A Large, Multi-Cell, Ecologically Engineered Passive Treatment System for Ferruginous Lead-Zinc Mine Waters

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Abstract A research-grade passive treatment system was constructed to receive 1000 L/minute of mine water from abandoned boreholes (pH 5.95, net alkalinity 29 mg/L $CaCO_3$, Fe 192 mg/L, Zn 11 mg/L, Cd 17 µg/L, Pb 60 µg/L and As 64 µg/L). The 2-ha system includes an oxidation pond followed by parallel treatment trains of aerobic wetlands, vertical flow bioreactors, re-aeration ponds, and horizontal-flow limestone beds and a final polishing wetland. Final effluent waters had pH >7 and contained < 1 mg/L total Fe and < 0.1 mg/L total Zn, with concentrations of Cd, Pb and As below detectable limits.

Key Words hard rock mining, metal mining, acid mine drainage, natural treatment systems

Introduction

This paper describes the initial evaluation of an innovative, ecologically engineered passive system designed to treat abandoned ferruginous Pb-Zn mine waters at the Tar Creek Superfund Site, part of the historic Tri-State Mining District (TSMD) of Oklahoma, Kansas and Missouri, USA. Significant quantities of Pb and Zn were produced from the TSMD from the 1890s through the 1960s. By the early 1970s when mining ceased, two and nine million tons of Pb and Zn, respectively, had been produced (McKnight and Fischer 1970). Due to extensive degradation of land and water resources and resulting risks to human and ecological health, the Tar Creek Superfund Site (representing the Picher Mining Field and the Oklahoma portion of the TSMD) was proposed for the U.S. Comprehensive Environmental Response, Compensation and Liability Act (Superfund) National Priorities List in 1981 and received final listing in 1983 (USEPA 2010).

During mining, large capacity dewatering operations pumped approximately 50,000 $m^3\ d^{-1}$ of water from the mines (Reed et al. 1955). Upon decline and cessation of mining, groundwater began to accumulate in the mine voids. By late 1979, metal-rich waters began to discharge via artesian pressure into Tar Creek and its tributaries. The first documented discharges of mine drainage were at a location near southeast Commerce, OK (Oklahoma Water Resources Board 1983) and were subsequently identified for passive treatment implementation (Nairn et al. 2009, 2010). These discharges, containing elevated Fe, Zn, Cd, Pb and As concentrations, represent about one-fifth of the contaminant mass loading from artesian discharges in the watershed. The multi-cell system is the first application of any full-scale mine water treatment at this Superfund site and in the TSMD.

Methods

For this study, periodic water quality and quantity data collection efforts for the subject discharges began in 1998, with regular monthly sampling beginning in 2004 and continuing to the present. The targeted discharges have circum-neutral pH (5.96 ± 0.06), total alkalinity of 405 ± 13 mg/L as $CaCO_3$ and combined flow rates of up to 1000 L/minute. Metals and sulfate concentrations are elevated above expected levels and degrade the receiving waters (LaBar et al. 2010). Design and construction details for the passive treatment system are summarized in Figure 1 and Table 1. The system consists of ten distinct process units including two parallel trains. Waters from three discharges (SA, SB, and SD) flow into an initial oxidation pond (1), followed by parallel surface-flow aerobic wetlands/ponds (2N and 2S), vertical-flow bioreactors (3N and 3S), re-aeration ponds (4N and 4S), horizontal-flow limestone beds (5N and 5S), and are recombined in a single polishing pond/wetland (6). Water first entered the system in December 2008 and monthly monitoring at all process unit influent and effluent locations began in January 2009. Methods and additional research efforts are further summarized in Nairn et al (2009, 2010).

***Table 1** Summary of process units, primary targeted water quality parameters and design function for the passive treatment system*

Process unit	Targeted parameter	Function
Oxidation pond (1)	Fe	• Oxidation, hydrolysis and settling of iron oxyhydroxide solids • Trace metal sorption
Surface-flow wetlands/ponds (2N/2SS)	Fe	• Solids settling
Vertical-flow bioreactors (3N/3S)	Zn, Pb, and Cd	• Retention of trace metal sulfides via reducing mechanisms
Re-aeration ponds (4N/4S)	Oxygen demand and odor	• Wind- and solar-powered re-aeration • Stripping oxygen demand and H_2S • Adding O_2
Horizontal-flow limestone beds (5N/5S)	Zn, Mn and hardness	• Final polishing of Zn as $ZnCO_3$ • Final polishing of Mn as MnO_2 • Adding hardness to offset bioavailability of any remaining trace metals
Polishing pond/wetland (6)	Residual solids	• Solids settling • Photosynthetic oxygenation • Ecological buffering

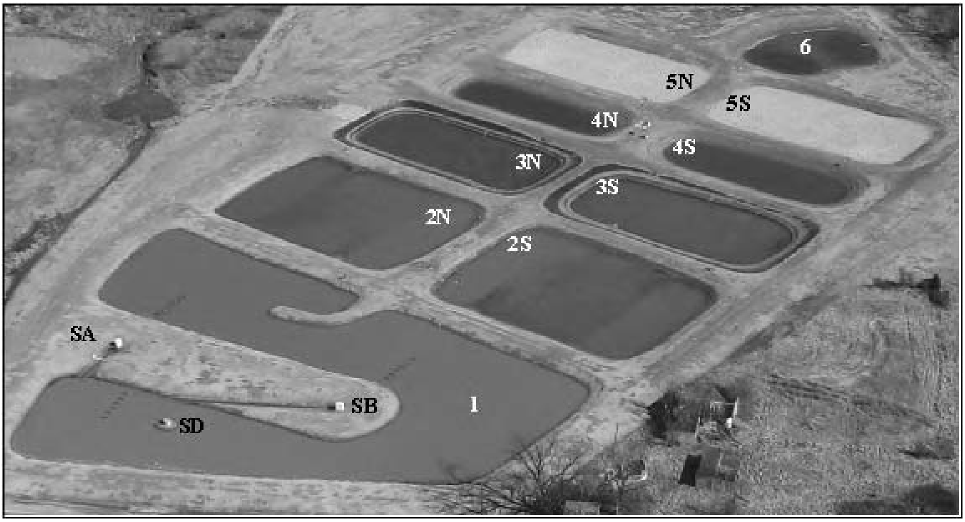

***Figure 1** Oblique aerial photograph of the first full-scale passive treatment system in the Tri-State Mining District taken February 4, 2009 showing mine drainage discharges and individual process unit designations*

Results and Discussion

In the year of operation, the passive treatment system performed as designed from a water quality perspective (Table 2). The net alkaline nature of the mine waters was maintained throughout the system as target metals were removed from solution. Due in part to degassing of elevated CO_2 concentrations in the artesian discharges, pH increased from <6 to >7 at final discharge. Coupled oxidative and reductive processes lead to fluctuating DO and ORP values throughout the system and a demonstrated seasonality as the rates of biological processes varied. The remaining discussion focuses on specific constituents of interest.

During this initial period of performance, flow-weighted mean total Fe concentrations decreased from 177 ± 2.33 mg/L to 0.57 ± 0.21 mg/L at the final outflow (Table 3). The great majority

***Table 2** Selected mean water quality data from artesian discharges and process unit effluents. All data are mg/L except pH (standard units) and alkalinity (mg/L as $CaCO_3$). BDL = below detection limits*

		pH	DO	Alk.	Fe	Zn	Cd	Pb	Mn	As	Ni	SO_4^{-2}
Discharges	SA	6.01	1.17	402	171	8.34	0.015	0.065	1.47	0.062	0.94	2209
	SB	5.97	1.04	371	178	8.15	0.016	0.069	1.51	0.064	0.94	2264
	SD	5.99	1.27	386	181	9.00	0.015	0.070	1.62	0.061	0.96	2343
Cell 1		6.10	3.83	161	30	6.71	0.003	0.029	1.48	BDL	0.87	2173
Cell 2	N	6.51	7.94	135	4.4	5.76	BDL	BDL	1.50	BDL	0.81	2199
	S	6.40	7.00	131	4.4	5.97	BDL	BDL	1.58	BDL	0.82	2216
Cell 3	N	6.85	0.35	262	1.3	0.24	BDL	BDL	1.36	BDL	0.045	2311
	S	6.84	0.28	242	1.1	0.28	BDL	BDL	1.35	BDL	0.042	2091
Cell 4	N	7.20	3.86	236	0.87	0.16	BDL	BDL	1.38	BDL	0.035	2076
	S	7.10	3.51	232	0.92	0.23	BDL	BDL	1.44	BDL	0.042	2099
Cell 5	N	6.98	0.65	229	0.57	0.087	BDL	BDL	1.28	BDL	0.033	2064
	S	6.95	0.42	227	0.63	0.109	BDL	BDL	1.40	BDL	0.033	2195
Cell 6		7.11	2.65	224	0.57	0.096	BDL	BDL	1.38	BDL	0.035	2057

of total iron removal occurred in the initial oxidation pond and parallel surface-flow aerobic wetlands/ponds, with mean removal rates of 21 ± 2.8 g $m^{-2}d^{-1}$ and 3.7 ± 3.4 g $m^{-2}d^{-1}$, with the latter rate being load-limited. A statistically significant relationship between area-adjusted iron removal rate and effluent water temperature did exist for this process unit ($r = -0.83$, $p < 0.01$) indicating greater removal under colder conditions as reported by Hedin (2008).

Flow-weighted mean total Zn concentrations decreased from 8.29 ± 0.08 mg/L to 0.10 ± 0.04 mg/L for the entire system. Zinc was targeted for retention via several mechanisms in individual process units of the treatment system, including sorption (Cell 1), ZnS precipitation (Cells 3N and 3S), and $ZnCO_3$ formation (Cells 5N and 5S). In the initial oxidation pond, Zn concentrations decreased to 6.71 ± 0.37 mg/L, representing an area-adjusted removal rate of 0.28 ± 0.05 g $m^{-2}d^{-1}$. Retention likely occurred through co-precipitation and sorption to iron oxyhydroxide precipitates. The tendency of these processes to occur at circum-neutral pH is well documented (e.g., Dzombak and Morel 1990). In the vertical-flow bioreactors, Zn concentrations decreased from 5.76 ± 0.81 mg/L to 0.24 ± 0.25 mg/L in Cell 3N and from 5.97 ± 0.87 mg/L to 0.28 ± 0.25 mg/L in Cell 3S. These cells were designed specifically to remove Zn and other trace metals through reductive mechanisms, converting free Zn and SO_4^{-2} to ZnS. Removal rates were much higher in these cells than in cell 1 (1.46 ± 0.27 and 1.45 ± 0.21 g $m^{-2}d^{-1}$ in cells 3N and 3S, respectively). Biological sulfate reduction in vertical-flow bioreactors is well-documented as a metal removal mechanism (e.g., Neculita et al. 2007) and was the primary Zn retention processes for this passive treatment system. In the horizontal-flow limestone beds, Zn concentrations decreased from 0.16 ± 0.21 mg/L to 0.09 ± 0.11 mg/L in Cell 5N and from 0.23 ± 0.23 mg/L to 0.11 ± 0.12 mg/L in Cell 5S. Relatively low influent Zn concentrations resulted in load-limited removal rates of 0.03 ± 0.04 and 0.02 ± 0.02 g $m^{-2}d^{-1}$ for cells 5N and 5S, respectively. These cells were designed to remove Zn through mechanisms specific to proper pE-pH conditions (e.g., Nuttall and Younger 2000). Although pE values (converted from field ORP readings) were typically within the needed range for amorphous $ZnCO_3$ and ZnO formation (-0.1 to +0.9 v), pH values were 6.95—7.20, below the needed pH values of 7.5—8.2.

Other metals of specific interest in these waters were Cd, Pb, and As. All three were removed to below detection limits (0.64, 19.5 and 22 µg/L, respectively) before the outflow of the second process units, presumably through sorptive processes. Although the vertical-flow bioreactors were designed to remove Cd and Pb as well as Zn, Cd and Pb rarely remained in measureable concentrations at this stage of the treatment system. The other trace metal found in significant concentrations in these waters was Ni. A small percentage (<10%) of Ni was removed through co-precipitation and sorption in Cell 1. However, the majority of Ni (≈ 95%) was removed via reductive mechanisms in the vertical-flow bioreactors. The concentration decreased from 0.81 ± 0.03 mg/L to 0.05 ± 0.04 mg/L in Cell 3N and from 0.82 ± 0.04 mg/L to 0.04 ± 0.03 mg/L in Cell 3S. Ni concentrations did not decrease significantly in the remainder of the system, with final system effluent concentrations of 0.035 ± 0.01 mg/L.

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