

PERFORMANCE OF AN ECOLOGICALLY-ENGINEERED MULTI-STAGE ACID MINE DRAINAGE AND MUNICIPAL WASTEWATER PASSIVE CO-TREATMENT SYSTEM¹

W.H. Strosnider², B.K. Winfrey and R.W. Nairn

Abstract: A laboratory-scale, four-stage continuous flow reactor system was constructed to test the viability of high-strength acid mine drainage (AMD) and municipal wastewater (MWW) passive co-treatment. Synthetic AMD of pH 2.6 and acidity of 1870 mg/L as CaCO₃ equivalent containing a mean 46, 0.25, 2.0, 290, 55, 1.2 and 390 mg/L of Al, As, Cd, Fe, Mn, Pb and Zn, respectively, was mixed at a 1:2 ratio with raw MWW from the City of Norman, Oklahoma and introduced to the system which had a total residence time of 6.6 days. During the 135-d experiment, dissolved Al, As, Cd, Fe, Mn, Pb and Zn concentrations were consistently decreased by 99.8, 87.8, 97.7, 99.8, 13.9, 87.9 and 73.4 %, respectively, pH increased to 6.8 ±0.1, and net-alkaline effluent produced. At a wasting rate of 0.69 % of total influent flow, the system produced sludge with Al, As, Cd, Cr, Cu, Fe, Pb and Zn at least an order of magnitude greater than the theoretical influent mix, which presents a possible environmental liability if not sustainably recovered or disposed. These results indicate that passive co-treatment is a promising approach that can be optimized and applied to improve water quality with minimal use of fossil fuels and refined materials.

Additional Key Words: arsenic, aluminum, iron, lead, zinc, cadmium, nickel, chromium, aqueous geochemistry, water quality, and sewage

¹ Paper was presented at the 2009 National Meeting of the American Society of Mining and Reclamation, Billings, MT, *Revitalizing the Environment: Proven Solutions and Innovative Approaches* May 30 – June 5, 2009. R.I. Barnhisel (Ed.) Published by ASMR, 3134 Montavesta Rd., Lexington, KY 40502.

² William H. Strosnider, Graduate Research Associate, and Robert W. Nairn, Associate Professor, Center for Restoration of Ecosystems and Watersheds, School of Civil Engineering and Environmental Science, University of Oklahoma, 202 West Boyd St. Norman, OK 73019, Brandon K. Winfrey, Graduate Research Assistant, Environmental Science and Technology Department, University of Maryland, 1109 H.J. Patterson Hall, College Park, MD 20742. Proceedings America Society of Mining and Reclamation, 2009 pp 1412-1432
DOI: 10.21000/JASMR09011412
<http://dx.doi.org/10.21000/JASMR09011412>

Introduction

Background

Treatment of acid mine drainage (AMD) and municipal wastewater (MWW) is central to maintaining global water resource quality. Untreated AMD causes water quality degradation in coal and metal mining regions worldwide (e.g., Bell and Donnelly, 2006). Discharges of untreated MWW degrade water resources in many developing nations (e.g., Gadgil, 1998; Kivaisi, 2001, Nelson et al., 2001). In developed nations, where MWW is generally addressed actively, treatment consumes considerable financial, material and energy resources (Muga and Mihelcic, 2008). Compared to passive methods, conventional MWW and AMD treatment are energy-intensive with higher operational and maintenance costs (Nelson et al., 2001; Younger et al., 2002; Muga and Mihelcic, 2008).

The passive treatment of AMD often requires an organic substrate for bacterial sulfate reduction (BSR) and other processes. MWW treatment can require electron acceptors for bacterially-mediated oxidation of carbon substrate, chemicals for pathogen removal, and physical or chemical filtration or flocculation for solids removal.

The possibility of using sulfate reducing bacteria (SRB) to treat AMD was first suggested by Tuttle et al. (1969). Numerous carbon sources, including horse and cow manure, chicken litter, ethanol, methanol, and municipal sewage sludge and compost, have been successfully applied to encourage BSR (Waybrant et al., 1998; Tsukamoto and Miller, 1999; Younger et al., 2002; Benner et al., 2002; Cocos et al., 2002; Watzlaf et al., 2000; McCollough et al., 2006; Zamzow et al., 2006; Luo et al., 2008). Generally, BSR is coupled with limestone dissolution in passive treatment cells such as reducing and alkalinity producing systems (RAPS) to maximize alkalinity generation and metals retention. However, BSR alone can be effective as Benner et al. (2002) and Cocos et al. (2002) have demonstrated.

Sewage sludge has been used as a BSR carbon source to treat AMD. Waybrant et al. (1998) observed sewage sludge to encourage the highest levels of sulfate reduction over seven other organic carbon sources. However, multiple studies have noted that mixtures of sewage sludge with multiple organic carbon sources generally promote higher sulfate reduction rates than single sources (Waybrant et al., 1998; Harris and Ragusa, 2000; McCullough et al., 2006).

MWW treatment must address suspended solids, oxygen demand and phosphorus concentrations. Suspended solids can be removed by biodegradation, settling, or filtration

through many types of media (Metcalf and Eddy, 1991). Oxygen demand is a function of the concentration of biodegradable organic matter, nutrients, and readily oxidized constituents. Oxygen demand can be lowered by bacterial respiration or reaction of labile organic matter and nutrients. For example, SRB and denitrifying bacteria utilize short-chain labile organic carbon thus lowering oxygen demand. Elevated reactive phosphorus levels are also ubiquitous with MWW. Reactive phosphorus levels can be decreased by flocculation with free Al(III) and Fe(III) ions (Metcalf and Eddy, 1991; Omoike and Vanloon, 1999).

Previous Co-Treatment Studies

Despite the amount of peripheral research regarding MWW and AMD, only one documented system has been intentionally constructed to simultaneously treat these effluents (Johnson and Younger, 2006). McCullough et al. (2008) documented fortuitous water quality improvement and BSR in an evaporation pond in which high-strength AMD was introduced to secondary MWW. The Johnson and Younger (2006) single-stage constructed wetland treatment system successfully improved the water quality of weak secondary MWW effluent (5-day biochemical oxygen demand of ~14 mg/L) and relatively weak (net-alkaline with ~3 mg/L Fe) AMD. The authors are not aware of any high-strength AMD and raw MWW co-treatment investigation, which is essential to addressing the approach's feasibility and applicability.

Methods

Experimental Design

The experimental setup involved four serial unit processes in quadruplicate (Fig. 1 and 2). The first unit processes are primary clarifiers where MWW and AMD mix, react, and solids settle. The second and third unit processes emulate a RAPS for dissolved oxygen (DO) stripping, alkalinity generation, and metal sulfide formation. The final unit processes are aerobic wetland mesocosms for Fe then Mn oxidation and precipitation. Each unit process was connected to the next via clear vinyl tubing and sampled at its outflow.

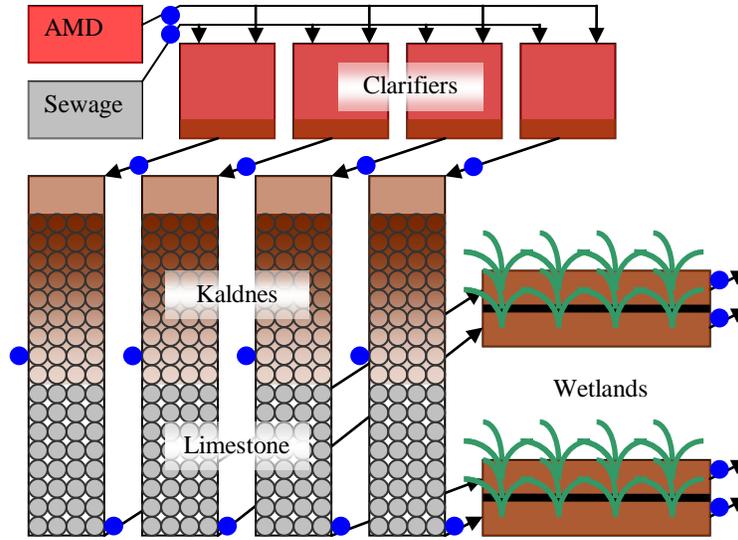


Figure 1: Conceptual experimental layout. Blue dots indicate sampling points.

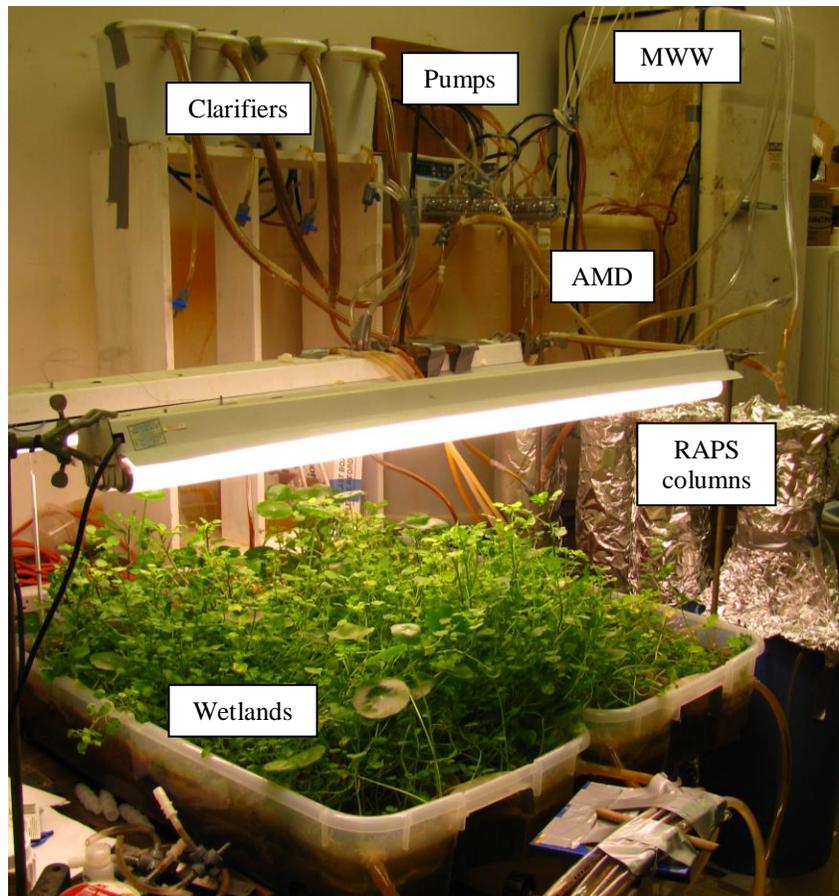


Figure 2: Photo of laboratory setup showing AMD and MWW reservoirs, peristaltic pumps, clarifiers, RAPS emulsion columns, grow-lights, and wetlands.

The primary clarifier unit process was sized for a relatively high retention time of 32 hr to allow for thorough solids settling and to encourage BSR (Table 1). Retention times of 1.5 – 2.5 hr are typical for MWW primary clarification systems (Metcalf and Eddy, 1991; Frigon et al. 2006). However, retention times of around 6 hr or greater commonly exist (Anderson, 1981; Gernaey et al. 2001). Four-cm deep single transverse baffles and 2.5-cm radius semi-circular weirs served as the physical structures in the 5-L LDPE basins that comprised this unit process. Sludge was wasted from the bottom of the clarifiers under gravity flow with a barbed HDPE T-connector attached to an HDPE valve and clear vinyl tubing.

Table 1. Design details and residence times for each unit process

Unit Process	Surface Area cm ²	Total Volume cm ³	Porosity	Void Volume cm ³	Residence Time hr
Clarifier	405	5020	1	5020	32
Kaldnes	154	8230	0.82	6750	42
Limestone	154	5850	0.5	2920	18
Wetland	5100	10600	1	10600	67
Overall	5810	29700		25300	159

The RAPS emulation columns were 91.5 cm in height and 12.5 cm in diameter. The bottom 38 cm of the columns were filled with high quality (>90% CaCO₃) limestone washed of all fines and separated by sieve analysis adapted from ASTM D422 with the fraction passing a 2.54-cm sieve yet retained by a 1.27-cm sieve. The remaining top 53.5 cm of the columns were packed with Kaldnes K3 biofilm media to provide SRB attachment surface. Kaldnes K3 media are polyethylene high surface area (500 m²/m³) components that are typically used in moving bed biofilm wastewater and drinking water treatment (Rusten et al., 2006). Following Pruden et al.'s (2007) findings of the importance of inoculation to sulfate reducing bioreactor performance, the Kaldnes zone was inoculated with 100 mL of RAPS substrate from two mature passive coal mine AMD treatment systems in Pittsburg and Latimer Counties, OK. Each column was wrapped in aluminum foil to emulate the lightless conditions in RAPS substrate.

The aerobic constructed treatment wetland mesocosms were two shallow LDPE storage containers. Each wetland was bisected longitudinally with plastic to create the necessary four treatment trains. Wetland soil was collected from an existing constructed mitigation wetland at

the Midwest City, Oklahoma MWW Treatment Plant. The mesocosms were surface flow and planted with *Hydrocotyle ranunculoides* and *Nasturtium officinale*. The wetlands were placed under timed grow-lights on a 12 hr/d cycle.

Temperature, pH, and specific conductance (SC) were determined using an Orion 1230 multimeter. An Accumet AR60 multimeter was used to determine DO concentrations. BOD was determined using the 5-day BOD Test following standard methods (APHA, 1998). Alkalinity titrations were conducted in accordance with standard methods (APHA, 1998) and Hach Method 8203 (Hach, 2006). Dissolved metals samples were filtered through 0.45- μ m nylon filters prior to preservation. Total and dissolved metals samples were preserved with concentrated trace metal grade nitric acid and stored at 4°C until microwave acid digestion following EPA method 3015. Digested total metals samples were filtered through 0.45- μ m nylon filters prior to analysis. Metals samples were analyzed via a Varian Vista-Pro® simultaneous inductively coupled plasma-optical emission spectrometer (ICP-OES) following EPA method 6010. Samples for anion analyses were stored at 4°C until filtered through Dionex OnGuard® II H cartridges and 0.2- μ m nylon filters. A MetrOhm® 761 compact ion chromatograph unit was used to quantify anion concentrations following EPA method 300.

Raw MWW collected after grit screening at the Norman, OK MWW treatment plant and synthetic AMD approximating that found at Cerro Rico de Potosí, Bolivia were introduced to the system at a 2:1 ratio (MWW:AMD) with peristaltic pumps at a combined flow rate (3.8 L/d) to produce an 18-hr residence time in the limestone stage, which is greater than the recommended minimum 15-hr design residence time suggested for anoxic limestone drains and the limestone drain components of RAPS (Younger et al., 2002). The system was gravity flow from the first (clarifier) to the last (wetland) unit processes. MWW was collected weekly, homogenized during pumping, and refrigerated at 4°C before introduction to the system. AMD was prepared weekly and stored at room temperature (20°C) until use. All unit processes were maintained at room temperature throughout the experiment. Sludge was wasted from the clarifiers in varying amounts at irregular intervals to investigate the influence of wasting rate on sludge total metal concentrations. Each treatment train continuously handled the mixed influent from March 6 to July 21, 2008 (135 d).

Data Analysis

Prior to statistical testing the data from each unit process was condensed by averaging each sampling period. This condensed data set was then used for statistical calculations, such as the grand mean. All data sets were tested for normality with the Anderson-Darling test and similarity of variance. Due to the prevalence of normality and equal variances when comparing the grand means, student's t-tests were applied. All statistical testing was completed within Microsoft® Excel to achieve 95% confidence.

Results and Discussion

Standard Operational Performance

Influent Characteristics. Influent characteristics were relatively uniform throughout the experiment (Tables 2 and 3). The high strength synthetic AMD was similar in composition to that generated in the base/precious metal mining district of Cerro Rico de Potosí, Bolivia (Strosnider et al., 2007). The mean alkalinity, biochemical oxygen demand (265 ± 94 mg/L), chloride (69 ± 3.8 mg/L), and sulfate concentrations place the MWW between the “medium” and “strong” designations of MWW created by Metcalf and Eddy (1991).

Table 2. Grand mean influent AMD and MWW physiochemical properties and sulfate concentration; n=10 for all except where noted.

	pH	DO	SC	Alkalinity	Net Acidity ^δ	Net Acidity ^τ	SO ₄ ²⁻
	s.u.	mg/L	uS/cm	mg/L as CaCO ₃ equivalent			mg/L
MWW	7.67	0.98	951	288	-287	-268	70
<i>s.d.</i>	<i>0.12</i>	<i>0.49</i>	<i>66</i>	<i>20</i>	<i>20</i>		<i>16</i>
AMD	2.60	7.69	3010	0	1870	1810	1920
<i>s.d.</i>	<i>0.04</i>	<i>0.64</i>	<i>112</i>	<i>0</i>	<i>91</i>		<i>140</i>

^δ Calculated with dissolved metal concentrations

^τ Calculated with total metal concentrations (n = 2)

Table 3. Grand mean influent AMD and MWW dissolved^δ (n=10) and total^τ (n=2) metal concentrations.

	MWW ^δ		MWW ^τ	AMD ^δ		AMD ^τ
	mean	s.d.	mean	mean	s.d.	mean
mg/L						
Al	0.108	0.018	0.692	45.8	3.2	46.3
As	<0.022		<0.022	0.25	0.14	0.38
Ca	39.6	4.5	40.5	82.8	3.5	90.6
Cd	0.0010	0.0003	0.0009	2.02	0.08	2.29
Cr	0.0036	0.0045	0.0066	0.027	0.034	0.012
Cu	0.0067	0.0021	0.029	0.0052	0.0028	0.088
Fe	0.315	0.091	0.719	292	23.8	268
K	16.3	0.58	16.6	0.46	0.62	0.02
Mg	21.1	2.99	18.2	26.1	1.3	26.5
Mn	0.056	0.010	0.063	54.6	3.0	54.4
Na	73.7	3.25	66.9	<0.0006		<0.0006
Ni	0.0103	0.0017	0.0048	0.145	0.026	0.192
Pb	0.015	0.0051	0.014	1.21	0.10	1.25
Zn	0.045	0.0402	0.526	391	21.6	388

Alkalinity Generation. Alkalinity was generated via biotic and abiotic processes. The pH maintained in the clarifiers and Kaldnes zones was sufficiently high to not preclude bacterial activity (Fig. 3). This pH allowed for DO suppression via bacterial activity, as well as other desirable abiotic and bacterially-mediated reactions. The alkalinity produced by the limestone zones was representative of real-world ALD performance (Cravotta, 2003; Watzlaf et al., 2004). The alkalinity provided by the MWW and generated by BSR and limestone dissolution was sufficient to produce net-alkaline effluent.

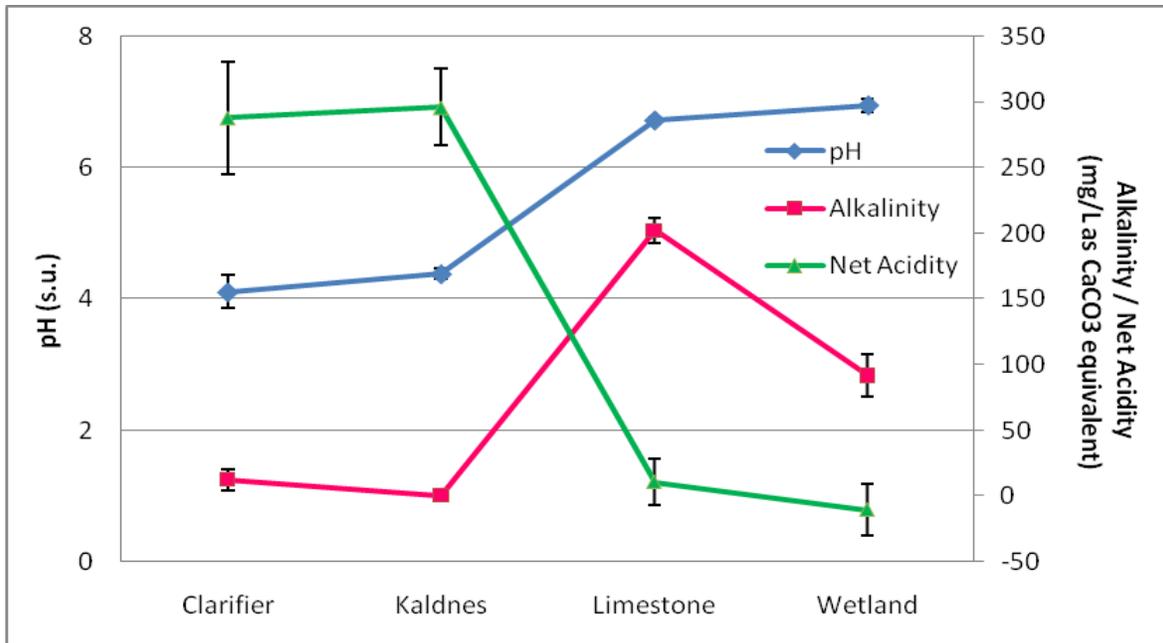


Figure 3. Grand mean of all sampling events (n=10) for pH, alkalinity and net acidity throughout the system. Error bars represent the 95% confidence interval constructed with the t statistic.

Aluminum. Al was primarily removed from solution in the clarifiers and limestone zones of the RAPS emulsion unit process (Fig. 4). In addition to combining with phosphate to form a relatively stable solid, Al can complex with particulate organic matter as well as react with dissolved organic carbon (DOC) and precipitate (Omoike and Vanloon, 1999). It is likely that all three of these removal mechanisms were occurring in the clarifier. Phosphate concentrations decreased in the clarifier from influent theoretical mix concentration of 7.7 mg/L to <0.75 mg/L. In the limestone zones pH increased to 6.72, which dramatically decreased Al solubility, likely forming insoluble amorphous Al(OH)₃ (Younger et al., 2002). This solid was flushed from the limestone during standard sampling events, resulting in a mean 77 mg/L of total vs. 0.053 mg/L of dissolved Al.

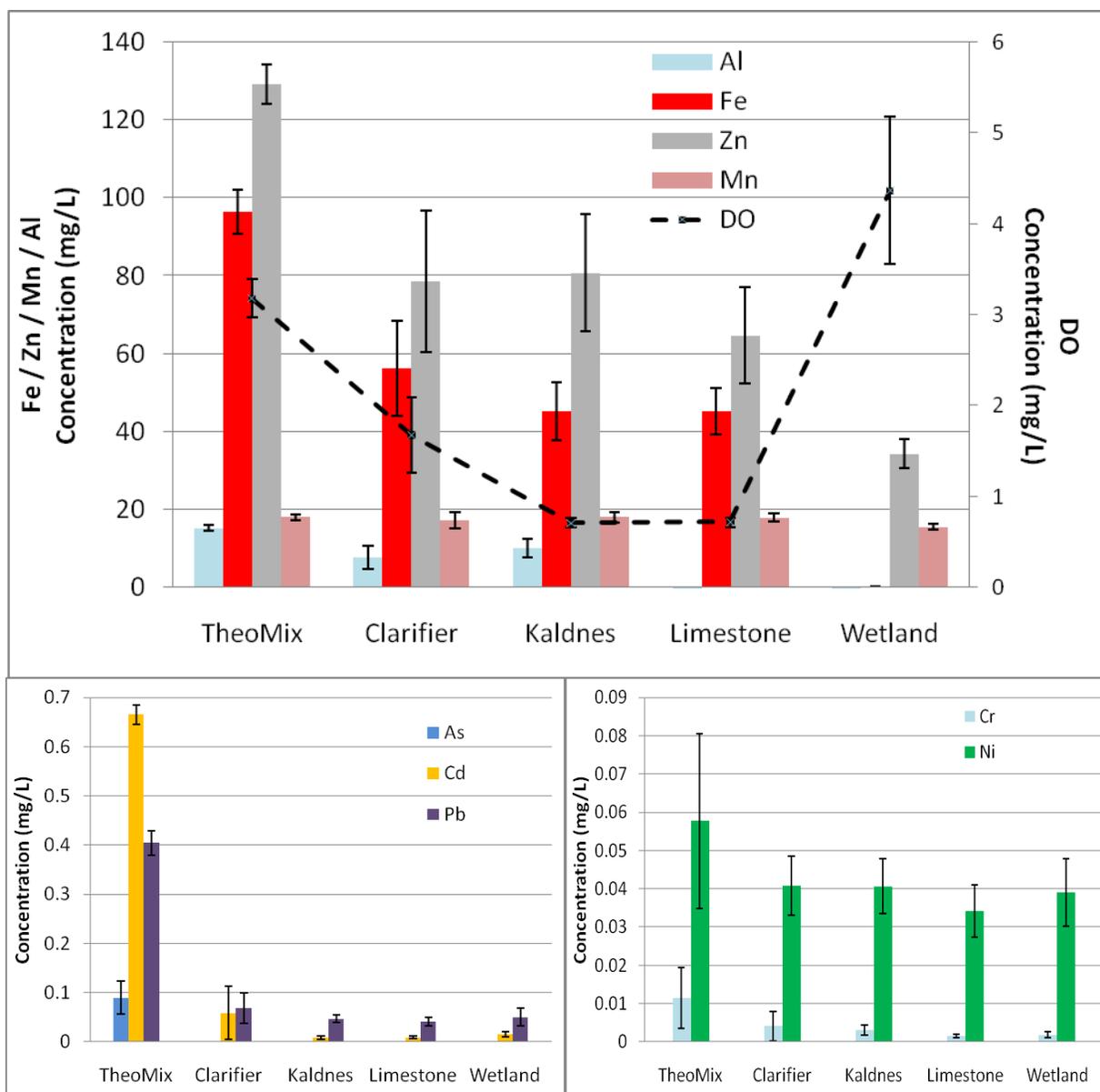


Figure 4. Grand mean of all sampling events (n=10) for dissolved metals concentrations with respect to DO. Error bars represent the 95% confidence interval constructed with the t statistic.

Arsenic. Due to the rapid removal of As to below detection limits (< 0.022 mg/L) in the clarifiers, the full extent of removal is unknown throughout the remainder of the system. It is most likely that As sorbed to Fe oxyhydroxides in the clarifiers. Extensive research has documented the affinity of As for Fe hydroxides, with amorphous Fe oxyhydroxides such as would be formed in the clarifier having the highest adsorption capacity (Mohan and Pittman, 2007).

Cadmium. Cd was removed in the clarifiers, likely from Cd sulfide formation and complexation with biotic and abiotic organic matter. Fristoe and Nelson (1983) demonstrated that between pH 4-5 Cd has a high affinity for organic ligands with which it will complex as well as adsorb to bacterial solids. Although Cd can complex with Fe oxyhydroxides (Olivie-Lanquet et al., 2001; Carroll et al., 1998), Cd increased within the wetlands, likely due to lack of an aerobic removal mechanism and evapoconcentration. Also, Zn sorption can suppress Cd sorption to Fe oxyhydroxides (Carroll et al., 1998) and significant Zn sorption likely occurred in the wetlands.

Chromium and Nickel. Cr and Ni were present in low concentrations in the AMD and MWW. Cr was also concentrated in the clarifier sludge and a significant decrease was noted between the theoretical influent mix and the wetland. Although there was no significant difference between the Ni theoretical influent mix and the wetland effluent, Ni was concentrated in the clarifier sludge.

Iron. Fe was removed from solution in the clarifier and wetland unit processes. Flocculation with phosphate likely removed some Fe from solution in the clarifier. Iron sulfide formation and combination with biotic and abiotic organic ligands (Fletcher and Beckett, 1987) also likely decreased dissolved Fe concentrations in the clarifier. In addition, the increase in pH from a mean of 2.60 to 4.11 caused some remaining Fe(III) precipitation by oxyhydroxide formation because Fe(III) is rapidly removed from solution in waters with pH > 4 (Younger et al., 2002). Fe(II) oxidation is unlikely to have occurred in the clarifiers due to low DO concentrations. Oxidation, hydrolysis, and sedimentation were the likely mechanisms of Fe removal in the wetland due to the high DO and pH. The limestone zones produced sufficient alkalinity which buffered pH through the wetlands during Fe oxidation and hydrolysis, a [H⁺]-producing process.

Key to the performance of the system, Fe remained unchanged through the Kaldnes and limestone unit processes and therefore did not armor the limestone. This indicates that the Fe(III) remaining in the AMD was reduced to Fe(II) in the clarifiers or Kaldnes zones, which allowed it to pass through the limestone without forming Fe(OH)₃ solids. The DO was driven below the suggested anoxic limestone drain design parameter of < 1 mg/L in the Kaldnes zones to limit the oxidation of Fe(II) within the limestone zones, which would also form Fe(OH)₃. Limestone in the presence of Fe(III) or Fe(II) and DO > 1 mg/L will become coated with Fe(OH)₃, dramatically lowering alkalinity production and porosity (Younger et al., 2002).

Manganese. Mn remained unchanged throughout the system until the wetlands. The oxidation and hydrolysis of Mn was possible because the pH was greater than 6 (6.95 ± 0.09) and Fe was driven to such low concentrations (to 0.18 ± 0.1 from 45 ± 6.0 mg/L) by the outflow of the wetlands. It is likely that Mn removal primarily occurred by the outflow of the wetlands where Fe concentrations were lower because Fe (II) will reduce oxidized forms of Mn when present (Watzlaf et al., 2004). In addition, Mn removal would be slightly greater if accounting was done for the evapoconcentration that occurred in the wetlands, which was estimated at 8.4%, assuming that Ca, Cl, and Na were conservative ions within the wetlands.

Lead. Pb was removed in the clarifier and remained unchanged throughout the subsequent unit processes. In the clarifier, Pb likely formed galena (PbS) or complexed with organic matter (Fletcher and Beckett, 1987) and sorbed to Fe oxyhydroxides (Carroll et al., 1998). Although Pb can sorb to Fe oxyhydroxides at the pH range found within the wetlands and should not be precluded by Zn sorption (Carroll et al., 1998), our study documented no significant difference between the limestone and wetland effluent dissolved Pb concentrations.

Zinc. Zn was primarily removed from solution in the clarifier and wetland. In the clarifiers, Zn sulfide formation and complexation with the biotic and abiotic organic ligands present in the MWW likely served as the primary Zn removal reactions (Fletcher and Beckett, 1987; Norton et al., 2004). In the wetlands, Zn removal was likely due to sorption to Fe oxyhydroxides. Zn has a high affinity for Fe oxyhydroxides, especially at the circumneutral pH present in the wetlands (Carroll et al., 1998).

Temporal Variability. Treatment efficiency of all metals was relatively stable throughout the duration of the standard operational run of the experiment. Zn is representative of the relatively quick stabilization and realization of peak performance (57 days) exhibited by each unit process and the whole system (Fig. 5).

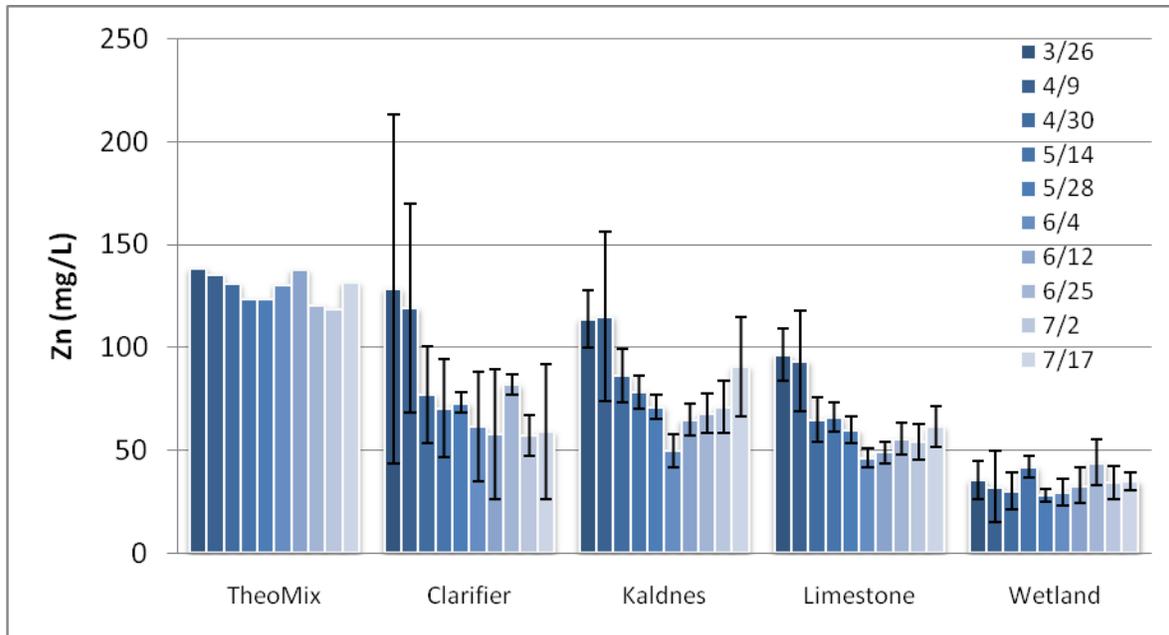


Figure 5: Mean dissolved Zn concentrations for each sampling period. Error bars represent one standard deviation above and below the mean. There are no error bars for TheoMix because it represents a single number, the 1:2 ratio of AMD to MWW.

Sulfate. Sulfate concentrations significantly decreased from the TheoMix to the Kaldnes zones, indicating that BSR could have been occurring in the clarifiers and/or Kaldnes zones (Fig. 6). Sulfate increased in the wetlands likely due to evapoconcentration. The high concentration of Zn present in the clarifiers and Kaldnes and limestone zones likely limited BSR rates. Zn concentrations ranging from 13 to 40 mg/L have been found to be toxic to SRB (Neculita et al., 2007). In addition, studies have suggested additive individual metal toxicity (Neculita et al., 2007), indicating that the other toxic metals within the system could have had an inhibitory effect on SRB. BSR rates also begin to decline at $\text{pH} < 5$ (Neculita et al., 2007). Therefore, it is assumed that BSR could have been greater if the AMD Zn concentrations were less and/or the ratio of MWW to AMD was increased to raise pH in the clarifiers and Kaldnes zones.

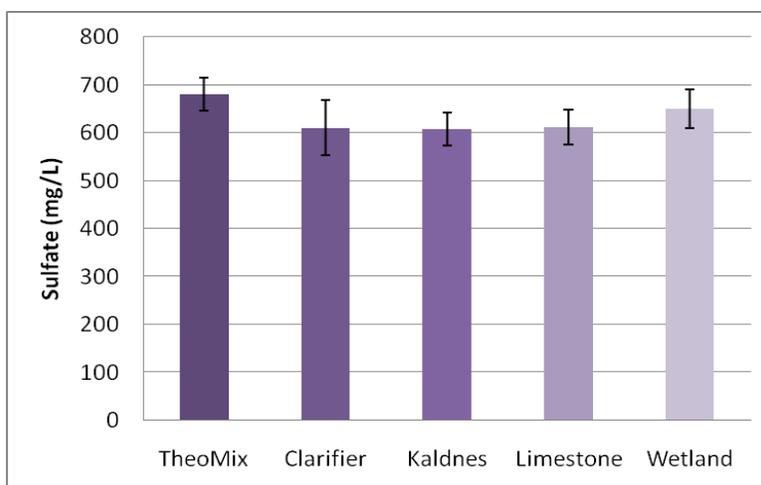


Figure 6. Sulfate grand mean of all sampling events (n=10). Error bars represent the 95% confidence interval constructed with the t statistic

Treatment rates. Treatment rates for key elements are presented in Table 4. Johnson and Younger (2006) reported 40-80% Fe removal in a constructed co-treatment wetland with a mean residence time of 14 hr receiving AMD with ~3 mg/L Fe. Although the residence time of the multi-stage co-treatment system was 10x that of the Johnson and Younger (2006) system, the multi-stage system demonstrated much higher % Fe removal while handling AMD with an Fe concentration approximately 100x greater. It should be noted that the multi-stage co-treatment system described was not optimized for maximum sustainable loading rates. The high % removal of key ecotoxic elements indicates that higher removal rates are likely achievable in an optimized system.

Table 4. Dissolved metal removal performance for key elements. Unit process removal is the percent difference between unit process inflow and outflow.

Metal	TheoMix mg/L	Final Outflow mg/L	Overall Removal %	Primary Unit Process of Removal	Primary Unit Process Removal		Primary Unit Process Treatment Rate			
					%	%	g/m ² -d		g/m ³ -d	
Al	15	0.035	99.8	Clarifier / Limestone	49.5	99.5	0.71	3.1	5.7	8.2
As	0.090	<0.022	87.8	Clarifier	87.8		0.007		0.060	
Cd	0.67	0.015	97.7	Clarifier	91.1		0.057		0.46	
Fe	96	0.18	99.8	Clarifier / Wetland	41.6	99.6	3.8	0.34	30	16
Mn	18	16	13.9	Wetland	13.6		0.018		0.88	
Pb	0.40	0.051	87.5	Clarifier	83.0		0.032		0.25	
Zn	129	34	73.4	Clarifier / Wetland	39.1	47.0	4.8	0.23	38	11

Sludge Generation

Approximately 0.69% of the total flow entering the clarifiers was wasted throughout the experiment. This wasting rate led to sustainable metals removal that did not compromise clarifier residence time. Sludge total Al, As, Cd, Cu, Mn, Ni, Pb, and Zn concentrations were negatively correlated with wasting rate (Fig. 7). The sludge contains concentrations of total Al, As, Cd, Cr, Cu, Fe, Pb, and Zn at least an order of magnitude greater than the dissolved theoretical influent mix. Sludge concentrations of total Mn and Ni were also greater than the dissolved theoretical influent mix, indicating that some degree of Mn and Ni removal was occurring in the clarifiers which could not be concluded from solely analyzing the theoretical influent mix and clarifier outflow data.

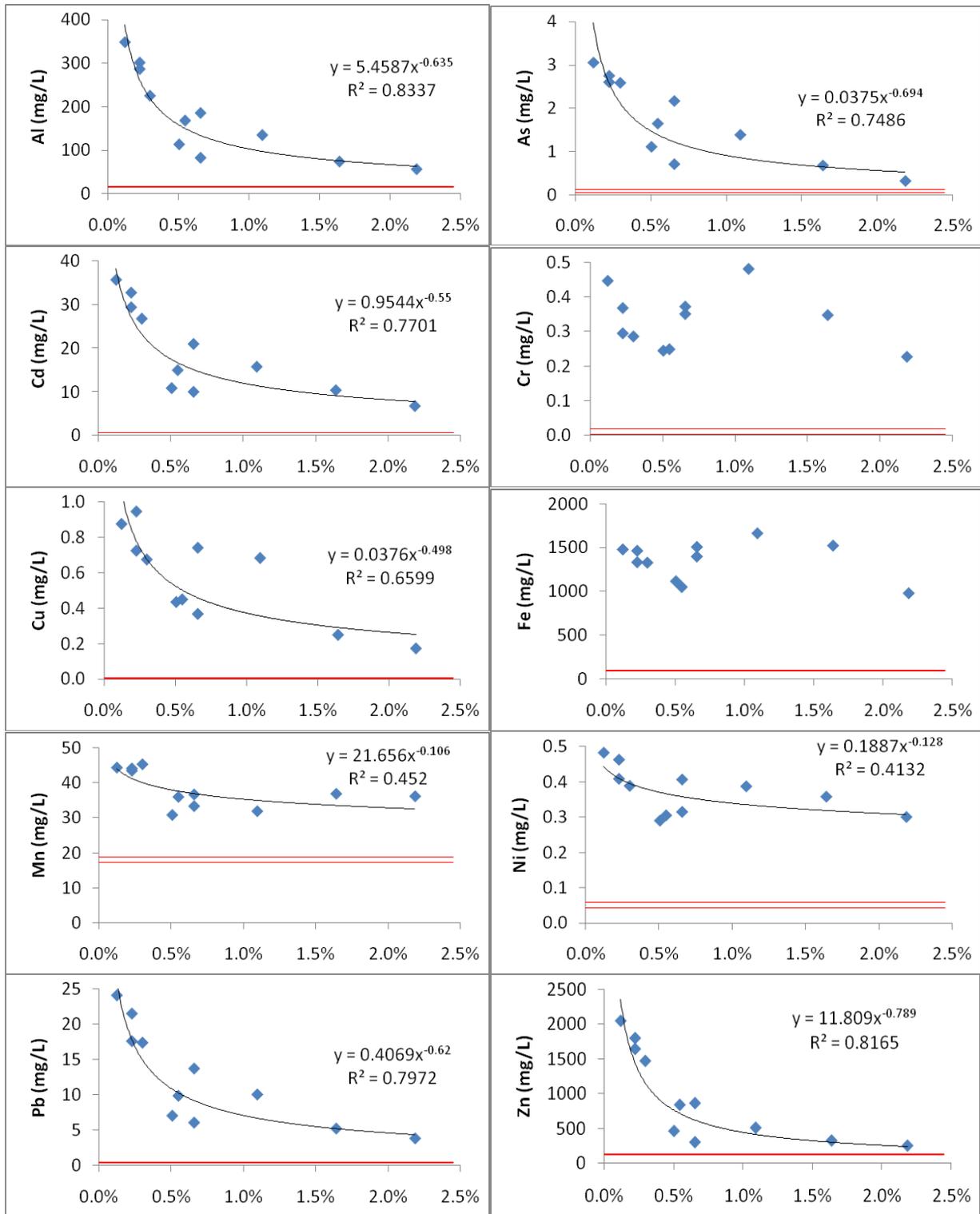


Figure 7. Total metals concentrations in sludge with respect to % clarifier outflow wasted. Red bars frame the 95% confidence interval constructed with the t statistic of the dissolved metals in the theoretical 1:2 AMD to MWW influent mix.

The sludge data indicate that the “more conservative” metals did not all behave conservatively within the clarifiers (Fig. 8). K was the only metal tracked for this study that behaved conservatively in the clarifier. The data indicate that Na appears to be dissociating from the sludge for the aqueous phase. Conversely, Mg and Ca appear to be complexing with the sludge.

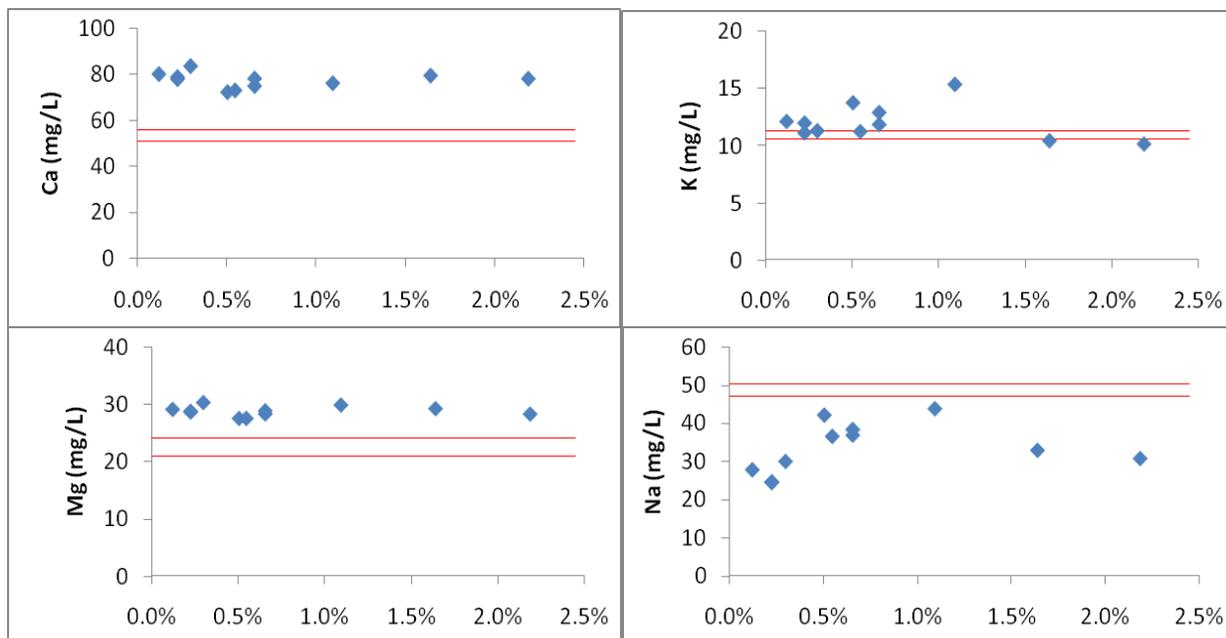


Figure 8. Total metals concentrations of possible conservative ions in sludge with respect to % clarifier outflow wasted. Red bars frame the 95% confidence interval constructed with the t statistic of the dissolved metals in the theoretical 1:2 AMD to MWW influent mix.

Conclusions and Recommendations

Results indicate that passive AMD and MWW co-treatment is a viable ecological engineering approach for the developed and developing world that can be optimized and applied to improve water quality with minimal use of fossil fuels and refined materials. The effect of increased loading rates, varied AMD to MWW mixing ratios, and the extent to which BSR can proceed in the presence of more commonly encountered Zn concentrations should be investigated to develop design guidance for full-scale co-treatment systems. The relatively quick treatment stabilization to peak performance indicates that full scale multi-stage co-treatment systems may reach maturity weeks after construction. However, the sludge produced can have

concentrations of ecotoxic elements orders of magnitude greater than is present in the mixed influent. This concentration may lend itself to metals reclamation, which if economically viable such as Fe reclamation from the oxidation ponds of standard passive treatment systems (Hedin, 2003), could be a continual source of revenue for large-scale passive co-treatment systems.

Acknowledgments

Dr. Keith Strevett and Dr. David Sabatini provided important experimental design guidance. Special thanks are extended to Beatriz Santamaria, Ronald Conlon, Alex Brewer, Jonathan Clifton, Darcy Lutes, and other University of Oklahoma Center for Restoration of Ecosystems and Watersheds personnel for laboratory assistance. Funding was provided by U.S. EPA Agreement FY04 104(b)(3) X7-97682001-0, USGS Agreement 04HQAG0131 and the University of Oklahoma Center for Restoration of Ecosystems and Watersheds.

Literature Cited

- American Public Health Association (APHA). 1998. Standard Methods for the Examination of Water and Wastewater. 20th Ed.
- Anderson, J.A. 1981. Primary sedimentation of sewage. *Water Pollution Control* 80(3): 413-420.
- Bell, F.G. and L.J. Donnelly. 2006. *Mining and its Impact on the Environment*. Taylor & Francis, New York.
- Benner, S.G., D.W. Blowes, C.J. Ptacek and K.U. Mayer. 2002. Rates of sulfate reduction and metal sulfide precipitation in a permeable reactive barrier. *Applied Geochemistry* 17: 301-320. [http://dx.doi.org/10.1016/S0883-2927\(01\)00084-1](http://dx.doi.org/10.1016/S0883-2927(01)00084-1).
- Carroll, S.A., P.A. O'Day and M. Piechowski. 1998. Rock-water interactions controlling zinc, cadmium, and lead concentrations in surface waters and sediments, U.S. Tri-State Mining District. 2. Geochemical interpretation. *Environmental Science and Technology* 32(7): 956-965. <http://dx.doi.org/10.1021/es970452k>.
- Cocos, I.A., G.A. Zagury, B. Clement and R. Samson. 2002. Multiple factor design for reactive mixture selection for use in reactive walls in mine drainage treatment. *Water Research* 32: 167-177 . [http://dx.doi.org/10.1016/S0043-1354\(01\)00238-X](http://dx.doi.org/10.1016/S0043-1354(01)00238-X).

- Cravotta, C.A. 2003. Size and performance of anoxic limestone drains to neutralize acidic mine drainage. *Journal of Environmental Quality* 32: 1277-1289. <http://dx.doi.org/10.2134/jeq2003.1277>.
- Frigon, D., R.M. Guthrie, G.T. Bachman, J. Royer, B. Bailey and L. Raskin. 2006. Long-term analysis of a full-scale activated sludge wastewater treatment system exhibiting seasonal biological foaming. *Water Research* 40: 990-1008. <http://dx.doi.org/10.1016/j.watres.2005.12.015>.
- Gadgil, A. 1998. Drinking water in developing countries. *Annual Review of Energy and the Environment* 23: 253-286. <http://dx.doi.org/10.1146/annurev.energy.23.1.253>.
- Gernaey, K. P.A. Vanrolleghem and P. Lessard. 2001. Modeling of a reactive primary clarifier. *Water Science and Technology* 43(7): 73-81.
- Hach. 2006. Digital Titrator Model 16900 Manual.
- Harris, M.A. and Ragusa, S. 2000. Bacterial mitigation of pollutants in acid drainage using decomposable plant material and sludge. *Environmental Geology* 40(1-2): 195-215. <http://dx.doi.org/10.1007/s002540000138>.
- Hedin, R.S. 2003. Recovery of marketable iron oxide from mine drainage. *Land Contamination and Reclamation* 11(2): 93-97. <http://dx.doi.org/10.2462/09670513.802>.
- Johnson, K.L. and P.L. Younger. 2006. The co-treatment of sewage and mine waters in aerobic wetlands. *Engineering Geology* 85: 53-61. <http://dx.doi.org/10.1016/j.enggeo.2005.09.026>.
- Kadlec, R.H and S.D. Wallace. 2009. *Treatment Wetlands*. CRC Press LLC.
- Kivaisi, A.K. 2001. The potential for constructed wetlands for wastewater treatment and reuse in developing countries: a review. *Ecological Engineering* 16: 545-560. [http://dx.doi.org/10.1016/S0925-8574\(00\)00113-0](http://dx.doi.org/10.1016/S0925-8574(00)00113-0).
- Luo, Q., T.K. Tsukamoto, K.L. Zamzow and G.C. Miller. 2008. Arsenic, selenium, and sulfate removal using an ethanol-enhanced sulfate-reducing bioreactor. *Mine Water and the Environment* 27: 100-108. <http://dx.doi.org/10.1007/s10230-008-0032-x>
- McCullough, C.D., M.A. Lund and J.M. May. 2006. Microcosm testing of municipal sewage and green waste for full-scale remediation of an acid coal pit lake, in semi-arid tropical Australia. *Proceedings of the 7th International Conference on Acid Rock Drainage*. <http://dx.doi.org/10.21000/jasmr06021177>.

- McCullough, C.D., M.A. Lund and J.M. May. 2008. Field-scale demonstration of the potential for sewage to remediate acidic mine waters. *Mine Water and the Environment* 27: 31-39. <http://dx.doi.org/10.1007/s10230-007-0028-y>.
- Metcalf and Eddy. 1991. *Wastewater Engineering: Treatment, Disposal and Reuse*. 3rd Ed. McGraw Hill.
- Muga, H.E. and J.R. Mihelcic. 2008. Sustainability of wastewater treatment technologies. *Journal of Environmental Management* 88: 437-447. <http://dx.doi.org/10.1016/j.jenvman.2007.03.008>.
- Mohan, D. and C.U. Pittman. 2007. Arsenic removal from water/wastewater using adsorbents – a critical review. *Journal of Hazardous Materials* 142: 1-53. <http://dx.doi.org/10.1016/j.jhazmat.2007.01.006>.
- Neculita, C., G.J. Zagury and B. Bussi re. 2007. Passive treatment of acid mine drainage in bioreactors using sulfate-reducing bacteria: critical review and research needs. *Journal of Environmental Quality* 36: 1-16. <http://dx.doi.org/10.2134/jeq2006.0066>.
- Nelson, M., H.T. Odum, M.T. Brown and A. Alling. "Living off the land": Resource efficiency of wetland wastewater treatment. *Advances in Space Research* 27(9): 1547-1556. [http://dx.doi.org/10.1016/S0273-1177\(01\)00246-0](http://dx.doi.org/10.1016/S0273-1177(01)00246-0).
- Norton, L., K. Baskaran and T. McKenzie. 2004. Biosorption of zinc from aqueous solutions using biosolids. *Advances in Environmental Research* 8: 629-635. [http://dx.doi.org/10.1016/S1093-0191\(03\)00035-2](http://dx.doi.org/10.1016/S1093-0191(03)00035-2).
- Olivie-Lanquet, G., G. Gruau, A. Dia, C. Riou, A. Jaffrezic and O. Henin. 2001. Release of trace elements in wetlands: role of seasonal variability. *Water Research* 35(4): 943-952. [http://dx.doi.org/10.1016/S0043-1354\(00\)00328-6](http://dx.doi.org/10.1016/S0043-1354(00)00328-6).
- Omoike, A.I. and G.W. Vanloon. 1999. Removal of phosphorus and organic matter removal by alum during wastewater treatment. *Water Research* 33(17): 3617-3627. [http://dx.doi.org/10.1016/S0043-1354\(99\)00075-5](http://dx.doi.org/10.1016/S0043-1354(99)00075-5).
- Pruden, A., N. Messner, L. Pereyra, R.E. Hanson, S.R. Hiibel and K.F. Reardon. 2007. The effect of inoculums on the performance of sulfate-reducing columns treating heavy metal contaminated water. *Water Research* 41: 904-914. <http://dx.doi.org/10.1016/j.watres.2006.11.025>.

- Rusten, B., B. Eikebrokk, Y. Ulgenes and E. Lygren. 2006. Design and operations of the Kaldnes moving bed biofilm reactors. *Aquacultural Engineering* 34: 322-331. <http://dx.doi.org/10.1016/j.aquaeng.2005.04.002>.
- Strosnider, W.H., R.W. Nairn and F.S. Llanos. 2007. A legacy of nearly 500 years of mining in Potosí, Bolivia: Acid mine drainage source identification and characterization. Proceedings, 2007 National Meeting of the American Society of Mining and Reclamation, Gillette, WY. <https://doi.org/10.21000/JASMR07010788>
- Tsukamoto, T. and G.C. Miller. 1999. Methanol as a carbon source for bioremediation of acid mine drainage. *Water Resources* 33(6): 1365-1370.
- Tuttle, J.H., P.R. Dugan, and C.I. Rendles. 1969. Microbial sulfate reduction and its potential utility as an acid mine water pollution abatement procedure. *Applied Microbiology* 17: 297-302.
- Watzlaf, G.R., K.T. Schroeder, R.L. Kleinmann, C.L. Kairies and R.W. Nairn. 2004. The Passive Treatment of Coal Mine Drainage. United States Department of Energy National Energy Technology Laboratory Internal Publication, 72 pp.
- Waybrant, K.R., Blowes, D.W. and Ptacek, C.J., 1998. Selection of reactive mixtures for use in permeable reactive walls for treatment of mine drainage. *Environmental Science and Technology* 32(13): 1972-1979. <http://dx.doi.org/10.1021/es9703335>.
- Younger, P., S.A. Banwart and R.S. Hedin. 2002. Mine Water: Hydrology, Pollution, Remediation. Kluwer Academic Publishers, Boston. <http://dx.doi.org/10.1007/978-94-010-0610-1>.
- Zamzow, K.L., T.K. Tsukamoto and G.C. Miller. 2006. Waste from biodiesel manufacturing as an inexpensive carbon source for bioreactors treating acid mine drainage. *Mine Water and the Environment* 25: 163-170. <http://dx.doi.org/10.1007/s10230-006-0128-0>.