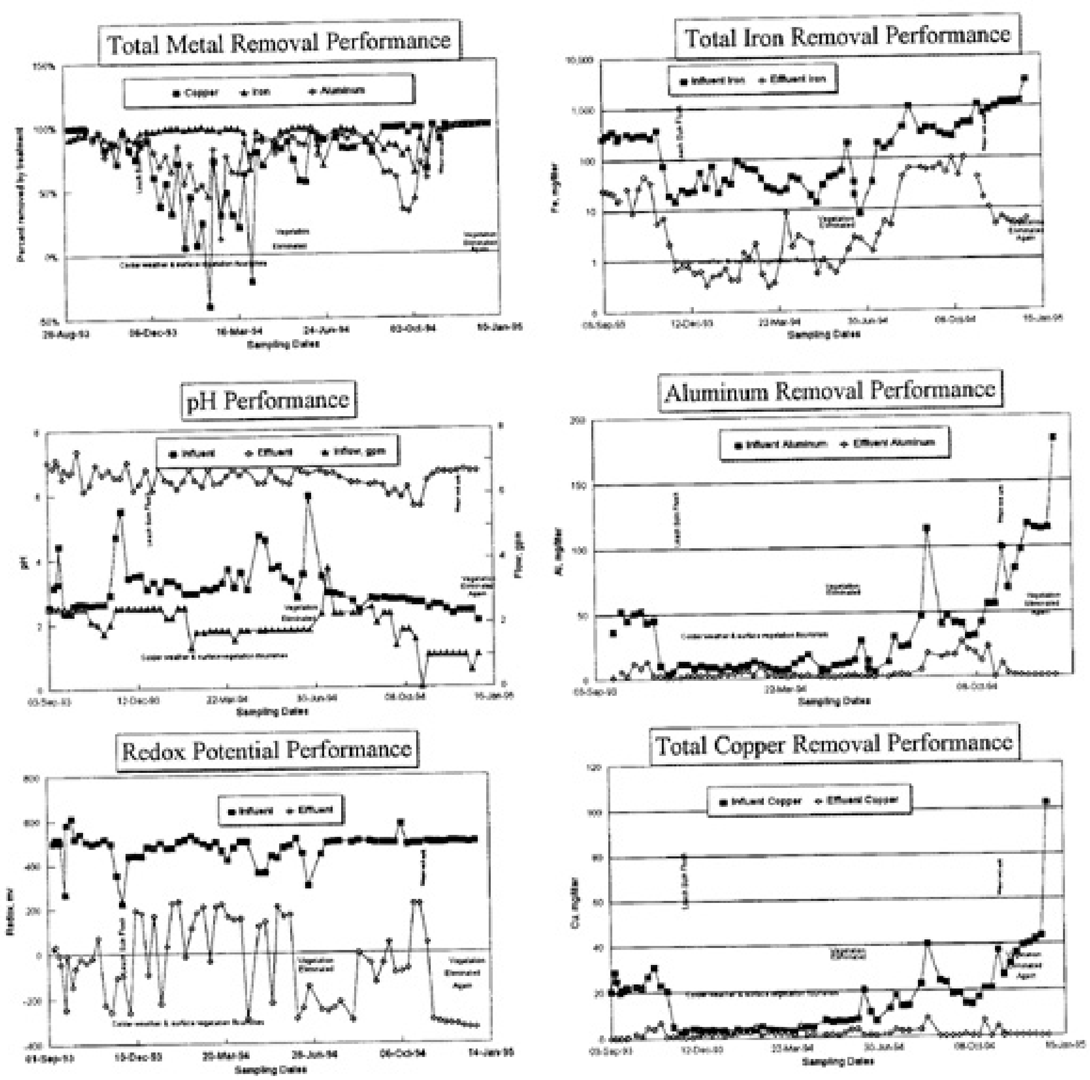

Figure 2. Ferris Haggarty Pilot-Scale Performance Data