

A PERFORMANCE COMPARISON OF ARSENIC, CADMIUM AND ZINC TREATMENT IN A DUPLICATE COLUMN STUDY OF AN ANAEROBIC BIOREACTOR OPERATED AT 4°C AND 25°C

Jonathan D.E. Kawaja¹, Dr. W. Douglas Gould¹, Lucie Morin¹, Al Mattes², and William F. A. Duncan³

¹Natural Resources Canada (CANMET) Mining and Mineral Science Laboratories, Mine Effluents Program, 555 Booth St., Ottawa, Ontario, Canada K1A 0G1

²Nature Works Remediation Corp., 1737 West River Road Cambridge, Ontario N1R 5S5

³Teck Cominco Metals Ltd., P.O. Box 1000 Trail, British Columbia V1R 4L8

ABSTRACT

This study provides a performance comparison of arsenic, cadmium and zinc treatment at mildly acid to neutral pH in an anaerobic bioreactor (ABR) column experiment operated at 4°C and 25°C. The materials and contaminants were based on a field scale system operated by Nature Works Remediation Corp. for Teck Cominco Metals Ltd. in Trail, BC. The majority of arsenic was removed within the oxic zones of the ABR columns. Although it was thought that arsenic removal at this stage was attributed to sorption to iron, it is now known to be zinc arsenate. The work showed cadmium and zinc removal improved in relation to the extent of anoxic conditions in the columns. In the most anaerobic zone of the columns (i.e., characterized by good sulphate reducing bacteria (SRB) activity) effective zinc removal required a stable SRB population, but was not necessarily temperature dependent. However, there was a direct and significant impact to microbial activity as a result of a temperature change. The work suggested that internal monitoring of DO and SRB can provide valuable information with respect to significant metal removal mechanisms, and the active volume in which metal sulphides can be significantly generated. The information can be used to: troubleshoot an under-performing system, and make appropriate amendments to improve system performance.

INTRODUCTION

Background

Over the past several years, the Mining and Mineral Science Laboratories (MMSL) has been examining the feasibility of (semi-) passive systems to mitigate mine drainage in Canada. In general, these systems utilize material to generate alkalinity (e.g., limestone) and provide a medium for microbial and chemical processes to precipitate metals in various forms, such as carbonates, hydroxides, or sulphides (e.g., biosolids generated from a pulp and paper mill).

This investigation relates to a passive biological treatment system at Teck Cominco Metals Ltd. in Trail, British Columbia (i.e., referred to as the Teck Cominco System (TCS)). At this site a combination of anaerobic bioreactors (ABRs) and vegetated cells are used to treat metal contaminated leachate containing arsenic, cadmium and zinc (Mattes et al., 2004). Although many reports on ABRs and engineered wetlands metal treatment systems are treated like “black boxes”, Teck Cominco through its own research and contracts with Nature Works has been

investigating many aspects of the processes for the past 5 years. To the best of MMSL's knowledge the system in Trail is generally successful in reducing initially high concentrations of metals to provincial irrigation quality objectives. However, there are times, during start-ups after shutdowns or in cold weather operation when zinc concentrations are higher than during stable summer operations.

Most recently the direction of MMSL work has shifted towards examining system performance at cold temperatures. Based on comparisons of the effect of temperature (25°C versus 4°C) on system performance, this report identifies useful parameters that can be used to: troubleshoot an under-performing system, and indicate the need for appropriate amendments required to improve system performance.

Experimental - Conceptual Design, Construction, and Operation

The two columns were clear Plexiglas, the piping was rigid PVC, and the influent and effluent tubing was Nalgene. A Masterflex peristaltic pump with very fine tubing was used to pump the synthetic contaminated leachate (i.e., the feed), which was directed vertically from the bottom-up. The total volume of each column was 15.6 L: the initial layer contained ~2 L of 6 mm CaCO_3 ; the next layer contained ~10.8 L of compost and sand (i.e., organic substrate); and on top there was 2.8 L of headwater. Refer to Table 1, for a summary of materials, dimensions, and physical parameters. The organic substrate was obtained from the effluent treatment ponds of Zellstoff Celgar Pulp Mill in Castlegar, British Columbia. Water was maintained over each column as a buffer between the organic substrate and the ambient air. Porewater sampling ports were located at column heights of 9 cm, 20 cm, 36 cm and 51 cm from the base (Figure 1).



Figure 1, Duplicate Column Study Setup in a Temperature controlled Room (4°C)

Table 1: Column Study Material Components

Cell	Materials/Components	Physical Parameters
Anaerobic Bioreactor (Total Volume 15.6L)	Bottom section: - 6 mm Limestone (CaCO_3)	Volume (V)= 2 L = 13% Cross Sectional Area (A) = 184 cm ² Height (h) = 11cm Porosity (n) = 0.255 Voidage (V_n) = 0.5 L Hydraulic Conductivity (k)= 7.17 cm/s
	Middle section: - Composted, Celgar Pulp mill biosolids - Industrial grade sand	Volume (V)= 10.8 L = 69% Cross Sectional Area (A) = 184 cm ² Height (h) = 59 cm Porosity (n) = 0.286 Voidage (V_n) = 3.1 L Hydraulic Conductivity (k)= 1.51 x 10 ⁻³ cm/s
	Top section: - Standing Effluent	Volume (V) = 2.8L = 18% Height (h) = 15 cm

The objective was to create a medium for limestone dissolution to produce alkalinity (Skousen, 1991; Zipper, 2001) as well as a solid support for the fermentative microbial populations (i.e., acid-producing bacteria (APB)) and sulphate-reducing bacteria (SRB). SRB also contribute to alkalinity when reducing sulphate (e.g., equation 1). APB metabolize complex and simple organics in the organic substrate to produce compounds such as ethanol and acetate that can be further metabolized by SRB. The microbial production of sulphides allows for cadmium and zinc sulphide precipitation (Song et al., 2001), and possibly arsenic (Newman et al., 1997). Equation 2 shows the reaction for divalent metals (Drury, 1999; Hedin et al., 1989).



Acclimatization of the bacteria took one month before operation at 25°C, a longer period of six months was chosen at 4°C (i.e., it was assumed that the bacterial growth would be much slower at 4°C). The acclimatization period involved: loading the columns with the synthetic feed solution; turning off the flow in order to provide for the consumption of DO; and the establishment of SRB throughout under no-flow conditions. The same columns were used for all phases. The feed contained ~126 mg/L [Zn^{2+}], ~25 mg/L [As^{5+} as AsO_4^{3-}], ~2 mg/L [Cd^{2+}], and ~218 mg/L [SO_4^{2-}] at a pH ~5.5. The proportion of feed contaminants was based on averages observed entering the TCS. At a flow of 77 L/m²/day, the feed met the criterion of 0.3 mol/m³/day used by Gusek et al. (1997); however, with the same concentrations, the loading was lower when tested at 4°C operation. Each experimental profile was operated for a period of two months. The first three sequential profiles operated at 25°C (Phases 1, 2, and 3) were discussed in a previous report (Kawaja et al., 2005). This report makes a comparison between experimental operation under “ideal” hydraulic loadings at 25°C (Phase 1), and the second of two sequential phases operated at 4°C (Phase 5):

At 25°C:

- (1) Phase 1, for a two month period the columns were operated at a hydraulic loading of 77 L/m²/day;
- (2) Phase 2, the hydraulic loading was doubled to stress the system for a two month period;
- (3) Phase 3, the hydraulic loading was returned to 77 L/m²/day to evaluate whether the system could re-establish its key operational conditions observed in Phase 1.

At 4°C:

- (4) Phase 4, for a two month period the columns were operated at a hydraulic loading of 72 L/m²/day;
- (5) Phase 5, for a two month period the columns were operated at a hydraulic loading of 20 L/m²/day (i.e., the loading rate was reduced based on the rule-of-thumb, for every 10°C drop in temperature the systems removal rates would be halved).

Phase 4 is not discussed because the flowrates used were too high for operation at 4°C, and monitoring suggested that the system’s performance was continually degrading.

Monitoring and Analyses

Once a week the input and outputs of each column, as well ports 1 through 4 were monitored with a WTW Multiline P4 Universal Pocket Meter for temperature, pH, redox potential (ORP), dissolved oxygen (DO), and conductivity. Samples were collected as follows: sample ports were sealed with a rubber stopper; a syringe inserted through the stopper and an adequate volume of solution was withdrawn for each parameter measured; and the solution was expelled from the syringe to the bottom of its sample bottle. A close fit between probe diameter and sample bottle opening ensured minimum aeration during measurement. As well, samples were collected for total arsenic, cadmium, zinc, iron, sulphate, and acidity/alkalinity. Samples for dissolved metals were filtered with a 0.45 μm filter before acidification. All samples for metal analyses were collected in 20 mL volumes and acidified with two drops of concentrated nitric acid. Total arsenic, cadmium, iron, and zinc in the mg/L range were determined using ICP-AES, and in the $\mu\text{g/L}$ range determined using ICP-MS. Sulphate was determined using a gradient elution HPLC, with a DIONEX column. Total acidity was determined using a two-endpoint (pH 4 and 8.3) titration using the NaOH technique to determine the equivalence point. Total alkalinity was determined in water by titration of a sample aliquot with a standard solution of dilute acid. A two-endpoint (pH 4.5 and 4.2) technique determined the inflection point or equivalence point of the titration. Before and after each adjustment in the experiment hydraulic loading rate: SRB, iron reducing bacteria (IRB), and APB were enumerated using a most probable number (MPN) determination from: the first, second, third and fourth pore water sample ports. For SRB determination, the bacteria were grown in modified Postgate medium C in 20 mL serum bottles (Postgate, 1984). The composition of the medium was as prescribed by Benner et al. (1999). IRB were completed as described by Gould et al. (2003). APB enumerations were carried out as described by Hulsof et al. (2003). Calculations on the results were analyzed using excel spreadsheets.

RESULTS

Generally, for each phase the last four weeks were accepted as representing a steady state; and therefore, served as the basis for the discussion. For Phase 1, residence times of 7 hrs, 18 hrs, 31 hrs, 44 hrs and 60 hrs; and for Phase 5, 25 hrs, 67 hrs, 120 hrs and 172 hrs; correspond to column heights of 9 cm, 20 cm, 36 cm, 51 cm, and 85 cm from the base (i.e., based on the loading rates and physical parameters listed in Table 1).

Figures 2, and 3 illustrate the rate at which pH, DO, and ORP changed within the columns. The limestone basin was the largest contributor to alkalinity. The microbial contribution to alkalinity was clearly reflected in the pH of Phase 1 after 20 hrs, but was not in Phase 5.

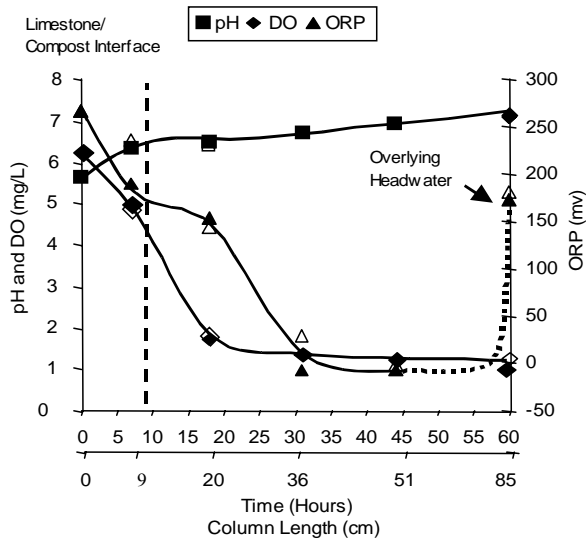


Figure 2: Phase 1 (25°C): pH, DO and ORP for each Column as a Function of Residence Time (Solid points represent Column 1; Open, Column 2)

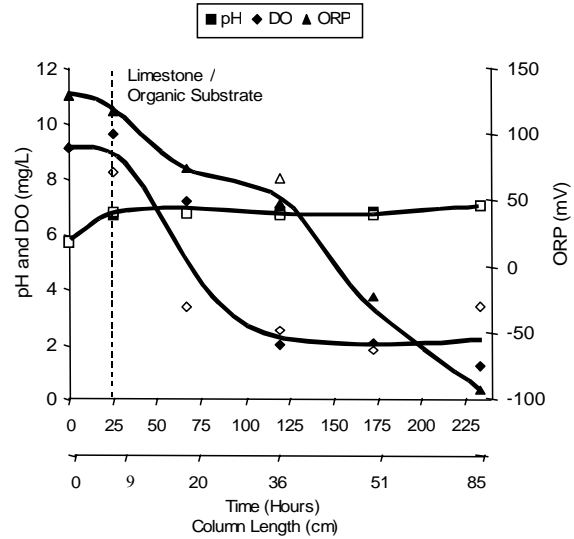


Figure 3: Phase 5 (4°C): pH, DO and ORP for each Column as a Function of Residence Time (Solid points represent Column 1; Open, Column 2)

The rate of DO removal accelerated in the organic substrate, and comparisons of each phase suggest that decreases in DO concentrations was in part determined by the contact time with the organic substrate. Temperature also appears to have an impact (e.g., four times the residence time at 4°C was required to lower the DO concentration to that of Phase 1).

On the other hand, an increase in residence time corresponded to a significant reduction in ORP, but a relationship with temperature was not apparent.

Arsenic, Cadmium and Zinc Treatment and Metal Attenuation

The graphs in Figures 4, and 5 shows the contaminant concentration at a given residence time for each phase. The best performance was observed in Phase 1, and the poorest performance was observed in Phase 5. As expected from theory, the decrease observed for cadmium was consistent with a four times reduction at 4°C compared to 25°C. This relationship cannot be observed for arsenic or zinc.

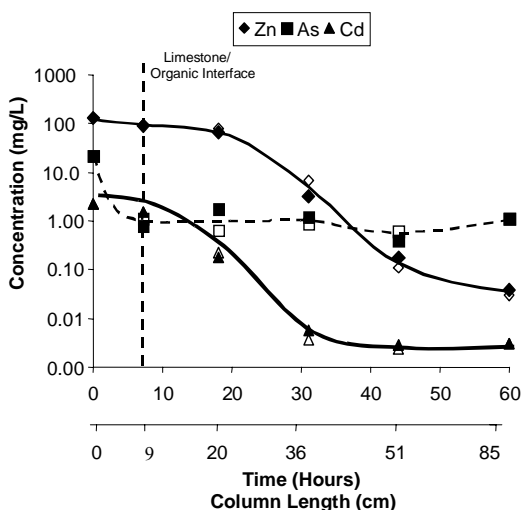


Figure 4: Phase 1 (25°C): Arsenic, Cadmium and Zinc (mg/L) for each Column as a Function of Residence Time (Solid points represent Column 1; Open, Column 2)

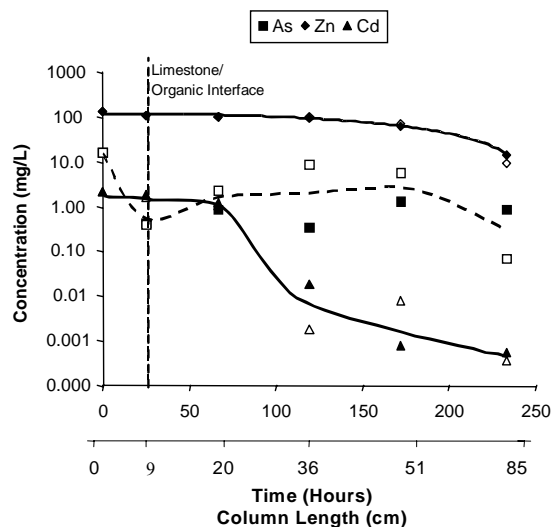


Figure 5: Phase 5 (4°C): Arsenic, Cadmium and Zinc (mg/L) for each Column as a Function of Residence Time (Solid points represent Column 1; Open, Column 2)

The trends in cadmium and zinc can be seen to be similar in Phase 1; however, the treatment of cadmium occurred preferentially. This was not so in Phase 5. In Phase 1 the total cadmium and zinc concentrations for each column were treated to below 0.003 mg/L and 0.06 mg/L, and in Phase 5 between 0.0005 mg/L and 11.6 mg/L respectively (Figures 4, and 5). The mass balance comparing the attenuation of zinc and sulphur shows that there was a strong 1:1 molar ratio at 25°C (Kawaja et al., 2005); however, the ratio weakened at 4°C. In all experimentation, the observed trends in total cadmium and zinc removal depicted a different treatment mechanism than that of the arsenic.

As indicated in Figures 4 and 5, the highest rate of arsenic removal in all the phases took place between the column's input and the limestone/organic substrate interface, and there was not a measurable effect by a change in temperature. Recent XRD analyses identified the attenuation product in the limestone to be zinc arsenate. Some arsenic persisted in the pore waters of the organic substrate, and the concentrations fluctuated in relation to total iron concentrations. As shown in Table 2, there was a good correlation between arsenic and iron throughout the biosolids of the columns, but the correlation was poorer between iron, and cadmium or zinc (i.e., although no iron was introduced in the feed solution, solid analysis shows the presence of iron in the column's substrate to be 17.4 mg/g). The fluctuations in arsenic concentrations in each column at

different sample ports, as observed in Figure 5, were more pronounced at 4°C. Total and dissolved analyses of arsenic, cadmium, zinc and iron in the overlying water show that most of the cadmium and zinc were dissolved; however, the majority of iron and arsenic were not (Kawaja et al. 2005).

Table 2: Summary of the Pearson Coefficient for the Average Pore Water Concentrations Over Time for Total Iron Vs Arsenic, Cadmium and Zinc at each Sample Location

Sample Location (25°C)	Fe Vs As	Fe Vs Cd	Fe Vs Zn	Sample Location (4°C)	Fe Vs As	Fe Vs Cd	Fe Vs Zn
Feed	0.39	-0.12	0.025	Feed	0.20	0.054	0.047
Port 1	0.88	-0.84	-0.74	Port 1	0.98	-0.50	0.16
Port 2	0.94	-0.63	-0.76	Port 2	0.74	-0.28	0.36
Port 3	0.84	0.73	-0.20	Port 3	0.55	-0.50	-0.14
Port 4	0.83	0.45	0.40	Port 4	0.71	0.14	0.31
Effluent	0.95	0.78	0.58	Effluent	0.88	0.38	0.78

A relationship between arsenic and DO could also be observed. Prior to Phases 1 and Phase 5 there was an acclimatization period, the intention of which was to encourage SRB populations prior to operations. During these two periods there was no feed flowing to the system, and the result was that the limestone basin areas of each column were anaerobic. During operation, a consistent feed loading provided DO that resulted in a trend towards oxic conditions during the initial residence times of the columns (i.e., at 4°C the cold temperatures resulted in higher DO concentrations for a longer period of time relative to 25°C). Arsenic concentrations were highest at the limestone/organic substrate interface from Day 0-15 of operation immediately following acclimatization.

Microbial Population Profiles – APB, IRB and SRB

After the initial acclimatization of the columns at 25°C (Day 0), an APB, IRB and SRB profile was completed at each sample port; another profile was conducted after the completion of Phase 1 (Day 58); one after the 4°C acclimatization (Day 0); and a final after Phase 5 (Day 84). Figures 6-11 illustrate the shift in each population's magnitude with respect to the columns length.

In general, following acclimatization at 25°C, each population was established at its peak level. IRB were not robust at the limestone/organic interface, but within the organic substrate, populations were slightly elevated. At 4°C microbial populations were consistently low for APB, IRB, and SRB. Some IRB and SRB activity was observed in the upper areas of the columns during Phase 5.

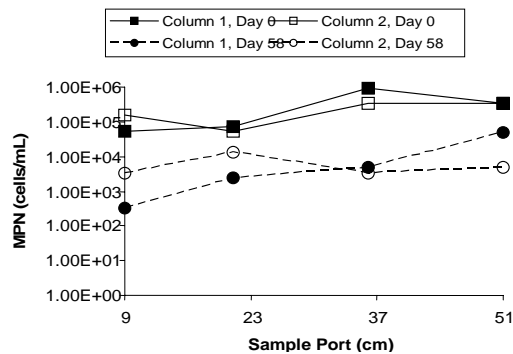


Figure 6: APB MPNs at 25°C as a Function of the Columns Height within the Pore Water of each Column

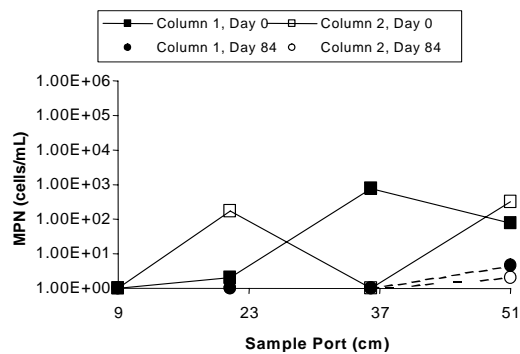


Figure 7: APB MPNs at 4°C as a Function of the Columns Height within the Pore Water of each Column

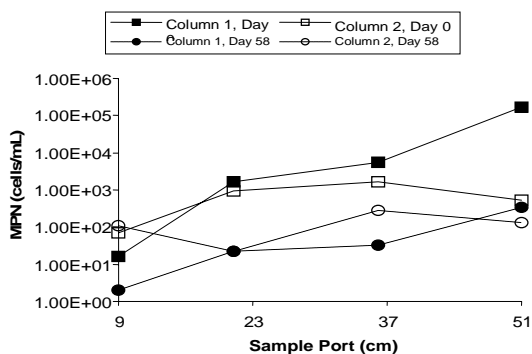


Figure 8: IRB MPNs at 25°C as a Function of the Columns Height within the Pore Water of each Column

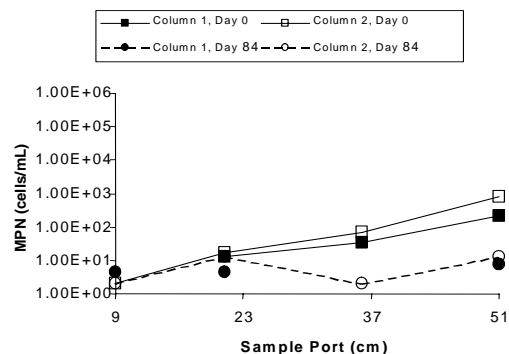


Figure 9: IRB MPNs at 4°C as a Function of the Columns Height within the Pore Water of each Column

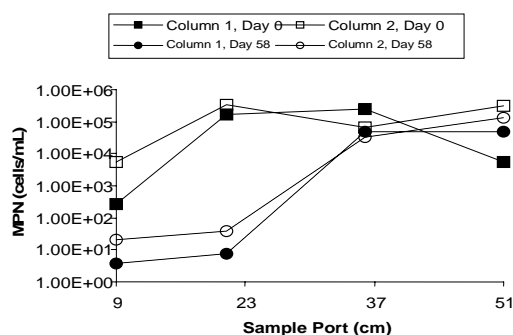


Figure 10: SRB MPNs at 25°C as a Function of the Columns Height within the Pore Water of each Column

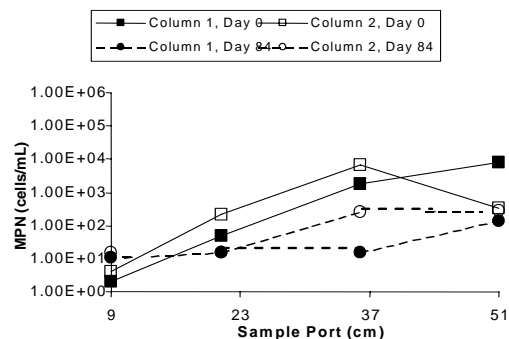


Figure 11: SRB MPNs at 4°C as a Function of the Columns Height within the Pore Water of each Column

DISCUSSION

The work provides evidence that arsenic attenuation was based on the formation of zinc arsenate in the limestone drain, and adsorption to iron at the columns overlying water, and was not a direct function of the anaerobic processes in the ABR columns. However, the mobility of small concentrations through the columns biosolids can be influenced by the reduction of iron by IRB (Johnson et al. 2004; McCreadie et al., 2000; Sorensen, 1982), the subsequent release of arsenic,

until their final co-deposition in the oxic headwater is the best explanation (Ball et al. undated; McGeehan, 1996; Smedley et al., 2002; Redman et al., 2002; Tingzong et al., 1997; and Yang et al., 2002). There is also evidence of zinc arsenate precipitation, and iron and arsenic co-precipitation at the TCS, but it is important to note that there is also evidence of arsenic attenuation in the anoxic zones of the TCS reported that could not be duplicated in this study. There was no measurable impact to arsenic removal based on temperature, but only redox conditions. Although cadmium and zinc were also treated in the oxic zones of the ABR, removal trends were different than that of arsenic, not correlated to iron, and more consistent with that expected for anaerobic attenuation. Bostick et al. (2001) identified zinc carbonates, oxides and sulphides as possible species in wetlands. Comparing the redox conditions, sulphate removal, SRB, as a function of both loading and temperature, with the mass balance of zinc and sulphur removal, provided the strongest evidence to support metal sulphide attenuation (O'Sullivan, A.D., 2004; Tuppurainen et al., 2002). SRB activity was determined, as a rate-limiting step for zinc removal, and as a result future studies should focus on how to counteract negative temperature impacts to SRB populations, as a means to maintain treatment performance. Under optimal operating conditions, as defined by the operational parameters in Phase 1, a retention time of 44 hrs was sufficient to establish SRB; however, operated as a passive system, the performance was significantly compromised by decreases in temperature. Therefore, site specific loading criterion is essential before operating an ABR and should not be strictly based on the literature, but demonstrated with rigorous pilot testing.

The next stage of the work will involve the sampling of the columns solids to perform mineralogical analyses, and chemical analyses of the substrate. The objective of this work will be to directly identify the attenuation products and their locations of disposition in the ABR.

Field design considerations reinforced and/or suggested by the study include:

(1) With respect to arsenic, a design should consider the placement of an oxic polishing step after an ABR to precipitate iron, thereby co-precipitating/adsorbing arsenic. The study suggests that this can be done passively. The mobility of arsenic at the limestone/organic interface during periods of acclimatization suggest that precipitated arsenic could possibly remobilize in anaerobic conditions (e.g., hypothetically, in the spring after a winter shutdown, or start-up after a prolonged work stoppage due to maintenance or repairs.) At the TCS arsenic release has only been observed following repairs or digging, and one explanation has been a change in the redox conditions in the cell being repaired.

(2) With respect to temperature, prolonged acclimatization periods, in itself, cannot be relied on to establish suitable quantities of SRB and their numbers appear to have a direct role in facilitating adequate attenuation of cadmium and zinc precipitation. Good controls (e.g., use of a feed reservoir and pump) can help in maximize retention time during cold periods. Without these controls the active volume that facilitates metal sulphide precipitation can be significantly hampered.

(3) Another control that was not addressed, but appears to be necessary in maintaining system integrity through periods of increased hydraulic loadings and/or cold temperatures, is the adoption of more “active” process controls, while still adhering the principles of low maintenance and costs (e.g., the use of reagents: acetate, ethanol, and sugar). These controls would involve the development of set-points for carbon reagent dosing to maintain SRB activity.

(4) Because there are a variety of possible attenuation products, more direct methods of monitoring performance should be developed and applied in the field to measure the redox conditions and microbial activity within ABRs. The results suggest that DO and SRB could be used as a relative guide to help assess and troubleshoot the “health” of an anaerobic bioreactor, by providing insight into what products are formed.

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REFERENCES

Ball, B.R., and K.V. Brix. Undated. Passive Treatment of Metalloids Associated with Acid Rock Drainage. Parametrix, Inc. Sumner, Washington.

Benner, S. G., D.W. Blowes, W.D. Gould. R.B. Herbert and C.J. Ptacek. 1999. Geochemistry of Permeable Reactive Barrier for Metals and Acid Mine Drainage. *Environmental Science & Technology*, 33, 2793-2799.

Bostick, B.C., C.M. Hansel, M.J. La Force, and S. Fendorf. 2001. Seasonal fluctuations in Zinc Speciation within a Contaminated Wetland. *Environmental Science & Technology*, 35, 3823-3829.

Drury, W.J. 1999. Treatment of Acid Mine Drainage with Anaerobic Solid-Substrate Reactors. *Water Environment Research*, Volume 71, Number 6, pg 1244-1250.

Gould, W.D., M. Stichbury, M. Francis, L. Lortie, and D.W. Blowes. 2003. An MPN Method for the Enumeration of Iron-Reducing Bacteria. *Sudbury 2003 Proceedings*.

Gusek, J. and T. Wildeman, 1997. Short Course #6 Treatment of AMD. Fourth International Conference on Acid Rock Drainage Vancouver, BC, Canada, May 31-June 6.

Hedin, R.S., R. Hammack, and D. Hyman. 1989. Potential Importance of Sulphate Reduction Processes in Wetlands Constructed to Treat Mine Drainage. *Constructed Wetlands for Wastewater Treatment - Municipal, Industrial and Agricultural*, pg 508-514.

Hulsof, A. H. M., D.W. Blowes, C.J. Ptacek, and W.D. Gould. 2003. Microbial and Nutrient Investigations into the Use of in Situ Layers for Treatment of Tailings Effluent. *Environmental Science & Technology*, 37, 5027-5033.

Johnson, D., B. and K.B. Hallberg. 2005. Biogeochemistry of the Compost Bioreactor Components of a Composite Acid Mine Drainage Passive Remediation System. *Science of the Total Environment*, 338, 81-93.

Kawaja, J.D.E., K. Morin, and W.D. Gould. 2005. A Duplicate Column Study of Arsenic, Cadmium and Zinc Treatment in an Anaerobic Bioreactor Based on a System Operated by Teck Cominco in Trail, British Columbia. *Proceedings of the 29th Annual British Columbia Mine Reclamations Symposium*, Abbotsford, BC.

Mattes A., W.F. Duncan, and W.D. Gould. 2004. Biological Removal of Arsenic in a Multi-Stage engineered Wetlands Treating a suite of Heavy Metals. *Proceedings of the 28th Annual British Columbia Mine Reclamations Symposium*, Cranbrook, BC.

McCreadie, H., D.W. Blowes, C.J. Ptacek, and J.L. Jambor. 2000. Influence of Reduction Reactions and Solid-Phase Composition on Porewater Concentrations of Arsenic. *Environmental Science & Technology*, 34, 3159-3166.

McGeehan, S.L. 1996. Arsenic Sorption and Redox Reactions: Relevance to Transport and Remediation. *Journal of Environmental Science and Health*, A31(9), 2319-2336.

Newman, D.K., T.J. Beveridge, and F.M.M. Morel. 1997. Precipitation of Arsenic Trisulfide by *Desulfotomaculum auripigmentum*. *Applied and Environmental Microbiology*, 63, 5, 2022-2028.

O'Sullivan, A.D., M. B. Moran, and M.L. Otte. 2004. Accumulation and Fate of Contaminants (Zn, Pb, Fe and S) in substrates of Wetlands Constructed for Treating Mine Wastewater. *Water, Air, and Soil Pollution* 157: 345-364.

Postgate, J.R. 1984. *The Sulphate-Reducing Bacteria*. Cambridge University Press: Cambridge, England.

Redman, A.D., D.L. Macalady, and D. Ahmann. 2002. Natural Organic Matter Affects Arsenic Speciation and Sorption onto Hematite. *Environmental Science & Technology*, 36, 2889-2896.

Skousen, J.G. 1991. Anoxic Limestone Drains for Acid Mine Drainage Treatment. *Green Lands* 21(4): 30-35.

Smedley, P.L., D.G. Kinniburgh. 2002. A Review of the Source, Behaviour and Distribution of Arsenic in Natural Waters. *Applied Geochemistry*, 17, 517-568.

Song, Y., M. Fitch, J. Burken, L. Nass, S. Chilukiri, N. Gale, and C. Ross. 2001. Lead and Zinc Removal by Laboratory-Scale Constructed Wetlands. *Water Environmental Research*, Volume 73, Number 1.

Sorensen, J. 1982. Reduction of Ferric Iron in Anaerobic, Marine Sediment and Interaction with Reduction of Nitrate and Sulfate. *Applied and Environmental Microbiology*, p. 319-324.

Tingzong, G., R.D. Delaune, and W.H. Patrick, Jr. 1997. The Influence of Sediment Redox Chemistry on Chemically Active Forms of Arsenic, Cadmium, Chromium, and Zinc in Estuarine Sediment. *Environment International*, Vol. 23, No. 3, pp. 305-316.

Tuppurainen, K.O., A.O. Vaisanen, J.A. Rintala. 2002. Zinc Removal in Anaerobic Sulphate-Reducing Liquid Substrate Process. *Minerals Engineering*, 15, 847-852.

Yang J., M.O., M.O. Barnett, P.M. Jardine, N.T. Basta, and S.W. Casteel. 2002. Adsorption, Sequestration, and Bioaccessibility of As(V) in Soils. *Environmental Science & Technology*, 36, 4562-4569.

Zipper C. and C. Jage. 2001. Passive Treatment of Acid-Mine Drainage with Vertical-Flow Systems. *Reclamation Guidelines for Surface Mined Land in Southwest Virginia. Powell River Project*. Virginia Cooperative Extension Publication 460-133, Virginia State University.