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EPA

SITE Technology Capsule

Pintail Systems Inc.'s Aqueous Biocyanide Process

Introduction

In 1980 the Congress passed the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), also known as Superfund, committed to protecting human health and the environment from uncontrolled hazardous waste sites. CERCLA was amended by the Superfund Amendments and Reauthorization Act (SARA) in 1986. These amendments emphasize the long term effectiveness and permanence of remedies at Superfund sites. SARA mandates implementing permanent solutions and using alternate treatment technologies or resource recovery technologies, to the maximum extent possible, to clean up hazardous waste sites.

State and Federal agencies, as well as private parties, are now exploring a growing number of innovative technologies for treating hazardous waste. The sites on the National Priorities List total more than 1,200 and comprise a broad spectrum of physical, chemical, and environmental conditions requiring varying types of remediation. The U.S Environmental Protection Agency (EPA) has focused on policy, technical, and informational issues related to exploring and applying new remediation technologies applicable to Superfund sites. One such initiative is EPA's Superfund Innovative Technology Evaluation (SITE) Program, which was established to accelerate development, demonstration, and use of innovative technologies for site cleanups. EPA SITE Technology Capsules summarize the latest information available on selected innovative treatment and site remediation technologies and related issues. These capsules are designed to help EPA remedial project managers, EPA on-scene coordinators, contractors, and other site cleanup managers understand the type of data and site characteristics needed to effectively evaluate a technology's applicability for cleaning up Superfund sites.

This capsule provides information on Pintail Systems, Inc.'s Aqueous Biocyanide Process, a bioremediation technology designed to treat aqueous process and waste solutions contaminated with cyanide and heavy metals. Applicable matrices include mine process solutions, mine drainage, tailings effluent, groundwater, and industrial process effluents. The technology consists of a proprietary biological culture of microorganisms, immobilized on a porous ceramic filtration media as an attached growth biofilm for aqueous treatment. Pintail Systems, Inc. has developed a companion technology for the *in situ* treatment of cyanide and heavy metals in ores, tailings, soils and sediments.

A field treatability study was performed on a cyanide and metal contaminated "pregnant solution" from a gold mine heap leach at the Echo Bay/McCoy Cove Mine Site, in Nevada. Information in this capsule emphasizes specific site characteristics and results of the treatability test. The capsule presents the following information:

- Abstract
- Technology description
- Technology applicability
- Technology limitations
- Process Residuals
- Site requirements
- Performance data
- Technology status
- Sources of additional information

Abstract

A two and one-half month field treatability study of an innovative biological treatment technology for the destruction of cyanide and immobilization of metals from an aqueous mine process stream was held at the Echo Bay/McCoy Cove mine site near Battle Mountain, Nevada.

The Aqueous Biocyanide Process, developed and operated by Pintail Systems, Inc. of Aurora, Colorado, biologically detoxifies cyanide and removes heavy metals from contaminated waste streams. The field treatability study was jointly sponsored by the Mine Waste Technology Program (MWTP), Activity III, Project 5, Biocyanide, and the Superfund Innovative Technology Evaluation (SITE) Demonstration Program.

The primary objective for the field treatability study was to determine the effectiveness of the bioremediation process in degrading Weak Acid Dissociable (WAD) cyanide from a metal laden, high cyanide "pregnant solution." The pregnant solution is the effluent form the heap leach process containing the extracted metals. The secondary objective of the study was to determine the ability of Pintail's process to remove and immobilize heavy metals from the pregnant solution.

Pintail Systems, Inc.'s Aqueous Biocyanide Process utilizes a specially selected and augmented consortium of microorganisms immobilized on a fixed media isolite. The isolite is loaded into bioreactors which can be controlled to provide specific environments for microbial degradation and immobilization pathways. For this study, an aerobic bioreactor was used in conjunction with an anaerobic bioreactor to provide the desired degradation and metal immobilization properties.

The field treatability study was conducted between June 11, 1997 andAugust 26, 1997. During this time, the period between June 11 to July 22 was devoted to customizing and optimizing the system to the site-specific waste characteristics. Once optimized, continuous testing was performed from July 23 and August 26.

Results from the study are summarized below:

- The average % WAD CN reduction attributable to the Biocyanide process was 89.3 during the period from July 23 to August 26. The mean concentration of the feed over this period was 233 ppm, while the treated effluent from the bioreactors was 25 ppm. A control train, used to detect abiotic loss of cyanide, revealed no destruction of cyanide (average control effluent = 242 ppm).
- Metals that were monitored as part of this study were As, Cd, Co, Cu, Fe, Mn, Hg, Ni, Se, Ag, and Zn. Significant reductions were noted for all metals except Fe and Mn. Average reduction in metals concentration after July 23 for all other metals were 92.7% for As, 91.6% for Cd, 61.6% for Co, 81.4% for Cu, 95.6% for Hg, 65.0% for Ni, 76.3% for Se, 94.6% for Ag, and 94.6% for Zn. Reductions for As, Cd, Co, and Se are probably greater than calculated due to non-detect levels in some effluent samples. A biomineralization mechanism is proposed for the removal of metals from solution. Biomineralization is a process in which microbes mediate biochemical reactions forming novel mineral assemblages on solid matrices.
- The Aqueous Biocyanide Process was operated for two and one-half months. During the first 42 days (June 11 to July 22) system performance was variable, and occasional downtimes were encountered. This was due to greatly higher cyanide and metals concentration in the feed than was encountered during bench-scale and design phases of the project. Once optimized for the more concentrated feed, the system performed well with continuous operation for 35 days (July 23 to August 26). The ability to "re-engineer" the system in the field to accommodate the new waste stream is a positive attribute of the system.

Technology Description

The Pintail Aqueous Biocyanide Process is a bioremediation technology for the treatment of cyanide and metals in process and waste water streams. The technology utilizes a proprietary method for identifying, isolating, and growing a specialized consortium of microorganisms designed to treat the specific contaminants and characteristics of the aqueous stream. Pintail uses microorganisms isolated from the environment of the aqueous stream and, if necessary, can augment the culture with microorganisms from their collection of microorganisms. The microorganisms in Pintail's collection were recovered from a wide variety of extreme environments and were isolated and adapted to treat specific contaminants. The optimized microbial consortium is then immobilized on a porous ceramic filtration media as an attached growth biofilm. Dependent on the application, one or more sets of microbial consortiums can be immobilized on separate media and used in tandem to achieve the treatment of complex waste streams.

For the current application, both aerobic and anaerobic microbial pathways were designed into a treatment train to degrade the cyanide and immobilize metals from the process stream. As part of this treatability design, a control train was used to determine abiotic losses of cyanide and metals. The system design is depicted in Figure 1 and described below.

Dual identical treatment trains are used in an alternating on-off mode. The reactors are operated as a plug-flow reactor system. The system is operated in 24 hour alternating cycles of treatment or reinoculation for the two biotreatment trains. A typical complete 48 hour operation cycle for one of the biotreatment trains would include a 24 hour treatment period, followed by a four to five hour flush of inoculation bacteria discharging to the drain, followed by a 20 hour bio-inoculation.

Cyanide and metals contaminated solutions from the mine are fed to the reactor system which contains both an aerobic treatment cycle and an anaerobic reactor. Optical level sensors on each aerobic tank turn a pump on and off to either transfer process solutions to the anaerobic reactors or to recycle aerobic bacteria/nutrient solutions back to the aerobic culture tank.

The treatment bacteria are maintained as live cultures in a continuous culture system. An aerobic culture and an anaerobic culture are maintained by scheduled nutrient and stock culture addition and are circulated through the aerobic and anaerobic biomass during the twenty-four hour flush and inoculation cycle and are returned to the bioculture tanks in a continuous loop.

Anaerobic cultures are applied to the anaerobic culture train during flush and inoculation cycles alternating between the biotreatment trains on a daily basis. A flush cycle of 4-5 hours is run between the treatment cycle and the full recycle inoculation. The flush cycle serves to discharge process solutions from the anaerobic tanks before recycling inoculation solutions to the culture tank. After drawing down during the flush cycle every day, the tank is topped off with fresh water.

Technology Applicability

The Aqueous Biocyanide Process is applicable to process and waste streams containing cyanide alone, or in combination with heavy metals. For the application tested in this study, the process was used to demonstrate its utility as a process to treat cyanide and metal contaminated process and waste streams derived from precious metal recovery. In these applications, cyanide is used as a lixiviant to extract and recover precious metals such as gold and silver from heap and vat leach mining practices. The spent solutions typically contain high levels of cyanide and heavy metals which must be treated prior to discharge. Cyanide is typically complexed with a wide variety of metal species and sulfur causing the cyanide to be environmentally persistent and difficult to be destroyed by natural processes. In addition, the effluents may contain high levels of metals and other constituents which may impact total water quality.

According to Pintail, the process is capable of treating all forms of cyanide, as well as treating heavy metals in the effluent. Standard processes for treating cyanide from heap and batch leach processes use peroxide to oxidize cyanide. The advantages of the Aqueous Biocyanide Process, as

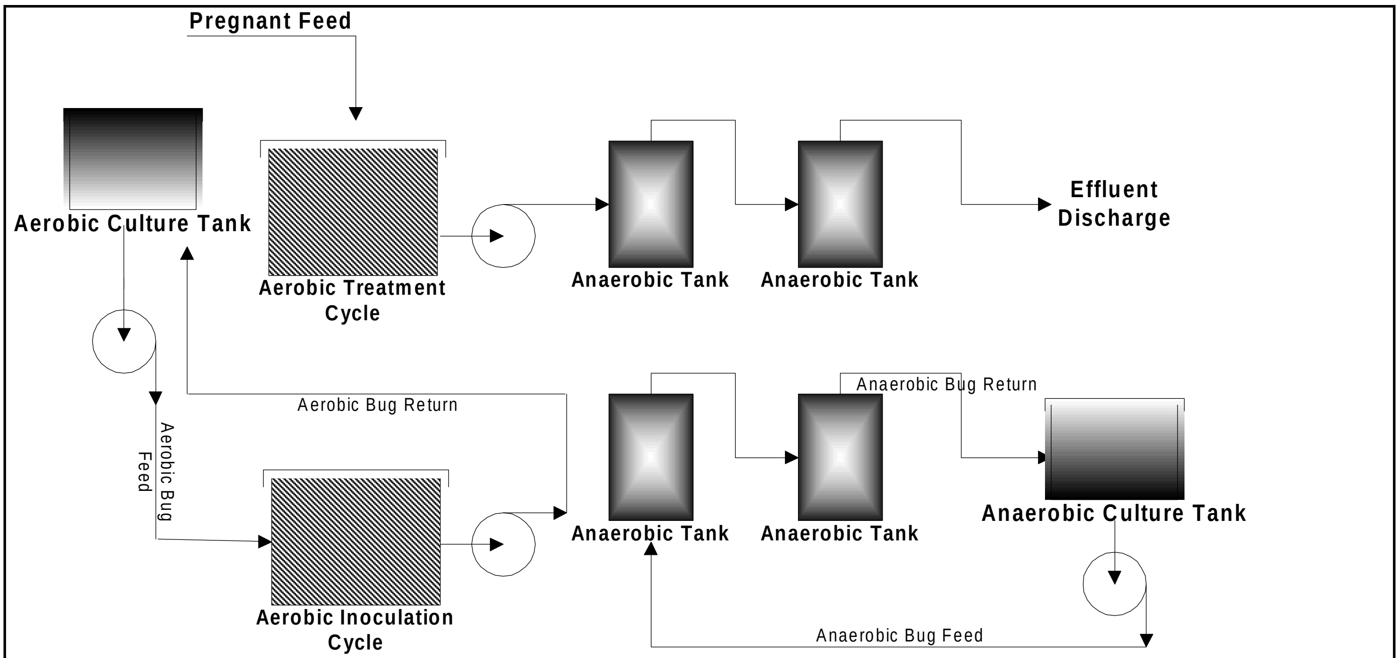

Figure 1. Dual train Aqueous Biocyanide System design depicting on-off mode. Top train is treating while bottom train is being re-inoculated.

compared to peroxide treatment, are:

- The biocyanide process is a biological treatment technology and does not utilize any hazardous or reactive chemicals.
- The process is inexpensive to operate once the bioreactors are constructed. The only consumables used are nutrients and bacterial cultures.
- The process treats heavy metals and may be engineered to treat other water quality impacting constituents. This eliminates the need to bring other technologies on-site.
- The Biocyanide Process may be engineered to recover precious metals (gold and silver) from waste streams during operation. This feature can offset costs during waste treatment.

In addition to mining wastes, the Aqueous Biocyanide Process may be used to treat cyanide contaminated wastewater from other industrial processes as well as contaminated groundwater containing heavy metals. Applicable wastewater streams may include electroplating wastes and effluents from spent aluminum pot liners. The biotreatment process can also be applied to the treatment of groundwater and surface water containing heavy metals and nitrates.

Pintail Systems, Inc. has also developed and applied, at full-scale, a biocyanide process for the *in situ* treatment of cyanide and heavy metals in spent ore and mine tailings. In the Spent Ore Biocyanide Process, bacterial solutions and nutrients are injected into the subsurface where entrained cyanide is destroyed and heavy metals are immobilized. Pintail has shown at other sites that this process greatly reduces rinsing of heap leach pads, and can minimize the impact of acid mine drainage from tailings and spent ore.

Technology Limitations

According to Pintail, proprietary colonies of bacteria or isolated native bacteria can detoxify WAD cyanide as high as 500 ppm and effectively treat aqueous waste streams containing soluble metals as high as 400 ppm. The bacteria are able to accommodate fluctuations in contaminant concentrations, however large variations in feed concentrations could be detrimental to the bacteria. A continuously mixed influent storage tank would eliminate fluctuations in contaminant concentration.

In addition, cool water temperatures (35-45^{o} F) could slow down biodetoxification and biomineralization. Water temperatures above 85^{o} F could also be harmful to the bacteria.

Process Residuals

The primary residual generated from the Pintail process is the solid media containing primarily dead bacteria and immobilized metals. This waste material can be stored in 55 gallon drums before being shipped off-site for disposal. The developer believes that the precious metals which are fixed on the support media can be separated and recovered and sold as a commodity.

Site Requirements

The Pintail process, as tested, requires an enclosed level 20 foot by 80 foot area capable of supporting the bioreactor and all necessary support equipment. Once the piping and pumps are installed, the system can be operational within three weeks. According to Pintail, the bacteria can be grown and be inoculated onto the porous ceramic media and acclimated to the waste stream in two weeks.

The technology utility requirements are minimal and consist of the following:

- 110 volt - single phase power
- potable water

Potable water should be available for field laboratory analytical procedures and process make up water as well as personnel decontamination. Storage tanks should be available for holding the treated water prior to discharge. A storage shed can be used to store nutrients such as ammonia and nitrogen.

Performance Data

Pintail Systems, Inc.'s Aqueous Biocyanide Process was used to treat a pregnant solution containing cyanide and heavy metal contaminants. The two and one-half month treatability test took place at the Echo Bay/McCoy Cove mine site near Battle Mountain, Nevada between June 11, 1997 to August 26, 1997.

The original system was designed and optimized based on the plan to treat a "barren solution" containing WAD cyanide concentrations in the tens of ppms and relatively devoid of heavy metal contaminants. However, upon mobilization of equipment to the site, the test feed was changed to a "pregnant solution" containing WAD cyanide concentrations between 250 to 350 ppm, and significant concentrations of heavy metals. Since the system was designed for the barren solution, significant redesign of the system on-site was necessary to treat the pregnant solution. Therefore, the period between June 11 to July 22 was devoted to customizing and optimizing the system to the pregnant solution characteristics. Once optimized, continuous testing was performed between July 23 and August 26. Therefore, the period between July 23 and August 26 will be used for performance assessment purposes.

The test system consisted of two identical treatment trains

(T-100 and T-200), and a control train (T-300). The control train was used to determine if any losses of cyanide or metals occurred due to abiotic mechanisms.

Four sample streams were evaluated as part of this treatability study. Streams included; (1) an influent stream designated as the “process feed” or “pregnant feed,” (2) a control effluent from the control train, (3) an effluent from the aerobic treatment cycle, and (4) the effluent from the entire treatment process. Concentrations of cyanide from the influent stream were compared to the treated effluent to determine system efficiency. Results from the aerobic effluent, as compared to the system effluent, were used to determine operating efficiencies of the individual aerobic and anaerobic segments.

Analyses for weak and dissociable (WAD) cyanide were performed by two different methods. On-site field analyses were performed on a daily basis using a Perstorp analyzer: a ligand exchange/flow injection amperometric method of analysis. Several samples, but not all field samples, were also analyzed by a laboratory distillation procedure; Standard Method 4500 CN.I. Total cyanide was also performed on samples submitted to the laboratory. Metals analysis of the process feed, treated effluent, and control effluent were performed on three composited samples taken each week. The samples were analyzed for the following metals: As, Cd, Co, Cu, Fe, Mn, Hg, Ni, Se, Ag, and Zn.

Cyanide Destruction

Table 1 summarizes WAD cyanide results from the study, and Figure 2 graphically depicts process efficiency during the performance assessment period as measured by WAD cyanide (field).

Table 1. Average WAD CN (mg/L) from 7/23 to 8/26.

	Influent	Control Effluent	Aerobic Effluent	Effluent	Average % Red.
Field Analysis	233 + 8 n=27	242 + 22 n=27	160 + 30 n=27	25 + 18 n=27	89.3 %
Lab Analysis	213 + 44 n=16	231 + 24 n=16	Not Measured	23 + 17 n=16	89.2 %

Note: the value after+ is the standard deviation; n is the number of samples analyzed

Results from the study demonstrate that, once optimized, the Aqueous Biocyanide Process was able to consistently reduce WAD cyanide by approximately 90%, based on an average influent value of 233 ppm and an average effluent

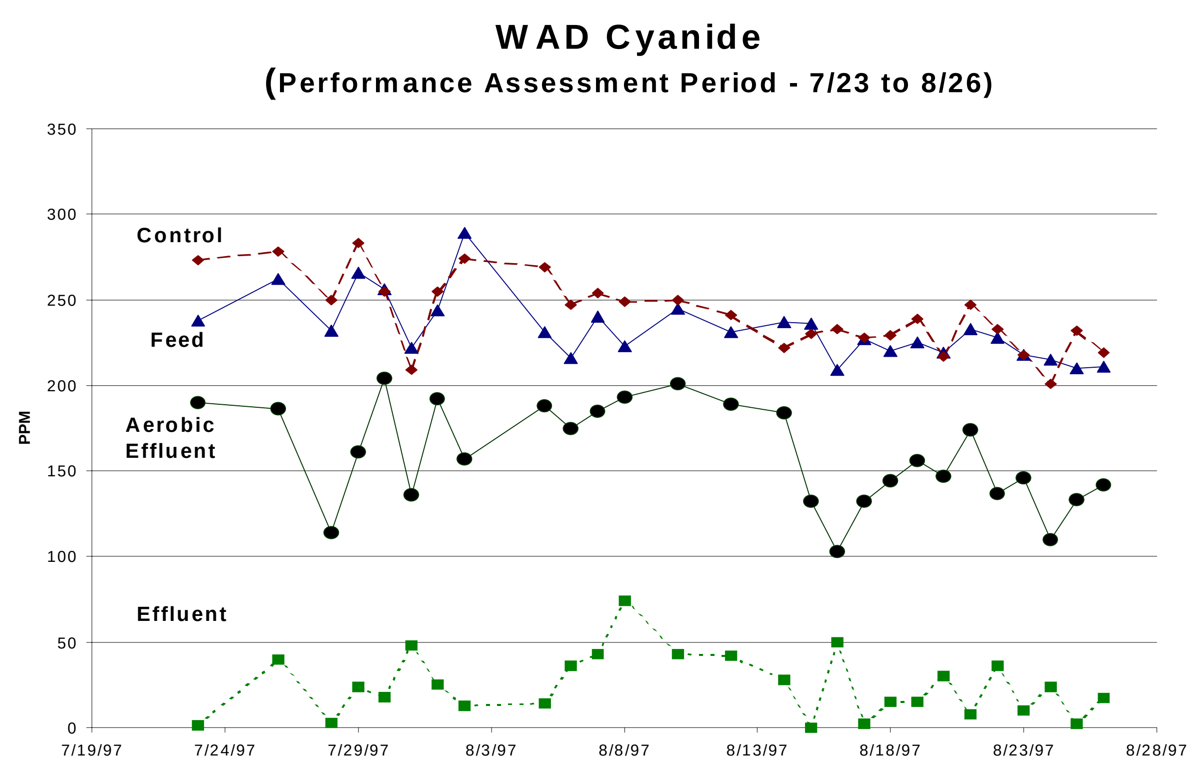

Figure 2. WAD CN concentrations over time.

value of 25 ppm. Furthermore, the WAD cyanide levels in the control effluent are statistically indistinguishable from influent concentrations, indicating that the biological system was responsible for the cyanide destruction.

Analyses for WAD cyanide were also performed on samples taken after the Aerobic Treatment Cycle. The average WAD cyanide concentration during the period between July 23 and August 26 was 160 ppm. This represents an average reduction in WAD cyanide of approximately 31% attributable to aerobic respiration processes.

Pintail offers the following explanation concerning the mechanisms of WAD Cyanide degradation in their treatment system:

- In the Aerobic Treatment Cycle, the microorganisms directly metabolize cyanide. The aerobic microorganisms can metabolize the more easily degradable metal-cyanide complexes such as Zn-cyanide. Degradation rates are relatively rapid. This phase reduces the toxicity load to the anaerobic system.

- In the Anaerobic Treatment Cycle, the microorganisms utilize cyanide as a co-metabolite. Degradation rates are relatively slow. Reduction of the more strongly complexed fraction of the WAD cyanide occurs.

- The combination of the aerobic/anaerobic system allows for the rapid destruction of easily degradable WAD cyanide in the aerobic phase as a pretreatment or conditioning step, in order to increase the efficiency of the slower anaerobic phase of the treatment.

Metals Removal

In addition to testing the cyanide destruction capabilities of the Aqueous Biocyanide Process, the system was secondarily evaluated for its ability to remove metal species from the pregnant feed solution. Table 2 presents a review of the metals data during the performance assessment period of the project. Figures 3 to 6 illustrate the effectiveness of the removal process for several select metals. The results from the analyses indicate that the process was able to immobilize and remove significant quantities of heavy metals from the process feed. Specifically, the metals arsenic, cadmium, mercury, and zinc exhibited reductions over 90%. Furthermore, the removal efficiency of these metals were consistent over time as depicted in Figures 3 to 6. The metals iron and manganese exhibited apparent increases in the effluent as compared to the feed. The apparent increase is probably due to inputs from process amendments in the form of humates. These metals are generally considered to be environmentally benign and do not add to the overall level of contamination.

The process of metals removal during cyanide detoxification has been observed from other studies performed by Pintail. The mechanism involves the formation of biologically mediated neo-mineral phases, termed biomineralization. Biomineralization is the process by which microorganisms catalyze and mediate inorganic reactions. A biomineral is defined to include both biologically formed authigenic minerals (pyrite, etc.) and complex bio-stabilized materials that are often clay- or gel-like (Fe,Al) silicates, sulfides and oxides of variable composition that are presumed to be thermodynamically metastable phases. Formation of biominerals on the solid media within the reactors removes the soluble metal contaminants from the aqueous phase and immobilizes them into a more stable mineral phase. This is preferable to ion exchange reactions in which metals are not covalently bonded to the substrate and can desorb.

Table 2. Average metals (μg/L) after 7/23.

Analyte	Influent	Control	Effluent	% Reduction
Arsenic	361.3+ 5.8	339.2+ 12.9	26.3+ 13.7	92.7
Cadmium	23.3+ 4.4	21.5+ 2.5	<1.95	>91.6
Cobalt	121.2+ 49.0	139.2+ 75.6	46.5+ 12.9	61.6
Copper	133,016.7+ 30,286.7	136,250.0+ 30,626.4	24,733.3+ 14,027.6	81.4
Iron	1,409.7+ 848.59	803.7+ 319.8	1,473.5+ 614.58	-4.5
Manganese	12.2+ 9.0	3.7+ 2.2	69.8+ 30.2	-470.9
Mercury	164.0+ 13.3	139.2+ 24.6	7.2+ 4.1	95.6
Nickel	1596.7+ 102.7	1646.7+ 26.6	559.3+ 221.3	65.0
Selenium	227.3+ 56.6	228.5+ 18.5	53.9+ 45.2	76.3
Silver	940.8+ 774.5	534.5+ 367.1	51.3+ 87.7	94.6
Zinc	8,597.7+ 1,604.3	8,573.3+ 926.2	465.0+ 194.4	94.6

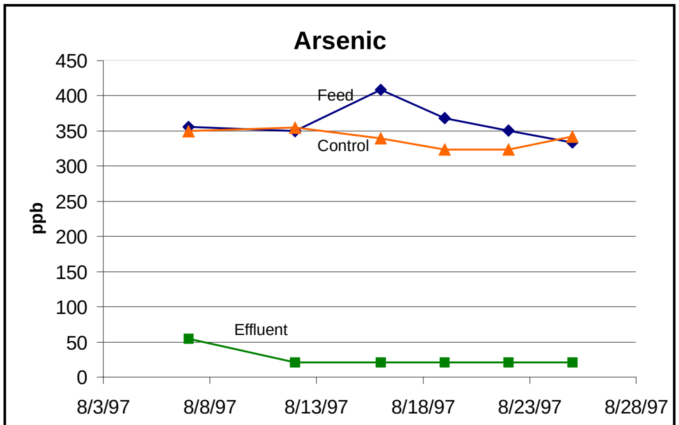

Figure 3

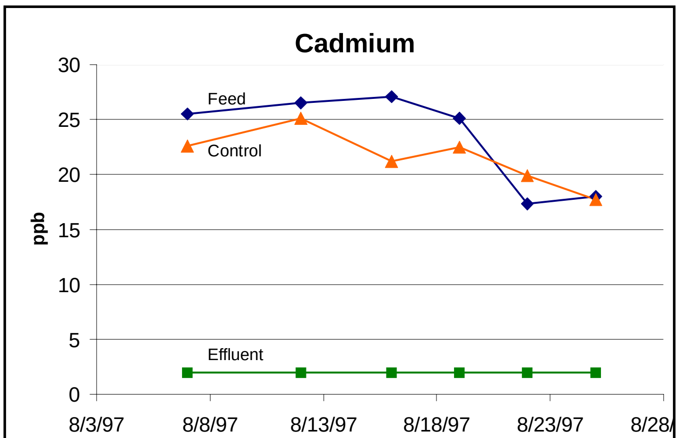

Figure 4

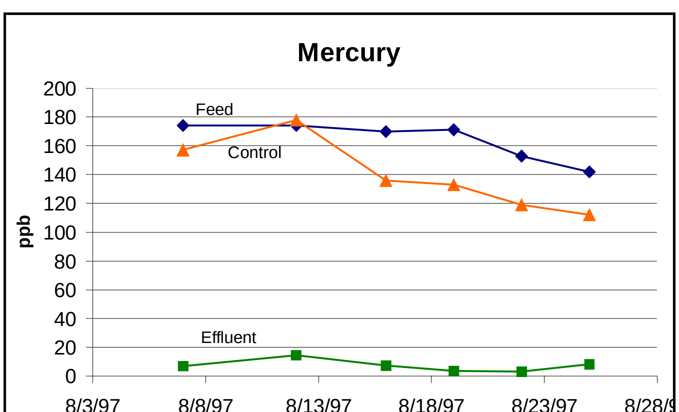

Figure 5

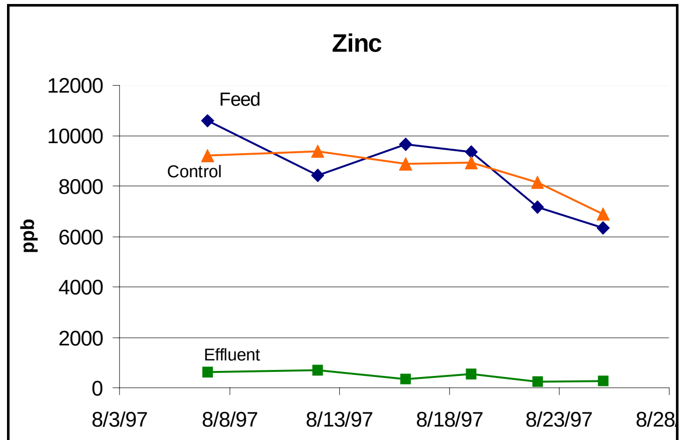

Figure 6

System Operability

The Aqueous Biocyanide Process was operated for two and one-half months. During the first 42 days (June 11 to July 22) system performance was variable, and occasional down-times were encountered. This was due to greatly higher cyanide and metals concentration in the feed than was encountered during bench-scale and design phases of the project.

Once optimized for the more concentrated feed, the system performed well with continuous operation for 35 days (July 23 to August 26). Specific process modifications included: (1) Periodic flushing of the anaerobic culture tank with clean water to remove built up levels of WAD cyanide; and (2) Adding additional tankage volume on the anaerobic system to increase residence time. These processes significantly improved the levels and consistency of WAD cyanide degradation. The ability to "re-engineer" the system in the field to accommodate the new waste stream is a positive attribute of the system.

One potential area of improvement would be to design a system that would minimize the channeling of fluids through the media. A common problem in many fixed media systems is the development of channels through preferred pathways in the media. This greatly reduces the available surface reaction area and reduces the efficiency of the system. There is some evidence that channeling did occur during the field tests.

Technology Status

Biotreatment processes for heap, tailings and process solution detox have been proven at other mine sites in a variety of environments. Biological processes are both site-specific and waste-specific and must be individually engineered and tested for each mine waste. Successfully adapting treatment bacteria to the spent ore environment is a key to developing successful bioremediation potential. Working with a biotreatment population that has been spe-

specifically adapted to the ore and augmented to improve cyanide metabolism insures that biotreatment will be effective.

Pintail has developed biological detoxification processes for the decomposition of cyanide and has applied them at several gold mines. The following case studies have been provided by Pintail Systems, Inc. The information and data contained within these case studies are not associated or validated by the USEPA SITE program.

Hecla Yellow Pine Mine

The first full-scale demonstration of *in situ* biotreatment processes took place at the Yellow Pine Mine near Yellow Pine, Idaho. Approximately 1.3 million tons of agglomerated oxide ore were treated. The goals of the project were to reduce WAD cyanide to 0.2 mg/L in leachate solutions, treat the source of the cyanide in the ore, and enhance gold production during detoxification operations. Furthermore, the site was a challenge to biotreatment processes due to low solution temperatures and extreme cold weather conditions throughout the operating season.

Results demonstrated complete cyanide detoxification (< 0.1 mg/L WAD cyanide) after a 5-month treatment period. In comparison, treatment time estimates for conventional chemical treatments (peroxide and sulfur dioxide/air) suggested two to four operating seasons for complete detoxification.

A secondary benefit of the biotreatment process was an enhanced gold production above predicted recoveries for water rinse operations. Biological solutions catalyze several biooxidation and biomineralization reactions that contribute to enhanced gold recovery.

Cyprus Copperstone Mine

An *in situ* cyanide detoxification was completed at the Cyprus Copperstone Mine located near Parker, Arizona. At this mine, 1.2 million tons of ore were biologically treated over a 70 day period. The goal was to reduce WAD and total cyanide from 30 to less than 0.2 mg/L in heap leachate solutions.

The rapid treatment (0.3 tons of solution per ton of ore) was attributable to high temperatures (80 to 90 degrees F) in the process solutions. Both WAD and total cyanides were reduced to less than 0.2 mg/L.

Disclaimer

While the technology conclusions presented in this report may not change, the data have not been reviewed by the EPA Quality Assurance/Quality Control office.

Sources of Further Information:

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