WATER TREATMENT ISSUES AND BIOTREATMENT SOLUTIONS FOR THE LANDUSKY MINE, MONTANA SPENT ORE HEAP LEACH PADS[1]

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Abstract. The Landusky gold heap leach mine in north central Montana is currently being reclaimed (see US Bureau of Land Management website http://www.mt.blm.gov). The majority of reclamation measures relate to minimizing current and future impacts to downstream waters. Management and seasonal treatment of approximately 2270 lpm (~600 gpm) of water is associated with the spent ore leach pads, primarily the 87 and 91 Pads.

Water in the 87 and 91 Pads have changed from a pH near 10, during mine operation and leaching, to the current pH of 6.5 to 5.5 and are still changing. As the Pad water pH becomes more acidic the dissolved co-contaminants of Al, Ni, Zn, Mn and Fe are starting to precipitate from solution. Past and present water management practices have included conventional water treatment using lime and ferric treatments and land application disposal (LAD) utilizing absorption by percolation through soils and nitrate-uptake by plants.

Pilot-scale tests of a biotreatment system configured to remove cyanide, nitrate and selenium (selenate) present in Pad waters, at concentrations of ~0.7 mg/L, ~260 mg/L and ~0.8 mg/L respectively, were successfully completed. A full-scale biotreatment system has been implemented at the Landusky site and operational parameters are being optimized. This paper describes aspects of the pilot-scale biotreatment test results, full-scale biotreatment system implementation and water pretreatment requirements demanded by the changing pad water chemistry.

Additional Key Words: selenium, cyanide, nitrate, bioremediation, microbes

Introduction

The Zortman-Landusky site in Montana contains ~850 million liters (~225 million gallons) of water in storage, with an additional contribution of ~568 million liters (~150 million gallons)

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annually. The bulk of the water is ponded under the heap material in lined heap leach pads with pH's ranging from ~5.5 to ~7. The water temperature is ~8° C and contains nitrate-N at ~260 mg/L, cyanide at ~0.7 mg/L (both Total and WAD cyanide are at approximately the same level) and selenium at ~0.8 mg/L (1). Contaminant effluent goals are nitrate <10 mg/L, cyanide <0.02 mg/L and selenium <0.05 mg/L.

From the Landusky side of the mountain all lower pads go into the barren pond, through and into Pad 87 and then over the hill to the Zortman side for treatment to Goslin Flats Land Application Disposal (LAD). Landusky 87 and 91 Pads contain the bulk of the contaminated waters requiring treatment. Currently, cyanide-containing water from Landusky pads 87 and 91 is being pumped to the Zortman Pond 82 and being treated with H_2O_2 before going to the LAD, Fig. 1.

Background

During biotreatability tests and throughout the on-site pilot-scale test, the Landusky 87 Pad site waters had three main contaminants of concern: nitrate, cyanide and selenium. Water temperature was a primary concern for treatment of these waters because of the requirement to treat these contaminants without heating. During the pilot tests, the 87 Pad water temperatures were ~7° C and water temperatures in the bioreactor system ranged from 5° to 16° C and averaged 8.3° C.

At the time of the pilot-scale tests, the general 87 Pad water appearance was clear with no precipitate or noticeable turbidity present. Pad water chemistry is summarized in Table 1. An initial treatability assessment optimized a non-pathogenic, proprietary culture for treatment of site waters. Denitrifying, selenium reducing and cyanide degrading microbes were supplemented with indigenous denitrifying bacteria to develop a robust microbial biofilm (2, 3, 4). Three separate, but complementary microbial mixes were prepared and optimized in the laboratory and scaled up at the site in existing tanks and carbon columns (5, 6).

Pilot-scale biotreatment of Pad 87 waters used three different flow rates to optimize nutrient composition and amount and to demonstrate nitrate, cyanide and selenium removal to target discharge criteria. Data was gathered to develop full-scale plant criteria, operational parameters and costing criteria.

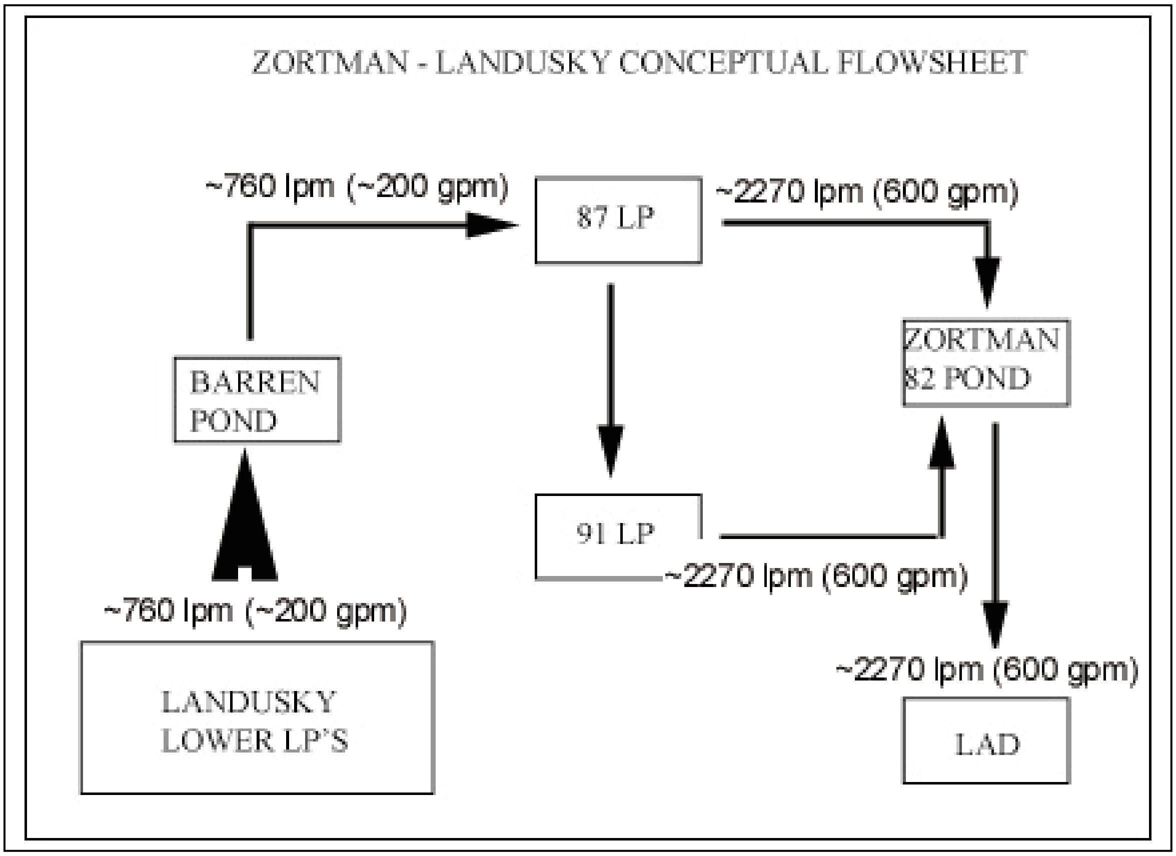

Figure 1. The Landusky water flow chart is based on seasonal pumping to pump up to ~570 million liters (~150 million gallons) annually to the LAD. There is also a capability to pump up to ~2650 lpm (~700 gpm) from the 87 Pad into the 91 Pad.

Modeling studies (7) predicted that changes in Landusky water chemistry could occur at some future time. Review of the predicted changes indicated that a water pretreatment system would be required to remove the expected precipitate from Pad waters before entering the bioreactor system. Because of the additional expense of a pretreatment system a decision was made to postpone pretreatment expenses until actually required.

Table 1. Pad 87 and 91 waters chemistry average values for the year preceding and during the pilot-scale test. (Values are in mg/L. pH is in standard units).

Parameter	87 Pad (Pre-test)	91 Pad (Pre-test)
pH	7.06	5.67
DO	1.53	N/A
TDS	8433	7930
Sulfate	4436	4170
NO_3-N	250	282.6
Se	0.85	1.17
CN-T	0.75	0.81
CN-W	0.72	0.69
Al	0.1	23.5
Fe	0.80	5.02
Ca	461	499
Mg	80.3	68.4
Mn	14.95	16.0
Ni	0.38	0.49
Zn	1.25	2.83

A biotreatment system was designed to treat ~1140 lpm (~300 gpm) year-round flow based on treatability assessments, pilot-scale testing, currently defined water chemistry and operational criteria to treat ~568 million liters (~150 million gallons) of leach pad water per year. A full-scale biotreatment system, consisting of three staged bioreactors, has been constructed over the existing liner at the Landusky 87 Pad.

During design construction of the full-scale biotreatment system 87 and 91 Pad recontouring and reclamation work continued. During this reclamation, water chemistry changes started to occur quite rapidly resulting in a decrease in pH. Water pH measurements varied from ~4.5 to ~6.7 for Pad 87 and increased in Pad 91 to ~6.6. A milky precipitate also formed in both 87 and 91 Pad waters. The precipitate did not affect the concentrations of nitrate, selenium or cyanide in either of the Pad waters. Jar testing and additional water chemistry analysis was completed to determine the pretreatment requirements and options to remove the precipitate from Pad waters.

Methods

Bioreactor Configuration**.**

Pilot-scale testing was conducted using existing on-site equipment to minimize testing costs. Applied Biosciences used a ~13.5 m^3 rectangular tank and a series of five 7’ x 8’ carbon tanks in carbon plant #3 to implement a site specific, staged treatment process. The reactors were filled with a microbial support material to support high density biofilm establishment.

Microbial Analysis/Characterization and Inocula.

Applied Biosciences completed all microbial analysis and characterization. All samples were stored at 4° C to inhibit microbial growth until analysis was performed. Baseline microbial characterization included microbial isolations and plate counts. Isolates were characterized by colony morphology and gram stain, and were slanted on appropriate media for future testing. Where appropriate, MIDI fatty acid profiles were used to fingerprint the microbial population to evaluate maintenance of appropriate microbial populations within the bioreactor. Microbial analysis and characterization data is used by Applied Biosciences to insure the microbial inocula established in site bioreactors is to predetermined, proprietary specifications. Microbial inocula for nitrate-, selenium- and cyanide-removal was supplemented with indigenous site microbes and delivered to the site for scale up.

Pilot-Scale Configuration.

87 Pad waters were fed directly into the rectangular tank and then through the 5-carbon tank system. This produced a very workable, but somewhat less than optimal treatment system.

Sample Point Description.

(1) Feed
(2) After the rectangular tank
(3) After 1 st carbon tank
(4) After 2 nd carbon tank
(5) After 3 rd carbon tank
(6) After 4 th carbon tank
(7) After 5 th carbon tank – Effluent

Sample Collection.

Samples were collected from each step in the treatment system. Samples were collected in sterile containers using methods to stabilize samples for the particular microorganism or analyte.

Samples for nitrate, nitrite, ammonia, selenium, total cyanide and weak acid dissociable (WAD) cyanide analyses were collected in sterile containers, filtered (0.45 μm), preserved and submitted to an EPA certified laboratory for analysis. Submitted samples included the following controls: a field duplicate, field cross contamination blank and calibration certification controls prepared with a known concentration of analyte. To help evaluate bioreactor performance, pH, dissolved oxygen (DO) and REDOX were measured at each sample point on a daily basis using calibrated instruments.

Jar Testing.

Jar test experiments used a laboratory six-paddle gang stirrer, Phipps & Bird Model #7790-400. The stirrer allowed for uniform conditions while the jars underwent rapid mixing, slow mixing and sedimentation. Experiments involved filling six beakers with 1 L water then adjusting the pH with either NaOH or lime. Samples were mixed for 2 min at 200 rpm, then mixed for 5 min at 10 rpm and then allowed to settle for 30 min. After settling, 100 ml samples were taken through the attached side tubes, allowing samples to be collected without disturbing the floc bed. Turbidity was measured with a factory calibrated turbidity meter and results reported in NTU (National Turbidity Units). Various flocculents were also examined, but were not found to be cost effective.

Results and Discussion

For long-term processes where native microbes are performing the degradations of interest, it is a good idea to configure a process around these microbes. This is because if they are present at high enough levels they can eventually replace introduced microbes over time, if given the right opportunities. This issue is addressed by the staged bioreactor system in the following ways. First, microbes naturally degrading nitrate in Landusky waters, have been isolated and combined with selenium reducing microbes and cyanide degrading microbes. Since selenium-reducing and cyanide-oxidizing microbes were not found in the Landusky waters a mixture of selenium reducing and cyanide degrading microbes were tested with site and other nitrate degrading microbes for development of stable biofilms, capable of removing these contaminants, from site waters in the laboratory.

A mixture of compatible microbes capable of growing together as a unit and performing mutually beneficial degradations can develop together as a unit or biofilm. The mixture of microbes used for the Landusky site has been demonstrated to be stable and effective in both laboratory and pilot-scale tests and can be thought of as a mixed microbe biofilm, performing the various contaminant transformations required. Analysis through plate counts and fatty-acid analysis showed that the biofilm established in the pilot-scale bioreactors was of the appropriate microbes and at the relative densities expected. Total microbial density in the bioreactor was $>10^{12}$ microbes per gram of support material.

Pilot-scale tests were conducted at three flow rates and ambient temperatures during September and October; average water temperatures were ~8.3° C. The 9.5 lpm (~2.5 gpm) flow rate was used to validate system performance. The 28.4 lpm (~7.5 gpm) flow rate was used to test various nutrients, as requested in the terms of the contract, including a balanced C:N:P and vitamin supplemented nutrient prepared by Applied Biosciences. Only when using the Applied Biosciences nutrient was the discharge criteria for nitrate-N met at this flow rate. Other nutrients were used in the same stoichiometric amounts. The 56.8 lpm(~15 gpm) flow rate was used to further optimize the nutrient amounts and addition times and to further develop full-scale capital and operational cost estimates. All flow rate tests were conducted for either 1 or 2 weeks following an equilibration period.

Nitrate, selenium and cyanide were removed from Landusky 87 Pad waters to or below discharge criteria during pilot-scale tests, Fig. 2, 3 & 4. Although the data is not presented here, analysis of nitrite and ammonia were made during the pilot-scale test period. Analysis showed that nitrite and ammonia levels were normally below 1.0 mg/L in both feed and effluent samples. However, both nitrite and ammonia levels tended to be slightly higher in effluents during the 28.4 lpm (~7.5 gpm) test period when nutrients with higher protein contents were examined.

No tracer studies were conducted to determine fates of contaminant components, but from past laboratory testing, using balanced nutrient sources, it is expected that the bulk of the nitrate was converted to nitrogen gas. Other possible nitrogen containing compounds or intermediates were not measured. Laboratory tests indicate that selenate and selenite were reduced to elemental selenium that remained in the bioreactor system and that cyanide was converted to carbon dioxide, nitrate and ammonia, Fig. 3 & 4.

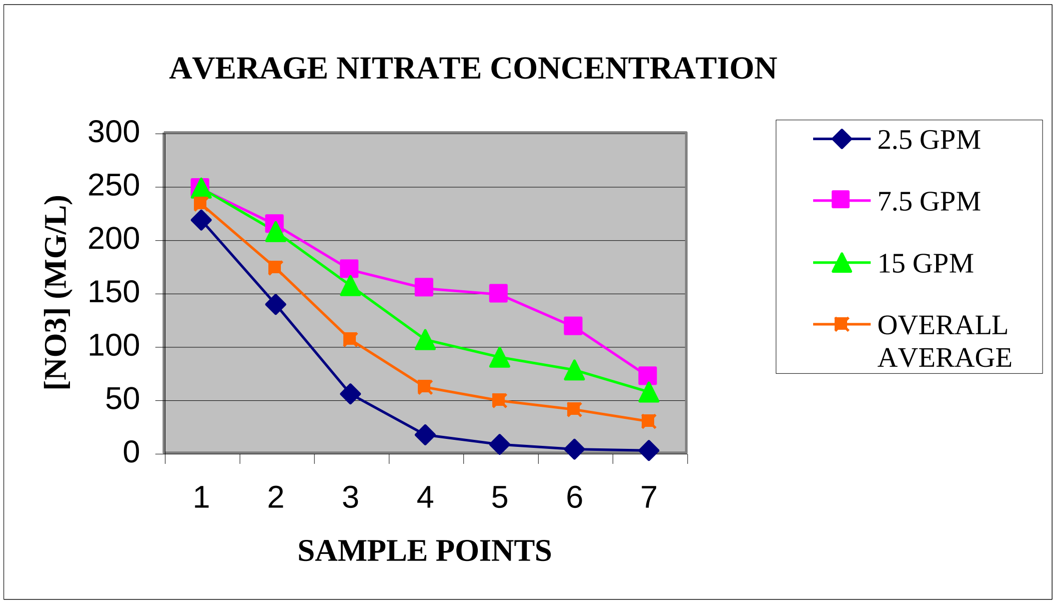

Figure 2. Average nitrate concentration at each sample point during pilot-scale tests.

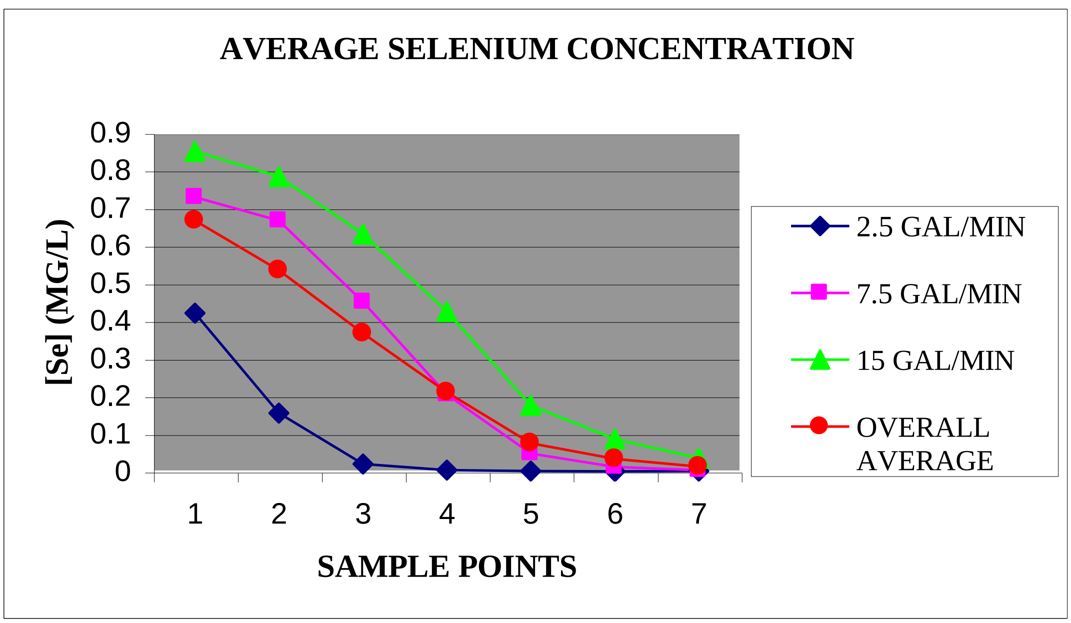

Figure 3. Average selenium concentration measured at each sample point in the bioreactor system.

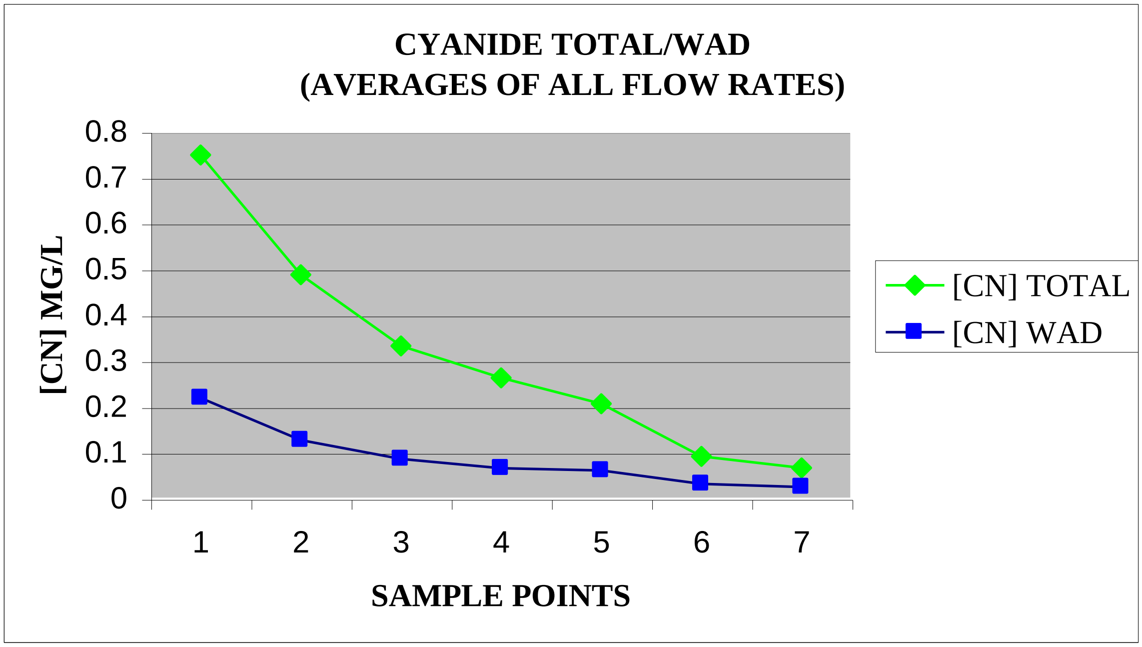

Figure 4. Average Total and WAD cyanide concentrations.

Nitrate and selenium removal bioprocesses require anaerobic conditions and cyanide biodegradation requires oxygen. These conditions were achieved at the biofilm level through the establishment of carefully selected microbial cultures that were demonstrated to form a robust biofilm in site waters. Based on laboratory and pilot-scale testing conducted in part under the EPA Mine Waste technology Demonstration Program (8), the Landusky biotreatment system at 0.8 mg/L selenium is expected to run ~15 years before harvesting of reduced selenium and bioreactor biofilm regeneration is required. This information is based only on accumulation of elemental selenium within the bioreactors.

Nutrient costs determined from pilot-scale tests were based on actual nutrient amounts required per 1,000 gal treated at the 2.5 and 15 gpm flows. The nutrient amounts and costing were similar to those previously determined by the EPA (8) - ~$0.55/1,000 gallons treated.

The process uses a balanced nutrient formulation, a portion of the nutrients delivered to the system provide energy needed to remove contaminants, provide electron donors and acceptors and to maintain the biofilm. Shorter contaminant contact times require the biofilm metabolic state be maintained at a higher activity level, which requires more energy, thus, slightly larger nutrient amounts. Nutrients are also required for synthesis of new cellular materials and there is a higher requirement at higher flow and thus higher metabolic rates. In some systems, bioconversions can be achieved with less complex nutrients such as methanol or simple sugars, these simpler nutrient formulations or compounds do not provide the proper C:N:P balance and other micronutrients required for long-term biofilm stability and optimal contaminant removal. With less than balanced nutrients, the biofilm must be in a state of steady die-off to provide missing nutrients to the living cells for cell growth and bioremediation.

To effectively address removal of these particular contaminants, nitrate must be addressed first since the nitrate oxygen is more easily reduced than the oxygen of selenate or selenite. Therefore, in order to reduce selenate and selenite in the presence of nitrate a process must be designed in a manner that addresses nitrate first. It is not necessary to remove all the nitrate before selenate and selenite can be reduced, but it is important that reduction oxidation (redox) potentials be such that nitrate is the primary target initially. Keeping the redox potential in this range somewhat reduces the effectiveness of both nitrate and selenium reduction. This can be minimized by using a staged bioreactor system with microorganisms selected specifically for a combined reduction of both nitrate and selenium.

The Landusky waters are further complicated by the presence of cyanide, present as complexed cyanide (total cyanide) and weak acid dissociable (WAD) cyanide. The biooxidation of cyanide requires oxygen. Again a staged bioprocess addresses this problem best using microbes that will degrade cyanide under low oxygen conditions. In a staged bioprocess, the reduction of nitrate and selenate/selenite provide the oxygen, on a microenvironment level, that microbes can use to oxidize cyanide. Again, as in the case of nitrate and selenium reduction, this process will not be effective as a process configured specifically for cyanide biooxidation, but can be effectively addressed in a staged bioprocess with sufficient retention time. Following the analysis of Landusky pilot-scale test data, a three-stage bioreactor system with an ~18 hour retention time was designed and built.

The sampling data available presented only snapshots of the water chemistries over time. Because of the value differences obtained for any one analyte at any particular location during any year, it is difficult to tell what has happened within the Pads. Averaged data are presented in Table 2. Jar test data and precipitate analyses helped clarify the nature of the precipitate occurring in the 87 and 91 Pad waters.

Modeling studies conducted by Robertson GeoConsultants Inc. (7), not presented here, predicted that changes in Landusky water chemistry could occur. Although the changes in water chemistry were predicted, they were undoubtedly influenced by the ongoing reclamation. would require installation of a water pretreatment system to remove the expected precipitate from Pad waters before entering the bioreactor system. Because of the additional expense of a pretreatment system a decision was made to postpone pretreatment expenses until actually required.

Precipitates in the 87 and 91 Pads were different in appearance, and analysis indicated that they also were different in composition. Two separate analyses, one precipitate/water sample collected after filling the bioreactors and another precipitate from Jar Test analysis, indicated that the 87 Pad precipitate was higher in Fe and Mg while the 91 Pad precipitate was higher in sulfate, Al, Mn and Zn, Figure 5. At the native pH neither the 87 nor 91 Pad precipitate contained significant amounts of Ni or Se.

Table 2. An overview of 87 and 91 Pad water chemistry changes.

Parameter	**87 Pad (Pre-test)**	**87 Pad (Post-test)**	**91 Pad (Pre-test)**	**91 Pad (Post-test)**
pH	7.06	4.5 to 6.7	5.67	6.55
DO	1.53	N/A	N/A	N/A
TDS	8433	8053	7930	7898
Sulfate	4436	4464	4170	4141
NO_3-N	250	250	282.6	283.7
Se	0.85	0.85	1.17	1.32
CN-T	0.75	0.86	0.81	0.748
CN-W	0.72	0.40	0.69	0.12
Al	0.1	24.9	23.5	13.4
Fe	0.80	1.01	5.02	4.82
Ca	461	461	499	547
Mg	80.3	179	68.4	78.4
Mn	14.95	31.5	16.0	16.0
Ni	0.38	0.84	0.49	0.47
Zn	1.25	3.19	2.83	2.83

Figures 6 and 7 show the amount of additional precipitate that can potentially be removed from 87 and 91 waters through treatment by settling/filtration and or pH adjustment. Settling times of 24 hours demonstrated that much of the precipitate present at native pH's can be removed. As can be seen in Figure 6 & 7, significant additional amounts of Al, Fe, and Zn can be removed through pH adjustment of 87 Pad waters. Similar results were observed with 91 Pad waters with the additional benefit of a greater sulfate removal. pH adjustment of 87 and 91 waters did not increase Se removal.

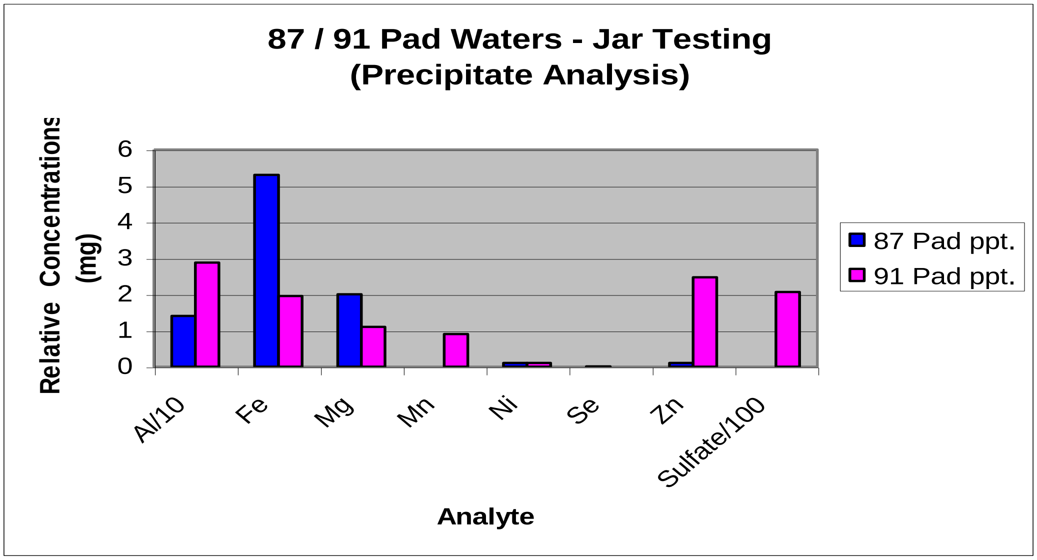

Figure 5. 87 and 91 Pad precipitate comparison.

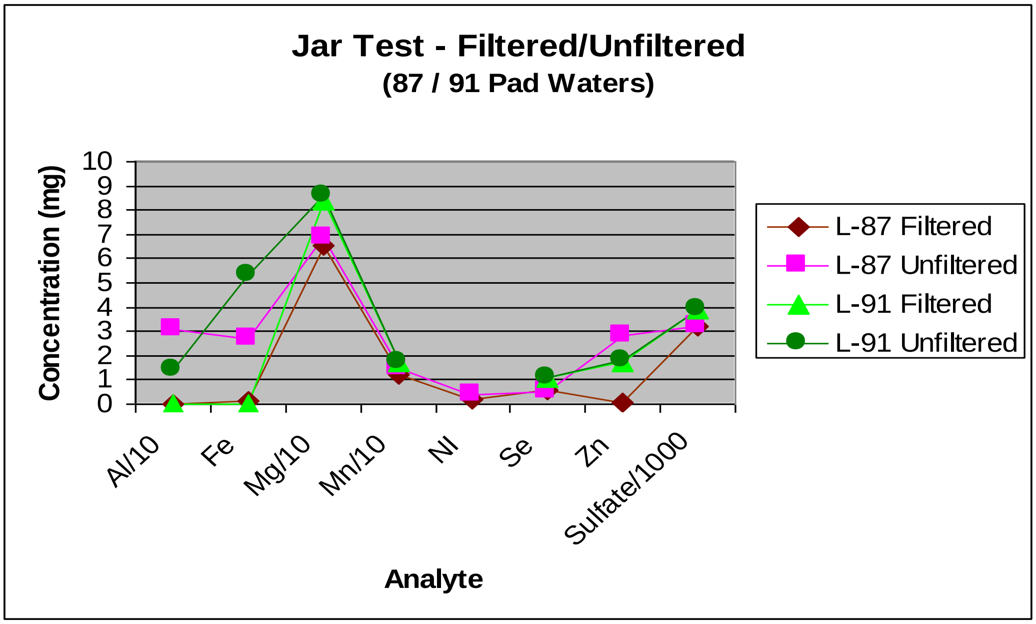

Figure 6. Jar Test analysis showing a comparison of filtered and unfiltered 87 and 91 Pad waters.

Figure 8 shows the turbidity decreases obtained through pH adjustment with NaOH or lime. Correlation of pH adjustment with analyte concentration and turbidity indicates that a pH of 8.0 for 87 Pad waters or a pH of 8.5 for 91 Pad waters removes >90% of the metals that can be

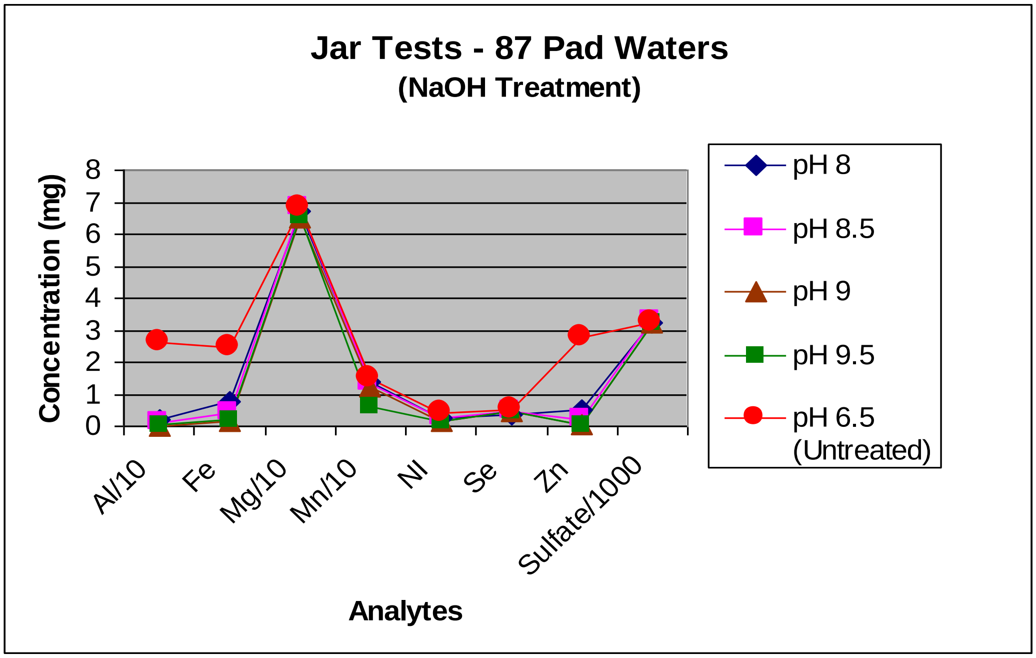

Figure 7. Jar Testing of Pad 87 Waters showing the effect of pH on removal of selected analytes.

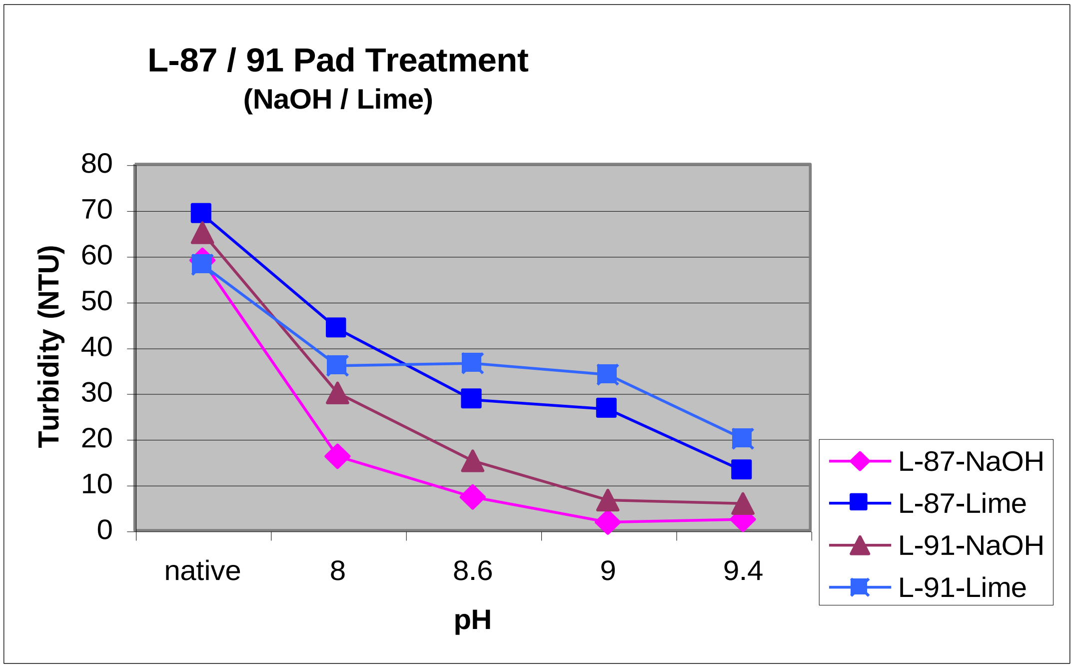

Figure 8. 87 and 91 Pad NaOH and Lime treatment Comparisons.

removed through pH adjustment. Testing with combinations of NaOH and lime with various Nalco polymers including 8108 and 8105 showed no additional benefit on analyte removal. Additionally, it is readily evident from Figure 8, that larger amounts of lime, thus a higher pH would be required to reach the same turbidity levels/contaminant removals as obtained with smaller amounts of NaOH and lower pH.

Conclusions

For best performance of any biotreatment or chemical treatment system, a constant-chemistry water feed must be supplied. Since the biological treatment systems tested at the Landusky use live microorganisms, this is particularly important. To achieve a constant feed for the Landusky bioreactor system, with the recent and expected water chemistry changes, a pretreatment system will ensure precipitate removal and a relatively constant biotreatment system feed water. Additional conclusions:

- Pilot-scale tests of the Applied Biosciences biotreatment system using Landusky 87 Pad waters was successful
- Nitrate, cyanide and selenium removal to target discharge criteria was demonstrated at ambient site water temperatures
- A biotreatment time long enough to remove nitrate also removed cyanide and selenium to target discharge criteria – target contaminant levels were achieved at all flow rates
- Pilot testing indicated that a retention time of 18 hr would be sufficient to reduce contaminant concentrations to target levels
- A NaOH-based pretreatment system is recommended to minimize sludge formation prior to processing water through the biotreatment system – a lime-based pretreatment system would reduce the amount of sodium in the Landusky water system

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