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A COMBINED PASSIVE SYSTEM FOR THE TREATMENT OF ACID MINE DRAINAGE

**BY
PASCALE CHAMPAGNE-HARTLEY**

**A Thesis presented to
the Faculty of Graduate Studies and Research
in partial fulfillment of the requirements
for the degree of
Doctor of Philosophy in Engineering*
Department of Civil and Environmental Engineering
Carleton University
Ottawa, Ontario
Canada**

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The undersigned recommend to the Faculty of Graduate Studies and Research
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A Combined Passive System for the Treatment of Acid Mine Drainage

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ABSTRACT

Acid mine drainage (AMD) mitigation at Canadian mine sites using passive treatment technologies requires a combined strategy aimed at minimizing the impact of climatic variability of system performance. In this research, a vertical-flow combined passive system was developed, which consists of four components with specific treatment functions: an oxidation/precipitation stage for excess iron removal; a peat biofilter for metal sorption and the establishment of anoxic conditions; sulphate reducing bacteria for alkalinity generation and sulphate reduction; and an anoxic limestone drain for alkalinity addition. A substantial portion of the research focused upon the peat biofilter component, because the removal mechanisms involved in this type of application and the impact of operational parameters on its performance were least understood.

Four laboratory investigations aimed at understanding AMD mitigation were undertaken in this research. (1) Physical/chemical characterization of the peat. (2) Kinetic and equilibrium studies to determine the sorption capacity of the peat. (3) Peat column experiments to assess the impact of substrate/amendment addition, constituent loading, hydraulic loading, water table elevation and ambient temperature on AMD mitigation. (4) Evaluation of a bench-scale combined passive system.

The peat column sorption study conducted at 0°C demonstrated that constituent and hydraulic loading had an impact on metal retention where: $LQ-L[] < HQ-L[] < LQ-H[] < HQ-H[]$, with a general metal breakthrough order of $Cd < Mn < Zn < Al < Ni < Cu < Fe$. At 20°C, sulphate-reducing conditions developed in the HQ columns leading to an increase in effluent pH and metal removal. Sequential extraction indicated that Fe, Cu and Al were typically bound to the organic matter fraction, while Mn, Zn, Ni and Cd were primarily associated with the exchangeable fraction. Substrate/amendment addition improved metal retention in the peat columns when a more readily available source of alkalinity was provided.

A bench-scale combined system dosed with 95 L/m²/d moderate-strength synthetic AMD was operated for 10 months under continuous flow conditions. Removal efficiencies of 99.7%, 99.9%, 99.9%, 98.6% and 99.9% were observed for Fe, Al, Zn, Mn, Ni, and Cu, respectively, while Cd remained fairly mobile through the system. Sulphate concentrations reduced by 73.1% and the highly acidic drainage was neutralized with an effluent pH of 7.2 and alkalinity of 1350 mg/L.

ACKNOWLEDGEMENTS

I would like to thank my supervisors, Dr. P. Van Geel and Dr. W. Parker for their guidance throughout this project. Their comments and observations were appreciated throughout this challenging endeavour.

The Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged for its continued funding throughout my graduate studies. I would also like to acknowledge Simmering and Associates, Continental Mushrooms Inc. and Compostes du Quebec for supplying the *Sphagnum* peat and substrates necessary for this project. I would also like to thank Nimal DaSilva for his help in the ICP analysis and Seprotech Laboratories for supplying us with chemical analyses at a reduced cost.

I would also like to acknowledge Paul Smolkin and Nural Kuyucak from Golder Associates; as well as Genevieve Bechard, Doug Gould and Dave Koren from CANMET for their feedback and insights during the proposal stage of this project. Special thanks to Henri Dinel for his help during the peat characterization study and his continued interest and friendship, Syed Wasay for his guidance during the sequential extraction experiment and Carl Weatherell for the endless supply of reading material on acid mine drainage.

This project would not have been possible without the help of some very special and talented 4th year students: Lorri MacLennan, Thomas Levy, John Sourial and Rinaldo Cristiano who worked on various aspects of this project. Your dedication was truly inspiring.

Many thanks to my family, friends and colleagues for their endless support and encouragement. Special thanks to my husband, Joel, and daughters: Alexandra, Rachel and Camille, whose love and devotion have helped me keep sight of my goals throughout all of my graduate studies.

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CHAPTER 1

INTRODUCTION

1.1 ACID MINE DRAINAGE

Over the last two decades, the mitigation of acid mine drainage (AMD) has become the most significant environmental issue concerning the mining industry. In North America, AMD generation from mining activities has been reported as early as 1698 (Paine, 1987). At active mine sites and some inactive mine sites, comprehensive systems have been developed to collect and treat acidic effluents and seepages. However, the mining industry has the potential to generate large volumes of AMD and acid generation may persist for hundreds of years after mining operations have ceased. Thus, long-term treatment may be required for AMD contaminated effluent streams, even under the best reclamation scenarios, in order to meet increasingly stringent environmental standards (MEND, 1994; Filion and Ferguson, 1989).

Research aimed at understanding and controlling AMD has been ongoing since the beginning of the twentieth century when AMD was identified as an environmental problem. Liming is a common and effective treatment practice to neutralize acidity and precipitate heavy metals. However, this method of treatment becomes expensive due to the extensive period during which treatment is required. Lime neutralization also produces large volumes of potentially hazardous sludge, has high maintenance and operation requirements, and may fail to comply with new, more demanding environmental regulations (MEND, 1994). Hence, efforts by industry and governments are now focusing on the development of new technologies for preventing and treating AMD.

1.1.1 WHAT IS ACID MINE DRAINAGE

Acidic drainage evolves from the chemical and biological oxidation of sulphide minerals contained in tailings and waste rock, mainly pyrite and pyrrhotite, upon exposure to oxygen and water. It is typically generated at mining sites and, as such, is commonly referred to as acid mine drainage (AMD). Few documented cases of acidic drainage sites exist outside of the mining industry.

In the mining environment, mine workings expose sulphide bearing rock surfaces, while, ore processing generates mine wastes in the form of tailings deposits and waste rock piles, which represent the primary sources of acidic drainage. Tailings deposits are a very fine processing waste material (0.01-1 mm particle size) produced on site when the ore is crushed and processed to remove a valuable metal concentrate. The concentrate is then sent to a smelter for further processing and the tailings, which can amount to more than 99% of the original ore, are accumulated in a disposal area. Waste rock ranges in size from a few millimeters to 1 m. It is typically low grade ore that can not be economically processed (Béchar, 1993). Tailings have long been considered an environmental hazard, and consequently, measures were generally taken to reduce their impact on the environment. On the other hand, environmental problems associated with waste rock have only recently been recognized. In the past, these materials were often disposed of at random in piles or used as fill (Ledin and Pedersen, 1996).

AMD often exhibits increased acidity and low pH values which can solubilize many trace metals. The extent of metal complexation and concentrations are dependent upon the composition of the material undergoing oxidation and the oxidizing environment (Béchar, 1993). AMD may contain very high concentrations of total dissolved solids, sulphate, ferrous iron, aluminum and base metals such as lead, copper, nickel, cadmium, zinc or silver depending on the type of mining operation. In

cases where sufficient alkaline materials are present to neutralize acid production, sulphide mineral oxidation can lead to drainage that has a near-neutral pH, but extremely high levels of major ions such as calcium, magnesium and sulphate (Durkin and Herrmann, 1996; Ritchie, 1994a).

1.1.2 IMPACT OF ACID MINE DRAINAGE

The characteristics of mine drainage and its impact on the environment vary widely. The most noticeable evidence of AMD is the reddish brown staining associated with the effluents, which consists mainly of ferric salt precipitates. These precipitates are a source of turbidity, however, they do not, as such, present an environmental problem. Of greater importance in terms of environmental impact are drainage waters containing elevated levels (1 to > 100 mg/L) of trace metals such as cadmium, copper, zinc, etc. which are solubilized due to low pH levels. Major ions such as calcium, magnesium and sulphate can also reach unacceptably high levels, from an environmental standpoint, in near-neutral mine drainage waters (Ritchie, 1994a).

If left uncollected and untreated, AMD can impact the surrounding environment acidifying the soil, killing local vegetation, and contaminating groundwater and local surface waters. Water contaminated with AMD may not be suitable for drinking, agricultural and industrial use, or the support of flora and fauna. In the United States, 10 000 miles of local waterways and 24 000 acres of impoundments and reservoirs are estimated to have been contaminated by acidic drainage (Béchar, 1993).

1.1.3 ACID MINE DRAINAGE IN CANADA

In Canada, approximately one third of the mine sites in British Columbia, Saskatchewan, Manitoba, Ontario, Quebec, New Brunswick, Newfoundland, Yukon and Northwest Territories

generate AMD. These provinces and territories have operating or abandoned acid-generating mine sites, which cover a total area of over 15 000 ha. These sites represent largely accumulation from the last 50 years of mining since the Second World War. It is estimated that with the mining of lower grade ores and the likelihood of increasing annual mineral production, the accumulation of an equal quantity of acidic tailings and waste rock could be achieved over the next 20 years (Filion and Ferguson, 1989).

Canada is a producer of several base metals (copper, zinc, cadmium and lead), precious metals (gold, silver), coal and uranium. Base and precious metals are usually obtained from sulphide ores and are mined across the country. The main generators of AMD at these mining sites are sulphide tailings. Coal is produced in the Atlantic region (New Brunswick and Nova Scotia) and Western Canada (Alberta, Saskatchewan and British Columbia). Western Canadian coals are very low sulphur coals, rarely exceeding 0.8% total sulphur. By comparison, Atlantic coals are high pyritic sulphur coals, averaging 4-10% total sulphur. Consequently, the generation of AMD in the Atlantic region coal fields is more of a problem than in Western Canada. Uranium is mainly produced from mines in Ontario (Elliot Lake area) and Saskatchewan (Rabbit Lake and Cluff Lake areas). The Elliot Lake location has the highest number of acid generating uranium tailings sites containing a total of over 100 million tons. (Paine, 1987).

Canadian AMD characteristics are outlined in a report prepared by Mine Environment Neutral Drainage - MEND (1994). The study incorporates data of 72 effluent streams from 14 metal (gold, copper, lead and zinc) and uranium mines. The quality of the AMD produced exhibits seasonal trends and there is considerable variability in the level of metals present depending on the site and mining operation. Overall, zinc, iron and aluminum are generally found in highest concentrations. The highest concentrations of copper and zinc are usually recorded in the spring, while lead, iron

and cobalt tend to peak in the winter. Conversely, zinc concentrations are at their lowest in the summer and fall, while the lowest concentrations of copper and cobalt are reported in the fall (Kilborn, 1996).

The quantity of AMD generated also varies depending on site and season. Small regraded coal mines can have an average flow of 58.8 L/min, while a flow rate of over 6000 L/min has been recorded for AMD from a tailings impoundment spanning 230 ha at Sullivan Mine in British Columbia (Béchar, 1993). In general, flow rates are higher in the spring and fall than in summer and winter. As a consequence, sulphate and acidity levels are at their highest in the winter and lowest in the spring due to dilution effects.

1.2 APPROACHES TO ACID MINE DRAINAGE PROBLEM

Pollution control is now a major concern in any mining operation. To comply with increasingly stringent government regulations and standards, the mining industry has developed and continues to develop measures to identify and reduce the impact of mining activities on the environment. In the United States, mining companies spend close to \$1 million each day on AMD prevention and abatement (Cohen, 1996). Once the potential for acidic drainage generation has been recognized, through AMD prediction techniques, AMD mitigation strategies can develop along three lines: (1) prevention of AMD generation; (2) control of AMD migration; (3) AMD collection and treatment.

1.2.1 PREDICTION

The prediction of acid generation potential and metal leaching are important from both an environmental and economic perspective. Testing is generally conducted to identify problem materials and develop suitable disposal techniques to prevent the generation or control the

migration of AMD. This can significantly reduce long-term environmental problems and associated financial liabilities.

A detailed understanding of site hydrogeochemistry and the mineralogy of reaction products are essential in determining the fundamental chemistry and reaction mechanisms of sulphide waste materials. Also of great importance are an understanding of site specific conditions and the factors controlling acid generation and drainage water quality. In the last decade, improved analytical protocols have been developed for identifying acid generating sulphide waste materials and predicting the concentration of pollutants to be expected in drainage waters (Broughton and Robertson, 1992).

The main goal, in terms of AMD generation prediction, is to obtain a better understanding of the acid generating process, improve static and kinetic predictive approaches which assess whether a site is likely to produce AMD, and finally, develop computer models to simulate the various components of acid generation and the contaminant migration process in tailings and waste rock (Filion and Ferguson, 1989). Models that can predict the performance of dry and wet covers on stacked tailings and waste rock piles are also being evaluated (Feasby and Tremblay, 1995).

1.2.2 PREVENTION

Prevention encompasses any measure designed to prevent the formation of AMD at the source by inhibiting sulphide oxidation. In theory, this can be achieved by excluding at least one of the elements essential for acid generation, or by controlling the environment to retard the rate of acid generation to an insignificant level (Robertson and Barton-Bridges, 1988). The prevention of acid generation requires one or more of the following control strategies: exclusion of water, exclusion of

oxygen, removal or isolation of sulphides, pH modification, control of bacterial action, or freezing (Kilborn, 1996; Feasby and Tremblay, 1995; Robertson, 1987).

Prevention is the most desirable acidic drainage abatement approach because if acid drainage generation is not initiated, then there is no risk of transport and subsequent contamination to the receiving environment. Current alternative prevention approaches include blending, alkaline addition, bactericides, sulphide isolation, underwater disposal, covers and liners (Broughton and Robertson, 1992; MEND, 1991). However, to date, preventive management strategies do not provide a long-term solution to the problem of AMD. Material failure due to the acidic environment, chemical leaching and the costs associated with the maintenance of some prevention measures are some of the reasons limiting the success of these approaches on a long-term basis.

1.2.3 CONTROL

Once acidic drainage generation is initiated, the next line of defense is to prevent contaminated drainage from migrating into the receiving environment. Water is the primary transport mechanism for the oxidation products. Thus, AMD migration is best controlled by employing strategies which, physically, constrain the flow of water through the diversion of surface waters flowing toward the waste, the interception of or isolation from ground water flow, and the prevention of precipitation infiltration into the sulphide waste (Broughton and Robertson, 1992).

Current AMD control measures typically involve the placement of dry covers and liners over the waste rock pile or tailings impoundment to limit infiltration. This is generally combined with upstream diversion of uncontaminated surface water and groundwater through ditches, cutoff walls or interceptor wells, and pumping (Robertson and Barton-Bridges, 1988). Measures implemented

for AMD migration control in waste rock piles typically differ from those used in tailings impoundments due to the difference in particle size and, hence, the permeability of these wastes.

1.2.4 COLLECTION & TREATMENT

To date, complete prevention and control of drainage from AMD-generating sites has not been demonstrated. Consequently, the collection and treatment of AMD is necessary to comply with established environmental standards. Collection and treatment of contaminated drainage is often the preferred approach, especially at older operating sites and abandoned mines (Kilborn, 1996).

The collection of surface flow is usually readily achieved. Subsurface flows, however, must be diverted to the surface using collection trenches, wells or cutoff walls before they can be collected for treatment (Robertson, 1987). Conventional methods are generally quite effective in treating acidic drainage. However, the potential long-term technical and financial liabilities associated with conventional treatment strategies have increased research interests in developing effective passive treatment options which could be considerably less costly.

1.3 ACID MINE DRAINAGE TREATMENT ALTERNATIVES

Acid mine drainage treatment systems can either be active or passive in nature. Active systems require continuous operation and maintenance, while passive systems are intended to function with limited intervention, care and maintenance. The most commonly utilized technology for active treatment is chemical neutralization. Treatment of AMD by passive strategies generally falls into one of four categories: anoxic limestone drain (ALD) neutralization, biosorption, bioreactors (alkalinity generation and sulphate reduction) and wetland treatment.

1.3.1 ACTIVE TREATMENT

Active treatment most commonly relies on chemistry to reduce the environmental impact of AMD. Generally, the pH is raised by the addition of alkaline materials. Once neutralized, heavy metal ions hydrolyze forming metal hydroxides which then precipitate out of solution. The mixture is often mechanically aerated to accelerate metal oxidation and precipitation. Finally, the neutral overflow containing reduced ions, is discharged to the receiving environment.

Robertson (1987) estimated that each tonne of pyrite in the waste has the capacity to produce approximately 3 tonnes of acidity as CaCO_3 , which when neutralized, would produce about 7 tonnes of dry sludge. The treatment produces a low density, high moisture content sludge, the mass of which will eventually greatly exceed the mass of the sulphide wastes responsible for the acid generation and will, hence, create a disposal problem. Reported sludge densities can vary from 1 to 30% solids depending on the metal concentration of the drainage and the sophistication of the treatment process (Kuyucak, 1995).

Lime as CaO or Ca(OH)_2 is the most commonly used neutralizing agent for the treatment of acidic drainage due to its high reactivity, low cost and availability. Treatment is generally effective and the discharged water meets regulatory standards. However, lime treatment does result in the formation of a voluminous metal hydroxide sludge. As such, many recent studies in the field of chemical neutralization of AMD have focused on process modifications aimed at generating denser sludges. Investigators have also reported that denser sludges can be obtained from the use of alternate neutralizing agents. These include: limestone (CaCO_3), caustic soda (Na_2SO_4), sodium (NaOH) or magnesium (Mg(OH)_2) hydroxide, sodium (Na_2S) or calcium (CaS) sulphide, and

ammonia (NH_3). Some wastes and by-products from industries have also been examined as potential lime substitutes for the treatment of AMD (Kilborn, 1996; Kuyucak, 1995).

Physico-chemical emerging technologies such as ion exchange, solvent extraction and membrane processes (reverse osmosis, ultrafiltration, microfiltration) are employed for site specific treatment applications (Kuyucak, 1997). Electroprecipitation processes have also been shown to achieve similar treatment efficiencies as chemical methods through the precipitation of metal hydroxides or metal ion adsorption (Cohen, 1996). However, none of these methods have been shown to be technically and economically feasible for treating AMD on a large scale.

Active treatment technologies, while they offer sound short-term AMD abatement measures, may not offer cost effective long-term solutions. These processes, both chemical and physical, are severely limited in that they cannot be used to treat the sometimes excessive sulphate concentrations associated with most acidic drainage. These processes also require large capital operations and maintenance costs. Chemical treatment imparts a high degree of hardness to the water (Cohen, 1996). Precipitation must be continuous and the large volumes of sludge produced from such measures require additional treatment and/or disposal. The sludge itself can constitute an environmental hazard, as it is a potential source of metal contaminated leachate if exposed to moderately low pH waters.

Although mining companies operating active mine sites can afford to treat AMD, active treatment is not financially attractive if treatment is required on a continuous basis after mining operations have ceased. For instance, at Waite-Amulet a chemical lime treatment plant built in 1984 at a cost of \$1.8 million, continues to neutralize AMD at an annual cost of \$300 000 to \$400 000. Keeping technical staff on-site in remote areas to operate treatment plants after mine closure is another

concern. Although efforts have been made to optimize current active treatment technologies to reduce sludge production, as well as operating and maintenance costs, these can not be considered long-term solutions to the AMD mitigation problem (Béchar, 1993).

1.3.2 PASSIVE TREATMENT

One of the most promising developments in the treatment of AMD was the recognition of the role of natural processes in the removal of acidity, sulphate and metals from drainage waters. Observations that natural wetlands could mitigate AMD led to the construction of over 300 small engineered wetlands to treat coal AMD in the United States. Most of these wetlands do not currently meet regulatory effluent standards and require a final chemical treatment step (Kleinmann, 1989). This can probably be attributed to the fact that the mechanisms involved in AMD mitigation by wetlands are very complex and are still under investigation. As such, in the past, the design of constructed wetlands has often been from a “black-box” approach. Wetland technology for AMD treatment is still in the experimental stage and may represent a viable alternate treatment technology.

Other passive treatment strategies are also being actively researched as promising treatment options. Major passive processes investigated to date include: wetlands, alkalinity generating and sulphate reducing (SRBs) bioreactors, anoxic limestone drains (ALDs) and biosorbents. In general, they have been found to be suitable for the treatment of low-flow and low-strength AMD (Kuyucak, 1997).

The effectiveness of passive treatment systems and their potential for long term use will depend upon operational conditions. Passive systems have been shown to be most effective in AMD

treatment when designed on a site-specific basis in terms of influent characteristics and geographical location. The aim is to enhance the self-regenerating nature of biological processes and promote interaction between the chemical, physical and biological processes of the system. Operational objectives of passive systems are to decrease acidity through neutralization and sulphate removal, and the precipitation of soluble metals (Silver, 1989). The following criteria have been established for the development of future passive treatment strategies (Béchar, 1993):

1. The treatment process should be effective, effluent streams should comply with regulatory discharge standards
2. The treatment of AMD should not create other environmental problems
3. Materials used for AMD treatment should be renewable, since treatment will be required over an extended period of time
4. Materials should be readily available, since continuous treatment is required
5. The process should be economic
6. The system should be simple to operate, requiring little or no maintenance

Passive treatment appears to have a significant advantage over conventional chemical neutralization, primarily due to reduced operating costs (Gusek, 1995). Passive measures offer the added advantage of operational reliability, while requiring minimal operational control. Passive treatment systems can achieve substantial reductions in net acidity, sulphate levels and soluble metal concentrations, even when subjected to variable influent loadings. While for optimum performance, conventional treatment feed rates must be continually adjusted. They produce less sludge than conventional treatment practices, however, they do, in general, require more space (Hellier *et al.*, 1994).

1.3.3 APPLICATION OF PASSIVE TREATMENT IN CANADA

The primary federal legislation relating to AMD is the Metal Mining Liquid Effluent Regulation (MMLER). Provincial and other regulatory agencies must utilize these standards or more stringent criteria to regulate effluent discharges from mine sites. The ability of passive treatment systems to meet the MMLER will be a function of influent drainage quality and the effectiveness of the system.

To date, much of the research and field applications of passive treatment systems have been aimed at the treatment of acidic coal drainage from the Appalachian region of the United States. Little information is available regarding the applicability and effectiveness of passive treatment systems under Canadian climatic conditions or at Canadian mine sites. Insufficient information is available to assess the potential life expectancy of various passive treatment processes. As well, limited or no information exists regarding the long-term handling and disposal of potentially toxic waste products containing elevated metal concentrations. For passive systems these are typically accumulated in aerobic ponds, wetland vegetation, bioreactor substrates and biosorption materials (Kilborn, 1996).

Canada has been recognized as a world leader in research and development for AMD mitigation. Since 1988, provincial and federal governments, along with the mining industry have funded a cooperative research program to find better approaches to predict, prevent, control and treat AMD (MEND, 1994). One promising approach is the use of combined passive treatment strategies for the treatment of AMD. However, much research is needed to identify individual and combined treatment mechanisms, determine long-term effectiveness and life expectancy at Canadian mine

sites, evaluate applicability under Canadian climatic conditions, and establish design configurations for optimum treatment.

1.4 OBJECTIVES

The main objective of this study was to develop and characterize a combined passive treatment system for the mitigation of AMD under conditions representative of those encountered at Canadian metal mining operations. The combined system consists of four components with specific treatment functions: an oxidation/precipitation basin for excess iron removal; a peat biofilter for heavy metal sorption and the establishment of anoxic conditions; sulphate reducing bacteria bioreactor for alkalinity generation and sulphate reduction; and an anoxic limestone drain for alkalinity addition. The peat biofilter was considered to present the greatest degree of uncertainty in terms of combined passive treatment system performance, hence, a large portion of the thesis research efforts were focused on this component.

In order to achieve this goal, the following tasks were undertaken:

1. Characterization of the physical/chemical properties of the peat.
2. Determination of the sorption capacity of the peat biofilter for heavy metals under varying temperature, pH, constituent loading and hydraulic loading conditions.
3. Determination of temperature profiles and establishment of anoxic conditions via organic substrate biodegradation by aerobic bacteria in the peat biofilter under varying temperature conditions.
4. Development and evaluation of the proposed combined passive treatment system at the bench scale using moderate strength synthetic AMD under continuous dosing conditions.

CHAPTER 2

BACKGROUND

2.1 CHEMISTRY OF ACID MINE DRAINAGE GENERATION

Acid mine drainage results from the oxidation of sulphide minerals, primarily pyrite and other iron sulfides, in coal waste, mill tailings, waste rock piles and abandoned mines. The acidic drainage is generated from a series of complex and interactive chemical, microbiological and physical processes occurring within the mine waste environment. Chemical aspects of AMD include acid generation, metal leaching and acid neutralization; while microbiological aspects are concerned with the bacterial acceleration of chemical reaction rates. The physical aspects of the AMD include hydrogeological processes which are responsible for AMD transport to active chemical and biological oxidation or neutralization sites, as well as for transport to the receiving environment. The combination of these processes leads to the release of acidity, sulphate and dissolved metals from the mine waste environment.

2.1.1 ALKALINITY, ACIDITY AND PH

The alkalinity and acidity of a solution are determined on the basis of its constituent bases and acids, respectively. In terms of the Lewis acid-base classification system, an acid is defined as an electron-pair acceptor and a base is an electron-pair donor. Thus, in general, an electron deficient species can act as a Lewis acid, while a species with a lone pair of electrons can act as a Lewis base.

The presence of alkalinity indicates an excess of chemical constituents containing less protons or Lewis acids than a specified analytical reference species (titration endpoint) when compared to constituents containing more protons than the reference species. The alkalinity of a solution represents its ability to neutralize acidic constituents. Alkaline materials and chemical reactions which provide hydroxide (OH^-), carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) species are generally the most significant alkalinity contributors in mine waste environments.

Conversely, the presence of acidity indicates an excess of constituents containing more protons than the specified analytical reference species (titration endpoint) with respect to constituents containing less protons than the reference species. The acidic character of AMD can be attributed to two types of constituents; protons (H^+) and metal ions (M^{n+}). Proton acidity generally results from the reaction of various constituents with water which produces H^+ ions. Transition metal ions, such as Fe^{3+} , typically exist in solution with a certain number of water molecules bonded to them (*e.g.* $\text{Fe}(\text{H}_2\text{O})_6^{3+}$). The metal or mineral acidity of these metal ions arises from the loss of a proton from an attached water molecule as it reacts with water in the AMD solution.

The pH is a measure of the acidic, neutral or basic nature of a solution. It is expressed as the logarithm of the reciprocal of hydrogen ion concentration in moles per liter. Since the pH only accounts for the presence of H^+ ions, it does not represent the level of acidity of a solution such as AMD, where much of the acidity may be contributed by the presence of elevated dissolved metal ion concentrations.

2.1.2 ABIOTIC ACID MINE DRAINAGE GENERATION REACTIONS

Sulphide minerals are the predominant source of acidity (H^+), sulphate (SO_4^{2-}) and dissolved metals associated with acidic drainage from mine wastes. The oxidation of the sulfide minerals, oxidation of ferrous iron (Fe^{2+}), hydrolysis of ferric iron (Fe^{3+}), and precipitation of metal hydroxides and hydroxysulphates are the principal reactions involved (MEND, 1991).

2.1.2.1 OXIDATION OF PYRITE AND PYRRHOTITE

The most abundant sulphide minerals in base- and precious-metal mine tailings and waste rock piles are pyrite (FeS_2) and pyrrhotite ($Fe_{(1-x)}S$). The oxidation of pyrite by molecular oxygen and water occurs according to the following reaction:

The ferrous ion may then be further oxidized by molecular oxygen to ferric iron

and then hydrolyzed by water and precipitated as ferric hydroxide

Combining the series of oxidation steps results in an overall reaction which yields a total of 4 moles of H^+ for each mole of pyrite oxidized:

Other forms of ferric iron precipitation can also occur, such as goethite (α -FeOOH), or schwetmannite ($\text{Fe}_8\text{O}_8(\text{OH})_6\text{SO}_4$), with these reactions releasing differing amounts of acidity. The generation of AMD as a result of pyrite oxidation is summarized in Figure 2-1.

Figure 2-1: Mechanisms of Pyrite Oxidation (Snoeyink and Jenkins, 1980)

The oxidation of pyrrhotite, the second most abundant sulphide mineral in mining operations can proceed to full completion through the reaction:

or can proceed to only partial completion, generating Fe^{2+} and elemental S^0 through the reaction

In both the complete and partial pyrrhotite oxidation, the ferrous iron released can be further oxidized and precipitated as in Equations (2-2) and (2-3). The elemental S^0 generated from the partial pyrrhotite oxidation can subsequently be utilized in the oxidation of sulphide to sulphate (Blowes *et. al*, 1995b) as described in section 2.1.2.2.

2.1.2.2 SULPHIDE OXIDATION

The sulphide to sulphate oxidation is a series of reactions which involve sulfides (S^{2-}), disulphides (S_2^{2-}), elemental sulphur (S^0), various sulphur intermediates, and sulphate (SO_4^{2-}). Depending upon environmental conditions in the mine waste environment, one or more of these equations may be rate limiting, affecting the overall extent of acid generation as predicted by Equation (2-4).

Sulphur exists in the form of S_2^{2-} in sulfide minerals such as pyrite (FeS_2) and chalcopyrite ($CuFeS_2$). A potential series of reactions, using molecular oxygen and water as oxidants, for the oxidation of S_2^{2-} is given by (MEND, 1991):

yielding an overall reaction of:

The net reaction generates 2 moles of acidity for each mole of sulphide oxidized.

2.1.2.3 ALTERNATE OXIDANTS

In the absence of molecular oxygen, ferric iron (Fe^{3+}) present in the mine waste environment or as a product of pyrite oxidation by oxygen (Equations (2-1) and (2-2)), can be utilized to oxidize sulphide minerals. These reactions can actually generate more acidity than oxidation by molecular oxygen. For instance, the oxidation of each mole of pyrite by 14 moles of ferric iron yields 16 moles of acidity (Blowes and Ptacek, 1994).

The oxidation of ferrous iron has been shown to be the rate-limiting step in AMD generation (Gray, 1997). There is a propagation cycle between ferrous iron oxidation (Equation (2-2)) and pyrite oxidation (Equation (2-9)). Ferric iron (Fe^{3+}), a product of Equation (2-2), acts as an oxidant for the pyrite reaction in Equation (2-9), while the ferrous iron (Fe^{2+}) produced can be utilized as an oxygen reductant in the reaction presented in Equation (2-2).

Manganese is another possible pyrite oxidant which is commonly found in the mine waste environment. In this case, the oxidation of each mole of pyrite by 12 moles of manganese generates 16 moles of acidity (MEND, 1991).

Neither of these reactions involve iron oxidation or precipitation. If the aqueous ferrous iron or manganese were to precipitate as metal hydroxide compounds, the net acidity gained by the waste environment would be enhanced further.

2.1.2.4 OTHER SULPHIDE MINERALS

Other sulphide minerals such as sphalerite (ZnS) and galena (PbS) could also be present in the mine waste environment, depending on the type of mining operation. In this case, however, the net oxidation of these minerals using molecular oxygen and water as oxidants will not generate net proton acidity as would be the case with pyrite or pyrrhotite oxidation (MEND, 1991). For example, the oxidation of galena would proceed through the following reaction:

resulting in an overall reaction of:

Net acidity could be generated if galena were oxidized in the absence of molecular oxygen by oxidants such as ferric iron or manganese. A further source of acidity resulting from the sulphide mineral oxidation by oxygen or other forms of oxidants would be the hydrolysis or precipitation of aqueous metals (Pb^{2+} or Zn^{2+}) from solution as metal hydroxide or metal carbonate minerals (MEND, 1991).

2.1.3 ROLE OF MICROORGANISMS IN ACID MINE DRAINAGE GENERATION

The oxidation of sulphide minerals such as pyrite and pyrrhotite in waste rock piles and tailings impoundments can generate acid as a result of both abiotic and microbially catalyzed chemical reactions. Temperature and pH appear to be determining factors for microbial growth in mine waste environments. The oxidation of sulphide minerals is an exothermic process which can release significant amounts of heat. Interior temperatures of 80°C have been recorded in waste rock heaps (MEND, 1991). Microorganisms (mainly bacteria) which are indigenous to the AMD environment and actively contribute to acid generation or amelioration, are either acidophilic or acid-tolerant. Acidophilic microorganisms typically have pH optima for growth between 2 and 4, while acid-tolerant microorganisms will generally grow best at pH levels above those generally encountered in AMD, but are capable of activity in very low pH environments (Johnson, 1995).

2.1.3.1 OXIDIZING BACTERIA

Thiobacillus ferrooxidans has been the most extensively reported acidophilic organism associated with metal sulphide oxidation in AMD environments. However, other bacteria of the genera *Thiobacillus*, *Leptospirillum*, *Sulfolobus*, *Sulfobacillus* and *Metallogenium* have also been implicated in the mediation of acid generation from sulphide minerals at pH levels below 4. Most of these microorganisms exhibit high tolerances to various metal ions and also to some anions such as arsenate and a majority are chemolithotrophs.

Thiobacillus ferrooxidans is an obligate acidophile that has a pH range of 1.0 to 3.5 and an optimum pH level of approximately 2.0. It is an autotrophic mesophile with a temperature optimum near 35°C. *Thiobacillus ferrooxidans* is capable of obtaining energy from the oxidation of a number of metal sulphides, as well as reduced sulphur compounds such as thiosulphate (S-

SO_3^{2-}), sulphide (S^{2-}) and elemental sulphur (S^0). It can also derive energy via the oxidation of ferrous iron to ferric iron (Evangelou and Zhang, 1995).

Other *Thiobacillus* species are unable to oxidize iron but do oxidize reduced sulphur compounds to sulphuric acid (H_2SO_4). They are typically mesophiles with optimum growth observed between 25 and 30°C. *Thiobacillus thiooxidans* is the most acid-tolerant of the thiobacilli with growth occurring over a pH range of 0.5 to 4.0. *Thiobacillus thioparus*, *Thiobacillus denitrificans*, *Thiobacillus novellus* typically function optimally within pH levels of 6.0 to 8.0. *Thiobacillus denitrificans* can use nitrate or nitrite as a terminal electron acceptor for the oxidation of reduced sulphur compounds. *Thiobacillus novellus* is a chemolithoheterotroph capable of growth on inorganic and organic substrates (Gould *et al.*, 1994).

Leptospirillum ferrooxidans is a gram-negative, mesophilic, acidophilic, obligate autotroph which is capable of oxidizing ferrous iron, but not sulphur. However, it has been noted to attack sulphide minerals under highly acidic conditions (MEND, 1991). *Leptospirillum* bacteria are usually as abundant as *Thiobacillus ferrooxidans* in acidic environments at temperatures equal to or above 20°C; while at lower temperatures, *Thiobacillus ferrooxidans* predominates.

Sulfolobus spp. and *Sulfobacillus* spp. are acidophilic, thermophilic bacteria which can grow autotrophically at pH levels of 1 to 3 over a temperature range of 50 to 90°C. They are capable of both iron and sulphur oxidation under these extreme environmental conditions. A filamentous bacterium, *Metallogenium* spp., has been implicated in the establishment of acid conditions in mine waste environments at pH levels in the range of 3.5 to 4.5 (Gould *et al.*, 1994).

2.1.3.2 BIOLOGICALLY MEDIATED ACID MINE DRAINAGE GENERATION REACTIONS

A succession of pH-dependent microbial activities are thought to be responsible for establishing the conditions that are necessary to promote the growth of sulphur and iron oxidizing bacteria responsible for the production of AMD in mine waste environments. It has been suggested that the acidification of pyrite occurs as a function of three dependent processes; abiotic reactions, biologically mediated reactions and bioleaching. Abiotic reactions generally predominate above pH levels of 4.5. At pH levels below 4.5, iron-oxidizing bacteria such as *Thiobacillus ferrooxidans* catalyze the oxidation of ferrous iron to ferric iron. Bioleaching of metals is also associated with microbial activities that enhance AMD generation. Thus, the production of acid and high metal concentrations via these mechanisms are the main characteristics of the process of AMD generation (Blowes *et al.*, 1995a).

Two distinct modes of microbiological sulphide mineral oxidation may contribute to the generation of acidic drainage in mine waste environments. These are often referred to as the direct and indirect mechanisms. The main difference between the two mechanisms is the requirement for oxygen in the direct mode, while chemical oxidation of sulphides by ferric iron or other oxidized metals can take place in anoxic environments; although the microbial regeneration of the oxidized metal does require oxygen. In general, both mechanisms operate concurrently within the mine waste environment. The interaction between the direct and indirect pathways is illustrated in Figure 2-2.

Direct oxidation requires intimate contact between the microorganism and the metal sulphide mineral due to its low solubility. Either or both of the iron and sulphur components can be oxidized by bacteria yielding metal sulphates, ferrous sulphate and elemental sulphur (Silver, 1989). The indirect oxidation mechanism, on the other hand, does not require contact between the microorganism and metal sulphide mineral. Metal sulphides are chemically oxidized by dissolved

ferric iron, or another oxidized metal such as manganese, which is consequently reduced. Acidophilic metal-oxidizing microorganisms then regenerate the dissolved metal in its oxidized form. This recycling of oxidized dissolved metals allows for sulphide mineral oxidation to proceed (Johnson, 1995).

Figure 2-2: Bacterial Oxidation of Pyrite by Direct and Indirect Pathways (Johnson, 1995).

In the case of pyrite oxidation in the presence of molecular oxygen, pyrite is first oxidized directly by acidophilic bacteria such as *Thiobacillus ferrooxidans* resulting in the formation of ferrous sulphate

which is then directly oxidized to ferric sulphate

Combining the two direct mechanisms yields the following overall biological oxidation reaction

At low pH levels, the ferric sulphate produced by the bacterial oxidation of sulphide minerals could dissociate and result in the oxidation and solubilization of additional metal ions according to the following reaction

Acidophilic bacteria can then regenerate ferrous iron to ferric iron by the indirect oxidation mechanism

The elemental sulphur produced from the chemical oxidation of pyrite using ferric iron as an oxidant, can be subsequently oxidized to sulphuric acid by either *Thiobacillus ferrooxidans* or other acidophiles

In the absence of molecular oxygen, elemental sulphur can be chemically oxidized as follows.

It should be noted that indirect microbial oxidation mechanisms are not limited to metal sulphides; arsenides, carbonates, oxides and silicates can also be solubilized by these biological reactions. In other words, metals that are not present as sulphide minerals, may be leached as a result of indirect mechanisms (Silver, 1989; MEND, 1991).

2.1.4 METAL LEACHING

Another concern associated with AMD is the potential toxicity of elevated dissolved metal concentrations released as a result of acid-generating processes. The aqueous concentration of a metal in solution will depend upon the solubility limit of that metal, the relative concentrations of other dissolved metal species and the pH level of the solution.

There are five principle mechanisms which have an impact on increased dissolved metal concentrations at lower pH levels: (1) oxidation of sulphide minerals; (2) enhanced solubility; (3) ion exchange/sorption; (4) complexation; and (5) kinetic limitations. These mechanisms are collectively referred to as metal leaching (MEND, 1991).

The oxidation of metal sulphide, the fundamental acid generation reaction, releases dissolved metals. For instance, ferrous iron (Fe^{2+}) is released upon oxidation of pyrite (FeS_2) and lead is released upon oxidation of galena (PbS).

The solubility of many non-sulphide minerals is enhanced at acidic pH levels. Higher dissolved metal concentrations are, therefore, directly correlated to the acid-generating process which tends to lower solution pH.

At elevated concentrations of H^+ ions in solution, these protons begin to occupy sorption sites which would normally be available for the sorption of dissolved metals under more neutral pH conditions. As a consequence of this reduced capacity for exchange or removal from solution, higher concentrations of dissolved metals will remain in solution.

Dissolved metals also have the ability to complex with anions such as sulphate, which are typically found in the mine waste environment in a process known as complexation. The complexation of aqueous metals can lead to total dissolved metal concentrations which are higher than those predicted from solubility limits alone.

Factors such as the residence time of water within the waste rock pile or tailings impoundment and/or the flowpath length of the water through the mine waste environment can be significant for certain processes to occur. In such cases, the kinetic processes rather than chemical equilibrium for dissolved metal reactions must be considered due to the time and space dependency of the reaction.

Mechanisms through which microorganisms can impact metal solubility and mobility are numerous and complex. These range from direct processes including metal transformation and intracellular uptake, to indirect processes such as the production of ionic groups and compounds which render the metal more or less mobile through complexation (Ledin and Pederson, 1996).

Metal leaching is a very complex process which is site specific. This process is also dependent upon the rate and extent of acid-generating and acid-neutralizing reactions, and microbiological involvement which add to the complexity. To date, the degree of metal leaching at AMD-generating sites is difficult to predict because the degree of interaction amongst individual mechanisms is not clearly understood.

2.2 EVOLUTION OF ACID MINE DRAINAGE AT MINE SITES

The generation of acidic drainage and the release of dissolved metals from sulfide-bearing rock, such as tailings impoundments, waste rock piles, or even exposed bedrock following construction can vary considerably. Research efforts are generally aimed at the mining industry since most acidic drainage is generated at mining sites and is dependent upon the type of mining operation. External factors and the waste generating environment will also affect the evolution and composition of AMD.

2.2.1 EVOLUTION OF ACID MINE DRAINAGE

Most base metal, precious metal, coal and uranium mines contain sulphide minerals either in the ore or surrounding waste rock. When these sulphide minerals, particularly pyrite and pyrrhotite, are exposed to oxygen and water, they can begin to oxidize almost immediately. At this point, the pH is near neutral and most of the oxidation is chemical (via oxygen). The acidity released is quickly neutralized by alkaline materials present in the waste environment.

As the alkalinity is consumed, the chemical reactions continue to produce acid, sulphate and liberate heavy metals associated with the waste deposit. The pH decreases in stages depending on the type of alkaline materials present and metal dissolution is limited by pH-solubility controls. The mineral species believed to be responsible for AMD neutralization at the three predominant pH stages are (Ritchie, 1994b):

- Calcium-based carbonates pH 5.5 to 6.4
- Aluminum hydroxides pH 4.3 to 5.0
- Iron hydroxides and jarosites pH 3.0 to 3.7

As the reactions continue further, temperature and acidity increase, resulting in an increased rate of chemical reaction. At a pH level of approximately 4.5, bacteria and ferric iron catalyze the reactions, and rates can be 20 to 100 times faster than the original chemical reaction rate (Broughton and Robertson, 1992; Fillion and Ferguson, 1989). At this stage, elevated acidity, sulphate and dissolved metal levels can be detected in the solution of the drainage environment.

There is also considerable lateral movement of moisture within the waste environment due to infiltration or groundwater seepage into the AMD generating environment. The acid generating front can be recognized by the reddish brown colour associated with the oxidized waste rock (Roberston and Barton-Bridges, 1990).

As drainage travels along the flow path, it reacts with the surrounding soil and rock material, changing the pH and contaminant concentrations in the drainage. Acidity may be neutralized by alkaline materials encountered along the flow path. Over time, the acid drainage front migrates along the flow path and eventually emerges and impacts the receiving environment. Acidic drainage and metal leaching to surface waters may not become apparent for many years after the start of mining operations. However, once initiated they can continue for hundreds of years.

A schematic diagram of the space dependence of sulphide mineral oxidation and associated chemical reactions within a waste rock pile is illustrated in Figure 2-3 (Ritchie, 1994a). Three distinct regions can be identified. The outer region is non-reactive in terms of AMD generation since all of the oxidizable material has been oxidized. In the middle region, oxidation of the sulphide mineral is actively occurring and the oxidation products interact with other chemical constituents present in the mine waste environment. This region represents the acid generating front, however, depending on the type of constituents present in the mine waste environment (*e.g.*

carbonates), neutralizing reactions could also take place in this middle region. The lower boundary of this middle region is defined as the point where oxygen concentrations are negligible. Within the inner region, the only products of sulphide mineral oxidation are those transported down by water infiltration (Ritchie, 1994b). Thus, there is interaction of these oxidation products with other chemical constituents present in this region of the mine waste environment and these include acid neutralization reactions. The size, shape and location of each of these regions depend on the rate at which the sulphide-bearing material is oxidized, as well as on gas-transport and water transport mechanisms within the waste environment (Ritchie, 1994a).

Figure 2-3: Schematic Representation of AMD Generation and Transport Processes in a Sulphide-Bearing Waste Rock Pile (Ritchie, 1994a).

2.2.2 FACTORS AFFECTING ACID MINE DRAINAGE EVOLUTION

The processes which control the rate of acid generation and migration in waste rock piles and tailings impoundments, while chemically and biologically similar, are very different in terms of the physical characteristics and can make prediction and control complicated, especially in waste rock piles. Recognition of the differences between conditions applicable to waste rock piles and tailings impoundments is key to both recognizing AMD potential and potential drainage water quality problems; and to evaluate technically and economically effective control measures. The main

factors which require consideration include: sulphide and alkaline material distribution with respect to acid-generating and acid-neutralizing reactions; surface area of the sulphide-bearing material. oxygen transfer, temperature and seepage flow paths affecting the rate of oxidation; as well as the presence of microorganisms which can eliminate the rate-limiting step for iron oxidation by oxygen at lower pH levels.

2.3 ACID MINE DRAINAGE COMPOSITION

Drainage composition can vary widely between AMD generating sites, and is dictated by the physical, chemical, mineralogical and microbiological properties of each site. Physical characteristics include the size, density, source of the waste material; as well as the hydrological properties of the site. The mineral composition of the waste and surroundings determine its susceptibility to chemical and biological oxidation reactions and its potential buffering capacity. The type of mining operation, coal mining versus metal or uranium mining, will also have a large influence on AMD composition. The Metal Mine Liquid Effluent Regulation (MMLER) limits in grab samples for various AMD constituents are presented in Table 2-1.

Table 2-1: Canadian MMLER Limits for Various AMD Constituents (Kilborn, 1996)

Parameter	MMLER Limit
pH	5.0
SO ₄	-
TSS	50 mg/L
Fe	-
Al	-
Mn	-
Cu	0.6 mg/L
Ni	1.0 mg/L
Pb	0.4 mg/L
Zn	1.0 mg/L
Co	-
Cd	-
As	0.5 mg/L

2.3.1 COAL MINING ACID MINE DRAINAGE COMPOSITION

Typical characteristics of AMD from coal mining operations in the Appalachian region of the United States have been reported by Bhole (1994) and Paine (1987). The ranges of component concentrations are summarized in Table 2-2. Paine (1987) suggested that similar ranges in constituent levels should also be expected from Canadian coal mining operations.

Dissolved salts other than sulphates (calcium, magnesium) may also be present in AMD from coal mine drainage. The expected concentration range for total dissolved salts is generally in the order of 100 mg/L to 30 000 mg/L. These levels can lead to a reduction in the quality of potable surface and groundwater supplies. Elevated dissolved heavy metal concentrations can also be encountered. However, these are often not directly associated with AMD from this type of mining operation.

Table 2-2: Reported Characteristics of AMD from Coal Mine Drainage (Paine, 1987)

Parameter	Suggested Range
Flow Rate	57 - 157 L/s
PH	1.4 - 6.2
Acidity (CaCO ₃)	0 - 45 000 mg/L
SO ₄	1 - 20 000 mg/L
TSS	5 - 3 000 mg/L
Fe	1 - 10 000 mg/L
Al	1 - 2 000 mg/L
Mn	1 - 50 mg/L

2.3.2 METAL AND URANIUM MINING ACID MINE DRAINAGE COMPOSITION

A study conducted by MEND (1994) examined the character and composition of 72 individual untreated AMD streams from 30 different uranium and metal mining sites across Canada. Their findings are summarized in Table 2-3. In general, AMD from metal and uranium mining operations contained elevated concentrations of the heavy and trace metals which are present in the mining

ore. The highest flow rates were associated with major water collection systems providing influent streams to existing treatment strategies. Low flows typically originated as drainage from waste rock piles or seepage from tailings impoundments and dams.

Table 2-3: Range in AMD Composition Reported From Canadian Metal and Uranium Mining Operations

Parameter	Composition		
	< 10 L/s (%)	10 - 100 L/s	> 100 L/s
Flow Rate (%)	42	35	33
Suspended Solids (%)	< 10 mg/L 44	10 - 100 mg/L 47	> 100 mg/L 9
Acidity (CaCO ₃) (%)	< 100 mg/L 23	100 - 10 000 mg/L 65	> 10 000 mg/L 12
SO ₄ (%)	< 100 mg/L 10	100 - 10 000 mg/L 78	> 10 000 mg/L 12
Fe (%)	< 1 mg/L 13	1 - 1 000 mg/L 79	> 1 000 mg/L 8
Al (%)	< 10 mg/L 60	10 - 1 000 mg/L 21	> 1 000 mg/L 19
Mn (%)	< 1 mg/L 38	1 - 100 mg/L 49	> 100 mg/L 13
Cu (%)	< 0.1 mg/L 29	0.1 - 10 mg/L 49	> 10 mg/L 22
Ni (%)	< 0.1 mg/L 29	0.1 - 1 mg/L 40	> 1 mg/L 31
Pb (%)	< 0.1 mg/L 43	0.1 - 1 mg/L 32	> 1 mg/L 35
Zn (%)	< 1 mg/L 42	1 - 10 mg/L 21	> 10 mg/L 37
Co (%)	< 0.1 mg/L 30	0.1 - 1 mg/L 46	> 1 mg/L 14
Cd (%)	< 0.01 mg/L 41	0.01 - 0.1 mg/L 45	> 0.1 mg/L 14

*Percentage of reported mining streams falling within the specified parameter range

Higher acidity values were usually reported for drainage from waste rock piles associated with gold mines and copper/gold/silver mines. These high acidity levels tended to be correlated with maximum sulphate concentrations and lower pH values. The majority of pH values reported for Canadian metal and uranium mines fall between 2 and 5 (MEND, 1994). The most important

concern associated with high acidity and low pH levels is the mobilization of heavy metal ions (Ritchie, 1994a). The highest pH values in the MEND (1994) study were associated with tailings ponds at copper/zinc mines.

Waste rock piles generated from gold mining activities yielded the highest range of iron, aluminum, manganese, nickel and lead concentrations indicating the potential detrimental effect of gold mining operations on their receiving environments. The highest lead and zinc concentrations were reported for underground drainage from lead/zinc mines. Maximum copper, nickel, cobalt and cadmium metal ion concentrations were associated with waste rock pile drainage from copper and nickel mines, seepages from uranium tailings dams and copper/zinc mine water, respectively (MEND, 1994). Ritchie (1994a) noted that heavy metal concentrations in the range of 1 to 200 mg/L led to reductions in aquatic flora and fauna, as well as in the quality of surface and groundwater supplies. Very few AMD streams contained detectable levels of arsenic in the MEND (1994) study. The maximum concentration reported was 0.32 mg/L which fell below the MMLER limit of 0.5 mg/L. These detectable arsenic concentrations were recorded at four different combined metal mining operations across Canada: a Quebec copper/zinc/lead mine; an Ontario copper/zinc mine; a British Columbia copper/silver/gold mine; and a British Columbia lead/zinc/silver mine.

The highest suspended solids concentrations have been associated with waste rock piles from gold mining operations, as well as from combined waste rock pile and underground mine working drainage streams from lead/zinc mines. Consideration of suspended solids parameter is of importance because it could potentially influence the effectiveness of the overall AMD treatment process.

2.4 CHEMISTRY OF ACID MINE DRAINAGE MITIGATION

The impact of AMD generation can be minimized by decreasing the net acidity, thereby increasing the pH toward more neutral levels and precipitating aqueous metals from solution. This can be accomplished in the tailings or waste rock environment through a series of geochemical reactions forming a process referred to as acid neutralization. The process involves the dissolution of neutralizing minerals in conjunction with aqueous reactions.

2.4.1 ABIOTIC ACID MINE DRAINAGE NEUTRALIZATION REACTIONS

Neutralization can be conceptualized as the interaction of acid-neutralizing minerals with acid-generating minerals via a liquid transport medium such as water. In an acid-generating mine waste environment, the relative contents of acid-neutralizing and acid-generating minerals and their corresponding rates of reaction will establish the character of the drainage from a tailings impoundment or waste rock pile. The neutralizing minerals are progressively consumed, until the material becomes exhausted. Once this occurs, if the rate of acid generation has not been successfully attenuated, the detection and impact of AMD in the receiving environment will be enhanced.

2.4.1.1 NEUTRALIZATION VIA AQUEOUS REACTIONS

Ions can combine with other ions to form aqueous complexes in a chemical interaction commonly referred to as complexation. The most important reactions in terms of AMD neutralization involve carbonate (CO_3^{2-}) and hydroxide (OH^-) ion complexes. These are often the most significant ion species contributing to the total alkalinity of a water, although other species such as ammonia and boron can also contribute to some level depending upon the geochemistry of the site.

The primary aqueous carbonate species are carbonate (CO_3^{2-}), bicarbonate (HCO_3^-), carbonic acid (H_2CO_3^0) and dissolved CO_2 which are related through the following pH-dependent reactions:

The concentration of H_2CO_3^0 is dominant at pH levels below 6.3, CO_3^{2-} is dominant at pH levels above 10.3 and HCO_3^- is the dominant species between pH levels of 6.3 and 10.3. At pH values in the latter range, significant buffering action can occur which can allow the pH to remain fairly constant despite the addition of acidity or alkalinity (Snoeyink and Jenkins, 1980).

This pH buffering capacity can have major implications in terms of AMD neutralization. For instance, the continuous dissolution of carbonate minerals adding carbonate (CO_3^{2-}) ions to acidic water will tend to increase the pH as free H^+ ions combine with carbonate ions to form bicarbonate (HCO_3^-) ions and then carbonic acid (H_2CO_3^0), thereby consuming a total of 2 H^+ ions. This reaction will be dominant until a solution pH of 6.3 is reached. Above this level, carbonate ions will continue to combine with H^+ ions forming HCO_3^- raising the pH above 6.3. However, only one H^+ ion can be neutralized for each carbonate ion added to the water because the formation of HCO_3^- rather than H_2CO_3^0 is favored above this pH level. In fact, as the pH continues to rise, H_2CO_3^0 begins to break down to HCO_3^- releasing H^+ ions. Thus, additional alkalinity is required to neutralize the acidity generated from bicarbonate acid and raise the pH above 6.3.

Hydroxide ions (OH^-) can also neutralize acidity by reacting with H^+ ions and producing water.

However, neutralization by hydroxide is usually less significant than carbonate neutralization in mine waste environments unless the site specific geochemistry dictates otherwise. This is mainly because concentrations of free OH^- ions below pH levels of 7 are very low. As well, the formation of various metal hydroxide complexes such as AlOH^+ and $\text{Fe}(\text{OH})_2^+$ occurs even at acidic pH levels which consumes any of the free OH^- ions present in solution (MEND, 1991).

2.4.1.2 NEUTRALIZING MINERALS

The principal acid-neutralization mechanisms affecting the pH of AMD waters are the dissolution of carbonate and hydroxide minerals. The dissolution and, hence, neutralizing capacity of various mineral groups, has been reported to occur in series depending upon the pH of the drainage water. The sequence of pH-buffering reactions observed in mine waste environments results in the development of a series of pH regions that can control the mobility of dissolved metals such as aluminum, chromium, nickel, cadmium, copper, cobalt and lead. The following sequence of mineral groups and equilibrium pH ranges has been established based upon complexation and mineral-solubility calculations (Blowes and Ptacek, 1994; MEND, 1991):

- Calcium-based carbonates 5.5-6.9
- Iron-based carbonates 5.1-6.0
- Aluminum-hydroxide-bearing minerals 4.3-5.0
- Iron-hydroxide-bearing minerals 3.0-3.7

Major calcium-based carbonate minerals include calcite (CaCO_3) and dolomite ($\text{CaMg}(\text{CO}_3)_2$), while the main iron-based carbonate minerals include siderite (FeCO_3) and ankerite ($\text{CaFe}(\text{CO}_3)_2$) (Blowes and Ptacek, 1994). The extent to which each of these minerals can release carbonate to neutralize acidity before its solubility limit is reached depends upon environmental factors such as

solution pH and the relative concentrations of other metal species in solution (Snoeyink and Jenkins, 1980).

Aluminum-hydroxide-bearing minerals include combinations of metals and hydroxides such as gibbsite ($\text{Al}(\text{OH})_3$), boehmite (AlOOH) and basaluminite ($\text{Al}_4(\text{OH})_{10}\text{SO}_4$). Amorphous ferric hydroxide ($\text{Fe}(\text{OH})_3$), goethite (FeOOH) and potassium jarosite ($\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$) are representative of the major iron-hydroxide bearing minerals (Blowes and Ptacek, 1994). As with carbonate minerals, the neutralization capacity of hydroxide-based minerals is dependent upon environmental factors such as pH and the concentration of other dissolved ions in solution. As well, the degree of crystallinity with some of these minerals can affect their solubility (MEND, 1991).

Once the acid-neutralizing carbonate and simple hydroxide species have been depleted, the dissolution of aluminosilicate minerals can become an important acid-neutralization mechanism. The main species generally include chlorite ($(\text{Mg, Al, Fe})_6(\text{Si, Al})_4\text{O}_{10}(\text{OH})_8$), muscovite ($\text{KAl}_2(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH},\text{F})_2$) and feldspars ($(\text{KNa})\text{AlSi}_3\text{O}_8$). Dissolution of aluminosilicates typically occurs at low pH levels and at very slow rates. The extent of acid-neutralization by aluminosilicate dissolution reactions will be limited by the completion of the acid-neutralizing reaction as a result of contact time between the acid-neutralizing materials and the acidic drainage.

2.4.1.3 PHOSPHATE AS A NEUTRALIZING AGENT

Phosphate can also be utilized as a means of precipitating iron and aluminum and neutralizing pH levels. This is achieved through the following sequence of reactions:

These reactions will occur preferentially in the sequence provided in Equation (2-23). After the completion of iron and aluminum precipitation reactions, the pH level increases due to the phosphoric acid formation which consumes H^+ ions. Once in this form, phosphate is then available for uptake by microorganisms and plants via biological processes (Kalin *et al.*, 1994).

2.4.2 ROLE OF MICROORGANISMS IN ACID MINE DRAINAGE MITIGATION

Microorganisms can be involved in AMD abatement primarily via metal reduction, sulphate reduction and other alkalinity generating processes. The extent to which each process may contribute to AMD neutralization depends upon AMD composition, availability of necessary electron donors and acceptors, redox potential, as well as temperature and pH conditions within the mine waste environment.

2.4.2.1 REDUCING BACTERIA

Acidophilic heterotrophic bacteria present in the AMD environment may be involved in AMD mitigation, as well as iron and manganese cycling. Some of these bacteria such as *Acidiphilicum* spp play a passive role by metabolizing organic materials that are potentially toxic to iron-oxidizing bacteria, thereby inhibiting biologically mediated iron oxidation reactions (Johnson, 1995). Other species have demonstrated the ability to reduce ferric iron, present either as soluble or as solid phase compounds, to ferrous iron (Johnson, 1995).

Manganese and iron reduction may also contribute to the neutralization process. A great variety of microorganisms can directly reduce manganese and iron by using them as final electron acceptors under anaerobic conditions. These organisms include heterotrophic bacteria such as *Pseudomonas*, *Clostridium* and *Desulfovibrio*. The ability to reduce ferric iron is widespread amongst acidophilic heterotrophic bacteria and has been reported for *Thiobacillus ferrooxidans* growing on elemental sulphur. The reduction of ferric iron is of significant importance in AMD mitigation because it yields ferrous iron which then reacts with sulphide produced by sulphate reduction, and ultimately results in alkalinity generation.

Sulphate reducing bacteria (SRB) encompass a heterogeneous group of species with very diverse functions. No truly acidophilic bacteria capable of sulphate reduction have been reported (Johnson, 1995). SRB use simple organic compounds as electron donors under anaerobic conditions ($E_h < 150$ mV); usually resulting from the degradation of carbohydrates, proteins and other components of dead biomass. SRB typically depend on other microorganisms to supply the required substrates as they are unable to use complex organic molecules directly. Sulphate reduction leads to permanent alkalinity when a product of reaction, hydrogen sulphide (H_2S), is released permanently from the mine waste environment (Gould *et al.*, 1994).

Other biologically mediated processes which can contribute to AMD neutralization by ultimately consuming H^+ ions include: ammonification by various microorganisms and enzymes; denitrification mediated by a number of bacterial species such as *Pseudomonas*, *Paracoccus*, *Flavobacterium*, *Alcaligenes*, and *Bacillus* spp.; and methane generation by methanogenic bacteria ($E_h < 330$ mV).

2.4.2.2 BIOLOGICAL REDUCTION

There are several microorganisms capable of mediating reduction reactions and generating alkalinity (Gould *et al.*, 1994). The most significant group in terms of AMD mitigation are the sulphate reducing bacteria (SRB). Sulphate reducing bacteria are strictly anaerobic bacteria which, in the absence of oxygen and nitrate, utilize simple organic compounds as electron donors for the reduction of sulphate employed as the electron acceptor. For instance using lactate as a simple carbon source

Sulphate reduction produces the bicarbonate (HCO_3^-) and hydrogen sulphide ions (HS^-) which attract free hydrogen ions (H^+) producing carbonic acid (H_2CO_3^0) and hydrogen sulphide (H_2S). At reduced pH levels, H_2S gas will be released permanently from the system. Sulphide can also be immobilized within the system by forming elemental sulphur or by reacting with iron or other metals to form insoluble metal sulphide precipitates which will ultimately generate alkalinity.

The production of ammonia has also been reported to contribute to neutralization. Ammonia can be produced from organic nitrogen by ammonification. Nitrogen in organic matter occurs mainly in the amino form, NH_2^- . The enzyme-catalyzed hydrolysis of urea yields ammonia and carbon dioxide:

In acidic to neutral conditions, ammonia is rapidly transformed to ammonium ions through the consumption of hydrogen ions.

For every ammonium ion produced, one proton is removed from solution, thereby directly neutralizing AMD. In systems where oxygen is not available but nitrate is present, a number of anaerobic microorganisms, including some SRB, can utilize nitrate as a final electron acceptor and reduce it to nitrogen gas through the following pathways in a process referred to as denitrification. In AMD containing nitrate, neutralization results from H^+ consumption during the reduction processes. For example, denitrification from formaldehyde can proceed in AMD mitigation through the following proton consuming reaction

In the absence of oxygen, nitrate and sulphate, methanogenesis can also contribute to the neutralization of acidic drainage. As with SRB, methanogens cannot use complex molecules for growth directly and depend on other microbial populations to consume and breakdown more complex organics and supply their substrates. The methanogens then utilize these very simple compounds to produce methane (CH_4). For example, the methanogenesis from acetate can participate in AMD mitigation through the following proton consuming reaction

A variety of microorganisms can directly reduce manganese and iron, using them as final electron acceptors under anaerobic conditions leading to alkalinity generation. As previously discussed, the ability to reduce ferric iron is widespread amongst acidophilic heterotrophic bacteria, however, little information is available on the mechanisms involved in microbial reduction of iron and manganese. It has been suggested that alkalinity is generated from the dissociation of $\text{Fe}(\text{OH})_3$:

Iron reduction, using sulphate and hydrogen gas along with a simple carbon source, generates ferrous iron which reacts with sulphide produced by the reduction of sulphate. The following overall reaction for ferric hydroxide dissociation, iron reduction and consequent alkalinity generation has been postulated (Gould *et al.*, 1994).

In this case, both sulphate and iron reduction are necessary to remove sulphide and iron from solution and also to prevent them from re-oxidizing (Gould *et al.*, 1994).

2.5 PASSIVE TREATMENT SYSTEMS

Passive treatment systems were initially considered attractive to treat AMD due to their lower costs of construction, operation and maintenance, and their ability to operate at remote locations with limited operational requirements, as compared to conventional chemical treatment schemes. In addition, acid generation at many mine sites is likely to continue for decades after decommissioning of the mine. As such, there is a financial incentive for continued research and development of these low-cost and low-maintenance treatment strategies.

Passive treatment systems utilize chemical, biological and physical removal processes that occur naturally in the environment to modify AMD characteristics. In combination, these processes have the potential to effectively generate alkalinity, neutralize pH levels, reduce dissolved iron and other metal concentrations, as well as reduce sulphate concentrations.

Passive treatment strategies for AMD mitigation are classified into four major categories (Kilborn, 1996): (1) wetlands; (2) anoxic limestone drains; (3) biosorption systems; and (4) bioreactors.

2.5.1 CONSTRUCTED WETLANDS

Wetlands are composite ecological systems where a variety of physical, chemical, microbial and plant-mediated processes occur which can cause significant changes in the water chemistry. Early investigations (Eger *et al.*, 1980; Eger and Lapakko, 1988) indicated that natural wetlands had a significant capacity for trace metal removal and, hence, were a potential alternative for AMD mitigation. Subsequent studies involving drainage from coal (Wheeler, *et al.*, 1991; Kalin *et al.*, 1990; Tarutis and Unz, 1989) and metal mine (MEND, 1990; Pett *et al.*, 1990) sources reported that heavy metal concentrations and low pH levels encountered in AMD could not be successfully mitigated under natural conditions. However, it was found that redirecting flow paths through the system, as well as the addition of organic amendments and nutrients to these natural systems enhanced alkalinity generation conditions which improved metal removal and neutralized the pH.

General removal mechanisms which have been identified in natural and constructed wetlands include metal oxidation/precipitation, metal adsorption/complexation by organic substrates, sedimentation, filtration of suspended and colloidal particles, active plant uptake and microbial sulphate reduction followed by precipitation of metal sulphides (Cohen, 1996). Plant growth and decay in wetlands provide a constant source of organic substrate. The organic matter provides ion-exchange and adsorption sites while stimulating a consortium of bacterial activity, which promotes a number of biotic and abiotic processes. Wetland vegetation also provides attachment sites for bacterial growth, and flow channels, thereby increasing the contact between the microorganisms and nutrients within the system.

In most wetlands where a free water surface exists, aerobic conditions exist throughout the water column and anaerobic conditions develop mainly below the sediment surface as shown in Figure 2-4. Metals are removed in the aerobic zones by oxidation, precipitation, adsorption and complexation reactions, while neutralization is primarily achieved in anaerobic zones by SRB activity. The increase in alkalinity is generally associated with other chemical and microbial reactions, such as the dissolution of limestone beds.

Figure 2-4: Schematic of a Free Surface Flow Wetland (Kalin & Van Everdingen, 1987).

In recent years, optimization of constructed wetlands has improved AMD treatment efficiency. Constructed wetlands can be classified as either aerobic or anaerobic wetlands, or a combination thereof. Sequential treatment using combinations of aerobic and anaerobic wetland cells have been reported to be effective in generating alkalinity and attenuating AMD (Kepler and McCleary, 1994; Brodie *et al.*, 1991). An example of staged aerobic and anaerobic constructed wetland cells is illustrated in Figure 2-5.

Figure 2-5: Schematic Representation of a Staged Constructed Wetland (Cambridge, 1995).

Anaerobic wetlands are generally employed to treat drainage waters which contain elevated concentrations of iron and aluminum or acidities greater than 300 mg/L as CaCO_3 . Subsurface flow through a 30 to 45 cm deep organic substrate under anaerobic conditions promotes chemical and microbial processes which generate alkalinity. The substrate usually consists of low-cost, high organic content materials such as spent mushroom compost, sawdust, manure, hay or peat which act as a nutrient source for reducing bacteria. A neutralizing source such as limestone is also generally included below the substrate layer (Kleinmann, and Hedin, 1993).

Aerobic wetland cells, on the other hand, are typically 15 to 45 cm deep water columns designed to maximize oxidation reactions which cause the precipitation of metals, primarily iron and/or manganese, as oxides and hydroxides. The precipitates are then incorporated into the wetland sediment. This type of wetland is most effective for drainage waters which are alkaline in nature (Hedin, 1996). As dissolved metals are oxidized, a net increase in acidity is generally observed in these systems due to the release of H^+ ions and/or the consumption of alkalinity associated with oxidation reactions.

2.5.1.1 PHYSICAL, CHEMICAL AND BIOLOGICAL CONSIDERATIONS

The low treatment efficiencies reported in some natural and constructed wetlands can probably be attributed to the heterogeneous nature of wetland systems. The horizontal and vertical distribution of nutrients, organic and inorganic substrates, redox zones, water chemistry, microbial productivity, and flow hydraulics through the system are not homogeneous (Kilborn, 1996). However, it is possible to minimize the degree of this non-homogeneity and improve AMD mitigation efficiency by introducing design modifications.

Wetlands differ in terms of substrate and water chemistry, vegetative cover and density, flow hydraulics, retention time, treatment area and other design characteristics (Witthar, 1993). The efficiency of natural and constructed wetlands in treating AMD will depend upon the composition and loading of the acidic drainage in relation to the physical characteristics of the system (Watson *et al.*, 1989). Enhancement of both microbial activity and plant productivity is also critical in establishing long-term metal removal and pH neutralization. It is essential to recognize that opposing mechanisms such as oxidation and reduction, neutralization and acidification, and

solubilization and precipitation can take place throughout the wetland systems unless they are compartmentalized by specific design constraints.

The design of constructed wetlands should consider the impact of precipitation and spring runoff on the constituent loading, flow hydraulics, sediment transport and erosion (Taylor *et al.*, 1993; Stark *et al.*, 1990). Adequate flow hydraulics and retention times are necessary to ensure maximum contact between the microorganisms, organic substrate and drainage. A number of sizing recommendations have been proposed for AMD generated from coal mining operations. These are based on criteria such as hydraulic loading and influent pH, iron and manganese values (Wildeman, 1991; Wieder *et al.* 1989). Hellier *et al* (1994) recommended a composite sizing index for determining wetland area based on the influent acidity, iron and manganese loadings. Drainage alkalinity is also important in the design and sizing of wetlands. In most instances, coal mine drainage with a net alkalinity, as opposed to a net acidity, can be treated using a simple aerobic systems (Kleinmann *et al.*, 1991).

Organic substrates commonly employed in constructed wetlands include: mushroom compost, sphagnum peat, hay, sawdust and wood shavings (Taddeo and Wieder, 1991). A study by Gross *et al.* (1993) examined the potential use of agricultural by-products such as manure, chicken litter, barley mash and rice hulls as alternate organic sources. Cattail, bulrush, sedges and *Sphagnum* peat are the most common vegetation encountered in natural and constructed wetlands. These species are highly tolerant to the low pH and elevated metal loading conditions imposed by AMD streams (Kalin *et al.*, 1990; Pesavento, 1987). Periodic use of fertilizers is recommended for most wetland operations in order to promote plant growth and enhance the efficiency of the system.

Cattails, peat and other wetland plants have appreciable cation exchange capacity and can bioaccumulate significant quantities of heavy metals (Pett and Lane, 1990; Sencindiver and Bhumbra, 1988). Metals can also adsorb onto metal precipitates formed as a result of oxidation and reduction reactions. However, many of the metal removal mechanisms involved are temporary and reversible. Processes such as accumulation and decay of organic detritus over a period of time can produce an oxygen demand in excess of what the wetland vegetation can replenish, resulting in the development of extensive anaerobic or facultative zones.

2.5.1.2 SYSTEM PERFORMANCE

The performance of wetland systems reported in the literature is highly variable. This is attributed to the fact that in many cases, wetland systems have been designed using a black box approach. Six multi-cell surface flow constructed wetlands receiving coal mine drainage in Pennsylvania were examined by Dietz *et al.* (1994). The total treatment surface area of the wetlands ranged from 92 m² to 1340 m². Metal removal efficiencies among the wetlands ranged from 35% to 50% for iron, from 0% to 50% for aluminum and from 0% to 30% for manganese. In addition to metals, the wetland treatment systems also decreased acidity concentrations by 40% to 90%.

Hellier (1989) reviewed data from 144 wetlands receiving AMD from Pennsylvania mine sites and assessed that wetlands with average influent net acidities of less than 200 mg/L were typically effective in mitigating effluent iron concentrations, but not manganese concentrations. For the 3000 m² Simcoe wetland operation near Coshocton Ohio, average reductions of total iron, acidity, alkalinity and sulphate were observed to be 62%, 74%, 70% and 7%, respectively, over a treatment period from November 1985 to October 1989 (Stark *et al.*, 1990). Total manganese and suspended solids, on the other hand increased by 5% and 25%, while the pH remained fairly constant at 6.5.

Twelve staged, aerobic wetlands managed by the Tennessee Valley Authority (TVA) have treated AMD from coal mining operations since the early 1980's and have consistently complied with U.S. monthly average effluent limits. The wetlands were generally hydraulically loaded between 0.02 to 0.24 L/day/m², and ranged in surface area from 1200 to 25 000 m² and in depth from 15 to 20 cm. Average discharge parameters were reported as follows: pH 6 to 9, iron < 3 mg/L, manganese < 2 mg/L, and total suspended solids < 35 mg/L (Brodie, 1993). At the Fabius Impoundment 1 (5700 m²), also managed by the TVA, iron was reduced from 69 mg/L to 0.9 mg/L, manganese from 9.3 mg/L to 1.6 mg/L, and the pH was raised from 3.5 to 6.8 (Brodie, 1991).

Most of the studies involving the treatment of AMD from coal mining sources reported iron removal rates which were much higher than manganese removal rates (Hellier, 1989). Results from laboratory mesocosm experiments (Tarutis and Unz, 1994) indicated that the generation of sulphide by bacterial sulphate reduction could effectively retain iron, but not manganese within anoxic soils. This was attributed to the lower solubility of iron sulphide, compared to manganese sulphide, under the operational pH range of the experiments.

To date, the majority of constructed wetland research has focused on the treatment of AMD from coal mining operations in the United States. The removal of iron, manganese and aluminum in wetland systems has, thus, been documented. However, there have been very few reported results on other metals common to Canadian metal mine AMD streams such as copper, lead, nickel and zinc. The concentrations of these metals in wetland systems could influence the degree of toxicity tolerated by wetland plants and microorganisms, and, hence affect the potential long-term viability of such systems.

Eger and Lapakko (1989) did observe overall nickel reductions ranging from 39% to 86% in four 6 m x 30.5 m wetland cells treating AMD from a metal mine in Minnesota. Short-term tests demonstrated that other trace metals, namely; copper, cobalt and zinc, were reduced by 83% to 94%. Later, test work was also performed on aerobic and anaerobic configurations at the same site for hydraulic residence times ranging from 18 to 48 hours (Eger, 1994). Aerobic overland flow systems were successful at removing copper, cobalt, nickel and zinc from neutral mine drainage. Nickel, which was the main metal contaminant, was reduced by approximately 90%. An anaerobic sulphate reduction system was able to treat AMD for a period of two years, increasing pH levels from 5 to >7 and reducing metal concentrations by more than 90%.

Many systems have attempted to maximize flow contact with the substrate by reducing short-circuiting and controlling velocities using hay bales and serpentine paths. A problem encountered in treating AMD with wetland systems is that they are surface-flow operations where the opportunity for contacting root-zone plants and sediments is limited. McIntire and Edenborn (1989) reported a significant increase in pH (2.9 to 6.5) and alkalinity, as well as a decrease in iron when AMD was forced through the anaerobic zone. The formation of iron sulphide accounted for 20% to 28% of the iron removed from coal mining AMD in a constructed cattail wetland (Calabrese *et al.*, 1991), indicating that sulphur reduction was a significant removal mechanism. However, a study by Taddeo and Wieder (1991) suggested that the importance of this iron retention mechanism in sediments would differ from wetland to wetland depending upon operating conditions, microbial populations and AMD constituent loadings.

Seasonal variability was observed in the Simcoe wetland operation near Coshocton, Ohio with iron removal being highest in summer and lowest in spring (Stark *et al.*, 1990). These results are consistent with the fact that summer is the season of lowest hydraulic loading and highest

biological treatment efficiency, while spring presents the highest hydraulic loadings due to spring runoff and relatively low biological activity in wetland systems. Taylor *et al.* (1993) reported that storm events could alter flow hydraulics within the system and, hence, negatively impact the performance of constructed wetlands designed to treat coal mine drainage.

The development of the vegetative cover, and addition of peat and organic amendments can play significant roles in the treatment efficiency of constructed wetland systems. Once the wetland vegetation cover and populations of microorganisms are established, the self-sustaining and self-regenerating nature of the wetland system can be maintained through periodic fertilization which provides plant nutrients. The composition, rate and frequency of the applied fertilizer will depend on influent composition. Studies have shown that the presence or addition of peat in constructed wetlands can enhance the removal of metals significantly due to the high sorption capacity of the peat substrate (Eger *et al.*, 1994).

Once well established, a wetland system will generate large deposits of organic sediments which can be decomposed further and provide anaerobic zones. Efficient wetlands accumulate metals and other precipitation products which are then stored in the substrate and biomass. This is a particularly important consideration at Canadian operations where the metal loadings in AMD exceed those in the United States (Kilborn, 1996). At some time, the treatment components in a wetland will become saturated with metals and reaction products, and will need to be regenerated, replenished or replaced. Wetland studies have yet to address the issue of waste generation and the disposal of treatment products.

2.5.2 ANOXIC LIMESTONE DRAINS

Anoxic limestone drains (ALDs) treat AMD having a net acidity by adding alkalinity to the water. These systems consist of underground crushed limestone beds through which the oxygen-depleted AMD streams are conducted. ALDs are typically buried to exclude oxygen, hence minimizing the occurrence of limestone armouring with metal hydroxide precipitates. Burial of ALDs also allows for the development of high CO₂ partial pressures which increases alkalinity concentrations beyond those possible under normal atmospheric conditions (Kilborn, 1996).

In ALDs, the acidic drainage passes through the drain where the acidity reacts with the limestone releasing carbonic acid (Brant *et al.*, 1995; Brodie *et al.*, 1991).

The carbonic acid then reacts with the limestone to produce alkalinity.

As the pH increases above 6.3, bicarbonate becomes the dominant dissolved species; thus as the acidity reacts with the limestone, alkalinity is generated directly.

In short, ALDs increase calcium concentrations, increase alkalinity, reduce acidity, and as a consequence, increase pH levels. Metal removal generally occurs downstream from the ALD under aerobic conditions. At near neutral pH levels, the introduction of highly alkaline water allows for the oxidation, hydrolysis and precipitation of metal hydroxides.

2.5.2.1 PHYSICAL CHARACTERISTICS

Anoxic limestone drains are essentially trenches filled with crushed limestone through which the contaminated AMD flows by gravity. The system is typically sealed under plastic and geotextile fabrics, and covered by a fairly impermeable soil. Figure 2-6 provides a schematic representation of a typical ALD.

In general, high calcium limestone is the most effective material for ALDs (Kilborn, 1996). The size of crushed limestone utilized in the drain is a compromise between enabling free flow and allowing sufficient surface area for dissolution. Faulkner and Skousen (1994) suggested that larger particle sizes (8-25 cm) along with finer particles (2-4 cm) should be used in ALDs to increase hydraulic conductivity and reduce the potential for plugging.

Figure 2-6: Schematic Representation of a Typical ALD (Hedin *et al.*, 1994)

Anoxic limestone drains are generally shallow in depth, and contain an effective limestone thickness of 1 to 2 m which is covered by a minimum of 0.6 m of soil. Traditionally, ALDs have been narrow in width (0.6 m to 1.0 m), with sufficient length to provide the required retention time for chemical equilibrium based upon the predicted flow regime of the site. However, drains of 10 m to 20 m wide have also been shown to be effective, and produce alkalinity concentrations similar to the narrower systems configurations (Gazea *et al.*, 1996; Hedin *et al.*, 1994).

Retention times ranging from 14 hours to 23 hours have been suggested by various authors (Faulkner and Skousen, 1994; Hedin and Watzlaf, 1994; Hedin *et al.*, 1994). It has been noted, however, that retention times beyond 23 hours will not achieve further alkalinity in ALD systems (Kilborn, 1996).

A plastic cover and geotextile fabric are usually placed over the crushed limestone to prevent oxygen penetration and to maintain high CO₂ partial pressures (Brodie *et al.*, 1993). Placement of a geotextile fabric on top of the cover helps protect the plastic from rupture during construction and resists root penetration. The geotextile fabric is then covered with a minimum of 0.6 m of compacted soil (Brodie *et al.*, 1991) and seeded with shallow root vegetation. A compacted clay cap is usually preferred since it is a more effective oxygen barrier.

2.5.2.2 INFLUENT REQUIREMENTS

Anoxic limestone drains are most effective for influents with dissolved oxygen concentrations < 1 mg/L, ferric iron (Fe³⁺) and aluminum (Al³⁺) concentrations < 1 mg/L, sulphate concentrations < 2000 mg/L and pH levels below 5.5 (Wildeman, *et al.*, 1997; Kepler and McCleary, 1994; Brodie

et al., 1991). Higher concentrations of dissolved oxygen within the influent allow the oxidation of ferrous iron (Fe^{2+}) to ferric iron (Fe^{3+}).

When highly acidic metal contaminated water contacts limestone, the first reaction to occur is the neutralization of proton acidity. This reaction raises the pH level of the drainage. As the pH level increases, the solubility of metal hydroxides decreases. Thus, the presence of dissolved ferric iron or aluminum concentrations above the recommended levels can cause the precipitation of metal hydroxides. Between pH levels of 3 to 4, ferric iron begins to precipitate as ferric hydroxide, while aluminum precipitates as aluminum hydroxide between pH level of 4 to 5. The formation of metal hydroxides can result in limestone armouring and a decrease in limestone dissolution, or system plugging and reduced flow. Ziemkiewics *et al.* (1997) investigated seven armoured open limestone channels which were able to reduce AMD acidity by 4 to 62%. In general, steeper channel slopes were found to be more effective because flow velocities could maintain hydroxide precipitates in suspension.

As the pH rises above 4.5, the bicarbonate concentration begins to increase and the solubility of metal carbonates may be exceeded, causing the precipitation of siderite and then rhodochrosite. With each precipitation reaction, calcium is released into solution which increases the potential for gypsum (CaSO_4) formation within the ALD at high influent sulphate concentrations ($>2000 \text{ mg/L}$). Gypsum can decrease the rate of limestone dissolution due to armouring, as well as reduce the flow through the system. In both cases, the ability of the ALD to generate alkalinity is reduced and failure of the system can occur (Kilborn, 1996).

2.5.2.3 SYSTEM PERFORMANCE

The generation of alkalinity in an ALD is limited by the solubility of the limestone. The maximum alkalinity concentrations achievable by use of an ALD are reported to be approximately 300 mg/L as CaCO_3 under high CO_2 partial pressures, with a maximum sustained concentration of approximately 275 mg/L. Comparatively, an open limestone system equilibrated to atmospheric CO_2 concentrations can only produce alkalinity in the range of 50 to 60 mg/L (Hedin *et al.*, 1994).

Anoxic limestone drains can successfully neutralize AMD which has an acidity of < 300 mg/L as CaCO_3 (Gazea, *et al.*, 1996; Hedin, 1996). If the influent contains greater levels of acidity, the ALD may not be able to produce a net alkaline effluent and further downstream alkalinity addition may be required, to meet effluent standards. The chemical composition and toxicity of the ALD effluent will depend upon the quality of the AMD influent.

The presence of organic matter and microorganisms has been shown to reduce ALD effectiveness. At a number of sites where hay was added to enhance ALD effectiveness, the rate of limestone dissolution decreased because the hay encouraged microbial growth which reduced the available pore space and the surface area available for dissolution. In addition, the hay was found to clog openings within the system and cause hydraulic failure (Faulkner and Skousen, 1994).

Anoxic limestone drains require little maintenance, usually limited to periodic site inspections and vegetation cover maintenance, which can be carried out once or twice a year. The ALD should be replaced once chemical reactions exhaust the limestone, dissolution of the limestone causes the surface to subside, or flow channelization is initiated, thereby reducing the retention time and exposure of the AMD to the limestone effective surface area. Although long-term data is not

available, research suggests that ALDs can be expected to be effective for 20 to 80 years, and perhaps even longer (> 100 years) depending on the influent characteristics (Brodie et al., 1993).

2.5.3 BIOSORPTION SYSTEMS

Wetlands for AMD mitigation were initially designed to imitate natural *Sphagnum* peat moss wetlands which exhibited relatively high adsorption capacities for heavy metals. Investigations conducted on a white cedar bog in Minnesota (Eger and Lapakko, 1988; Eger *et al.*, 1980) revealed that the natural peatland removed 80% of the nickel and nearly 100% of the copper from tailings drainage. Removal by peat accounted for more than 90% of the total metal reduction. In Canada, Kalin *et al.* (1990) reported that elevated heavy metal concentrations and low pH levels in coal AMD in Nova Scotia caused considerable damage to peat bog natural vegetation, with the exception of *Typha* and *Sphagnum* species. Subsequent studies showed that, natural *Sphagnum* moss is not always readily available, is difficult to transplant, and generally accumulates metals to toxic levels after several months of exposure to mine drainage (Hedin and Nairn, 1993). As a consequence, alternative biosorption technologies based on the action of living and non-living biomass, including peat, have been developed.

Acid mine drainage abatement using biosorption treatment systems relies on the removal of metal ions from solution via sorption processes onto biological sorbents. The main sorption mechanisms involved include surface adsorption, ion exchange, complex formation and precipitation with either living or non-living biomass. Biosorption has also demonstrated potential in the metal recovery process and could be employed as an alternative to more costly conventional strategies such as ion-exchange resins (Tsezos *et al.*, 1989).

2.5.3.1 LIVING BIOSORPTION SYSTEMS

Living organisms have been used in a number of studies to treat AMD. In laboratory microcosms, Tarleton *et al.* (1984) examined the mechanisms by which natural *Sphagnum* peat removes dissolved iron from coal AMD. They concluded that the formation of organically bound iron was the principal manner in which the iron was removed from solution.

Smith and Kalin (1989) evaluated the use of an underwater meadow formed by attached macrophytic algae, *Nitella flexilis*, for treating drainage water from a uranium mine in Northern Saskatchewan. The underwater meadow of algae acts as a filter which, through continuous growth and decay, effectively transfers the contaminants radium²²⁶ and to a lesser extent uranium, from the water to the sediment. This natural, self-sustaining and maintenance free treatment system is referred to as the Chara process.

Laboratory experiments (Vatcharapijarn *et al.*, 1994), using microbial mats immobilized on glass wool, were performed to evaluate the removal of zinc and manganese from contaminated waters. Vatcharapijarn *et al.* (1994) reported that extracellular metal deposits could be responsible for minimizing toxic effects in the biological system. As such, metal precipitation induced by altering surrounding water chemistry rather than cell sorption and deposition (Stevens *et al.*, 1989) may represent a preferred removal mechanism in microbial mats because living cells are protected, thereby extending the viability of the system.

Microbial mats composed of heterotrophic and autotrophic microorganisms (mainly blue-green algae *Oscillatoria* sp., green filamentous algae and *chromatium* sp.) have also been used in constructed ponds to reduce the dissolved manganese and iron concentrations from mine drainage

(Phillips *et al.*, 1995; Bender and Phillips, 1994; Phillips *et al.*, 1994). In this case, the microorganisms are held together by slimy secretions, that fix the ecosystem to a variety of substrates. Since these mats are both nitrogen fixing and photosynthetic, they are self-sufficient solar-driven ecosystems with few growth requirements.

Studies involving biosorption by living systems is on-going, however, processes have not yet been tested on a large scale. To date, pilot pond studies using microbial mats have only examined treatment performance under low flow rates of 2 to 5 L/min. As well, microorganisms are being genetically engineered to sequester metals such as gold, silver, platinum, cadmium, cobalt, copper, uranium and mercury mainly for the purpose of metal extraction and recovery (Ledin and Pedersen, 1996; Smith *et al.*, 1994).

2.5.3.2 NON-LIVING BIOSORPTION SYSTEMS

The utilization of non-living biomass and natural materials for reducing metal concentrations in mine drainage has also been reported. The high metal sorption capacity of peat has long been recognized. Peat has been characterized as a natural material composed largely of humic compounds. Humic substances containing carboxyl, amino, quinone, hydroxyl and other functional groups are responsible for surface adsorption, ion exchange, chelation and complex formation with metals in solution. Experiments have been conducted by several authors examining adsorption capacity of peat, and other natural adsorbents high in humic and cellulose content, for various metals. The studies generally involved laboratory investigations and were not specifically aimed at AMD mitigation. These are summarized in Table 2-4. It should be noted, the heterogeneity of peat materials within and between locations, the various degrees of decomposition and differences in experimental testing often make comparisons between studies difficult.

Table 2-4: Heavy Metal Removal by Natural Adsorbents

Author	Adsorbent	Metals Treated
Bunzl (1974a)	Peat	Pb
Bunzl (1974b)	Peat	Pb
Bunzl <i>et al.</i> (1976)	Peat	Pb, Cu, Cd, Zn, Ca
Wolf <i>et al.</i> (1977)	Peat	Pb, Cu, Cd, Zn, Ca
Chaney & Hundemann (1979)	Peat	Cd
Dissanayake & Weerasooriya (1981)	Peat	Cu
Lapakko & Eger (1981)	Peat, woodchips, tailings, till	AMD (Cu, Ni, Co, Ni)
Pakarinen <i>et al.</i> (1981)	Peat	Cu, Pb, Zn, Mr:
Kadlec & Rathbun (1983)	Peat	Cu
Tarleton <i>et al.</i> (1984)	Peat	AMD
Gosset <i>et al.</i> (1986)	Peat	Cu, Cd, Zn, Ni
Azab & Peterson (1989)	Activated charcoal, biomass, compost, peat, nutshells, bone	Cd
Bencheikh-Lehocine (1989)	Peat	Zn
Howard, <i>et al.</i> (1989)	Woodland litter & humus, charcoal	AMD
Lee & Low (1989)	Woodland moss	Cu
Chen <i>et al.</i> (1990)	Peat	Cu
Chistova <i>et al.</i> (1990)	Peat	Fe, Cu, Cr, Zn, Ni, Pb, Ba
Trujillo <i>et al.</i> (1991)	Peat immobilized in beads	Al, Cd, Zn, Ca, Mn, Mg
D'Avila <i>et al.</i> (1992)	Peat	Cu, Cd, Cr, Pb, Ni
Brown (1993)	Peat	Cu, Cd, Zn, Pb, Al
Sharma & Foster (1993)	Peat	Cr
Ho <i>et al.</i> (1994)	Peat	Cu
Ho <i>et al.</i> (1995)	Peat	Ni
Spinti <i>et al.</i> (1995)	Peat immobilized in beads	Fe, Al, Pb, Cu, Cd, Zn, Ca, Mn, Mg, Na
Arnfolk <i>et al.</i> (1996)	Peat, organic soils, minerals	Cd, Cr ³⁺ , Cr ⁶⁺ , Hg, Pb
Gardea-Torresdey <i>et al.</i> (1996)	Peat	Cu
McKay & Porter (1997)	Peat	Cd, Cu, Zn
McKay <i>et al.</i> (1998)	Peat	Co, Cu, Cd, Zn, Ni

The removal mechanisms involved in the retention of metals onto peat are often difficult to identify and have been the subject of much debate. Ion-exchange, surface adsorption, chemisorption, complexation, adsorption-complexation and precipitation mechanisms have been proposed by various authors. These will depend upon the nature of the peat utilized and the degree of pre-treatment applied to the material, as well as the composition of the metal solution requiring treatment (Brown *et al.*, 2000).

Bunzl (1974a, 1974b) investigated the adsorption of lead with humic substances such as peat. He reported that the principal mechanism responsible for the removal of lead from solution was ion-exchange. In a later study involving the adsorption of dissolved metals in mixtures, Bunzl *et al.* (1976) found a selective removal order where lead > copper > zinc > cadmium was noted for metal adsorption by peat at pH levels ranging between 3.5 to 4.5. Gosset *et al.* (1986) reported a similar preferential adsorption order: nickel > copper > cadmium $\approx$ zinc for pH levels between 0 and 6.5. Several studies examining the order of affinity for metal ion sorption onto peat reported consistent results. The following orders of affinity were suggested by Pakarinen *et al.* (1989): lead > copper > zinc > manganese; Chistova *et al.* (1990): iron > copper > chromium > zinc > nickel; Chen *et al.* (1990): lead > copper > calcium > magnesium = zinc for eutrophic peat, and lead > calcium > copper > magnesium = zinc for oligotrophic peat.

Research by Arnfalk *et al.* (1996) investigating peat and other types of soil materials and minerals indicated a chromium (III) > lead > cadmium $\gg$ chromium (VI) > mercury preference of adsorption for a pH range of 0.5 to 12. The organic content of soils was found to be the most significant parameter affecting metal uptake, followed by other parameters such as surface area, particle size and extractable metal content. The trend in relative sorption capacities observed by McKay *et al.* (1998) at pH 4.5, copper > zinc > nickel > cadmium, was noted to be the same as the order of decreasing absolute electronegativities for these metals. This supported the findings of a previous study by McKay and Porter (1997) examining copper, zinc and cadmium sorption. A study conducted by Brown (1993) demonstrated that the removal of individual copper, cadmium, zinc, lead and aluminum ions by peat was lower in mixtures than in single ion solution due to competitive inhibition. However, the total adsorption capacity of the peat increased. The order of metal sorption onto peat observed through these various studies has generally been consistent over a wide range in pH for results presented on the basis of moles of metal ion per mass of peat.

Adsorption equilibrium experiments using heavy metals such as copper (McKay and Porter, 1997; Ho *et al.*, 1994; Brown, 1993; Lee and Low, 1989; Kadlec and Rathbun, 1983), cadmium (McKay and Porter, 1997; Brown, 1993; Chaney and Hundemann, 1979), nickel (Ho *et al.*, 1995), zinc (McKay and Porter, 1997; Brown, 1993; Benchikh-Lehocine, 1989), chromium (Sharma and Foster, 1993), aluminum (Brown, 1993) and lead (Brown, 1993; Wolf *et al.*, 1977) demonstrated that both the Langmuir and Freundlich isotherm models could adequately describe the sorption of these metals onto peat. However, the Langmuir model was generally reported to provide a better correlation with the experimental data and was applicable over a wider pH range (Brown *et al.*, 2000). In these same studies, kinetic experiments indicated that the adsorption equilibrium of the heavy metals was generally reached within 2-hour contact periods. Investigators examining the adsorption of heavy metal mixtures onto peat (McKay and Porter, 1997; Gosset *et al.*, 1986; Lapakko and Eger, 1981; Wolf *et al.*, 1977; Bunzl *et al.*, 1976) observed that up to 12 hours were necessary to achieve equilibrium.

In most cases, peat was found to be an effective adsorbent for dissolved heavy metals. The adsorption studies were usually performed over a wide range of pH levels. The process was found to be pH dependent, the optimum generally ranging between 4 and 5 (Bencheikh-Lehocine, 1989). The peak adsorption for copper onto peat was reported to occur at a pH of 4.0 (Gardea-Torresdey *et al.*, 1996; Gosset *et al.*, 1986), while pH values over 5.5 and 5.0 were required for zinc and cadmium, respectively (Gosset *et al.*, 1986) and a pH range of 4.0-7.0 was adequate for zinc removal (Ho *et al.*, 1995; Gosset *et al.*, 1986). Metal cations were completely desorbed at pH levels of 1.5, except for nickel which was found to bind strongly to peat and to desorb only at pH levels below 1.5 (Gosset *et al.*, 1986).

The impact of the presence of metal cations such as calcium on heavy metal sorption was examined by Wolf *et al.* (1977). They indicated that the presence of calcium ions influenced heavy metal sorption by peat. Increasing the ratio of $\text{Ca}^{2+}/\text{H}^+$ ions in the peat phase was found to enhance the sorption of heavy metals. However, increasing calcium concentrations in the solution was reported to reduce the sorption capacity. Dissanayake and Weerasooriya (1981), observed that the presence of sodium cations in solution also reduced the adsorption of copper onto peat.

Results from batch experiments (Lapakko and Eger, 1981) indicated that peat, till and tailings were capable of removing trace metals from waste rock drainage. Lapakko and Eger (1981) also found that metal removal capacities of these biosorbents increased with increasing pH and increasing dissolved metal concentrations. Studies exploring the use of forest products with significant humic content were undertaken by Howard *et al.* (1989). They concluded that the reduction of dissolved metal concentrations from abandoned mine drainages using forest litter and humus represented a promising biosorbent material alternative.

The utilization of commercial non-living biomass to reduce dissolved metal concentrations from mine waste environments has also been reported. One biosorbent material used to treat AMD is BIO-FIX (Biomass-foam immobilized extractant). BIO-FIX beads are fabricated from dried non-living biomass such as marine algae (*Ulva* sp.), blue-green algae (*Spirulina* sp.), yeast (*Saccharomyces cerevisiae*), common duckweed (*Lemna* sp.), and finely ground peat (*Sphagnum* peat moss), blended into a high-density polysulfone dissolved in an organic solvent. BIO-FIX beads are generally enclosed in meshed polypropylene bags and placed either in a trough or directly into a waste stream, or in conventional equipment (Kilborn, 1996). Metals which were successfully removed from effluents included arsenic, cadmium, copper, silver, lead, manganese and zinc.

Bennett *et al.* (1991) and Jeffers *et al.* (1989) recommended using BIO-FIX to adsorb contaminants from dilute AMD streams containing metal concentrations below 15 mg/L.

The use of another biosorbent, AlgaSORB II, was proposed by Darnall *et al.* (1989). This bio-recovery system is a preparation of immobilized algae, mainly *Chlorella vulgaris*, and has been found to be effective at recovering metals such as copper, mercury or cadmium from contaminated groundwaters. The levels of these metal ions can be reduced in concentration from low ppm levels to low ppb levels (Darnall *et al.*, 1989).

Médiaflex_{MC} is a commercial biosorbent material that acts as a biofilter. It is composed of *Sphagnum* peat moss, as well as a carbon material, referred to as biofil, that has adsorptive and chemical precipitation properties. The treatment capacity of Médiaflex for various types of wastewaters, including AMD, containing metals such as iron, zinc, copper, nickel, chromium, and cadmium has been tested under Canadian climatic conditions (Bélanger *et al.*, 1995). A Médiaflex biofilter (15 m x 36 m) was reportedly able to treat drainage from an abandoned copper mine in a basin with a capacity of 6000 m³ using flow rates in the order of 250 m³/d.

Other biosorbents have also been investigated, including: calcium-alginate to remove cadmium, barium, uranium and zinc from uranium mine tailings drainage water; chitosan (a natural biopolymer from chitin) and immobilized algal biomass (*Spirulina* sp.) in preformed polyurethane foam (Kilborn, 1996).

2.5.3.3 SYSTEM PERFORMANCE

A large number of dissolved metals have been reported to be removed using commercial and natural biosorbents (arsenic, barium, cadmium, copper, iron, mercury, lead, manganese, molybdenum, radium, selenium, zinc, uranium). The few field studies available regarding biosorption and AMD mitigation using live biomass focused primarily on iron and manganese removal and on metals released from uranium mine tailings (molybdenum, radium, selenium, uranium). Manganese (Mn^{2+}), a dissolved metal species common to both metal and coal mine drainage, is difficult to remove from solution without chemical treatment due to the high pH required to form insoluble manganese oxide, carbonate or sulphide precipitates (Kilborn, 1996).

Living cells can only be used to treat effluent where metal concentrations are below levels that are toxic to the microorganism. Immobilized, non-living biomass has been shown to tolerate low pH and high temperatures better than conventional ion exchange materials. Problems associated with metal toxicity, adverse climatic conditions, and the costs of nutrient supply and culture maintenance can be avoided with the use of non-living biomass as biosorbents (Kilborn, 1996).

To date, no data exists regarding long-term performance of biosorption systems designed to treat AMD. Most living ecosystems presented are reported to be resilient, self-sustaining and maintenance-free ecosystems with few growth requirements (Phillips *et al.*, 1995; Bender and Phillips, 1994; Phillips *et al.*, 1994; Smith and Kalin, 1989). However, occasional nutrient addition has been necessary and should be expected on a periodic basis. Microbial mats are expected to persist for long periods without nutrient supplements once adequate growth has been established (Bender and Phillips, 1994). In the long-term, systems are expected to become clogged with metal precipitates, or the conditions that facilitate contaminant removal may be compromised.

Available sorption sites in BIO-FIX beads saturate quickly, and as such, require frequent eluting and recharging to ensure effective dissolved metal removal (Jeffers *et al.*, 1989). In general, the higher the concentration of dissolved metals in the drainage, the more frequently the biomass must be eluted to remove the metals.

New material, such as peat or other non-living biosorbents, must be added on a periodic basis to passive treatment systems such as constructed wetlands to promote heavy metal removal by providing new adsorption sites. Similarly, in biosorption systems containing living microorganisms, saturated biomass will eventually have to be removed and replaced by fresh materials. The introduction of new biomass provides a lower metal content and therefore higher metal sorption and uptake potential than the old biomass, thereby enhancing the treatment efficiency of the systems (Kilborn, 1996). In order to maximize the life of the biosorption system, living or non-living materials must be replaced before the dissolved metal adsorption/absorption capacity of the biosorbent is exhausted.

2.5.4 BIOREACTOR SYSTEMS

Bioreactor treatment systems are, in essence, highly optimized wetland treatment systems without the wetland plants. They are strictly dependent on a bacterial consortium that can metabolize biodegradable substrates and eventually generate short chain organic acids. The short chain organic acids are then available to promote the growth of sulphate reducing bacteria. As in wetland systems, microbial activity within bioreactors can be supplemented with inorganic chemical reactions, such as pH neutralization via limestone dissolution or other neutralizing agents (Eger *et al.*, 1997).

Bioreactors rely on several microbial reactions requiring different levels of oxygen to treat AMD. A cellulose-based organic material is required by the system on a periodic basis. The substrate is degraded by cellulolytic bacteria which generate free sugars and other metabolites. Aerobic and facultative heterotrophs can then further metabolize these products to provide substrates for the fermentative anaerobes. Under anaerobic conditions, the free sugars are fermented to short chain organic acids or short chain fatty acids which are suitable substrates to support the growth of the sulphate reducing bacteria (SRB). The SRB then reduce sulphate to hydrogen sulphide which reacts with dissolved metal ions forming low solubility metal sulphide precipitates.

The SRB concurrently consume hydrogen ions and produce carbon dioxide which generates alkalinity, thereby increasing pH levels due to the reduced concentration of free hydrogen ions and the buffering effect of the bicarbonate buffer system. Other biologically mediated reactions can also contribute to alkalinity generation depending upon AMD composition. These include activities by ammonia producers, methanogens, and metal reducing bacterial species (Kilborn, 1996).

In general, bioreactor systems fall into one of three categories: (1) open aerobic systems where the surface is exposed to the atmosphere; (2) closed anaerobic systems where the surface is not exposed to the atmosphere; and (3) bioreactive walls placed at the leading edge of an underground acidic plume.

2.5.4.1 OPEN BIOREACTOR SYSTEMS

Open reactor systems that have been investigated for acid mine drainage mitigation have included open pit, biotrench, and Acid Reduction Using Microbiology (ARUM) configurations. The Noranda Technology Centre evaluated the feasibility of utilizing SRB for the treatment of AMD in

open pits and underground mines (Kuyucak and St-Germain, 1994; Kuyucak *et al.*, 1991). The process involved the addition of a SRB inoculum along with the necessary substrates and nutrients to the acidic drainage. Reducing conditions in the pit then promoted the growth of SRB, resulting in alkalinity generation, acidity reduction, metal precipitation and, hence, AMD mitigation within the pit or *in situ*.

In a study undertaken by CANMET, a biotrench system was constructed to treat acidic drainage at Halifax International Airport (Béchar, 1993). The system consisted of three 16.8 m x 1 m x 1 m clay-lined cells in sequence. The cells were physically separated by a clay wall and the drainage was allowed to meander through each of the three cells, before being returned to a downstream ditch. Partially decomposed straw and wood shavings were added to the cells as a source of carbon to promote the growth of SRB (Béchar *et al.*, 1995; Béchar *et al.*, 1991).

ARUM systems are essentially highly optimized wetland systems which, through their design and configuration, exploit the ability of anaerobic microbial reducing processes to generate alkalinity, reduce acidity, raise pH levels and precipitate metals. A schematic representation of the ARUM Test Cells System is presented in Figure 2-7. Microbial alkalinity-generating processes are usually confined to sediments, thus, in order to optimize AMD treatment, ARUM cells extend reducing conditions throughout the entire water column (Fyson *et al.*, 1995b). Drainage flowing slowly through ARUM cells is then treated by sediment bound anaerobic microbial processes.

Figure 2-7: Schematic Layout of Test Cell System for ARUM (Kalin and Smith, 1997).

Test cell systems were designed to produce a self-sustaining, sediment-based AMD treatment system. In general, the systems were comprised of 2 to 3 oxidation cells to allow iron precipitation, 2 to 3 holding ponds, and 2 to 3 ARUM cells to provide reducing conditions and promote alkalinity generation (MEND, 1993b). Test cell systems have been implemented to treat AMD from copper/zinc mine drainage in Northwestern Ontario (Kalin and Smith, 1997; Kalin, 1989), nickel tailings near Sudbury (Fyson *et al.*, 1995b; Kalin and Smith, 1991) and coal mine seepages in Cape Breton, Nova Scotia (Kalin *et al.*, 1994; Kalin, 1989) using various organic substrates.

2.5.4.2 CLOSED BIOREACTOR SYSTEMS

Pilot-scale anaerobic reactor systems were developed to treat metal contaminated drainage in an underground coal mine and at a smelting residues waste environment in Pennsylvania (Dvorak *et al.*, 1992; Dvorak *et al.*, 1991). Bacterial sulphate reducing conditions were established within the bioreactors with spent mushroom compost serving as a readily degradable source of carbon. The formation of insoluble metal sulfides through biologically mediated reactions was identified as the most significant metal removal mechanism (Dvorak *et al.*, 1991). Alkalinity generation was attributed to both bacterial sulphate reduction and limestone dissolution (Dvorak *et al.*, 1992).

2.5.4.3 BIOREACTIVE WALLS

Sulphate reducing porous reactive walls have been proposed as an effective alternative for the abatement of AMD. At many sites, waters affected by sulphide mineral oxidation migrate downward, to aquifers underlying the mine waste environment, and are transported through the groundwater system eventually discharging into a surface receiving stream (Blowes *et al.*, 1995c). To mitigate AMD, porous reactive walls are installed in the path of the groundwater plume. This is accomplished by excavating a portion of the aquifer and replacing the original material with a permeable reactive mixture. The reactive mixture, which is composed of an organic substrate, is designed to achieve dissolved metal removal and alkalinity generation by enhancing bacterially mediated sulphate reduction and metal sulphide precipitation conditions (Benner *et al.*, 1997a; Benner *et al.*, 1997b). Significant changes in sulphate, trace metals and alkalinity concentrations were observed following the installation of a reactive barrier in an aquifer contaminated with effluent from mine tailings (Benner *et al.*, 1999). SRB populations were noted to be 10 000 times greater and bacterial activity 10 times higher within the barrier than in the up-gradient aquifer.

2.5.4.4 SUBSTRATE REQUIREMENTS

Each of the bioreactor systems described previously requires a biodegradable carbon source to promote bacterial growth, and ultimately, sulphate reduction. The use of agricultural products such as flax, timothy hay, wheat straw and alfalfa or spent mushroom compost as potential carbon sources has been the objective in many investigations, primarily for economic reasons and availability. To date, there is no agreement among researchers regarding the best substrate for optimal microbial growth and activity.

Béchar *et al.* (1994) indicated that in the biotrench system alfalfa was a better substrate for AMD mitigation than either straw or timothy hay. Alfalfa was also found to be a more effective substrate compared to potato waste and hydroseeding mulch in studies by Fyson *et al.* (1995a) and Fyson *et al.* (1994). Shelp *et al.* (1994) reported that natural peat could provide a suitable source of carbon for SRB. In addition, natural peat offers a microflora capable of complexing metals, forming relatively insoluble sulphide minerals, and surviving exposure to extreme acidic conditions.

The ability of yard waste, horse manure, sawdust and municipal compost to sustain sulphate reduction and AMD treatment was examined by Eger and Wagner (1995). Overall, municipal and yard waste composts were most effective substrates. In their experiment using packed-bed reactors, Chang *et al.* (2000) tested organic wasted materials such as oak chips, spent oak, mushroom compost, waste paper recycling plant sludge and organic-rich soils as electron donors for sulphate reducers treating synthetic AMD. They noted that raw biomass (oak chips) was less satisfactory than biologically (spent oak, mushroom compost) or chemically (waste paper sludge) treated materials. Cellulose polysaccharides were the main components consumed in the waste materials. They concluded that hydrolytic fermentative anaerobes must be present to degrade polysaccharides to fatty acids and alcohols that can then support the growth of sulphidogens. From their observations and the assumption that the bacterial consortium can utilize a quarter of the substrate content, they suggested that the removal of 1 kg of sulphate would require 2.5 kg of substrate.

Reactivity and permeability must both be taken into consideration in selecting an organic substrate for bioreactive walls. Batch tests conducted by Waybrant *et al.* (1995) using various organic mixtures of sewage sludge, leaf mulch, wood chips, sheep manure and sawdust revealed that multiple sources of organic material were the best candidates for use in bioreactive walls. Higher sulphate reduction rates were recorded with multiple mixtures as compared to single source

mixtures. It was concluded that a long-term effectiveness could be achieved due to the differing decomposition stability of each organic carbon source contained within the multiple organic mixture (Waybrant *et al.*, 1997). Similar conclusions supporting the use of multiple mixtures were drawn by Kuyucak and St-Germain (1994). An example of a multiple mixture of organic materials which is commonly used as a substrate is spent mushroom compost which generally consists of a mixture of manure, hay, straw, corn cobs, and wood chips conditioned with gypsum and limestone (Dvorak *et al.*, 1992). Hence, mushroom compost represents a multiple mixture of organic materials, as well as a source of neutralizing agents.

Eger and Wagner (1995) cautioned that bioreactor systems could only offer short-term treatment unless a labile organic compound source is provided on a continual basis. The use of methanol, lactate, pyruvate and acetate as electron donors and carbon substrates for 7 metal tolerant strains of SRB was studied by Hard *et al.* (1997). After a 5-day incubation period, sulphate reduction was found to be highest in cultures grown on methanol and lactate. Since the amount of methanol consumed per gram of biomass produced was generally less than for lactate, they recommended that methanol be utilized as a labile source of carbon for sulphidogens. Tsukamoto and Miller (1999) examined the addition of methanol and lactate as an amendment to a depleted manure substrate to reactivate a bioreactor that had lost > 95% of its SRB activity. The addition of lactate caused a 69% reduction in sulphate, while the addition of methanol resulted in an 88% reduction in sulphate. Methanol was suggested as the preferred substrate due to its inherent properties: cost, low freezing point and low viscosity; that make it more suitable for remote, high elevation sites where low temperatures could hamper the use of aqueous solutions.

Cheese and dairy wheys have been suggested as effective and inexpensive labile carbon sources for sulphate reduction in open systems (Drury, 1999; Christensen *et al.*, 1996; Borek *et al.*, 1995).

Drury (1999) investigated the addition of liquid cheese whey as an additional electron donor source to stimulate SRB activity in packed-bed reactors filled with a 2:1 ratio of cow manure and sawdust solid substrate mixture. Reactors supplied with cheese whey produced AMD effluents with a pH value of 6.5, alkalinity of 550-700 mg/L, sulphate reduction of 80-98% and dissolved metal removals of 84%, 40%, 99.7%, 99%, 99% and 89% for iron, manganese, zinc, copper, cadmium and arsenic, respectively. On the other hand, a pH value of 5.5, alkalinity of 50-300 mg/L, sulphate reduction of 40-60% and dissolved iron, manganese, zinc, copper, cadmium and arsenic concentration removals of 10%, 2%, 96%, 99%, 99% and 84% were reported for reactors not receiving the liquid cheese whey addition.

As an alternative, floating *Typha* vegetation covers have been investigated (Kalin and Smith, 1997; Kalin *et al.*, 1993; Smith, 1990; Kalin and Scribailo, 1988; Kalin, 1987) as a self-sustaining and self-regenerating organic carbon sources in ARUM systems.

2.5.4.5 SYSTEM PERFORMANCE

The capacity of bioreactor systems to mitigate high acidity, low pH levels and elevated dissolved metal concentrations resulting from AMD have been found to be variable to date. The studies reviewed generally noted increases in pH in the order of 1.1 to more than 3.0 pH units. Acidity reduction in the drainage ranged from 53% to 100% (Kilborn, 1996). Metal removal efficiency was found to be a function of initial pH level, dissolved metal concentrations and hydraulic loading to the bioreactor system, with higher hydraulic retention times required for lower pH levels and higher dissolved metal contents (Lyew *et al.*, 1994).

In the CANMET Biotrench study (Béchar *et al.*, 1991), encouraging results were obtained over one field season. Sulphate reduction was noted, aluminum concentrations in the effluent water fell to undetectable values, and significant quantities of iron were removed. The addition of sucrose and small amounts of urea promoted bacterial growth throughout the reactor. With heavy late summer rains and the eventual onset of winter, process effectiveness declined due to higher flow rates (up to 60 L/min) and freezing.

In closed anaerobic systems consisting of two independent 4500 L tanks loosely packed with a compost mixture conditioned with gypsum and limestone, Dvorak *et al.* (1991) recorded greater than 98% removal of manganese, zinc, cadmium and nickel at flow rates ranging between 0.07 to 0.131 L/min. They were able to sustain their Palmerton system through cold winter conditions with the addition of sucrose as a carbon source. For drainage water containing relatively high concentrations of copper and nickel, Eger and Wagner (1995) found that municipal and yard waste compost were effective in increasing the pH of the drainage from 5 to over 6.5 while reducing trace metal concentrations by over 99% for field flow rates ranging between 0.006 to 0.07 L/min.

An ARUM system composed of four 100 m x 20 m wide test cells received 1 L/min nickel mine AMD and demonstrated removals of > 88% iron, 77% nickel, 39% sulphur in 1992 (Fyson *et al.*, 1995a). The results of the system had improved within a two-year period, when removals of > 98% iron, 95% nickel and 45% sulphur were recorded. In a similar study (Kalin *et al.*, 1994), early results from test cells constructed to treat coal seepages in Eastern Canada demonstrated some reduction in acidity and iron concentration. The flow rate was highly variable throughout the year ranging from 16 m³/d to 366 m³/d. As a consequence, in spring and summer, retention times decreased below that necessary for the reduction process to take place due to high flow rates. From this field experiment, it became evident that flow control is essential in order to obtain high quality

effluent (Kalin *et al.*, 1994). Phosphate rock was utilized as a means of precipitating iron and aluminum and raising pH in coal mine drainage. It was noted that the placement and grain size of the phosphate rock are very important for successful application.

A full-scale porous reactive wall 15 m wide, 4 m in thickness and 3.6 m in depth, was installed in 1995 to intercept and treat mine drainage flowing within an aquifer at a rate of flux of 288 m³/year through the wall (Blowes *et al.*, 1997). After passing through the bioreactive wall, it was reported that downstream sulphate concentrations had been reduced by > 50% and iron concentrations by > 95% (Benner *et al.*, 1997c). A pH increase from 5.8 to 7.0 was also observed, along with an increase in alkalinity from 0 to 50 mg/L as CaCO₃ in the influent water to 1000 mg/L to 2000 mg/L in the effluent water (Benner *et al.*, 1997a). Sulphate and dissolved metal concentrations were found to exhibit trends suggesting a greater degree of sulphate reduction at the top and bottom (sulphate < 500 mg/L) of the porous reactive barrier than in the middle (sulphate > 1500 mg/L). This was attributed to the higher flow rates through the middle portion of the bioreactive wall (Benner *et al.*, 1999).

Kilborn (1996) recommended that in addition to recording typical chemical parameters such as pH, acidity and dissolved metal concentration, the Eh at various locations within the reactor should be monitored, since SRB can only survive at Eh values of less than -150 mV and methanogens require an Eh of less than -330 mV. The role of microorganisms in AMD mitigation have not been thoroughly identified and characterized. A sulphate reducing bacteria consortium, anaerobic and aerobic cellulolytic bacteria, cellulolytic fungi, methanogens, and heterotrophic fermentative organisms were found to be present in laboratory reactors, and their role in AMD mitigation investigated to some extent in small laboratory microcosms (Bécharde *et al.*, 1993).

The cellulolytic and heterotrophic organisms required to generate the carbon substrate for SRB grow best at moderate temperatures in a near-neutral pH environment. They are sensitive to temperature and are expected to become ineffective below 0 to 5°C and above 37 to 40°C. Sulphate reducing bacteria tend to grow best at near neutral conditions and at moderate temperatures in the range of 20 to 30°C. They will generally not grow at pH levels below 5. As a result, the initial cell of any treatment system should be designed with sufficient buffering capacity to raise the pH to greater than 5.0 for the system to sustain SRB growth (Béchar, 1993).

To be effective in the treatment of AMD, the total microbial consortium must be active. The treatment system should have an anaerobic zone to support the SRB and have sufficient volume to allow a 10 to 14 day hydraulic retention time. It is recommended that the bioreactor system have an iron oxidation and removal stage, for the influent, to reduce the amount of iron sulphides produced within the bioreactor. In order to prevent winter freeze-up, open bioreactors should have a minimum depth of 1.5 to 2.0 m (MEND, 1993b). This depth, combined with the protective effect of the overlaying substrate, should allow the system to operate throughout the winter.

Open, closed and reactive wall bioreactor systems for treatment of AMD will require periodic maintenance. The organic substrates used in the bioreactor are expected to require supplementation with fresh substrate every six to twelve months. Eventually, the degraded organic material will become saturated with iron and other precipitated metals, and will have to be removed and replaced with fresh substrate material. This is estimated to be required every three to seven years, depending on the initial flow rate and the metal ion content of the AMD being treated (Kilborn, 1996).

Although long-term data is not available, it is anticipated that with proper maintenance, as well as periodic substrate and nutrient addition, the open, closed and reactive wall bioreactor systems could operate indefinitely unless exposed to extreme climatic conditions. The detrimental effects of extreme temperatures on the system and the consequent loss in treatment efficiency are expected to affect open bioreactor systems the most. However, it should be noted that highly variable flow rates could negatively impact AMD mitigation in closed and reactive wall systems as well.

2.6 COMBINED PASSIVE TREATMENT SYSTEMS

The applicability of passive treatment systems for the long-term mitigation of acid mine drainage is a function of contaminant loading, climate, treatment efficiency required and life expectancy of the system. The mitigation of AMD at Canadian mine sites using passive treatment technologies requires a combined strategy which aims at minimizing the impact of climatic variability on the treatment performance of the system.

2.6.1 LIMITATIONS OF INDIVIDUAL PASSIVE TREATMENT SYSTEMS

In the past, the majority of research and field studies involving passive systems have focused on the treatment of acidic coal drainage in the Appalachian region of the United States. In general, acid mine drainage from metal mining operations exhibits lower pH levels, as well as higher dissolved metal concentrations and acidity than AMD generated from coal mining activities. Canadian AMD displays strong seasonal variability in contaminant loadings and flow rates; typically, low flow rates and high metal concentrations in winter, and high flow and low metal concentrations in the spring due to spring runoff, have been recorded. Canadian mine sites are also characterized by harsh winters and short growing seasons.

2.6.1.1 CONSTRUCTED WETLANDS

Constructed wetlands are a technically and economically viable treatment alternative for the mitigation of AMD. The application of constructed wetlands in Canada requires further research specific to Canadian coal and metal mining sites to assess the impact of Canadian climatic conditions. Wetland systems for Canadian operations should be designed based on an understanding of the interactions between the chemical, physical, microbial and vegetative components of the system, rather than the traditional black-box approach.

Wetland treatment efficiency is a function of the operating temperature due to the large biological component of the system. Microbial substrate degradation and bacterially-mediated sulphate reduction reaction rates will be reduced at lower temperatures. The success of wetlands during winter operation will depend upon the temperature regime throughout the water column and should be designed to minimize the impact of low temperatures on the hydraulics and microbiological components of the system.

The use of wetland systems as an AMD mitigation strategy emerged approximately two decades ago. However, due to the black-box approach which was often employed in designing these systems, a wide range of system performances, viabilities and life expectancies have been reported. Many of the wetlands built in the United States do not meet effluent criteria throughout the year and require an active chemical treatment step (Kleinmann, 1989).

The long-term response of constructed wetland systems to seasonal variations in metal loadings is unknown and requires further research. Fluctuations in treatment efficiencies corresponding to these seasonal variations in flow rate and metal loading should be anticipated, unless the system is

optimized to ensure a maximum contact between the microorganisms, organic substrates, and the treatment components of the wetlands.

Constructed wetlands are designed to be efficient accumulators of metals and reaction products, which are stored in the substrate, sediments, microorganisms and vegetation. It is anticipated that the removal and disposal of metal hydroxide precipitates will be required every 10 years in aerobic wetland systems, while anaerobic wetlands will require the removal and disposal of depleted substrate every 30 years (Gusek, 1995). The accumulation of heavy metals in the microfauna and flora of wetland systems receiving AMD will eventually reach levels which are toxic to the living biomass and vegetation. This renders the long-term applicability (> 100 years) of wetland systems without major reconstruction works doubtful.

2.6.1.2 ANOXIC LIMESTONE DRAINS

Anoxic limestone drains offer an effective and inexpensive form of passive alkalinity addition for acid mine drainage having dissolved oxygen, ferric iron and aluminum concentrations below 1 mg/L, and sulphate concentrations less than 2000 mg/L. These systems may only have limited applications at Canadian mine sites where the presence of more elevated concentrations of these parameters will cause premature system failure by armouring and/or clogging.

In general, ALDs are not a stand-alone mitigation method for AMD. They simply add alkalinity to the effluent stream, which may in turn improve the effectiveness of downstream treatment systems, and cause precipitation of metal hydroxides. The chemical composition and toxicity of the ALD effluent will depend upon the influent quality. Few studies have examined the effect that the presence of other metals (copper, nickel, lead, zinc), common to Canadian mining operations, may

have on the effectiveness of the system. As a result, the ability of ALD effluent to meet Canadian water quality criteria is uncertain.

Anoxic limestone drains have primarily been applied in the treatment of coal drainage in the Appalachian region of the United States. The impact of temperature on alkalinity generation and ALD effectiveness has not been specifically investigated. However, past studies do not indicate that ALDs will be less effective in more extreme northern climates. Exothermic reactions associated with AMD generation and neutralization, assisted by the insulating capacity of the snow and soil cover, may allow the ALD to remain open and operational throughout the winter.

The research conducted to date suggests that ALDs can be expected to be effective for 20 to 80 years (Brodie *et al.* 1992) and perhaps even longer (> 100 years) depending on the influent quality. Eventually the volume of limestone available will be exhausted causing the overlaying surface to subside or channelized flow to develop, rendering the system ineffective. Another concern is the potential for the retention of metals and the development of hydroxides under low dissolved oxygen conditions (< 1 mg/L) over an extended period of time (> 100 years).

2.6.1.3 BIOSORPTION SYSTEMS

It is currently difficult to assess the applicability of biosorption systems for AMD mitigation at mine sites under Canadian climatic conditions due to the lack of research regarding this topic. Biosorption systems using non-living materials are expected to be more successful than living biomass because of the difficulty in maintaining growth, and treatment efficiency under severe winter conditions. Biosorption alternatives employing immobilized biomass in a column system analogous to ion-exchange show promise as an intermediate form of passive treatment.

The potential toxicity of effluents released from these systems is also unknown, although studies involving biosorbents have reported reductions in concentrations of a large number of metals (Arsenic, barium, cadmium, copper, iron, mercury, lead, manganese, zinc, radium, selenium, uranium, molybdenum). In general, changes in water quality have been documented, but little information concerning removal processes and mechanisms has been presented. The potential for long-term use (> 100 years) of these technologies also needs to be assessed.

To date, biosorption systems can not be considered an effective stand-alone treatment alternative. However, with on-going research they may develop into a final or intermediate passive treatment step for AMD having high flow volumes and low to moderate metal concentrations. In the long-term, biosorption systems are expected to become clogged with metal precipitates or the conditions that facilitate contaminant removal may be compromised.

2.6.1.4 BIOREACTOR SYSTEMS

Experimental investigations involving microbial reactor systems have mainly focused on the mitigation of low flow (< 1 L/min) and low to moderate strength AMD streams. One field-scale study (Bécharde *et al.*, 1995) was designed to treat a flow rate in the order of 23 L/min, however, the treatment system only operated successfully for a 13 week period. In the future, the potential success of open and closed bioreactor systems as stand alone treatment strategies will depend on their ability to treat higher flow rates more common to Canadian mining operations. However, AMD mitigation under higher flow rates would require larger quantities of substrate, as well as larger surface areas to provide the necessary detention times, which may not be economically viable. Thus, for higher flows or concentration loadings, bioreactor systems may have to be utilized in combination with other passive or active treatment systems.

The treatment efficiency of open bioreactors may be limited by extreme climatic conditions unless special design considerations are employed to address this issue. In comparison, AMD mitigation using closed systems and bioreactive walls is generally unaffected by climate and can be designed to be operated year-round.

With proper maintenance and replacement of the organic substrate as it is metabolized, bioreactor systems have the potential to be stable for an extended period of time. Data regarding the performance of these systems over an extended treatment period is unavailable at this time. However, it is anticipated that with proper maintenance, open and closed bioreactor systems, and bioreactive walls could operate indefinitely and show the most promise as potential long-term (> 100 years) passive treatment alternatives.

2.6.2 APPLICABILITY OF PASSIVE TREATMENT STRATEGIES

Passive treatment strategies offer a significant advantage over conventional lime treatment, primarily due to reduced operating costs. Their applicability in Canadian mining environments, however, remains uncertain. In addition, insufficient information is available to assess the potential life expectancy of passive treatment systems.

Maintenance requirements for passive treatment systems are generally less than for conventional active treatment systems. Anoxic limestone drains require the least maintenance since they do not rely on biological components. Systems incorporating biologically-mediated treatment will require the replacement of certain components once metal saturation levels are reached, as well as periodic substrate and nutrient additions.

Very few studies have presented handling and disposal strategies for the potentially toxic waste products created by concentrating metals in wetland plants and substrate, cellulosic substrate of bioreactors, or biosorption materials. Sludges may contain gypsum, heavy metal hydroxides, heavy metal arsenates, calcium arsenates and heavy metal sulphides. As such, the stability of the material and long-term toxicity is an important concern.

The mitigation of AMD streams using combined passive strategies is an aspect of passive treatment toward which further research should be directed. Each treatment technology presents unique advantages, which, if used together, could provide an optimal treatment system. These types of combined passive treatment systems are more likely to achieve treatment efficiency producing effluents meeting water quality regulations throughout the entire year at Canadian mine sites.

2.6.3 EXISTING COMBINED PASSIVE TREATMENT SYSTEMS

It has been recognized that, the applicability of individual passive treatment strategies is influenced by the composition of the drainage, flow variations and climatic conditions. As a consequence, a field of research has evolved which attempts to combine the strengths of individual passive treatment systems. A summary of selected combined passive treatment systems composed of various treatment components is presented in Table 2-5. Drainage generated at Canadian mine sites is often characterized by low pH levels and a high dissolved metal content. It is believed that, under Canadian climatic conditions the successful mitigation of AMD will be most effectively achieved with the application of combined passive treatment systems.

Table 2-5: Summary of Selected Combined Passive Treatment Systems

Contributors	AMD Source	Location	Components	Dimensions	Constituent of Interest
Brodie, 1991	Coal Mine	Tennessee	ALD	5-15 ft (w) x 2-10 ft (h) x 260-1400 ft (l)	Alkalinity, pH ↑
Brodie <i>et al.</i> , 1991			Oxidation/Precipitation	N/A	Fe, Mn, TSS ↓
Brodie, 1993		Alabama	Acrobic Wetlands (Staged)	1200-25 000 m ²	Fe, Mn ↓
Brodie <i>et al.</i> , 1993			Rock Filter	N/A	Mn ↓
Cambridge, 1995	Copper/Tin Mine	England	ALD	N/A	Alkalinity, pH ↑
Cambridge, 1997			Anoxic Cell	N/A	Oxygen ↓
			Acrobic Wetland	N/A	Fe, As ↓
			Anaerobic Wetland	N/A	Alkalinity, pH ↑ Zn, Cd, Cu, Fe ↓
Eger <i>et al.</i> , 1997	Copper/Nickel Mine	Minnesota	Rock Filter	N/A	Mn ↓
			Wetlands (Staged)	930 m ²	Fe, Ni, Zn, Cu, Co ↓
			Peat Berm (Staged)	0.3-0.6 m (h)	Ni, Zn, Cu, Co ↓
			Limestone Berm (Staged)	4-60 m (l) x 1 m (h)	Alkalinity, pH ↑
Frostman, 1993	Iron Mine	Minnesota	Wetlands (Staged)	8000 ft ²	Mn, Fe ↓
Kepler & McCleary, 1994	Coal Mine	Pennsylvania	Peat Berm (Staged)	10 ft (l) x 3 ft (h)	Ni, Zn, Cu, Co ↓
			ALD	N/A	Alkalinity, pH ↑
			Wetland	N/A	Fe ↓
			SAPS (Staged)	15-25 m (w) x 10-60 m (l) x 1.6-1.9 m (h)	Alkalinity, pH ↑, Fe ↓
Kuyucak, 1993			[Compost + Limes]		
Kuyucak & St-Germain, 1994	Synthetic	Noranda Research	Lime-Organic Mixture	20-30 L	Alkalinity, pH ↑
			ALD	4 L	Fe, Al, Cu, Zn, Cd, As ↓
			Biosorption	4-30 L	Alkalinity, pH ↑
			Oxidation/Precipitation	254 m ² / 242 m ³	Fe ↓
MEND, 1993b	Copper/Zinc Mine	Ontario	ARUM/Precipitation	188 m ² /188 m ³	Alkalinity, pH ↓
(Staged)				Cu, Ni, Al, Fe ↑	
Living Biosorption Mat			188 m ²	Cu, Ni, Al, Fe ↑	
Fyson <i>et al.</i> , 1995b					
Kalin & Smith, 1997					

Fourteen constructed wetland systems were established for the treatment of coal mine drainage by the Tennessee Valley Authority (TVA) (Brodie, 1993; Brodie, *et al.*, 1993; Brodie, 1991; Brodie *et al.*, 1991). The TVA recommended the use of staged aerobic wetlands as a preferred approach for the treatment of low-quality AMD. Staged systems consisted of an ALD as a source of alkalinity addition; an aerobic settling basin to allow the precipitation of oxidized iron as iron hydroxide; and two or three aerobic constructed wetland cells for iron and manganese removal (Brodie, 1993). Brodie *et al.* (1991) reported that ALDs increased the buffering capacity of the constructed wetlands, and thus, enhanced the effectiveness of wetland treatment systems. Mine drainage with high dissolved iron (> 50 mg/L) content and zero alkalinity was also ameliorated using staged wetland systems. However, system longevity had not been assessed under these loading conditions and problems related to the structural and hydraulic stability, as well as system clogging were anticipated.

Kepler and McCleary (1994) also recognized that constructed wetland mitigation of AMD was limited by the alkalinity-producing capacity of the systems. The application of successive ALDs for alkalinity generation beyond 300 mg/L was not viable due to concerns associated with dissolved oxygen. Therefore, ALDs could only mitigate of 300 mg/L of net acidity. As an alternative, they introduced the use of compost wetlands to promote bacterially mediated sulphate reduction and alkalinity generation required in excess of that produced by ALDs. Successive alkalinity-producing systems (SAPS), were designed to combine ALD technology with sulphate reduction mechanisms to effectively neutralize drainage pH and reduce dissolved metal concentrations from coal mining AMD. SAPS promote the vertical flow of AMD through organic wetland substrate and into limestone beds located beneath the organic compost. In addition, SAPS require smaller treatment areas than those associated with compost wetland treatment alone.

Although this combined treatment strategy shows promise, to date, its applicability in the treatment of AMD from metal mining operations and under Canadian climatic conditions remains unknown.

Studies involving field scale open reactor systems or ARUM (Kalin and Smith, 1997; Fyson *et al.* 1995b; MEND, 1993b) have demonstrated that AMD mitigation can be successfully optimized by enhancing individual treatment mechanisms occurring in wetlands. The ecologically engineered systems included an oxidation cell to oxidize ferrous iron to ferric iron which could then be precipitated as ferric hydroxide in a settling pond. The oxidation stage was followed by microbial treatment cells where sulphate reduction via SRB and iron reduction via iron reducing bacteria (Vile and Wieder, 1993; Wieder, 1993) were designed to generate alkalinity to raise the pH of the drainage. Sulphate reduction via SRB also produced low solubility metal sulphides which precipitated out of solution. Floating vegetation covers were utilized to reduce oxygen penetration into the microbial reduction cells and provide organic substrates to drive microbial processes.

A separate iron oxidation cell, rather than the use of ALDs or compost wetlands, was suggested for AMD containing elevated iron loadings (Kalin and Smith, 1997). Iron hydroxide production and clogging would ultimately reduce the effectiveness of the latter two processes. Although the oxidation step decreases the pH level, it also reduces the volume of sludge produced in the reduction stage which would interfere with the microbial treatment stage. These systems have been shown to be effective at flow rates below 1 L/min. System performance under freezing winter temperatures and higher flow conditions generated by spring runoff were not discussed. It is expected, however, that the living vegetation cover would not survive the winter conditions and would have to be regenerated in the spring for the efficiency of the system to be reestablished.

A combined passive treatment system was devised for the mitigation of AMD from an abandoned mine site at Wheal Jane located in Cornwall in the south-western part of England (Cambridge, 1997; Cambridge, 1995). Elevated dissolved metal concentrations (cadmium, zinc, copper, iron, aluminum, arsenic) and low pH of the drainage indicated that pre-treatment was necessary prior to the staged constructed wetland system. The pre-treatment stage included an ALD preceded by an anoxic cell containing cattle manure and straw which effectively reduced dissolved oxygen concentrations and maintained the iron in ferrous form, thereby preventing it from precipitating. An aerobic wetland cell designed principally to remove iron and arsenic followed the ALD. An anaerobic cell then allowed for the removal of zinc, copper and cadmium via SRB and metal sulphide precipitation under reducing conditions. The final stage of passive treatment involved a rock filter in which water moved through a rock/gravel substrate on which algal growth was promoted. The purpose of the rock filters was to provide a final polishing step for metals such as manganese.

Cambridge (1995) noted that the aerobic cell required a large land area to provide effective treatment. In addition, during the winter months in colder climates, the total capacity of the aerobic cell would be significantly reduced by freezing. The anaerobic cells proved to be less affected by the winter climate, however, it was expected that under more extreme conditions, the performance of the anaerobic stage would also be reduced. To date, the application of rock filters for the mitigation of coal and metal AMD has not been addressed in the literature. Thus, further research is necessary to assess their potential as alternative passive treatment strategies.

Results from a peat/wetland demonstration project treating iron mining AMD in Minnesota were discussed by Frostman (1993). Processed peat with a low degree of decomposition was introduced into certain sections of 4 wetland treatment cells. The purpose of peat addition was to promote

heavy metal (copper, nickel, cobalt, zinc, manganese, iron) removal through adsorption mechanisms and provide a substrate for anaerobic sulphate reducing conditions to develop. From this study, it was concluded that the addition of a biosorption component could enhance the performance of existing wetlands in the mitigation of metal AMD. However, Frostman (1993) also indicated that AMD with moderate pH levels (5 to 6) and relatively low metal concentrations were more conducive to treatment using peat/wetland configurations than AMD characterized by low pH and high metal content.

Eger *et al.* (1997) presented a peat/limestone treatment system installed at a nickel/copper mine in Minnesota. The system was composed of a series of limestone berms with a mixture of peat and peat screenings between the berms and was designed as a pre-treatment measure prior to discharge into a wetland treatment system. The system has been successful in neutralizing the drainage, and copper and nickel removals have been reported at 85% and 65%, respectively. Treatment life-time estimates for nickel, which is removed primarily by adsorptive mechanisms, have predicted acceptable system performance for a period of 6 to 7 years before saturation of the peat is reached. Copper removal, on the other hand, is mainly attributed to pH change resulting from the dissolution of limestone and should continue well beyond 7 years.

Bench-scale experiments were undertaken at the Noranda Technology Center to evaluate the performance of individual passive treatment technologies and assess the potential for AMD mitigation using combined passive systems (Kuyucak, 1993). The results indicated that a lime-organic matter (LOM), biosorption (BIOS) and ALD configuration in series would probably be successful. It was surmised that the lime-organic matter mixture would generate alkalinity via SRB and limestone dissolution. The biosorption component would adsorb heavy metals, while the ALD

would provide additional alkalinity to promote iron and manganese precipitation as metal hydroxides in an oxidation pond downstream of the ALD.

Laboratory tests were conducted which examined the LOM/BIOS/ALD configuration, as well as BIOS/ALD and LOM/ALD configurations (Kuyucak and St-Germain, 1994). Results of the study are presented in Table 2-6. The LOM/BIOS/ALD and BIOS/ALD systems were able to raise pH levels from 2.4 to 6.3, while the LOM/ALD system raised the pH to a level of 7.2. The BIOS/ALD system performance was not affected by low temperatures. The LOM/ALD system exhibited the best overall sulphate and metal removal in terms of effluent water quality. However, it should be noted that the LOM/BIOS/ALD system was tested at almost twice the volumetric flow rate than the other configurations which could have affected the performance of the system. It is also possible that a BIOS/LOM/ALD system configuration where biosorption would take place prior to sulphate reduction, thereby removing some of the heavy metals, might be more effective.

Table 2-6: Treatment Efficiency of Various Passive Treatment System Configurations

Parameter	Initial	LOM/BIOS/ALD	BIOS/ALD	LOM/ALD
Flow Rate (L/m ³ /d)		27	14.7	14.6
pH	2.4	6.3	6.3	7.2
SO ₄ (mg/L)	6300	2287	nr	nr
Fe (mg/L)	325	21	3.8	0.1
Al (mg/L)	220	0.7	< 0.7	0.7
Cd (mg/L)	1.8	< 0.25	< 0.25	0.01
Cu (mg/L)	60	< 0.25	< 0.25	0.01
Zn (mg/L)	460	181	276	8
Mn (mg/L)	50	nr	nr	15
As (mg/L)	1.5	< 0.25	< 0.25	0.13

nr = Parameter value not reported in publication

CHAPTER 3

PROPOSED COMBINED PASSIVE TREATMENT SYSTEM

From the studies presented in the previous section, it can be concluded that significant AMD mitigation can be achieved by combining individual passive treatment alternatives. However, the majority of research presented to date has focused on the use of combined passive strategies involving wetlands. The main concerns associated with the use of wetlands under Canadian climatic conditions is the reduced treatment efficiency during the winter season due to freezing and loss of vegetative cover effectiveness. The performance of wetland systems can also be reduced during the spring season, due to high flow rates and reduced biological activity. As mentioned previously, the mitigation of AMD at Canadian mine sites using passive treatment technologies requires a combined strategy which aims at minimizing the impact of climatic variability on the treatment performance of the system.

3.1 SYSTEM COMPONENTS AND REMOVAL MECHANISMS

The proposed combined passive treatment system is comprised of four individual treatment components in series: (1) iron oxidation, (2) peat biofilter, (3) sulphate reduction, and (4) anoxic limestone drain. The combined system is designed to function in vertical percolation and horizontal flow configurations. A conceptual representation of the proposed combined system under field application is illustrated in Figure 3-1. The treatment function of individual components and the design issues associated with these are outlined in Table 3-1.

Figure 3-1: Conceptual Representation of Proposed Combined Passive Treatment System

Table 3-1: Combined Passive Treatment System Components Functions and Requirements

System Component	Treatment Function	Design Requirements
Iron Oxidation	<ul style="list-style-type: none"> ➤ Oxidation ➤ Precipitation 	<ul style="list-style-type: none"> ➤ HRT
Peat Biofilter	<ul style="list-style-type: none"> ➤ Metal Sorption ➤ Anoxic Conditions 	<ul style="list-style-type: none"> ➤ Organic Amendment ➤ Neutralizing Agent ➤ HRT
Sulphate Reducing Bacteria	<ul style="list-style-type: none"> ➤ Sulphate Reduction ➤ Metal Sulphide Precipitates ➤ Alkalinity Generation 	<ul style="list-style-type: none"> ➤ Organic Amendment ➤ Reducing Conditions ➤ pH > 5.0 ➤ HRT
Anoxic Limestone Drain (ALD)	<ul style="list-style-type: none"> ➤ Alkalinity Addition ➤ pH Increase 	<ul style="list-style-type: none"> ➤ Anoxic Conditions ➤ Fe, Al, DO < 1 mg/L ➤ Sulphate < 2000 mg/L ➤ HRT

3.1.1 IRON OXIDATION

A pre-treatment stage involving the oxidation of ferrous iron to ferric iron followed by the precipitation of ferric hydroxide has been recommended for AMD containing elevated iron concentrations (Kalin and Smith, 1997). In this stage, the oxidation of ferrous iron is achieved by allowing the AMD to flow over a rock surface at shallow depth which would encourage oxygen exchange and enhance the formation of ferric hydroxide. The precipitate is subsequently allowed to settle in a detention pond. The purpose of this step is to remove some excess iron from the AMD. Although the oxidation of iron may result in a decrease in the pH level, it also reduces the amount of iron retained within the biofilter, the potential for armouring in the ALD and the production of iron sulphide precipitates in the reduction stage. These factors can interfere with the overall treatment process and reduce the life expectancy of the system.

3.1.2 PEAT BIOFILTER

Peat biofilters have been developed for the treatment of domestic and industrial wastewater. They have been successful in the treatment of such discharges for several reasons. Firstly, the processed *Sphagnum* peat employed in biofilters exhibits the same adsorptive properties demonstrated by the peat in natural and constructed wetland systems. Thus, it has a high capacity for contaminant adsorption. Secondly, peat is a highly porous material that promotes microbial growth within its pore space and allows for the treatment of wastewaters via, in large part, aerobic biodegradation. Thirdly, aerobic biodegradation reactions are exothermic, which combined with the insulative properties of the peat sustains microbial activity throughout the entire year. As such, peat biofilters typically do not freeze during the winter season and, when designed adequately, have been reported to treat municipal and industrial wastewaters efficiently throughout the year under winter conditions (Brooks *et al.*, 1984).

To date, the use of peat biofilters in combination with other passive treatment strategies has not been investigated for the amelioration of AMD generated at Canadian metal mine sites. Peat biofilters can essentially serve three purposes in AMD mitigation; removal of heavy metals, development of anoxic conditions, and insulation of the treatment system.

Peat is a natural, inexpensive non-living biosorbent composed largely of humic compounds. Its high adsorption capacity for heavy metals has been demonstrated in several studies (Table 2-4). The humic substances contain functional groups which enable surface adsorption, ion exchange, chelation and complex formation with the dissolved metals in solution. These represent the main biosorption mechanisms responsible for the removal of heavy metals from AMD. A rise in pH level can generally be associated with the reduction in metal acidity through the peat biofilter.

Anoxic conditions can be developed in the peat biofilter by promoting microbial activities that consume oxygen. This is accomplished by introducing small dosages of readily biodegradable organic substrate which can be consumed under aerobic conditions in the upper layer of the peat biofilter. As aerobic bacteria degrade the substrate, oxygen serves as an electron acceptor until dissolved oxygen concentrations are no longer sufficient to sustain aerobic biodegradation. Dissolved oxygen concentrations are expected to decrease with peat biofilter depth. The addition of a neutralizing agent, such as limestone, may also be necessary to enhance biodegradation activity under severely acidic drainage conditions.

In addition to producing anoxic conditions, organic substrate biodegradation by aerobic bacteria serves another useful purpose. Aerobic biodegradation reactions are typically exothermic. The heat generated can then be retained within the peat biofilter which can act as an insulator due to its physical properties. By creating an insulation layer it may be possible to protect the system from extreme climatic conditions and to maintain treatment effectiveness throughout the winter season.

3.1.3 SULPHATE REDUCING COMPONENT

The third stage of the proposed combined passive treatment system involves the use of SRB. Under the reducing conditions generated by the peat biofilter and in the SRB zone, microbially-mediated sulphate reduction reactions generate alkalinity and produce sulphide that forms low solubility metal precipitates, thereby allowing for a further increase in pH level and removal of dissolved metals. This treatment process requires a source of carbon substrate, such as mushroom compost, municipal compost or some other form of organic compound.

3.1.4 ANOXIC LIMESTONE DRAIN

As a final treatment step, the drainage water flows horizontally through an ALD. The main purpose of the ALD is to add alkalinity and provide a final polishing step in terms of heavy metal removal. For optimal performance, the ALD requires anoxic conditions, as well as reduced dissolved iron (<1 mg/L), aluminum (<1 mg/L) and sulphate (<2000 mg/L) concentrations. These conditions are achieved by percolating the AMD through the preceding components.

3.2 LIMITING FACTORS

There are several environmental and operational factors that can ultimately affect the performance of individual components and the combined passive treatment systems. These limiting factors must be identified and quantified in the proposed combined passive treatment systems, in order to assess the potential applicability of a particular treatment configuration to the full-scale mitigation of AMD. The proposed combined passive treatment is comprised of four main treatment components: iron oxidation/precipitation, peat biofilter, biological reduction (SRB) and ALD. Each of these individual components is expected to have its own limitations which could impact the overall treatment efficiency of the entire system.

Investigations involving this system should focus on (1) identifying removal mechanisms in each component; (2) determining the impact of constituent and hydraulic loadings, as well as initial pH levels on treatment efficiency; (3) organic substrate and amendment selection; and (4) applicability of the combined system for AMD mitigation at Canadian mine sites and under Canadian climatic conditions.

3.2.1 *pH*

One of the largest problems associated with passive treatment of AMD is the pH of the influent drainage. Although some acidophilic bacterial species have been identified and characterized in mine waste environments, in biological treatment components, the microbial activities that can be associated with AMD mitigation are generally inhibited by low pH levels. For instance, SRB typically require pH levels above 5 in order to reduce sulphate to sulphide. As well, it is possible that aerobic bacteria may not be able to degrade organic substrates at the pH levels typically encountered in AMD without the addition of an alkaline amendment.

pH levels also affect physical/chemical treatment mechanisms. Depressed pH levels will reduce the biosorption effectiveness of peat. As the pH level decreases and, hence, the concentration of H^+ ions in solution increases, the functional groups or available sorption sites become occupied by the excess H^+ ions in solution. The number of sites available for sorption with dissolved heavy metals is thus reduced.

3.2.2 *CONSTITUENT LOADINGS*

The loading of metals can also impact the effectiveness of the passive treatment system. Individual components will respond differently to elevated metal concentrations. Toxic concentrations and accumulation of dissolved heavy metals can influence biodegradation activities of the aerobic bacteria in the peat biofilter. The effectiveness of ALDs is limited by iron, aluminum and dissolved oxygen concentrations greater than 1 mg/L which can cause system armouring. ALDs are also negatively affected by sulphate concentrations above 2000 mg/L.

The life expectancy of the peat biosorption and ALD components of the proposed passive treatment system are dictated by the metal concentrations of the AMD. At higher loadings, the finite number of adsorption sites on the peat biosorption material are expected to become occupied more quickly than under moderate to low metal concentrations. The life of the ALD can also be reduced by higher dissolved metal concentrations. When acidic drainage containing elevated metal concentrations comes into contact with limestone, metal hydroxides are formed. Ferric hydroxide armours the limestone, limiting its further dissolution, while other metal hydroxides, especially aluminum hydroxides, form precipitates which plug flow paths and eventually decrease the permeability of the ALD.

3.2.3 HYDRAULIC LOADING

Hydraulic loading has been reported to be a significant problem in passive treatment operations. High flow rates resulting from spring runoff and seasonal variability are difficult to predict and must be designed for accordingly. The consequences of elevated hydraulic loadings could include metal desorption in the peat biofilter and shortened residence time for treatment leading to fluctuations in the mitigation efficiency of the system.

3.2.4 SUBSTRATE AND AMENDMENT SELECTION

The periodic addition of substrate and amendments is required for biologically-mediated treatment strategies. In the proposed combined treatment system, the peat biofilter and SRB require organic substrates in order to enhance aerobic biodegradation and sulphate reduction, respectively. The selection of a substrate for each of the treatment components could be a controlling factor affecting the life expectancy of that component. Thus, both component life expectancy and treatment effectiveness should be considered in selecting organic and nutrient amendments.

3.2.5 TEMPERATURE

Temperature has been reported to be a major limiting factor in biologically-mediated treatment strategies. The effectiveness of the system can be lost entirely if the system freezes during the winter season and is unable to mitigate higher flow rates during spring runoff. In the proposed combined passive treatment system, the introduction and eventual characterization of a self-insulating system is aimed at reducing the detrimental impact of the extreme climatic conditions generally encountered at Canadian mine sites.

3.3 OVERVIEW OF EXPERIMENTAL APPROACH

To assess the performance of the proposed combined passive treatment system, laboratory investigations were undertaken to identify treatment mechanisms and quantify constituent removal and pH and alkalinity increases in the overall system, as well as individual system components. A series of four experiments were performed using moderate strength synthetic AMD. The main objective for each of these experiments is discussed briefly in the following sections.

3.3.1 ACID MINE DRAINAGE CHARACTERISTICS

In order to represent AMD that would be generated at Canadian mine sites, a moderate strength synthetic AMD was utilized for the laboratory experiments. Moderate strength AMD, encountered as a result of metal mining activities, would typically contain elevated concentrations of heavy metals in addition to iron, aluminum and manganese and a pH below 4. The AMD composition presented in Table 3-2 was utilized as the standard for base metal constituent concentrations. The mixture was prepared using metal sulphate salts and distilled water; the synthetic AMD recipe

utilized can be found in Appendix A. Experiments examining the impact of metal loading or pH variation will be evaluated and reported in reference to the moderate strength composition.

**Table 3-2: Moderate Strength
Acid Mine Drainage**

<i>Constituent</i>	<i>Concentration (mg/L)</i>
pH	3.0
Fe(II)	200
Al(III)	90
Zn(II)	100
Cu(II)	20
Cd(II)	6
Mn(II)	25
Ni(II)	20
SO ₄	3000

3.3.2 LABORATORY INVESTIGATIONS

The proposed combined passive treatment system for the mitigation of surface AMD comprises of four individual treatment components; iron oxidation and precipitation, peat biofilter, sulphate reduction, and anoxic limestone drain. Processed *Sphagnum* peat moss was utilized for the peat biofilter component due to its high adsorptive capacity and the reported success in its application as a biofilter for the treatment of municipal and industrial wastewaters. The anticipated primary functions of the peat biofilter included: adsorption of heavy metals and establishment of anoxic conditions via aerobic biodegradation.

The multi-purpose nature of this proposed peat biofilter had not been investigated to date. As such, a significant portion of this study focussed on the physical, chemical and biological characterization of the peat biofilter component and the mitigation of AMD within this component. Acid mine drainage removal mechanisms associated with iron oxidation and precipitation, sulphate reduction and alkalinity generation via SRB, and ALDs have been reported in previous studies. Thus, the performance of the iron oxidation, ALD and sulphate reducing components of the proposed system were evaluated only as part of the combined passive treatment system.

To satisfy the objectives, laboratory investigations were undertaken in the following four stages:

1. Physical/chemical characterization of peat
2. Adsorption of heavy metals onto peat
3. Impact of constituent loading, hydraulic loading, aerobic biological degradation and the development of anoxic conditions within the peat biofilter
4. Evaluation of combined passive treatment system performance

3.3.2.1 PEAT CHARACTERIZATION

The physical and chemical characterization experiments of the *Sphagnum* peat moss were conducted according to procedures outlined by the Ministry of Northern Development and Mines of Ontario (1989) and according to the American Society for Testing and Materials (ASTM) standards for peat, soils and organic materials (1996). Characterization of the peat utilized in this study will allow for comparisons with future experiments employing different sources of peat or, potentially, other sources of organic biosorption material.

3.3.2.2 HEAVY METAL ADSORPTION – PEAT BATCH EXPERIMENTS

The capacity of the peat biofilter for heavy metal adsorption was evaluated using batch experiments. The synthetic moderate strength AMD mixture was employed to establish the adsorption kinetics of the heavy metal mixture with the peat biosorbent over a 24 hour period, although past studies indicate that equilibrium should be reached within a 12 hour period. Since pH and temperature have been noted to affect the adsorption capacity and possibly adsorption kinetics, the experiment was performed at two different initial pH levels (2.5 and 5.0), and under three different temperatures (10°C, 20°C and 30°C).

Adsorption equilibrium isotherms for the individual heavy metals contained in the standard AMD mixture were determined at four different pH levels (2, 3, 4 and 5). Constants for the Langmuir isotherm model were subsequently derived from the data. The results of these experiments indicate the adsorption potential that might be achieved in a field system and the impact of pH, temperature and competitive adsorption of different metals on the performance of the system.

3.3.2.3 ACID MINE DRAINAGE MITIGATION – PEAT COLUMN EXPERIMENTS

The effects of hydraulic and constituent loadings on the removal of metals in a peat filter were examined using column experiments. The study focussed on four cases; (1) high flow - low metal concentration, (2) high flow - high metal concentration (3) low flow - low metal concentration, and (4) low flow - high metal. The experiment was conducted at two temperatures (20°C and 0°C). Constituent loadings applied to the peat filter included the moderate strength metal concentrations presented in Table 3-2 as the elevated loading case, while 25% of these metal concentrations was employed to represent low metal loading. The results of this study will allow estimation of break-through times for peat filters treating AMD. Upon completion of this study, all the columns were

dosed with a 5% dilution of the high concentration synthetic AMD solution for 10 days. The purpose of this experiment was to investigate the desorption potential of heavy metals within the peat filter. The impact of low heavy metal concentration influent drainage and near neutral pH levels, as might be expected during rainfall events or spring runoff, on heavy metal sorption in the peat filter was evaluated.

Investigations relating to the characterization of the peat biofilter in terms of aerobic biodegradation resulting in oxygen consumption were conducted under two temperature regimes, 20°C and 0°C. These conditions emulate summer and winter conditions, respectively, for which the temperature profile of the peat biofilter and the performance of this component were quantified. For each set of experiments, columns containing different mixtures of neutralizing agents and organic substrate were utilized. Amendments of interest in this study included pulp and paper sludge, 30% limestone-pulp and paper sludge and 10% lime-pulp and paper sludge mixtures.

The water saturation and the thickness of the unsaturated zone were also expected to affect the availability of oxygen for the degradation process. They, in turn, limit the depth of the aerobic zone within the column. To determine the effect of these parameters on the performance of the biofilter, the water saturation was varied by changing the water pressure at the base of the column, thereby, fixing the location of the water table and the thickness of the aerobic zone. The impact of changing the water level on the development of anoxic conditions, metal removal and system viability was thereby assessed to evaluate the applicability of this component at the field scale under varying operating conditions.

3.3.2.4 COMBINED PASSIVE TREATMENT SYSTEM STUDY

Once the metal removal, oxygen consumption and pH conditions within the peat biofilter were established under varying operational conditions, a bench-scale system containing all the elements of the combined passive process was constructed and the system performance was assessed using synthetic AMD. The peat biofilter component design was determined on the basis of the results obtained in the previous batch and column experiments. From the literature, it was estimated that empty-bed hydraulic retention times of 5-10 days and 10-30 days would be necessary for mitigation in the peat biofilter and sulphate reduction components, respectively. In comparison, the oxidation and ALD components, only required an empty-bed hydraulic retention time on the order of 1 day. The combined process was operated for a 10-month period to ensure that a pseudo steady-state had been achieved. These results will indicate the expected performance of the combined system under operating conditions representative of the environment encountered at Canadian mining facilities.

CHAPTER 4

PEAT CHARACTERIZATION

4.1 EXPERIMENTAL PROCEDURES

4.1.1 CHEMICAL CHARACTERIZATION

The chemical characterization of the peat employed in this study examined the elemental composition, extractable ions, cation exchange capacity, moisture content, ash content, organic matter content, fiber content, pH and optical density of the material. Experimental methods described in the following sections were generally derived from the American Society for Testing and Materials (ASTM) Standards, Manuel de Méthodes d'Echantillonnage et d'Analyse des Sols (McKeague, 1978) or Laboratory Methods for Testing Peat (Riley, 1989).

4.1.1.1 EXTRACTABLE IONS

The peat was divided into eight samples, oven-dried and finely ground ($<500\ \mu\text{m}$). Three 500 mg specimens from each sample were shaken in 100 mL of 0.5 N HCl for 30 minutes to displace any mobile cations and saturate adsorption complexes with H^+ . The specimens were then filtered using Whatman No. 41 filter paper and the filtrate collected. The filtrate was then analyzed for the following elements using ICP conducted at Agriculture Canada: arsenic, calcium, cadmium, cobalt, copper, chromium, lead, magnesium, nickel, phosphorous, potassium, selenium, sodium and zinc.

4.1.1.2 *ELEMENTAL COMPOSITION*

The total heavy and trace metal contents of the peat were determined using the wet-ashing method of sample preparation (McKeaggu, 1978) and given on a ppm of oven-dried peat basis. 50 mL of concentrated HNO_3 was added to three 1.0 g oven-dried and finely ground ($<500 \mu\text{m}$) peat specimens. The mixture was covered and boiled for at least 1 hour at a temperature of $100\text{--}150^\circ\text{C}$. After cooling, 20 mL of concentrated HClO_4 was added and the mixture was covered and boiled for another hour at a temperature of $200\text{--}250^\circ\text{C}$. The mixture was allowed to cool, after which, 10 mL of concentrated HF was added. The mixture was covered and boiled for an hour at 80°C . Next the mixture was uncovered, the temperature raised gradually to 250°C and the mixture was boiled until all but 3 mL had been evaporated. After cooling, 25 mL of 1 N HCl was added to dissolve any residue present and the mixture was covered and brought to a boil, then allowed to cool. Oxidation of Cr^{3+} with 10 mL of 30% H_2O_2 followed. The excess H_2O_2 was evaporated. Once the digestion was completed, 5% HCl was added to increase the volume of the solution to 50 mL. The element concentrations were then determined using Inductively Coupled Plasma Emission Spectrometry (ICP) conducted at Agriculture Canada.

4.1.1.3 *CATION EXCHANGE CAPACITY*

The cation exchange capacity of the peat was determined using the $\text{HCl}\text{--}\text{Ba}(\text{OAc})_2$ method as described by Day *et al.* (1979). The peat was divided into eight samples, oven-dried and finely ground ($<500 \mu\text{m}$). Three 500 mg specimens from each sample were shaken in 100 mL of 0.5 N HCl for 30 minutes to remove cations and saturate adsorption complexes with H^+ . The specimens were then filtered using Whatman No. 41 filter paper and the filtrate discarded. Excess acid was removed from the peat by rinsing with distilled water. The adsorbed H^+ was then replaced with Ba^{2+} ions by shaking in 100 mL of 0.5 N $\text{Ba}(\text{OAc})_2$ for 30 minutes. The specimens were filtered

using Whatman No. 41 filter paper and the filtrate collected. The filtrate was then titrated with 0.1 N NaOH using phenolphthalein indicator. The cation exchange capacity was computed from the following relationship.

$$CEC (meq / 100 g) = \frac{(\forall N)100}{M_p} \quad (4-1)$$

Where the cation exchange capacity is given as meq/100 g of oven-dried peat, $\forall$ is the volume of NaOH titrated (mL), N is the normality of the NaOH solution and M_p is the mass of the peat specimen (g).

4.1.1.4 MOISTURE CONTENT

The moisture content of air-dried peat was determined for sieved and ground samples, since both sieved and ground samples were utilized in the characterization analyses. The test was conducted according to ASTM Standards (D 2974-87). The peat was divided into eight samples, sieved using a ¼" sieve and allowed to air-dry for a 72-hour period. Half the mass of each of the eight samples was finely ground (<500 µm). Specimens containing 10.0 g of sieved peat and 2.0 g of ground peat were dried at 90°C for 48 hours. Due to the highly organic nature of peat, a drying temperature of 90°C was used instead of 105°C to avoid the loss of organic material. After a 2-hour cooling period in a desiccator, the final specimen mass was recorded. The moisture content was taken as the difference between the initial and final specimen mass.

$$Moisture (\%) = \frac{A - B}{B} 100\% \quad (4-2)$$

Where the moisture content is expressed on a dry mass basis, A is the initial mass of the air-dried peat specimen (g) and B is the sample mass remaining after drying at 90°C (g).

4.1.1.5 *ASH AND ORGANIC MATTER CONTENT*

The ash and organic matter content of the peat was determined by igniting the dried specimens from the moisture content procedure according to ASTM Standards (D 2974-87). After moisture content determination, the eight sieved specimens from the moisture content procedure were placed in a muffle furnace. The temperature was gradually brought to a temperature of 440°C and the samples were ignited for a 2-hour period and then allowed to cool for another 2 hours in a desiccator. The specimens were then weighed. The mass remaining after ignition is the ash content and includes mineral impurities such as sand.

$$Ash (\%) = \frac{D}{B} 100\% \quad (4-3)$$

The organic matter content is the fraction of material that has been ignited and volatilized.

$$Organic Matter (\%) = \frac{(B - D)}{B} 100\% \quad (4-4)$$

Both values were reported on an oven-dried mass basis; where D is the mass of ashes remaining after ignition (g).

4.1.1.6 *FIBER CONTENT*

The fiber content of the peat was determined using the laboratory method outlined by ASTM Standards (D 1997-91). The peat was divided into eight samples, sieved using a ¼" sieve and air-dried. Specimens weighing 3-5 g were placed in 100 mL of 5% sodium hexametaphosphate, mixed thoroughly and allowed to stand in this dispersing agent for 18 hours. The specimens were placed on a shaker at 180 rpm for 10 minutes. Then, the specimens were poured over a 100 mesh (150 µm) stainless steel sieve and the peat was washed until the water passing through was clear. Next, the sieve and peat were placed in a 2% HCl bath for more than 10 minutes to dissolve any

carbonates present. After the HCl bath, the peat was washed for 10 minutes to remove any residual HCl. The specimens were then filtered using Whatman No. 41 filter paper and the filtrate discarded. Finally the specimens were dried at 90°C for 24 hours, allowed to cool for 2 hours in a desiccator and the weight of the fibers remaining was recorded.

$$Fiber (\%) = \frac{F}{B} 100\% \quad (4-5)$$

Where the fiber content is expressed on an oven-dried mass basis and F is the mass of fibers remaining after the procedure (g).

4.1.1.7 pH

The pH of the peat in water and in calcium chloride was determined according to the methods described by Lévesque *et al.* (1980). The peat was sieved using a ¼" sieve and divided into 16-3.0 g samples which were allowed to air-dry over a 72-hour period. 50 mL of distilled-deionized water was added to eight of the peat samples, while 50 mL of 0.01 M CaCl₂ was added to the remaining eight samples. The samples were shaken on a reciprocating shaker at 100 rpm for a 30 minute period. The pH of the solution was then measured using a WWRbrand pH/mV/Temperature Meter (model 34105-002), a pH probe with temperature compensation.

4.1.1.8 OPTICAL DENSITY

The optical density, also referred to as the pyrophosphate index and E₄:E₆ ratio, was determined using a modified Kaila (1956) method of sample preparation. The peat was divided into eight batches, air-dried and finely ground (<420 µm). Three 1.0 g samples from each batch were shaken for 16 hours with 10 mL of 0.025 M Na₄P₂O₇ solution. The samples were filtered using Whatman No. 42 filter paper. Once filtered, 8 mL of 0.025 M Na₄P₂O₇ was added to 2 mL of filtrate. The

absorbances of the solution at 465 nm, 550 nm, and 665 nm were measured. The values obtained at 550 nm were multiplied by 100 to yield the Kaila index, while the $E_4:E_6$ ratio was obtained from the absorbances measured at 465 nm (E_4) and 665 nm (E_6).

4.1.2 PHYSICAL CHARACTERIZATION

The degree of compaction of the peat is likely to impact liquid and contaminant transport through a peat column. Thus, the physical characterization of the peat included the characterization of the dry density, water holding capacity and hydraulic conductivity of the material for the range of compaction expected in the column and overall system experiments. Experimental methods described in the following sections were generally derived from ASTM Standards or Laboratory Methods for Testing Peat (Riley, 1989). A volumetric water content calibration curve for time domain reflectometry (TDR) was also defined and was utilized for in-situ volumetric water content determination during the column experiments portion of this study.

4.1.2.1 DRY DENSITY

The dry density of the peat under varying degrees of compaction was determined using a method derived from ASTM Standards (D 4531-86). The peat was sieved using a ¼" sieve and air-dried for a 72-hour period. The moisture content of the peat was determined as outlined in Section 4.1.1.4 using 10.0 g samples of air-dried peat. Six PVC columns with 10.1 cm inside diameters were compacted with known masses of peat in 10.0 cm lifts to a depth of approximately 54.0 cm. The dry density was then computed, for each column, from the mass of oven-dried peat per volume of column.

$$\text{Dry Density (kg / m}^3\text{)} = \rho_d = \frac{M}{aL} \quad (4-6)$$

Where the dry density is expressed on a dry mass basis. M is the mass of the oven-dried peat (kg), a is the cross-sectional area of the column (m^2) and L is the peat depth in the column (m).

4.1.2.2 *HYDRAULIC CONDUCTIVITY*

The hydraulic conductivity of the peat under varying degrees of compaction was calculated using a modified version of the ASTM Standard Method (D 4511-93). The previously prepared columns were flooded for a period of 24 hours, using a constant head set up, at which point the flow into each column equaled the flow out. For a constant hydraulic head differential of 51.5 cm across the soil column, water samples were collected at 1-minute intervals in a pre-weighed set of beakers. The weight of water collected was determined and, assuming 1 g of water is equal to 1 cm^3 of water, the volume of water was collected and recorded. Next the cumulative volume of water collected was plotted against time and the flow rate was calculated from the straight portion of the curve. The hydraulic conductivity was then computed.

$$k(\text{cm/s}) = \frac{L}{a(\Delta H)} Q \quad (4-7)$$

Where k is the hydraulic conductivity, Q is the sustained flow rate (cm^3/s) and ΔH is the constant hydraulic head differential applied to maintain a corresponding sustained flow rate (cm). This procedure was repeated for constant hydraulic head differentials of 28.5 cm and 69.0 cm, and the average hydraulic conductivity was reported. Hydraulic conductivity values are typically corrected from the experimental water temperature to a reference temperature of 20°C. However, the analyses were conducted under laboratory conditions at recorded temperatures of 18.5°C to 21.0°C, hence, no temperature corrections were made.

4.1.2.3 *WATER HOLDING CAPACITY*

The water holding capacity of the peat under varying degrees of compaction was computed using a modification of ASTM Standards (D 2980-71). The peat was sieved using a ¼" sieve and air-dried for a 72-hour period. Six PVC columns with 10.1 cm inside diameters were compacted with known masses of peat in 10.0 cm lifts to a depth of approximately 54.0 cm as in the dry density procedure. The air-dried mass and volume of the peat in the column, as well as the mass of the empty columns were recorded. The columns were then flooded for a period of 24 hours, using a constant head set up, at which point the flow into each column equaled the flow out and the peat was saturated. Next, the flow was interrupted, suction equivalent to 38.1 cm of water was created at the base of the columns and the columns were gravity-drained under this suction for a period of 4 hours. The columns were then weighed. The procedure involving flooding and draining of the columns was repeated until consistent results were obtained.

$$\text{Water Holding Capacity (\%)} = \frac{M_w - M}{M} 100\% \quad (4-8)$$

Where the water holding capacity is expressed on an oven-dried mass basis, M_w is the mass of the wetted peat (g).

4.1.2.4 *VOLUMETRIC WATER CONTENT CALIBRATION CURVE FOR TIME DOMAIN REFLECTOMETRY*

A water content calibration curve for time domain reflectometry was defined for the peat employed throughout this study. An existing experimental setup in the Carleton University Geocryology Laboratory was utilized to determine the dielectric constant of the peat. A column, 20 cm in length, was packed with a measured initial air-dried mass of peat. Two 0.3 cm diameter and 15.0 cm long stainless steel probes were inserted into the peat column at a center-to-center distance of 1.95 cm

apart. The peat was moistened with a known volume of distilled water and the apparent length of the TDR probe was determined from the reflectometer oscilloscope reading, which was plotted using an x-y plotter. The dielectric constant was computed from the following relationship

$$K_a = \left[\frac{cH}{L} \right]^2 \quad (4-9)$$

$$H (ns) = \frac{L_a}{(2 cm / div)} 0.833 ns / div \quad (4-10)$$

Where K_a is the dielectric constant, c is the velocity of electromagnetic radiation in free space (30 cm/ns), L is the length of the TDR probe (15 cm) and L_a is the apparent length of the TDR probe measured from the x-y plot (cm) (daSilva *et al.*, 1998b). The experiment was repeated for several water volume additions to the peat column. The dielectric constant was plotted against the volumetric water content of the peat to obtain a water content TDR calibration curve.

4.2 RESULTS AND DISCUSSION

The results obtained from the analyses described in the previous section will form the basis for comparison between peats from different sources. The data are reported on a sieved oven-dried mass basis in the following sections. Appendix B contains the raw data from the chemical and physical characterization experiments. The material retained on the sieve consisted mainly of twigs, rocks and clumps of peat and represented 10 to 15% of the as received material by weight. The removal of these larger materials was necessary to ensure a more uniform material distribution and minimize channeling in the column experiment.

4.2.1 CHEMICAL CHARACTERIZATION

Total ion concentrations are generally regarded as the sum of the elemental composition fixed within the peat matrix and extractable fraction. Fixed ions are not expected to be leached into solution under system conditions; including high hydraulic loadings and highly acidic AMD environment. Extractable ions, on the other hand, will be mobile in the peat. The extractable ion determination, using HCl, provided a baseline for potential cation movement throughout the peat matrix. These represent the fraction of ions that is most likely to be displaced as a consequence of microbial activity and/or leaching at low pH levels. The results from the total element and HCl-extractable ions are presented in Table 4-1. The laboratory procedures and chemical analyses for the elemental composition and extractable ions were conducted at Agriculture Canada. It should be noted that since the potential leaching of iron, manganese, molybdenum and aluminum ions is not typically of concern in the agricultural industry, the extractable concentrations for these ions were not determined by the technician and could not be reported. Therefore, only the elemental composition fixed within the peat matrix was included in Table 4-1.

As can be seen from this table, copper, zinc and nickel are the most likely heavy metal ions, of interest in this study, to be leached from the peat matrix; the extractable fractions representing 39.4%, 44.5% and 21.5% of the total metal ion composition, respectively. This signifies that in the 1.9 kg of peat in the columns utilized in this study, a total metal mass of 225.3 mg of copper, 45.0 mg of zinc and 3.2 mg of nickel could be leached from the system. These extractable ion masses for copper, nickel and zinc represent only a fraction (< 1%) of the total metal mass which was supplied to each column in the synthetic AMD mixture.

Table 4-1: Total and Extractable Ion Concentrations in the Peat

Element	Total Ion Concentration (ug/g)	Extractable Ion Concentration (ug/g)
Ca	7420	2120
P	440	243
K	4180	219
Mg	4070	1180
Na	n.r.	390
Fe	3790 (fixed)	n.r.
Mn	16.6 (fixed)	n.r.
Mo	88.0 (fixed)	n.r.
As	93.6	34.4
Cd	0.8	b.d.
Co	24.1	6.3
Cr	15.8	b.d.
Cu	301	119
Ni	7.9	1.7
Pb	13.3	2.4
Se	5.7	b.d.
Zn	53.2	23.7

b.d. = below detection limit n.r. = value not reported

The results from the remaining chemical characterization procedures are presented in Table 4-2.

The potential for the total amount of cations adsorbed by the peat is represented by its cation exchange capacity (CEC). The higher the CEC the more heavy metals the peat can adsorb. The analysis yielded an average CEC of 119 meq/100 g of dry peat which indicates a moderate adsorption capacity relative to other peat materials (Lévesque *et al.*, 1980).

Table 4-2: Chemical Characterization Results for New Brunswick *Sphagnum* Peat

Parameter	Average	St. Dev.
CEC (meq/100 g)	119	4.4
Moisture Content (%)	11.2	3.0
Ash Content (%)	21.1	4.5
Organic Matter Content (%)	78.9	4.5
Fiber Content (%)	65.9	7.1
pH in H ₂ O	3.80	0.03
pH in CaCl ₂	3.00	0.02
Kaila Index	39.9	0.02
E ₄ :E ₆ Ratio	6.00	0.05

Compared to other peat materials (Lévesque *et al.*, 1980), the New Brunswick *Sphagnum* peat moss material utilized in this study was found to have a high ash content and correspondingly low organic matter content. Peat materials with higher organic matter content would generally have more functional groups for metal adsorption and would, therefore, be expected to have a higher adsorption capacity.

The pH of the peat material in solution is a means of expressing the degree of acidity of the peat material suspended in water or calcium chloride solution. pH measurements were made both in distilled water and CaCl_2 solutions because pH readings in water can be influenced by the presence of salts, whereas the observed pH in CaCl_2 solution is, in theory, independent of the initial salt concentration present in the soil. Values obtained in CaCl_2 solution are typically expected to be 0.5 to 0.8 pH units below those measured in distilled water, as was the case in this study, due to an increase in the release of H^+ ions by cation exchange (Lévesque *et al.*, 1980). The pH values of the peat material used in this study (3.0 and 3.8) were found to be fairly acidic (<4.5). The acidity of the peat will have an impact on its ability to adsorb metals onto the peat matrix. At lower pH levels and, hence higher H^+ ion concentrations, the H^+ ions in solution will occupy adsorption sites on the peat functional groups, thereby, reducing the number of sites available for metal adsorption. The acidity of the peat is also expected to affect the character of AMD as it percolates through the column environment. An acidic drainage effluent will result regardless of the metal removal processes occurring within the system, unless an alkalinity generating environment is developed (*e.g.* via sulphate reduction).

Optical density was utilized to assess the degree of decomposition of the peat. The Kaila or pyrophosphate index indicates the degree of humification of the peat, while the $\text{E}_4:\text{E}_6$ ratio empirically measures the polymeric character of the water-soluble soil humus. The higher the

pyrophosphate index or $E_4:E_6$ ratio, the more humified the sample, and hence, the more biologically stable the sample (Lévesque *et al.*, 1980). The values determined from these analyses indicate that the peat employed in this study showed a moderate to advanced state of humification, and hence, was relatively stable. These results concurred with the fiber content which was moderate compared to other peat materials (ASTM D4427, 1996) indicating a moderate degree of humification. A humified peat will generally not decompose easily and will, therefore, not act as a readily available carbon source for microorganismal growth in the column. This implies that a stable peat is more likely to retain its physical structure, and its ability to adsorb metals is less likely to be altered due to changing states of decomposition.

4.2.2 PHYSICAL CHARACTERIZATION

The physical characteristics of the peat including dry density, water holding capacity, and hydraulic conductivity were largely dependent on the degree of compaction of the peat material. In general, a dry density of 100 to 140 kg/m³ (Brooks *et al.*, 1984) is typically recommended for optimal performance in domestic wastewater treatment using peat biofilters. This range in density allows for the maintenance of the biofilter matrix and the growth of microorganisms required for treating domestic wastewater. No specific value had been suggested in the literature for peat filters employed to treat AMD. It was felt that a higher dry density was more appropriate since bacterial growth was expected to be much less than that in a filter treating domestic wastewater and it would also tend to strengthen the filter matrix. Hence, an average dry density of 200 kg/m³ was targeted in these physical characterization experiments with actual dry density values ranging between 170 to 219 kg/m³.

Water holding capacity tests performed on the columns indicated that water holding capacity generally increased with increasing dry density. The results are shown in Figure 4-1. Equation 4.11 represents the relationship between water holding capacity and dry density (ρ_d) ($R^2 = 0.975$).

$$\text{Water Holding Capacity (\%)} = 1.03\rho_d + 164 \quad (4-11)$$

Constant head experiments demonstrated that, within the range of dry densities tested, hydraulic conductivity decreased exponentially with increasing dry density. The results are presented in Figure 4.2 and the mathematical relationship represented by the following equation ($R^2 = 0.9995$).

$$\text{Hydraulic Conductivity (cm/s)} = 25.2e^{(-0.04\rho_d)} \quad (4-12)$$

Figure 4-1: Water Holding Capacity as a Function of Peat Dry Density

Figure 4-2: Hydraulic Conductivity as a Function of Peat Dry Density

This relationship is similar to the one described by Kennedy and Van Geel (2000) who conducted a study using New Brunswick *Sphagnum* peat. The water holding capacity (Eq. 4-11) and hydraulic conductivity (Eq. 4-12) relationships will be employed to physically characterize experimental conditions during the peat filter column experiments based upon the dry density of the material in the columns.

The volumetric water content TDR calibration curve was defined from the procedure described in section 4.1.2.3. It was assumed that water content values below 50% were not necessary due to the operational conditions under which TDR would be employed and water content evaluated. The resulting calibration curve between water content and dielectric constant (K_a) at 20°C can be found in Figure 4-3. The following relationship was derived from the data ($R^2 = 0.954$):

$$\text{Volumetric Water Content (\%)} = 1.23 K_a + 29.2 \quad (4-13)$$

The volumetric water content relationship (Eq. 4-13) will be utilized to determine the volumetric water content profile with depth in the substrate/amendment mixture study.

4.2.3 PEAT CLASSIFICATION

Results from the fiber content, ash content, pH and water holding capacity were utilized to classify the peat using the method outlined by ASTM Standards (D4427-92). From the results presented in Table 4.2 and Figure 4.1, the peat utilized in this study was characterized as hemic (33% < fiber content < 67%) , high ash (ash content > 15%), highly acidic (pH < 4.5) and moderately absorbent (300% < water holding capacity < 800%).

Figure 4-3: Peat TDR Calibration Curve

CHAPTER 5

HEAVY METAL ADSORPTION – BATCH EXPERIMENTS

5.1 EXPERIMENTAL PROCEDURES

5.1.1 METAL ADSORPTION ONTO FILTER PAPER

Comparing the metal concentration of filtered and unfiltered samples for a series of dilutions assessed the potential for retention of heavy metals onto the Millipore filter paper utilized throughout this study. Single metal solutions containing 5 mM concentrations of iron (Fe), aluminum (Al), zinc (Zn), manganese (Mn), copper (Cu), cadmium (Cd) and nickel (Ni) were made up using metal sulphate salts and distilled water. A 25 mL sample was filtered using a 0.45 μm Millipore filter and a corresponding 25 mL of unfiltered sample was collected. This procedure was repeated for serial dilutions of 1 mM, 0.5 mM, 0.1 mM and 0.01 mM concentrations. The samples were then acidified using 3 drops of concentrated HCl. Metal concentrations were determined using inductively coupled plasma (ICP) analysis conducted by the Department of Chemistry at Carleton University.

5.1.2 AMD ADSORPTION – KINETIC EXPERIMENTS

Kinetic experiments were aimed at determining the time required for steady-state conditions to be reached as a function of temperature and pH in an unbuffered multi-species ion solution. In all cases, duplicate experiments were conducted.

5.1.2.1 *EXPERIMENTAL AND SAMPLING PROCEDURES*

The synthetic AMD composition presented in Table 3-2 was utilized for the batch kinetic experiments. The initial pH of the synthetic AMD was adjusted to 2.5 using concentrated HCl. Prior to the experiment, milled New Brunswick peat was hand-sieved with a ¼" sieve and allowed to air-dry for a 24-hour period. Eighteen specimens were prepared by placing 1.0 g of peat in 250 mL serum bottles and mixing with 150 mL of the synthetic AMD solution. Three control specimens were included in the test; one containing 1.0 g of peat and 150 mL of distilled water (C1), the second containing containing 150 mL of distilled water and 0.0 g of peat (C2), and the third 150 mL of the AMD solution and 0.0 g of peat (C3). The initial pH of each mixture was recorded. The specimens were then shaken at 200 rpm in an incubator with a constant temperature of 20°C.

Samples were sacrificed at 15-minute intervals for the first three hours, then after 3.5, 4.0, 6.0, 12.0 and 24.0 hours of contact time. Upon collection, the final pH of the mixture was recorded. Next the samples were filtered using 0.45 µm Millipore filter paper and acidified with 3 drops of concentrated HCl. Metal concentrations were determined from ICP analysis performed in the Department of Chemistry at Carleton University. This procedure was repeated for the following experimental conditions: pH = 2.5, T = 10°C; pH = 2.5, T = 30°C; and pH = 5.0, T = 20°C.

5.1.2.2 *DATA ANALYSIS*

The individual metal ion concentrations removed from solution were plotted as a function of time. The time required to reach equilibrium adsorption conditions was then determined. It was surmised that pH, temperature and metal species would affect the time required to reach equilibrium. Results

obtained from these experiments were utilized to establish the minimum contact time necessary in the batch equilibrium study.

In each batch test, the first control (C1) was used to establish whether any metals would be leached from the peat material, while the second control (C2) was utilized to determine if any metals would be leached from or lost by adsorption to the serum bottle. The third control (C3) was employed to account for any removal of soluble metal ions from the AMD solution due to sorption onto the serum bottle wall under each of the experimental conditions.

5.1.3 HEAVY METAL ADSORPTION – EQUILIBRIUM EXPERIMENTS

Equilibrium experiments were conducted to evaluate the heavy metal adsorption capacity of the peat under various unbuffered pH conditions. In all cases, the tests were performed in duplicate.

5.1.3.1 EXPERIMENTAL AND SAMPLING PROCEDURES

Equilibrium experiments were conducted using single-component metal ion solutions containing 5 mM concentrations of iron (Fe), aluminum (Al), zinc (Zn), manganese (Mn), copper (Cu), cadmium (Cd) and nickel (Ni) under ambient laboratory conditions. Prior to the experiment, milled New Brunswick peat was hand-sieved with a ¼" sieve and allowed to air-dry for a 24-hour period. For each metal, four sets of 8 peat specimens weighing 0.0, 0.1, 0.25, 0.5, 1.0, 1.5, 2.0 and 4.0 g were placed in 250 mL serum bottles. The metal solutions were prepared using metal sulphate salts and distilled water. The initial pH of the single-component metal ion solutions was adjusted to 5.0 using concentrated HCl and 30% NaOH solutions where decreases and increases in pH were required, respectively. 150 mL of one of the single metal solutions was added to each sample

contained in the first set of 8 peat specimens. Next, the pH of the single-component metal ion solution was adjusted, in turn, to 4.0, 3.0 and 2.0 using concentrated HCl and 150 mL of each of the solutions with adjusted pH was added to the remaining three sets of 8 peat specimens. The samples were then shaken at 200 rpm for 24 hours. In total, sixty-four samples were prepared for each metal; thirty-two duplicate samples.

After a 24-hour contact period, the shaker was stopped and the final pH of each of the samples was recorded. The samples were then filtered using 0.45 µm Millipore filter paper and acidified with 3 drops of concentrated HCl. Metal concentrations were determined via ICP analysis performed by Seprtech Laboratories in Ottawa. This procedure was repeated for single-component metal ion solutions containing each of the heavy metals listed above with pH levels of 5.0, 4.0, 3.0 and 2.0.

5.1.3.2 DATA ANALYSIS

The apparent mass of metal adsorbed onto the peat at equilibrium was determined for each metal under the four pH conditions. The Langmuir isotherm model was selected to fit the data because it has generally been accepted for describing metal sorption onto peat in single-component metal ion solutions over a wide range of pH values (Brown *et al.*, 2000; McKay *et al.*, 1998; Viraraghavan and Dronamraju, 1995). It represents monolayer adsorption partitioning for which the monolayer saturation capacity can be estimated for each of the metals on the peat. In cases where monolayer adsorption behaviour could be observed from the results, constants for the Langmuir isotherm model were derived from the equilibrium data. The Langmuir expression is represented by the following equation.

$$q_e = \frac{q_s b C_e}{1 + b C_e} \quad (5-1)$$

Where C_e is the liquid-phase equilibrium concentration of the heavy metal of interest (mM/L), q_e is the equilibrium amount of metal adsorbed per unit weight of adsorbent (mM/g), q_s represents the metal adsorbed per unit weight of adsorbent in a mono-layer around the peat (mM/g), and b is the adsorption equilibrium constant related to the energy of adsorption (L/mM).

The Langmuir model for competitive adsorption was applied to describe adsorption equilibria in multiple metal ion systems (Butler and Ockrent, 1930). This simple isotherm model is based on the same assumptions as the Langmuir model for single metal ion solutions. For the n metals present in solution, the predicted equilibrium amount of each metal adsorbed per unit weight of adsorbent $q_{e,i}$ (mM/L) is given by:

$$q_{e,i} = \frac{q_{s,i} b_i C_{e,i}}{1 + \sum_{i=1}^n b_i C_{e,i}} \quad (5-2)$$

Where $C_{e,i}$ is the liquid-phase equilibrium concentration of each of the n metals in the mixture (mM/L), $q_{s,i}$ represents the metal adsorbed per unit weight of adsorbent in a mono-layer around the peat for each of the n metals in the mixture (mM/g) obtained from single metal ion isotherm analyses, and b_i is the adsorption equilibrium constant related to the energy of adsorption for each of the n metals in the mixtures (L/mM) obtained from single metal ions isotherm analyses.

The equilibrium amount of metal adsorbed onto the peat material was computed from the difference between the initial and equilibrium soluble metal ion concentrations in solution as per:

$$q_e = \frac{(C_o - C_e) \forall}{M} \quad (5-3)$$

Where C_o is the concentration in the bottle with 0.0g of peat (mmol/L), V is the volume of AMD (L) and M is the mass of peat (g). The concentration in the bottle with no peat added was employed to account for metal removal which may occur due to precipitation. The equation parameters and corresponding statistics were obtained by plotting the metal adsorption capacity (mmol) per mass (g) of peat as a function of solution equilibrium concentration (mmol/L). Final solution pH levels were plotted as a function of peat mass for the metals examined at each of the pH levels.

5.2 RESULTS AND DISCUSSION

The capacity of the peat for heavy metal adsorption was evaluated using the series of batch experiments described in the previous section. Where duplicate experiments were conducted, the results were combined and represented as distinct points in each data set, rather than the average of the duplicate experiments. The raw data from each of the analyses can be found in Appendix C.

5.2.1 METAL REMOVAL ONTO FILTER PAPER

Metal removal onto the Millipore filter paper was evaluated to assess the impact of the filtering process on the accuracy of metal concentration values. The results for individual metals were plotted as the percentage difference of the filtered and non-filtered concentrations versus the solution concentration and are presented in Figures 5-1. An exponential decay relationship was observed for all metals. The curves were then linearized by transforming the data to a log-log scale as shown in Figure 5-2. As can be observed from the linearized curves, the percentage differences in concentration between filtered and unfiltered samples with decreasing solution concentration increased more rapidly in copper, manganese, iron and nickel samples. Cadmium, on the other hand, was least affected by filtration under decreasing metal concentration conditions.

Figure 5-1: Metal Removal due to Filtration as a Function of Concentration

Figure 5-2: Log-Log Plot of Metal Removal due to Filtration as a Function of Concentration

Regression analyses were performed on the transformed data to obtain parameters F and n for the following exponential decay relationship, where C_M is the solution concentration (Mm).

$$\log \left[\frac{[(non - filtered) - (filtered)]}{(non - filtered)} \right] = \log F + n \log(C_M) \quad (5-4)$$

These parameters are presented in Table 5-1. As can be seen from Figure 5-1, filtered and non-filtered sample concentration differences of <2% were observed for 5 mM metal concentrations. Differences in concentrations were generally found to increase with decreasing concentration. At 0.01 mM concentrations differences in concentrations were generally found to be $\geq 20\%$ with the exception of cadmium for which a value of 8% was recorded. These results would indicate that the accuracy decreases significantly at these lower concentrations, as does the validity of the specific values. Molar concentrations on the order of 0.01 mM controlled the lower limit of experimental interpretation. As such, metal concentrations (mg/L) were reported to one decimal point digit throughout the remainder of this study.

Table 5-1: Computed Parameters and Statistics for Metal Removal due to Filtration as a Function of Concentration

Metal	Parameters		Statistics		
	Log(F)	(n)	R ²	St. Err. [log(F)]	St. Err. (n)
Fe	0.11	-0.66	0.955	0.09	0.08
Al	0.56	-0.45	0.985	0.03	0.03
Zn	0.50	-0.46	0.993	0.02	0.02
Mn	0.18	-0.67	0.932	0.11	0.11
Ni	0.14	-0.65	0.967	0.07	0.07
Cu	0.07	-0.78	0.977	0.07	0.07
Cd	0.33	-0.33	0.941	0.05	0.05

5.2.2 AMD ADSORPTION – KINETIC EXPERIMENTS

The peat was contacted with the synthetic AMD mixture described in Table 3-2 for three different temperature conditions (10°C, 20°C and 30°C) and two pH values (2.5 and 5). The aim of this experiment was to determine the time required to reach equilibrium conditions as a function of temperature and pH.

Response curves for each of the metals of interest are presented in Figures 5-3 to 5-9 and the pH variations under each of the experimental conditions in Figure 5-10. Samples were damaged and, hence, results were not available for the 0.25 and 12 hour contact times under the 10°C and pH of 2.5 experimental conditions. The time required to reach equilibrium (t_e) was assessed as the point where the slope of the kinetic curve was less than 111 (%)/(hr) between two consecutive contact times. The equilibrium percent removal (R_e), relative to the experimental control (C3), and the corresponding standard deviation (SD) for each of the metals in the mixture was estimated as the average of the percent removal values after equilibrium had been reached. The results are summarized in Table 5-2 for each of the metals in the mixture.

Table 5-2: Contact Time to Reach Equilibrium and Corresponding Equilibrium Percent Removals for Metals in AMD Mixture

		Fe	Al	Zn	Mn	Ni	Cu	Cd
20°C pH=5.0	t_e (hr)	4.0	12.0	3.5	4.0	4.0	3.0	6.0
	R_e (%)	14.4	39.1	15.9	9.3	18.6	61.2	21.7
	SD (%)	0.8	2.0	1.2	0.6	1.0	1.5	1.3
20°C pH=2.5	t_e (hr)	4.0	4.0	6.0	12.0	4.0	4.0	4.0
	R_e (%)	11.1	7.9	10.1	8.9	13.6	19.7	13.1
	SD (%)	0.7	0.8	0.3	0.8	1.3	0.9	1.3
30°C pH=2.5	t_e (hr)	4.0	4.0	6.0	12.0	6.0	4.0	6.0
	R_e (%)	13.6	6.5	20.1	11.0	17.2	16.6	22.2
	SD (%)	1.5	0.8	1.0	1.1	1.3	0.8	1.6
10°C pH=2.5	t_e (hr)	4.0	3.5	6.0	12.0	4.0	3.0	4.0
	R_e (%)	9.6	9.1	7.7	7.0	7.9	23.5	6.6
	SD (%)	0.5	0.3	0.6	0.6	1.4	1.2	0.8

Under the four experimental conditions, equilibrium concentrations for the metals composing the synthetic AMD mixture were generally reached within a 6-hour contact period, with a few exceptions. A 12-hour contact period was necessary for manganese (Fig. 5-6) to reach equilibrium at all temperatures conditions at a pH of 2.5. The lower contact period required at 30°C is likely due to reaction kinetics which might be more rapid at higher temperatures. This could also be explained by the fact that manganese did not generally exhibit a high affinity for sorption onto peat and could be displaced easily by other ions in a mixture due to competitive inhibition. At 20°C and a pH of 5, aluminum (Fig. 5-4) also required a 12-hour contact period. This latter phenomenon was attributed to chemical reactions, such as aluminum precipitation, taking place in the pH range of 5, which would require a longer contact time for the solution to equilibrate.

As can be seen from Table 5-2, the order of equilibrium contact times for the metals present in the AMD mixture was as follows: $\text{Cu} < \text{Zn} < \text{Fe} = \text{Ni} = \text{Mn} < \text{Cd} < \text{Al}$ at 20°C and a pH of 5; $\text{Cu} = \text{Al} = \text{Fe} < \text{Ni} = \text{Zn} = \text{Cd} = \text{Mn}$ at 30°C and a pH of 2.5; $\text{Cu} = \text{Al} = \text{Fe} = \text{Ni} = \text{Cd} < \text{Zn} < \text{Mn}$ at 20°C and a pH of 2.5, and; $\text{Cu} < \text{Al} < \text{Fe} = \text{Ni} = \text{Cd} < \text{Zn} < \text{Mn}$ at 10°C and a pH of 2.5. The results observed at 20°C and a pH of 2.5, are consistent with results obtained by Gosset *et al.* (1986) in their adsorption study using Cu, Cd, Zn and Ni. Working with single-component metal ion solutions at 20°C and an initial pH of 2.2 (unbuffered), the order of equilibrium contact time was reported as follows: $\text{Cu} < \text{Ni} < \text{Cd} < \text{Zn}$. Based upon the results from the kinetic study, a contact period of 24 hours was selected for the equilibrium experiments to allow equilibrium adsorption conditions to be reached for a pH range of 2 to 5, as well as under cold and laboratory temperature conditions.

Figure 5-3: Effects of Temperature and pH on Iron Adsorption Kinetics onto Peat

Figure 5-4: Effects of Temperature and pH on Aluminum Adsorption Kinetics onto Peat

Figure 5-5: Effects of Temperature and pH on Zinc Adsorption Kinetics onto Peat

Figure 5-6: Effects of Temperature and pH on Manganese Adsorption Kinetics onto Peat

Figure 5-7: Effects of Temperature and pH on Nickel adsorption Kinetics onto Peat

Figure 5-8: Effects of Temperature and pH on Copper Adsorption Kinetics onto Peat

Figure 5-9: Effects of Temperature and pH on Cadmium Adsorption Kinetics onto Peat

Figure 5-10: Batch Kinetic Experiment Solution pH Variation as a Function of Time

5.2.2.1 *EFFECT OF TEMPERATURE ON METAL ADSORPTION KINETICS*

Temperature was found to affect both the time required to reach equilibrium and the degree of metal adsorption onto the *Sphagnum* peat. Metal removal from the mixture using peat was found to increase with increasing temperature for iron (Fig 5-3), zinc (Fig. 5-5), manganese (Fig. 5-6), nickel (Fig. 5-7) and cadmium (Fig. 5-9). On the other hand, the degree of removal decreased with increasing temperature for aluminum (Fig. 5-4) and copper (Fig. 5-8). The latter observations could be the result of competitive adsorption and/or the increased solubility of some compounds at higher temperatures. Another plausible explanation for decrease in removal with temperature increase might be attributed to the weakening of sorptive forces between the peat binding sites and these metal ions which would occur with increasing temperature in an exothermic process as suggested by Viraraghavan and Dronamraju (1995). However, the multi-ion composition of the AMD mixture makes it difficult to distinguish between the competitive adsorption and the exothermic process responses.

The contact period necessary to attain equilibrium conditions increased with increasing temperature for aluminum, nickel, copper and cadmium (Table 5-2). The opposite trend was noted for manganese, while the contact time required for iron and zinc removal was relatively constant for the three temperature conditions. The differences in trend were attributed to competitive adsorption caused by the mixture of ions in solution, and the affinity of the metals for peat under the different temperature conditions.

5.2.2.2 EFFECT OF pH ON METAL ADSORPTION KINETICS

Another important operating parameter affecting metal sorption onto *Sphagnum* peat was the pH of the mixture. In general, the adsorption kinetic study yielded higher metal removals in the solution pH of 5.0 compared to the solution pH of 2.5 under the same temperature conditions, with the exception of manganese where no significant difference was noted. Thus, the removal of the metals from the AMD mixture using peat followed a similar trend to that of single-component metal ion solutions, where adsorption would be expected to decrease with decreasing pH (Gosset *et al.*, 1986; Bunzl *et al.*, 1976)

Comparing the results from the kinetic experiments at the same temperature and two pH levels, demonstrated that equilibrium conditions for zinc (Fig. 5-5), manganese (Fig. 5-6) and copper (Fig. 5-8) could generally be achieved more quickly at higher pH levels. The opposite trend was observed for aluminum (Fig. 5-4) and cadmium (Figure 5-9), while the contact time required to reach equilibrium for iron (Fig. 5-3) and nickel (Fig. 5-7) did not appear to be significantly affected by the variation in pH. Again, competitive inhibition was more than likely responsible for the behaviour relating kinetics and pH. A decrease in pH (Fig. 5-10) from 5.0 to 4.1 was also observed during the course of the experiment conducted at 20°C and a pH of 5. This was due, in part, to the acidity of the peat, and to the precipitation of iron, aluminum, and copper, at a pH of 5. The general trends reported in this section for the sorption of the synthetic AMD mixture under varying pH and temperature will be utilized to interpret observations in the column experiments.

5.2.3 HEAVY METAL ADSORPTION – EQUILIBRIUM EXPERIMENTS

Equilibrium experiments were conducted for the metals of interest at four different unbuffered pH levels to assess their adsorption capacity onto peat in 5 mM single-component metal ion solutions. The Langmuir constants were computed on a molar basis by fitting a curve to the sorption capacity (mmol-metal/g-peat) as a function of equilibrium metal concentration (mmol/L). These values along with their standard errors are listed in Table 5-3. The Langmuir isotherms for the metals and corresponding pH responses were plotted in Figures 5-11 to 5-17.

Table 5-3: Langmuir Adsorption Isotherm Constants and Standard Errors

Metal	pH	q_s (mmol/g)	St. Err (q_s) (mmol/g)	b (L/mmol)	St. Err. (b) (L/mmol)
Iron	5	0.62	0.01	1.84	0.16
	4	0.56	0.02	1.16	0.16
	3	0.50	0.03	1.11	0.22
	2	--	--	--	--
Aluminum	5	0.13	0.07	16.6	4.09
	4	0.88	0.11	0.62	0.18
	3	0.37	0.01	8.03	1.27
	2	--	--	--	--
Zinc	5	0.49	0.03	0.30	0.04
	4	0.48	0.04	0.28	0.04
	3	0.26	0.04	0.44	0.16
	2	--	--	--	--
Manganese	5	0.56	0.06	0.22	0.04
	4	0.54	0.06	0.21	0.05
	3	0.36	0.06	0.42	0.19
	2	--	--	--	--
Nickel	5	0.56	0.26	0.10	0.07
	4	0.47	0.20	0.13	0.09
	3	0.32	0.15	0.21	0.19
	2	0.17	0.12	0.31	0.24
Copper	5	0.63	0.04	1.36	0.35
	4	0.60	0.04	1.37	0.40
	3	0.46	0.03	2.06	0.56
	2	0.17	0.05	0.35	0.25
Cadmium	5	0.27	0.05	0.27	0.10
	4	0.25	0.08	0.26	0.18
	3	0.17	0.04	0.43	0.28
	2	--	--	--	--

Figure 5-11: Equilibrium Isotherms and pH Response for Iron Adsorption onto Peat

Figure 5-12: Equilibrium Isotherms and pH Response for Aluminum Adsorption onto Peat

Figure 5-13: Equilibrium Isotherms and pH Response for Zinc Adsorption onto Peat

Figure 5-14: Equilibrium Isotherms and pH Response for Manganese Adsorption onto Peat

Figure 5-15: Equilibrium Isotherms and pH Response for Nickel Adsorption onto Peat

Figure 5-16: Equilibrium Isotherms and pH Response for Copper Adsorption onto Peat

Figure 5-17: Equilibrium Isotherms and pH Response for Cadmium Adsorption onto Peat

Metal adsorption onto peat generally followed the monolayer adsorption model, as defined by the Langmuir isotherm for the initial pH values of 3, 4 and 5. The monolayer saturation adsorption capacities (q_s) for the individual metals decreased with decreasing pH, with the exception of aluminum (Fig. 5-12). The relative single metal sorption capacities observed on a molar basis as defined by the monolayer saturation adsorption capacity parameter was: $\text{Cu} \approx \text{Fe} > \text{Ni} \approx \text{Mn} \approx \text{Zn} > \text{Cd} > \text{Al}$ at a pH of 5; $\text{Al} > \text{Cu} \approx \text{Fe} \approx \text{Mn} \approx \text{Zn} \approx \text{Ni} > \text{Cd}$ at a pH of 4, and: $\text{Fe} \approx \text{Cu} > \text{Al} \approx \text{Mn} \approx \text{Ni} > \text{Zn} > \text{Cd}$ at a pH of 3 (Table 5-3). In examining the adsorption capacities of cadmium, copper, nickel and zinc, the responses were found to be fairly consistent at pH 3, 4 and 5: $\text{Cu} > \text{Ni} > \text{Zn} > \text{Cd}$ at pH 3; $\text{Cu} > \text{Ni} \approx \text{Zn} > \text{Cd}$ at pH 4; and, $\text{Cu} > \text{Ni} \approx \text{Zn} > \text{Cd}$ at pH 5.

The results at pH 4 were consistent with the relative equilibrium adsorption capacities reported by Lee and Low (1989) and McKay *et al.* (1998) under similar experimental conditions. Lee and Low concluded that the relative capacities were in the order of $\text{Cu} > \text{Cd} > \text{Zn} > \text{Ni}$ on a mass basis, which, when converted to molar basis yielded an order of $\text{Cu} > \text{Zn} > \text{Ni} > \text{Cd}$. Working with carefully pH buffered single-component metal ion solutions at pH 4.5, McKay *et al.* (1998) also obtained a relative order of $\text{Cu} > \text{Zn} > \text{Ni} > \text{Cd}$. They related this adsorption trend to the absolute electronegativity of the metal ions, where the more electronegative metal ions would be more strongly attracted to the peat surface.

In the literature, detailed equilibrium studies could not be found which included the sorption of aluminum, iron or manganese onto peat. This is probably because aluminum and iron are generally found to form metal hydroxide precipitates when accompanied by changes in the solution pH, which can complicate the experimental procedure. Under these conditions, it becomes difficult to identify the appropriate metal removal mechanism, sorption or precipitation.

5.2.3.1 *EFFECT OF pH ON METAL ADSORPTION EQUILIBRIUM*

Mono-layer saturation adsorption capacities of the metals onto the *Sphagnum* peat were generally found to increase with increasing pH, indicating a higher removal potential at higher solution pH. Iron, aluminum, zinc, manganese and cadmium did not appear to follow the mono-layer adsorption model for experiments conducted at an initial solution pH of 2 due to the low solution pH. In each of the batch experiments conducted at initial solution pH conditions of 2 and 3, the solution pH was found to increase with increasing peat mass addition, while at pH conditions of 4 and 5, the final solution pH was generally found to decrease with increasing peat sample weight. In the absence of significant metal precipitation, these changes were attributed to the nature of the adsorbent, which caused the pH of the solution to converge towards the natural pH of the peat material. The adsorption behaviour of the metal ions was consequently affected by the changing solution pH (Fig. 5-11 to 5-17). The pH of the solution was not adjusted, since the pH of the AMD would not be altered in the field.

The aluminum adsorption capacities (Fig. 5-12) were observed to increase rapidly with increasing equilibrium concentration, except at the initial pH of 2. This latter phenomenon was attributed to the large solution pH fluctuations (1.8 units) at this pH level. The solution would probably require a greater contact time to achieve a true sorption equilibrium under this pH condition. During the kinetic batch experiments, a greater contact time was also necessary for aluminum to reach equilibrium at higher pH levels (Table 5-2). Aluminum was found to precipitate significantly, as aluminum hydroxide, at an initial solution pH of 5, which resulted in fluctuations in solution pH. These factors led to aluminum mono-layer saturation adsorption capacities which were lower at pH 2 and 5, compared to pH 3 and 4 where sorption was the predominant removal mechanism.

Iron adsorption (Fig 5-11) also increased with increasing equilibrium concentration, except at the initial pH of 2 where the adsorption capacity decreased with increasing pH. This was attributed to the significant changes in pH (1.2 units) occurring at this pH level with increasing peat sample weight. At pH 4 and 5, the slight formation of an iron hydroxide precipitate was observed, especially in lower peat weight samples. The reduction in final solution pH for the equilibrium experiments conducted at pH 5 was attributed to the formation of this precipitate and the difficulty in initial solution buffering at this pH.

Manganese adsorption (Fig. 5-14) onto peat exhibited similar removal trends to that of iron under the same initial solution pH conditions. Adsorption capacities were significantly lower than that of iron under all pH conditions, however, and precipitate formation was not detected. Fluctuations in solution pH ranged from increases of 1.7, 1.8 units and a decrease of 0.8 at initial pH conditions of 2, 3 and 5 respectively.

Although zinc (Fig. 5-13) and cadmium (Fig. 5-17) mono-layer saturation adsorption capacities (Table 5-3) differed significantly, their sorption responses with increasing peat sample weight were relatively similar. Gosset *et al.* (1986) also noted a similar pH dependence between cadmium and zinc. These were found to increase with increasing equilibrium concentrations under all pH conditions, with exponential increases in adsorption capacities with increasing equilibrium concentrations for initial solution pH conditions of 2. The adsorption behaviour of these metal ions was continuously modified, and the adsorption capacity increased as the pH increased from the initial solution pH toward the natural pH of the peat material.

Nickel (Fig. 5-15) and copper (Fig. 5-16) were the only two metal ions to follow mono-layer adsorption behaviour at initial solution pH conditions of 2. This can be explained by the fact that

copper and nickel are reportedly more strongly bound by peat than other metals at low pH conditions (Gosset *et al.*, 1986). Gosset *et al.* concluded that above pH 3, the single-component metal ion adsorption behaviour of copper was very similar to that of nickel, but these differed at solution pH conditions of less than 3.

5.2.3.2 *EFFECT OF MULTI-ION COMPOSITION ON ADSORPTION EQUILIBRIUM*

In order to determine the relative effect of competitive inhibition on metal ion sorption from the AMD solution, the results obtained from the kinetic experiment were compared to those of the equilibrium experiment. The equilibrium concentrations of the AMD mixture measured at the end of the kinetic experiment conducted at 20°C and pH of 5, as well as the corresponding Langmuir parameters (q_s and b) obtained from the equilibrium experiments were applied to the single-component and multi-component Langmuir equations (Eq. 5-1 and Eq. 5-2) to predict the respective metal ion adsorption capacities at a pH of 5. The results were then compared to the actual adsorption capacity observed during the kinetic experiment under these experimental conditions. The results are summarized in Table 5-4.

The observed multi-component metal ion adsorption capacities were found to be much lower than the predicted single-component metal ion adsorption capacities. Values ranged from 0.12 of predicted for iron to 0.63 of predicted for Nickel. From these results, it was evident that the expected removal of individual metals in peat columns via sorption mechanisms will be greatly affected by the presence of other metal ion species in the AMD mixture, as well as solution pH and temperature.

Competitive adsorption was not found to be adequately represented by the multi-ion Langmuir model. This could be attributed to the fact that this model, as many other competitive models, assumes that the competing metal species have equal access to all adsorption sites (AWWA, 1990). In using peat as an adsorbent a variety of surface functional groups provide sites for adsorption. The ratio of observed to predicted multi-metal ion adsorptions would indicate that the metal ions are not governed by the same adsorption mechanisms. This premise is consistent with results obtained from the sequential extraction analyses as will be shown in Section 6.2.2.4. Thus, competitive metal adsorption using peat requires a complex analysis which accounts for the various types of surface adsorption mechanisms which can not be represented by simplified models such as the Langmuir model for competitive adsorption.

**Table 5-4: Effect of Multi-Component Solution Composition
on Metal Ion Adsorption at 20°C and pH 5**

	AMD Mixture C_{eq} (mmol/L)	Predicted Single-Ion (mmol/g)	Predicted Multi-Ion (mmol/g)	Observed Multi-Ion (mmol/g)	Observed/ Predicted Single-Ion	Observed/ Predicted Multi-Ion
Fe	2.79	0.51	0.21	0.06	0.12	0.29
Al	0.69	0.11	0.070	0.04	0.36	0.58
Zn	1.64	0.14	0.015	0.04	0.27	2.51
Mn	0.49	0.05	0.004	0.007	0.14	1.63
Ni	0.34	0.02	0.001	0.01	0.63	7.96
Cu	0.20	0.06	0.005	0.02	0.31	3.60
Cd	0.06	0.003	0.0003	0.002	0.58	7.46

CHAPTER 6

AMD MITIGATION – COLUMN EXPERIMENTS

6.1 EXPERIMENTAL PROCEDURES

6.1.1 COLUMN LEACHING/SORPTION TEST

Two 14.6 cm inside diameter, 61 cm long stainless steel columns were employed to establish the potential for leaching of metals from or sorption of metals onto the actual columns throughout the remaining experiments. To evaluate the potential for adsorption of metals, 3 L of the synthetic AMD solution presented in Table 3-2 was poured into the first column. To assess the metal leaching potential, 3 L of distilled water was poured into the second column. The pH was adjusted to 2.5 with concentrated HCl in each of the columns and an initial sample was collected.

The columns were covered to minimize evaporation and the solution was permitted to sit, undisturbed for a 3-week period. At that time, a final sample was collected from each column and the pH was measured. Samples were preserved by adding 3 drops of concentrated HCl at the time of sample collection. The initial and final metal concentrations were determined using ICP analysis provided by the Department of Chemistry at Carleton University.

6.1.2 IMPACT OF HYDRAULIC AND CONSTITUENT LOADING

The impact of hydraulic and constituent loading on heavy metal adsorption and sulphate reduction was tested at temperatures of 0°C and 20°C through column experiments. These were followed by

a sequential extraction procedure to determine the associative preference of each metal for the peat material under different loading conditions and temperature regimes.

6.1.2.1 *EXPERIMENTAL SET-UP*

Prior to packing, milled New Brunswick peat was hand-sieved with a 1/4" sieve and allowed to air-dry over a 24-hour period. Eight 14.6 cm inside diameter stainless steel columns were packed with peat in 10 cm lifts to a depth of 46 cm as illustrated in Figure 6-1. The columns were packed with an average dry density of approximately 194 kg/m^3 (Appendix D), corresponding to a saturated hydraulic conductivity of $1.02 \times 10^{-4} \text{ m/s}$ and a water holding capacity of 364%. Prior to testing, the columns were insulated with 2 layers of standard pipe insulation.

Figure 6-1: Peat Filter Test Column for Loading Experiment

To determine the impact of constituent loading, two of the columns were supplied synthetic AMD with the composition presented in Table 3-2, while the other two columns were fed a 25% $\forall/\forall$ dilution of the synthetic AMD mixture to distilled water. The impact of hydraulic loading was quantified by supplying a flow of 1.37 L/d (82 L/m²/d) to two of the columns, while the other two columns each received a flow of 0.685 L/d (41 L/m²/d). These loadings represented unsaturated flow conditions with empty bed hydraulic retention times of 5.65 and 11.3 days for the high-flow and low-flow cases, respectively. Four experimental conditions were tested by combining these constituent and hydraulic loadings: (1) high-flow, high AMD strength (HQ-H[]); (2) high-flow, low AMD strength (HQ-L[]); (3) low-flow, high AMD strength (LQ-H[]); and (4) low-flow, low AMD strength (LQ-L[]).

6.1.2.2 OPERATIONAL CONDITIONS

The columns were fed continuously for a period of 75 days at an ambient laboratory temperature of 20°C and an ambient temperature of 0°C in a cold room located in the Geocryology Laboratory at Carleton University. The temperature of the synthetic AMD feed solution was approximately 10°C. After the 75-day sorption period, all columns were fed a 5% $\forall/\forall$ mixture of the high strength synthetic AMD at twice their respective flow rates for 10 days. The purpose was to quantify the level of desorption that might be expected in the field during the spring, resulting in high flow and low constituent concentration drainage.

6.1.2.3 SAMPLING PROCEDURE AND ANALYSIS

Three times per week, a 20 mL effluent sample from each column was collected to measure dissolved oxygen, metal concentrations and pH. Dissolved oxygen concentrations were measured using a WWRbrand Dissolved Oxygen Meter (model 34105-004). The pH of the samples was

determined using a WWRbrand pH/mV/Temperature Meter (model 34105-002). The samples were then filtered with a 45 µm Millipore filter paper and acidified with concentrated HCl. Analysis of the samples for metal concentrations was conducted using ICP analysis in the Department of Chemistry at Carleton University. 15 mL samples were collected using a 20 mL syringe once a week for sulphate concentration analysis which was performed by Seprotech Laboratories.

6.1.2.4 SEQUENTIAL EXTRACTION PROCEDURE AND ANALYSIS

Once the adsorption/desorption experiments were completed, the peat from each column was dissected into five 9.2 cm layers from the top (1) to bottom (5) of the column. The layered sections of peat were then oven-dried at 104°C for a period of 24 to 48 hours. After drying, each layer was mixed thoroughly to obtain a more uniform material. The adsorption of metals onto the various fractions of the contaminated peat was assessed through a sequential extraction procedure outlined by Wasay *et al.* (1998) which has been employed and tested for use with peat materials. Heavy metals were assessed with respect to the following operationally-defined fractions of the peat material: (1) Water extractable fraction; (2) Exchangeable fraction; (3) Fe-Mn oxide bound fraction; (4) Organic matter bound fraction; and (5) Residual metal fraction. Some modifications to the referenced procedure were necessary to adapt the experiment to the peat material utilized in this study. These are described in detail in the subsequent sections.

6.1.2.4.1 WATER EXTRACTABLE FRACTION

Metals that are weakly bound to the peat were released through the water extractable fraction. For each of the dried peat layers, 5 random grab samples weighing approximately 10 g were collected. These samples were then mixed to form a representative composite sample. 100 mL of distilled water was added to 5 g of the blended samples and the mixtures were placed on a reciprocating

shaker for a period of 2 hours at 150 rpm under room temperature conditions. The solutions were then filtered with a 45 µm Millipore filter paper. The supernatant was collected and acidified with concentrated HCl. Metal concentrations were determined using ICP analysis in the Department of Chemistry at Carleton University. The solids retained, along with their filters, were returned to the sample bottle for exchangeable fraction analysis.

6.1.2.4.2 *EXCHANGEABLE FRACTION*

This procedure released metal ions that were physically bound by electrostatic attraction to negatively charged sites via cation exchange. The filters and solids retained from the water extractable procedure were mixed with 100 mL of 0.1 M calcium chloride (CaCl_2) and returned to the reciprocating shaker for 2 hours at 150 rpm under room temperature conditions. The solutions were then filtered with a 45 µm Millipore filter paper, the supernatant collected and acidified. Metal concentrations were determined using ICP analysis. The filtrates and solids retained were returned for Fe-Mn oxide-bound fraction analysis.

6.1.2.4.3 *OXIDE-BOUND FRACTION*

Heavy metals attached to the amorphous or poorly crystallized Fe-Mn oxides or equivalent materials were released during this procedure. 100 mL of 0.05 M hydroxylamine hydrochloride (NH_2OHHCl) was added to the filters and solids retained from the exchangeable fraction procedure. The samples were shaken at 150 rpm for 12 hours under room temperature conditions. The solutions were then filtered with a 45 µm Millipore filter paper. The supernatant was collected and acidified. Metal concentrations were determined using ICP analysis. The solids retained and filters were returned to the sample bottle for organic matter- and silicate mineral-bound fraction analysis.

6.1.2.4.4 *ORGANIC MATTER-BOUND FRACTION*

Metals bound to the organic matter were released via oxidation by adding 10 mL of distilled water and 10 mL of 30% peroxide (H_2O_2) to the filters and solids retained from the Fe-Mn oxide bound fraction procedure. The samples were digested for 30 to 60 minutes at room temperature. The solution was then digested at 85°C until the volume was reduced to a few milliliters. Peroxide (30%) was slowly added until the solution turned into ash and 10-15 mL remained. Next, 50 mL of 1 M ammonium acetate (NH_4Ac) was added and shaken overnight at 150 rpm under room temperature conditions. The purpose of this reagent was to unbind any solid metals adhering to the sample bottle and place them in the liquid phase. The solutions were then filtered with a 45 μm Millipore filter paper. The supernatant was collected, acidified and metal concentrations were determined using ICP analysis. The solids retained and filters were returned to the sample bottle for residual metal fraction analysis.

6.1.2.4.5 *RESIDUAL METAL FRACTION*

The heavy metals that were not released in the previous fractions were unbound by digesting the filters and solids retained from the organic matter-bound fraction analysis with strong acids at elevated temperatures. The procedure outlined by ASTM Standard D3974-81 no. 14 using hydrochloric acid and nitric acid was followed. The goal of this procedure was to break existing metal-silicate mineral bonds. The solutions were then filtered with a 45 μm Millipore filter paper. The supernatant was collected, acidified and metal concentrations were determined using ICP analysis.

6.1.3 SUBSTRATE/AMENDMENT MIXTURE FOR PEAT BIOFILTER

The characterization of the peat biofilter in terms of aerobic biodegradation that results in oxygen consumption and heat generation was performed using two sets of column studies. Column experiments were conducted at an ambient air temperature of 20°C and at 0°C. These conditions were aimed at emulating summer and winter conditions.

6.1.3.1 EXPERIMENTAL SET-UP

The impacts of aerobic biodegradation and the addition of organic substrates in the peat biofilter on the mitigation of AMD were examined through a series of column experiments. Two sets of six columns (61 cm X 14.6 cm ID) were constructed using stainless steel and instrumented as shown in Figure 6-2. Prior to packing, milled New Brunswick peat was hand-sieved with a ¼" sieve and allowed to air-dry over a 24 hour period. The columns were packed, in 10 cm lifts, with 46 cm of peat at an average dry density of 190 kg/m³ (Appendix D).

To each of the columns, a 10 cm layer of substrate/amendment mixture was added on top of the peat as a source of carbon and alkalinity for the peat biofilter. Three substrate/amendment mixtures were tested. The first was composed of 100% dewatered sludge with no neutralizing agent addition. The second, contained dewatered sludge and limestone in a 70/30 volumetric ratio, respectively. And the third, was composed of dewatered sludge and lime in a 90/10 volumetric ratio, respectively. The primary and secondary sludge mixture was obtained from the MacLaren Pulp and Paper Plant in Masson, Quebec. The experiment was conducted in duplicate. Therefore, for each set of 6 columns, two columns were supplied with each of the three substrate/amendment mixtures.

Figure 6-2: Peat Biofilter Test Column for Substrate/Amendment Mixture Experiment

The columns were instrumented with thermocouples and time domain reflectometry (TDR) probes located 5.0 cm, 18.5 cm, 32 cm and 45.5 cm from the base of the column as illustrated in Figure 6-2. The thermocouples were constructed of copper/constantan (Type T) wire. The tips were coated in Rust-O-Leum High Performance Epoxy (9192-white) supplied by Acklands-Grainger to protect the wire in the highly acidic AMD environment. The thermocouples were then connected to a data acquisition system which recorded the temperature profile within each column every 2 hours. The TDR probes consisted of two 15 cm long stainless steel rods, 3.2 mm (1/8") in diameter with a center-to center distance of 1.97 cm (0.776"). The apparent lengths of the TDR probes were measured from reflectometer oscilloscope readings that were then printed on an x-y plotter. The dielectric constants were calculated from Equations 4-9 and 4-10 and the volumetric water content determined from the calibration relationship provided by Equation 4-13.

6.1.3.2 *OPERATIONAL CONDITIONS*

One set of 6 columns was placed in a cold temperature room at 0°C located in the Geocryology Laboratory at Carleton University, while the other six columns were set up outside the cold room under ambient laboratory conditions (18-21°C). The columns were pulsed daily with 1.37 L of the synthetic AMD mixture presented in Table 3-2 corresponding to an empty bed hydraulic residence time of 5.65 days and a surface loading rate of 82 L/m²/d. The temperature of the synthetic AMD feed solution was approximately 10°C for the cold room columns and 20°C for the ambient temperature columns.

The degree of water saturation and the thickness of the unsaturated zone will affect the availability of oxygen for the biodegradation process, which limits the depth of the aerobic zone within the column. To determine the effect of these parameters on the performance of the biofilter, the water saturation was varied by changing the water pressure at the base of the column. This was accomplished by fixing the location of the water level. Three water levels were examined in this study: (1) 20 cm below the base of the column, (2) 15 cm above the base of the column, and (3) 30 cm above the base of the column. Each case was tested for a period of 28 days corresponding to 5 empty bed hydraulic retention times to ensure that pseudo steady state conditions had been reached within the columns.

6.1.3.3 *SAMPLING PROCEDURE AND ANALYSIS*

Initially, the columns were wetted on a daily basis with 1 L of distilled water for a period of one week. Once the columns were saturated, the experimental procedure involving dosing with AMD and sampling was initiated. Three times per week, a 20 mL effluent sample was collected from each column to measure dissolved oxygen and metal concentrations, and pH. Dissolved oxygen

concentrations were measured using a WWRbrand Dissolved Oxygen Meter (Model 4000). A WWRbrand pH/mV/Temperature Meter (Model 3000) was utilized to determine the pH of the solution.

The samples were then filtered with a 45 μm Millipore filter paper and acidified with 3 drops of concentrated HCl for sample preservation. Metal concentrations were determined via ICP analysis by Seprtech Laboratories in Ottawa. To determine effluent sulphate concentrations from each column, 15 mL samples were collected once a week and sent for analysis at Seprtech Laboratories in Ottawa. The acidity of the effluent was also measured for each column on a weekly basis using a procedure specific for AMD as outlined in Standard Methods for Water and Wastewater Quality (1994).

The vertical temperature profile within the peat was recorded every 2 hours by the data acquisition system. The volumetric water content vertical profile was assessed once a week. The TDR probes were connected to the reflectometer which plotted the apparent length of the probe. This procedure was conducted at 4 different depths for each of the columns.

6.2 RESULTS AND DISCUSSION

The effect of constituent and hydraulic loading on heavy metal adsorption using peat, as well as the impact of various amendment mixtures on column performance, were evaluated using the series of column experiments described in the previous section.

6.2.1 COLUMN LEACHING/SORPTION TESTS

Separate leaching and sorption tests were undertaken to determine if any significant amount of metals could be leached from or sorbed onto the stainless steel columns utilized throughout this study. The results are summarized in Table 6-1, with further details provided in Appendix D. Table 6-1 presents the differences between the initial and final concentrations of AMD and distilled water (DW). Positive values indicated potential sorption of metals onto the stainless steel column, while negative values indicated the potential leaching of metals from the stainless steel column.

Table 6-1: Column Leaching/Sorption Test

	Solution Concentration	Metal Concentration (mg/L)						
		Al (ppm)	Cd (ppm)	Cu (ppm)	Fe (ppm)	Mn (ppm)	Ni (ppm)	Zn (ppm)
AMD	Initial	87.8	6.30	19.7	203	25.6	20.7	104.6
	Final	87.4	6.50	19.6	207	26.0	21.1	106.4
	Initial-Final	0.38	-0.20	0.08	-3.61	-0.41	-0.38	-1.79
DW	Initial	< d.l.	< d.l.	0.03	< d.l.	0.03	< d.l.	< d.l.
	Final	0.17	< d.l.	0.06	1.72	0.08	< d.l.	< d.l.
	Initial-Final	-0.17	< d.l.	-0.03	-1.72	-0.05	< d.l.	< d.l.

< d.l. → Below detection limit

After a three-week contact period, a potential for sorption from the synthetic AMD solution onto the stainless steel columns was noted for Al (0.4%) and Cu (0.4%). Slight increases in synthetic AMD solution concentrations of Cd (3.2%), Fe (1.8%), Mn (1.6%), Ni (1.8%) and Zn (1.7%) were observed suggesting some level of leaching from the column. The leaching of Fe and Mn in the AMD column was supported by the small increases in Fe and Mn concentrations detected in the column containing distilled water. Al and Cu were also found to be leached from the AMD column in the distilled water experiment. However, in both experiments, the degree of leaching from or sorption onto the columns was found to be negligible, and was not expected to significantly impact the results of the column and overall system studies given the experimental mass loadings.

6.2.2 IMPACT OF HYDRAULIC AND CONSTITUENT LOADING

The impact of climatic, seasonal and operational variability on metal sorption onto peat was assessed using column experiments. Peat columns at 0°C and 20°C were subjected to different hydraulic and constituent loadings and the effluent concentrations were monitored. Upon completion of the experiment, the columns were dissected and a sequential extraction procedure was performed to identify and quantify the bonding behaviour of the metals under the various experimental conditions. The complete data arising from the loading and sequential extraction experiments can be found in Appendices E and F.

6.2.2.1 INFLUENT CONCENTRATIONS

Influent concentrations were monitored throughout the 85-day sorption/desorption experiment. Mean influent concentrations and standard deviations for the sorption and desorption phases of the experiment are tabulated in Table 6-2. The raw data are presented in Appendix D. During the 75-day sorption experiment, influent variabilities of 3% to 15% and 3% to 22% were noted for constituent loadings at 20°C and 0°C, respectively. The observed variabilities were considerably higher during the 10-day desorption portion of the experiment, due to the low influent concentrations and the fewer number of observations.

6.2.2.2 CONCEPTUAL MODEL

Each of the eight columns in the loading study represented a metal mitigation column with a step influent concentration at the start of the experiment, followed by a decrease in concentration and increase in flow step at the end of the experiment. The HQ-H[] columns were to simulate moderate

Table 6-2: Average Influent Concentrations for the Column Experiments at 0°C and 20°C

		High Constituent Loading				Low Constituent Loading			
		Sorption		Desorption		Sorption		Desorption	
		Mean	St. Dev.	Mean	St. Dev.	Mean	St. Dev.	Mean	St. Dev.
		(mg/L)	[obs.] (mg/L)	(mg/L)	[obs.] (mg/L)	(mg/L)	[obs.] (mg/L)	(mg/L)	[obs.] (mg/L)
0°C	pH	3.0	0.14[22]	3.9	0.16[2]	3.4	0.28[22]	4.0	0.23[2]
	DO	6.9	0.60[22]	6.9	0.14[2]	6.8	0.63[22]	6.2	0.56[2]
	SO ₄	3150	104[12]	183	12.7[2]	776	46.3[11]	194	9.19[2]
	Fe	197	9.02[22]	10.9	0.95[2]	51.3	2.72[22]	10.4	0.77[2]
	Al	90.9	4.63[22]	4.8	0.0[2]	21.4	2.46[22]	4.8	0.0[2]
	Zn	107	8.05[22]	5.2	0.41[2]	20.8	3.57[22]	5.0	0.45[2]
	Mn	24.9	1.21[22]	1.2	0.13[2]	6.1	0.81[22]	1.4	0.21[2]
	Ni	17.7	3.40[22]	1.3	0.04[2]	4.4	0.80[22]	1.3	0.63[2]
	Cu	18.3	1.89[22]	1.1	0.03[2]	4.9	0.38[22]	1.1	0.03[2]
	Cd	6.0	0.35[22]	0.5	0.06[2]	1.5	0.33[22]	0.5	0.13[2]
20°C	PH	3.1	0.29[21]	3.7	0.04[3]	3.6	0.32[21]	3.8	0.14[3]
	DO	5.9	0.36[21]	6.3	0.13[3]	5.9	0.57[21]	6.0	0.71[3]
	SO ₄	2999	36.9[9]	170	--[1]	803	54.3[9]	145	--[1]
	Fe	191	10.6[17]	9.9	1.28[3]	51.0	3.6[17]	9.9	0.43[3]
	Al	87.6	2.38[17]	4.4	0.36[3]	23.4	1.54[17]	4.3	0.27[3]
	Zn	93.1	13.7[17]	5.0	0.60[3]	21.5	2.70[17]	5.2	0.30[3]
	Mn	25.2	1.11[17]	1.4	0.21[3]	6.7	0.47[17]	1.4	0.05[3]
	Ni	20.3	1.24[17]	1.1	0.22[3]	4.9	0.52[17]	1.1	0.28[3]
	Cu	18.4	0.59[17]	1.0	0.07[3]	5.0	0.32[17]	0.6	0.46[3]
	Cd	6.10	0.53[17]	0.3	0.08[3]	1.7	0.13[17]	0.4	0.20[3]

strength AMD under operational design flow. The HQ-L[], LQ-H[] and LQ-L[] columns could represent seasonal variations in AMD discharge, such as a decrease in AMD generation in the fall due to changes in temperature; a decrease in flow due to summer drought conditions and a reduction in flow, and; AMD generation due to winter temperatures and partial freezing of water. The step decrease in AMD loading and increase in flow would be representative of spring runoff conditions which could result in the desorption of metals retained in the peat column. Seasonal temperature effects were simulated by conducting the experiment with a set of four columns at 0°C and the other set of columns at 20°C.

The total mono-layer saturation adsorption capacities for single-constituent metal ions in each of the experimental columns solutions are tabulated in Table 6-3. These were computed using the mean influent concentrations (Table 6-2), the Langmuir parameters obtained from the batch equilibrium experiments at a pH of 3 (Table 5-3) and the total mass of peat in the column (Appendix D). The total metal loadings for each of the experimental columns were also determined from the mean influent concentrations and duration of the sorption stage of the experiment, prior to the desorption stage where the 5% dilute AMD mixture was employed.

Table 6-3: Predicted Total Single-Ion Saturated Adsorption Capacities and Total Metal Loading for Each Experimental Column

		LQ-H[]		HQ-H[]		LQ-L[]		HQ-L[]	
		Total Cap. (mmol)	Total Load (mmol)	Total Cap. (mmol)	Total Load (mmol)	Total Cap. (mmol)	Total Load (mmol)	Total Cap. (mmol)	Total Load (mmol)
0°C	Fe	655	184	572	369	409	49.7	374	99.5
	Al	587	176	512	351	518	43.2	473	86.4
	Zn	179	85.3	156	171	51.7	17.4	47.2	34.8
	Mn	94.7	23.6	82.6	47.2	25.6	6.0	23.4	11.9
	Ni	31.3	15.8	27.3	33.1	8.0	4.2	7.3	8.3
	Cu	282	15.0	246	30.1	102	4.2	93.3	8.4
	Cd	6.3	2.8	5.5	5.6	1.6	0.7	1.4	1.4
20°C	Fe	594	178	571	356	352	49.3	359	98.7
	Al	535	169	514	338	452	46.7	461	93.5
	Zn	150	74.2	145	148	45.9	18.0	46.8	36.0
	Mn	87.2	23.9	83.9	47.8	24.5	6.6	25.0	13.2
	Ni	32.5	18.0	31.3	36.1	7.7	4.5	7.9	9.0
	Cu	258	15.3	248	30.7	89.6	4.2	91.4	8.3
	Cd	5.8	2.8	5.6	5.6	1.5	0.8	1.6	1.7

Without the addition of substrates or neutralizing amendments, adsorption and precipitation would be the primary removal mechanisms anticipated in the peat columns. From Table 6-3, it can be seen that adsorption capacities were generally significantly lower in the low constituent loading columns due to the lower influent concentrations. Due to the lower adsorption capacity associated

with the lower constituent loadings, metal breakthrough was expected to occur at lower total metal mass loadings in the low-concentration columns than in the high-concentration columns. Earlier breakthroughs are also expected in columns under higher hydraulic loading conditions because the saturation adsorption capacity of the peat is expected to be reached more rapidly.

By comparing the adsorption capacities and the corresponding total metal loadings for each of the columns (Table 6-3), it is evident that, under ideal single-component adsorption conditions, metal breakthrough, without considering dispersion or retardation effects, should only be observed in the HQ-H[] columns for cadmium, nickel and zinc, and in the HQ-L[] for cadmium and nickel. The impact of the desorption step should also be more evident in these columns due to the greater total metal mass loading to adsorption capacity ratios under these conditions. Results presented in Table 5-2 indicate that under lower temperature conditions, metal breakthroughs should generally be expected to occur at lower total mass loadings than in the columns operated at 20°C under similar loading conditions with the exception of copper and aluminum, where adsorption capacities were found to increase with decreasing temperature. Exothermic adsorption mechanisms would be suggested by an increase in adsorption capacity with decreasing temperature.

The addition of a multi-component metal ion solution (AMD) will create competitive sorption conditions. This will lead to metal ion breakthroughs occurring at lower total mass loadings than predicted as these become preferentially displaced by other metal ions in solution with higher affinities or binding capacities for the limited sorption sites on the peat. It is difficult to predict the impact of competitive sorption under different hydraulic and constituent loading conditions. However, Table 5-4 illustrates the preferential selectivity of metal displacement under high constituent loading conditions at 20°C and a pH of 5. For instance, manganese is more likely to be displaced from its sorption site than nickel.

Other removal mechanisms may also contribute to metal removal in the peat columns. Under appropriate concentrations, pH and/or redox conditions, some metal ions may precipitate out of solution in the form of metal hydroxides, metal carbonates, or metal sulphides, and be physically retained within the peat matrix. There is also a potential for biological processes to develop in time and contribute to metal removal due to the organic nature of the peat material and the presence of moderate sulphate concentrations. This will lead to metal sulphide precipitation reactions under sulphate-reducing conditions, resulting in an increase in effluent solution pH and alkalinity. In such a case, effluent metal concentrations may first be observed to increase due to partial breakthrough, followed by an apparent decrease in effluent concentrations as sulphate-reducing conditions develop. The establishment of a sulphate-reducing environment will largely depend on the dissolved oxygen concentrations in the peat column. The final dissolved oxygen concentration in the column will be a function of the influent dissolved oxygen concentration, the rate of oxygen consumption in the columns and the rate of aeration in the column. Sulphate-reducing conditions would be expected to develop more quickly under warmer temperature conditions due to the lower solubility of oxygen and higher biological kinetics leading to oxygen consumption at higher temperatures.

The results obtained from this experiment will, in theory, demonstrate the effect of flow, metal concentration and temperature on the response of a simple peat filter to a moderate strength AMD influent.

6.2.2.3 EFFLUENT CONCENTRATIONS

Metal concentrations were monitored throughout the 85-day sorption/desorption column experiment. Metal concentrations in the effluent from each of the experimental columns are presented in Appendix E and cumulative metal retentions are presented in Figures 6-3 to 6-6. Breakthrough was defined as the point where the cumulative effluent metal mass reached 10% of the cumulative metal mass added to the system at that time. This breakthrough definition was employed to identify breakthrough trends readily without the impact of effluent concentration variability. Table 6-4 summarizes the cumulative metal loading and volumetric loading required for individual metals to reach breakthrough under the various experimental column conditions. In columns where breakthrough was not observed, a percent retention was computed from the ratio of cumulative mass retained to total cumulative mass added, and averaged from days 12 to 75. These values are included in the discussion which follows.

Table 6-4: The Cumulative Constituent Loading and Volumetric Loading Required for Individual Metals to Reach Breakthrough

Metal	LQ-H[]		LQ-L[]		HQ-H[]		HQ-L[]	
	Metal Loading (mmol)	Volume Loading (L)	Metal Loading (mmol)	Volume Loading (L)	Metal Loading (mmol)	Volume Loading (L)	Metal Loading (mmol)	Volume Loading (L)
0°C	Fe	NBT	NBT	NBT	NBT	NBT	NBT	NBT
	Al	63.7	18.1	3.3	3.4	85.6	24.7	28.2
	Zn	28.7	16.1	5.6	18.9	61.1	35.6	10.3
	Mn	5.1	11.0	0.8	8.2	7.9	17.1	2.0
	Ni	7.4	27.4	4.1	64.6	7.5	30.8	5.7
	Cu	NBT	NBT	NBT	NBT	21.1	75.2	NBT
	Cd	0.4	5.5	0.08	8.1	0.9	17.8	0.1
20°C	Fe	NBT	NBT	5.9***	6.8	NBT	NBT	9.5***
	Al	109	34.3	NBT	NBT	NBT	NBT	NBT
	Zn	42.6	33.9	3.6	14.4	NBT	NBT	9.9***
	Mn	8.9	20.2	1.7	13.9	NBT	NBT	NBT
	Ni	11.0	32.6	NBT	NBT	NBT	NBT	1.9***
	Cu	NBT	NBT	NBT	NBT	NBT	NBT	NBT
	Cd	0.4	7.2	0.01	0.3	0.4	5.6	0.01

NBT = No Breakthrough

*** = Tended to reach 10% breakthrough and then retention increased

Figure 6-3: Cumulative Metal Retention Under Low-Flow High-Concentration Loading Conditions at (a) 0°C and (b) 20°C

Figure 6-4: Cumulative Metal Retention Under Low-Flow Low-Concentration Loading Conditions at (a) 0°C and (b) 20°C

Figure 6-5: Cumulative Metal Retention Under High-Flow High-Concentration Loading Conditions at (a) 0°C and (b) 20°C

Figure 6-6: Cumulative Metal Retention Under High-Flow Low-Concentration Loading Conditions at (a) 0°C and (b) 20°C

The removal of iron was generally found to be high in the peat columns where breakthrough was not observed with 98.8% (SD 0.42), 96.9% (SD 0.70), 99.0% (SD 0.42) and 96.7% (SD 0.83) under the LQ-H[], LQ-L[], HQ-H[] and HQ-L[] loading conditions tested at 0°C, respectively (Fig. 6-3a to 6-6a). Similar removals were observed in LQ-H[] (97.8%, SD 0.37) and HQ-H[] (98.9%, SD 0.40) columns at 20°C (Fig. 6-3b and 6-5b). Breakthrough did occur in the LQ-L[] and HQ-L[] columns at 20°C (Fig. 6-4b and 6-6b). In both cases, the removal efficiencies after 10% cumulative breakthrough were found to improve with time. After the addition of diluted AMD, desorption was noted in the HQ-L[] and LQ-H[] columns at 0°C and 20°C, respectively. This was indicated by the slight increase in cumulative effluent iron concentration during the desorption phase (Appendix E).

Overall, copper removal was also found to be high under each of the loading conditions (Fig. 6-3 to 6-6). Copper retentions of 99.4% (SD 0.16), 97.0% (SD 0.42), and 97.0% (SD 0.27) were respectively measured under LQ-H[], LQ-L[] and HQ-L[] loading conditions at 0°C (Fig. 6-3a, 6-4a and 6-6a), while removals of 99.3% (SD 0.04), 98.4% (SD 0.16), 99.7% (SD 0.02) and 98.8% (SD 0.06) were noted in the LQ-H[], LQ-L[], HQ-H[] and HQ-L[] columns at 20°C (Fig. 6-3b to 6-6b). Breakthrough was only observed in the HQ-H[] column at 0°C, after 55 days (75.2L) and a cumulative copper loading of 21.1 mmol (Table 6-4), which represented 8.6% of the single-component copper ion adsorption capacity of the column (Table 6-3). At 0°C, desorption was observed in the LQ-H[], HQ-H[] and HQ-L[] columns (Fig. 6-3a, 6-4a, 6-5a and Appendix E), while no desorption was apparent at 20°C.

Aluminum breakthrough was observed in all columns at 0°C (Fig. 6-3a to 6-6a), and only in the LQ-H[] column at 20°C (Fig. 6-3b). In the cold temperature columns, the order of breakthrough was noted as LQ-L[] (3.3 mmol) < HQ-L[] (28.2 mmol) < LQ-H[] (63.7 mmol) < HQ-H[] (85.6

mmol), which represented 0.6%, 6.0%, 10.8% and 16.7% of the total single-component aluminum adsorption capacity for each of the respective columns (Table 6-3). The cumulative loading in the LQ-H[] column at 20°C (Table 6-4) when breakthrough occurred, was found to be 20.5% of the adsorption capacity for the column (Table 6-3). The removal of aluminum was generally found to be high in the peat columns where breakthrough was not evident with 96.6% (SD 0.11), 99.1% (SD 0.32) and 97.9% (SD 0.24) under the LQ-L[], HQ-H[] and HQ-L[] loading conditions tested at 20°C, respectively (Fig. 6-4b to 6-6b). In all columns where breakthrough was reported, a notable increase in aluminum effluent concentration was observed during the desorption portion of the experiment (Appendix E).

Under low-temperature conditions, the breakthrough of cadmium (Fig. Fig 6-3a to 6-6a) occurred as follows: LQ-L[] (0.08 mmol) < HQ-L[] (0.1 mmol) < LQ-H[] (0.5 mmol) < HQ-H[] (0.9 mmol). These represented 5.0%, 7.1%, 6.3% and 16.4% of the total single-component cadmium adsorption capacity for each of the respective columns (Table 6-3). In the columns at 20°C (Fig 6-3b to 6-6b), the order of breakthrough was noted as LQ-L[] (0.01 mmol) $\approx$ HQ-L[] (0.01 mmol) < LQ-H[] (0.4 mmol) $\approx$ HQ-H[] (0.4 mmol); 0.6%, 0.6%, 6.9% and 7.1% of their respective column adsorption capacities. The diluted AMD was found to cause a desorption of cadmium in each of the columns as indicated by the small effluent concentration increase during this particular phase of the experiment. A slight recovery in removal efficiency was noted in the LQ-L[] column at 20°C.

Manganese breakthrough was observed in all of the columns at 0°C, as well as in the LQ-H[] and LQ-L[] columns at 20°C. In the room temperature columns, breakthrough occurred at manganese loadings of 1.7 mmol and 8.9 mmol for the LQ-L[] and LQ-H[] columns, respectively, or 6.9% and 10.2% of the single-constituent manganese adsorption capacity (Fig 6-4b and 6-3b). For the

cold temperature columns (Fig. 6-3a to 6-6a), LQ-L[] (0.8 mmol) < HQ-L[] (2.0 mmol) < LQ-H[] (5.1 mmol) < HQ-H[] (7.9 mmol), was the reported order of breakthrough representing 3.1%, 8.5%, 5.4% and 9.6% of the peat column single-constituent adsorption capacity for manganese (Table 6-2). In the peat columns where breakthrough did not occur, the removal of manganese was relatively high with 98.2% (SD 0.23) and 96.7% (SD 0.48) reported under the HQ-H[] and HQ-L[] loading conditions 20°C (Fig. 6-5b to 6-6b). In all columns which experienced breakthrough, desorption was noted following the addition of dilute AMD (Appendix E).

Zinc breakthrough was not observed under HQ-H[] loading conditions at 20°C. Instead, a removal efficiency of 93.7% (SD 2.48) was reported (Fig 6-5b). In the columns at 0°C, the order of breakthrough (Table 6-4) was noted as LQ-L[] (5.6 mmol) < HQ-L[] (10.3 mmol) < LQ-H[] (28.7 mmol) < HQ-H[] (61.1 mmol), representing 10.8%, 21.8%, 16.0% and 39.1% of the total single-component zinc adsorption capacity for each of the respective columns (Table 6-3). In the columns at 20°C, cumulative zinc loadings of 3.6 mmol (7.8%), 9.9 mmol (21.1%) and 42.6 mmol (28.3%) were determined for the LQ-L[], HQ-L[] and LQ-H[] columns, respectively (Fig. 6-3b, 6-4b and 6-6b). Recoveries in zinc removal efficiencies were observed in the LQ-L[], HQ-L[] and HQ-H[] columns throughout the course of the experiment at 20°C. Zinc desorption was not significant following the addition of dilute AMD in columns under HQ-H[], LQ-L[] and HQ-L[] loading conditions at 20°C and LQ-L[] loading conditions at 0°C.

Similar responses were reported for nickel at 0°C (Fig. 6-3a to 6-6a), where breakthrough occurred as follows (Table 6-4): LQ-L[] (4.1 mmol) < HQ-L[] (5.7 mmol) < LQ-H[] (7.4 mmol) < HQ-H[] (7.5 mmol), corresponding to 51.3%, 78.1%, 23.6% and 27.5% of the respective column single-component nickel adsorption capacities. At 20°C, HQ-L[] (1.9 mmol) < LQ-H[] (11.0 mmol) breakthroughs (Fig. 6-3b and 6-6b) were reported representing 24.1% and 33.8% of

predicted column adsorption capacities. In the columns where breakthrough was not observed, nickel retention was relatively high with 95.9% (SD 1.08) and 98.6% (SD 0.28) noted under the LQ-L[] and HQ-H[] loading conditions (Fig. 6-4b and 6-5b). In columns which experienced breakthrough, desorption was noted following the addition of dilute AMD.

Effluent pH values, dissolved oxygen (DO) concentrations and sulphate removal rates are plotted in Figures 6-7 to 6-9, respectively. Effluent pH values were relatively constant at 0°C (Fig. 6-7a), with mean values of 3.0 (SD 0.15), 3.3 (SD 0.20), 2.9 (SD 0.16) and 3.3 (SD 0.20) measured from day 12-75, in the LQ-H[], LQ-L[], HQ-H[] and HQ-L[] columns, respectively. The variability observed in the effluent pH was consistent with the variability in the influent pH (Table 6-2) during the sorption phase of the experiment.

At 20°C, low-flow effluent pH values were also constant (Fig. 6-7b). From days 12 to 75, the LQ-H[] and LQ-L[] columns recorded mean values of 3.2 (SD 0.13) and 3.5 (SD 0.27), respectively, and the variability was similar to that observed for the influent pH (Table 6-2). Under high-flow conditions, however, the effluent pH began to increase significantly after 19 days (26.0L) for the HQ-H[] column; and after 43 days (58.9L) for the low influent concentration column. The pH rises coincided with an increase in the hydrogen sulphide odour emanating from each column, indicating the presence of sulphate reducing bacteria in these columns.

Figure 6-7: Effluent pH Levels Under Different Loading Conditions at (a) 0°C and (b) 20°C

Figure 6-8: Effluent Dissolved Oxygen Concentration Under Different Loading Conditions at (a) 0°C and (b) 20°C

Figure 6-9: Sulphate Utilization Rates Under Different Loading Conditions at (a) 0°C and (b) 20°C

Effluent dissolved oxygen concentrations were markedly lower in the columns at 20°C (Fig. 6.8b), than those at 0°C (Fig. 6-8a). At 0°C, mean effluent DO concentrations of 5.8 mg/L (SD 0.51), 5.8 mg/L (SD 0.49), 6.5 mg/L (SD 0.45) and 6.6 mg/L (SD 0.51) were observed in the LQ-H[], LQ-L[], HQ-H[] and HQ-L[], respectively. Under warm temperature conditions, however, all effluent concentrations were less than 2 mg/L: 1.3 mg/L (SD 0.24), 1.4 mg/L (SD 0.27), 1.6 mg/L (SD 0.36) and 1.0 mg/L (SD 0.23) exiting the LQ-H[], LQ-L[], HQ-H[] and HQ-L[], respectively. The variability associated with the effluent DO concentrations was consistent with the variability noted in the influent data (Table 6-2).

Sulphate removal rates were computed from the hydraulic loading (Q , m³/d), the volume of peat in the column (V , m³), the mean influent concentration (S_o , mg/L) and the measured effluent concentrations (S_e , mg/L) as shown in Equation 6-1.

$$\frac{Q(S_o - S_e)}{V} \quad (6-1)$$

The highest sulphate removal rates were observed in the high-flow columns at 20°C (Fig. 6-9b). In the columns operating at 0°C (Fig. 6-9a), on the other hand, sulphate removal rates appeared to be high initially, but were found to gradually decrease with time.

The combination of increasing pH, low effluent DO and high sulphate utilization rates indicated the presence of anaerobic biological activity in the high-flow columns at 20°C, where the peat could act as the carbon source necessary for sulphate reduction to occur. As discussed previously, the establishment of sulphate reducing conditions is largely a function of DO availability, which depends upon the rate of re-aeration in the peat column and the solubility of DO. The rate of re-aeration was lower in the high-flow columns due to the higher hydraulic loading, which would result in more saturated conditions within the column and, hence, less opportunity for gas-phase

diffusion. DO solubility was expected to decrease with increasing temperature. The absence of microbiological activity under the colder temperature conditions, was probably due to the reduced kinetics of biological reactions at colder temperatures. Under sulphate reducing conditions, the primary metal removal mechanism would become metal sulphide precipitation, which would decrease effluent metal concentrations. The increased pH resulting from sulphate reduction could also promote the precipitation of metal carbonates.

6.2.2.4 *SEQUENTIAL EXTRACTION*

The aim of the sequential extraction procedure was to determine the dominant fractions to which metals were bound with depth within the peat filter. Sequential extraction was performed following the desorption phase of the column experiment. It is thus expected that some of the more weakly bound metals may have been displaced vertically or removed completely as a result of desorption. The metal mass retention per fraction bound for each of the five individual layers are tabulated in Appendix F. The notation employed with reference to the presentation of sequential extraction results was as follows: water extractable (W), exchangeable fraction (Ex), oxide-bound fraction (Ox), organic matter-bound fraction (OM) and residual metal fraction (RM).

6.2.2.4.1 *LOW-FLOW HIGH-CONCENTRATION COLUMN*

The distribution of metals within the LQ-H[] columns at 0°C and 20°C is illustrated in Figures 6-10a and 6-11a, respectively. Under these experimental conditions, aluminum, zinc, manganese, nickel and cadmium were found to be well distributed throughout the depth of the column. The breakthrough of these metals was noted in the LQ-H[] columns at both temperatures (Fig. 6-3) which would be consistent with an even distribution throughout the peat depth.

Figure 6-10: Metal Mass Retention Under Low-Flow High-Concentration Conditions at 0°C: (a) per layer and (b) per fraction bound.

Figure 6-11: Metal Mass Retention Under Low-Flow High-Concentration Conditions at 20°C: (a) per layer and (b) per fraction bound.

Breakthrough of iron and copper was not observed in either of the LQ-H[] columns (Fig. 6-3). As can be seen from Figures 6-10a and 6-11a, iron (63.3%, 70.7%) was largely retained within the first layer of the peat. Copper, on the other hand, was mostly retained within the first three layers at 20°C. This might suggest the likelihood of copper breakthrough prior to iron breakthrough.

The higher retention of iron and copper observed in the columns can be explained in terms of their binding fraction. Figures 6-10b and 6-11b demonstrate the percentage of total metal mass retained per fraction bound at 0°C and 20°C. The distribution of metal mass between the various bound fractions was consistent when comparing the distributions for the columns at 0°C and 20°C with the exception of aluminum. In each column, zinc (65.4%, 64.4%), manganese (49.6%, 57.0%), nickel (57.6%, 54.5%) and cadmium (72.3%, 71.8%) were associated with the exchangeable fraction, while copper (69.1%, 70.1%) and iron (46.2%, 56.4%) were bound to the organic matter fraction. It is plausible that the weakly bound zinc, manganese, nickel and cadmium were preferentially displaced by iron and copper ions. 10.6% and 7.6% of the iron, and 19.4% and 14.3% of the copper retained were bound to the exchangeable fraction at 0°C and 20°C, respectively. It should be noted that iron was present in higher concentrations than the other metals.

Aluminum was generally bound to the organic matter and residual fractions under these loading conditions. The association with the residual fraction was probably due to aluminum hydroxide precipitation within the column and/or the initial aluminum composition of the peat (Table 4-1). The relatively constant distribution of aluminum ions in association with this fraction throughout the depth of the column would suggest the latter (Appendix F). Aluminum precipitation would have resulted in a comparatively higher retention in the upper layers of the column due to the filtering affect of the peat material, as well as increased aluminum efficiencies, neither of which were observed.

The flushing of the columns with dilute AMD generally had a lower impact on copper and iron (Fig 6-3) which were largely bound to the organic matter fraction (Fig. 6-10b and 6-11b). A slight decrease in cumulative metal retention was noted for zinc, manganese, nickel and cadmium which were primarily associated with the exchangeable fraction. The desorption of aluminum was also observed which might have resulted the resolubilization of the ion under the different solution conditions and in the flushing of this metal from the peat matrix.

6.2.2.4.2 *LOW-FLOW LOW-CONCENTRATION COLUMN*

The responses of the columns to the LQ-L[] loading at 0°C and 20°C were similar to the response observed in the LQ-H[]. The distribution of metals with depth is presented in Figures 6-12a and 6-13a for the 0°C and 20°C cases, respectively. The breakthrough of zinc, manganese, nickel and cadmium occurred in the same relative order as in the LQ-H[] case (Fig. 6-4), however, nickel breakthrough was not reached at 20°C (Fig. 6-4b). Early breakthrough was reported for aluminum at 0°C, as well as for iron at 20°C (Table 6-4). Aluminum, zinc, manganese and cadmium were found to be evenly distributed through the depth of the LQ-L[] columns at both temperatures, consistent with the observed breakthrough of these metals under these experimental conditions.

The breakthrough of copper was not observed in either of the LQ-L[] columns (Fig. 6-4). As shown in Figures 6-12a and 6-13a, copper (80.3%, 76.6%) was strongly associated with the first layer of the peat column. Under these loading conditions, iron was also mostly retained in the first layer (51.3%, 51.5%) at both temperatures, however, there was a slightly higher distribution of iron in the lower layers as well (~10%), when compared to the LQ-H[] column (Fig. 6-10a and 6-11a). This distribution of iron in the column was probably due to the nature of the peat material, rather than the removal of iron. Concentrations determined for the lower layers of the peat column

Figure 6-12: Metal Mass Retention Under Low-Flow Low-Concentration Conditions at 0°C:
(a) per layer and (b) per fraction bound.

Figure 6-13: Metal Mass Retention Under Low-Flow Low-Concentration Conditions at 20°C:
(a) per layer and (b) per fraction bound.

(Appendix F), were within a similar range as those reported for the elemental composition of the peat (Table 4-1, Appendix B).

No significant changes in metal retention trends were noted compared to the LQ-H[] columns. The higher retention of iron and copper observed in the columns was probably due to their association with the organic matter fraction. Figures 6-12b and 6-13b demonstrate the percentage of metal mass retained per fraction bound at 0°C and 20°C for the LQ-L[] loading condition. The LQ-L[] columns were in reasonable agreement for all metals under both temperature regimes. At 0°C and 20°C, respectively, zinc (65.7%, 62.2%), manganese (63.4%, 61.5%), nickel (55.1%, 49.6%) and cadmium (73.6%, 71.3%) were largely bound to the exchangeable fraction, while copper (68.5%, 73.8%) and iron (50.9%, 61.0%) were primarily associated with the organic matter fraction. Once again, it is plausible that a weaker association of zinc, manganese, nickel and cadmium for the exchangeable fraction might have resulted in the preferential displacement of these metals by iron, copper or aluminum.

Nickel breakthrough was not observed at 20°C (Fig 6-4b). This was probably due, in part, to the adsorption capacity of the peat for this metal under competitive sorption. The early breakthrough of aluminum at 0°C and iron at 20°C was attributed to the initial flushing of the elevated background concentrations of both of these metals (Table 4-1) at the start of the experiment as noted from the initial decrease and subsequent recovery of their respective cumulative metal mass retention curves (Fig. 6-4). The gradual recovery of the cumulative metal retention curves noted for iron, manganese and zinc at 20°C (Fig. 6-4b) might suggest the establishment of sulphate reducing conditions and the start of biologically mediated metal sulphide precipitation. However, this trend could not be confirmed with the effluent pH (Fig. 6-7), DO (Fig. 6-8) and sulphate (Fig. 6-9) data.

The flushing of the columns with the dilute AMD did not significantly affect copper, iron, aluminum or zinc metal retention at either temperature regime (Fig 6-4). The desorption of manganese, nickel and cadmium was noted at 0°C, but the affect was dampened at 20°C, which could have been due to the impact of metal removal mechanisms other than sorption, such as metal sulphide precipitation (Fig. 6-12b and 6-13b).

6.2.2.4.3 HIGH-FLOW HIGH-CONCENTRATION COLUMN

The HQ-H[] column responses to the loadings at 0°C and 20°C are illustrated in Figures 6-14 and 6-15. Under these experimental conditions the breakthrough of all metals with the exception of iron was observed at 0°C (Fig 6-5a), while cadmium breakthrough alone occurred at 20°C (Fig 6-5b). At 0°C, the metals were generally found to be well distributed throughout the depth of the HQ-H[] column (Fig. 6-14a), which is consistent with the observed metal breakthroughs. Iron, exhibited slightly higher percentage retention within the top layers with a noted value of 36.7%. The response of the HQ-H[] column at 20°C was much different. Iron, aluminum and copper were largely retained within the top layers, while zinc, manganese, nickel and cadmium removal were associated with the mid-layers, with very little retention occurring in the final layer (Fig. 6-15a). This response is consistent with the comparatively low breakthrough noted in the column.

Figures 6-14b and 6-15b demonstrate the percentage of metal mass retained per fraction bound at 0°C and 20°C. At 0°C, metal retention was in reasonable agreement with that described in the two previous cases, where iron (53.9%) and copper (66.3%) were primarily associated with the organic matter fraction; zinc (59.5%), manganese (38.0%), nickel (49.2%) and cadmium (67.9%) were mostly retained by the exchangeable fraction; and aluminum demonstrated a strong association with the residual (42.5%) fraction as well as the organic matter fraction (41.6%). The higher

High Flow - High Concentration
T = 0°C

High Flow - High Concentration
T = 0°C

Figure 6-14: Metal Mass Retention Under High-Flow High-Concentration Conditions at 0°C:
(a) per layer and (b) per fraction bound.

Figure 6-15: Metal Mass Retention Under High-Flow High-Concentration Conditions at 20°C: (a) per layer and (b) per fraction bound.

retention of metals at 20°C. on the other hand, was found to coincide with a deviation from the preferred binding fractions reported in the two previous cases and at 0°C under the HQ-H[] conditions. In the second to fourth layers of the peat column (Appendix F), iron and copper, as well as zinc, manganese and nickel were mostly bound to the organic matter and residual fractions. This could be indicative of anaerobic biological activity and removal due to metal sulphide precipitation. The development of anaerobic conditions and the establishment of a sulphate reducing environment is supported by the low effluent DO concentrations (Fig. 6-7b) and high sulphate (Fig. 6-8b) utilization rates, as well as the significant increase in pH under the HQ-H[] loading conditions at 20°C.

The flushing of the columns with the dilute AMD had a much lower impact at 20°C than at 0°C (Fig. 6-5). At 0°C, a slight decrease in cumulative metal retention was noted for aluminum, zinc, manganese, nickel and cadmium which were primarily associated with the exchangeable fraction. At 20°C, the effect of desorption was minimal for most of the metals which was attributed to the increased association of these metals with the organic matter and residual fractions. Cadmium was the only metal which remained primarily bound to the exchangeable fraction, and coincidentally, exhibited breakthrough at 20°C. A slight decrease in metal retention was noted for cadmium, after the addition of the dilute AMD at 20°C

6.2.2.4.4 HIGH-FLOW LOW-CONCENTRATION COLUMN

The responses observed for the HQ-L[] columns at 0°C and 20°C were generally similar to the responses noted in the HQ-H[] columns. At 0°C, the breakthrough of zinc, manganese, nickel and cadmium occurred in a similar order as in the LQ-H[] and LQ-L[] cases (Fig. 6-3a, 6-4a and 6-6a). In the 20°C HQ-L[] column, the breakthrough trend resembled that obtained in the HQ-H[]

column with a few notable differences. The distribution of metals with depth is presented in Figures 6-16a and 6-17a for the 0°C and 20°C cases, respectively. As in the previous cases, aluminum, zinc, manganese, nickel and cadmium were generally found to be well distributed throughout the depth of the HQ-L[] column at 0°C which is consistent with the observed breakthrough of these metals under these experimental conditions (Fig. 6-16a).

The breakthrough of copper was not observed in either of the HQ-L[] columns (Fig. 6-6). From Figures 6-16a and 6-17a, it can be seen that copper was largely retained within the first two layers (49.5%, 45.9%) of the peat columns at 0°C (Fig. 6-16a) and the first layer (84.1%) of the peat column at 20°C. Under these loading conditions, iron was also mainly associated with the first layer (59.0%, 41.6%) at both temperatures. However, there appeared to be a significant distribution of iron in the lower layers of the column as well (~10%). As discussed previously, this distribution of iron in the column was probably due to the nature of the peat material, rather than the removal of iron. From Appendix F, it can be seen that the concentrations determined in the lower layers of the peat column, are once again within a similar range as those reported for the elemental composition of the peat (Table 4-1, Appendix B).

Figure 6-16b demonstrates the percentage of metal mass retained per fraction bound at 0°C for the HQ-L[] loading condition. No significant changes in metal retention trends were noted compared to the HQ-H[] columns. At 0°C, the higher retention of iron and copper observed in the columns was attributed to the association of these metals with the organic matter fraction. Zinc (63.4%), manganese (56.6%), nickel (54.5%) and cadmium (71.2%) were largely bound to the exchangeable fraction, while copper (69.3%) and iron (52.1%) were primarily associated with the organic matter fraction.

Figure 6-16: Metal Mass Retention Under High-Flow Low-Concentration Conditions at 0°C:
(a) per layer and (b) per fraction bound.

Figure 6-17: Metal Mass Retention Under High-Flow Low-Concentration Conditions at 20°C: (a) per layer and (b) per fraction bound.

The metal mass retained per fraction bound at 20°C is presented in Figure 6-17b. Zinc breakthrough was not observed at 20°C (Fig 6-4b). The early breakthrough of iron (Table 6-4) was attributed to the initial flushing of the elevated background concentrations (Table 4-1) at the start of the experiment as noted from the initial dip and subsequent recovery of the cumulative metal mass retention curve (Fig. 6-6b) for this metal. As discussed for previous cases, the relatively constant distribution of iron in association with the residual fraction throughout the depth of the column would support this assumption (Appendix F).

The gradual recovery of the cumulative metal retention curves noted for iron, manganese, zinc and nickel at 20°C (Fig. 6-6b) might suggest the establishment of sulphate reducing conditions and the start of biologically mediated metal sulphide precipitation. The establishment of a sulphate reducing environment was confirmed with the rise in effluent pH (Fig. 6-7), low effluent DO concentrations (Fig. 6-8) and elevated sulphate (Fig. 6-9) consumption rates. This was further supported by the fact that iron, aluminum, zinc, manganese, nickel and copper were highly retained within the organic matter and residual fractions, overall and in the individual layers, especially in the mid-layers of the column.

As with the HQ-H[] case, the flushing of the columns with the dilute AMD had a much lower effect on metal retention at 20°C than at 0°C (Fig. 6-6). The desorption of aluminum, zinc, manganese, nickel and cadmium was noted at 0°C. At 20°C, on the other hand, the effect of desorption was negligible for most of the metals, with the exception of cadmium for which complete metal breakthrough was observed. A slight decrease in metal retention was noted for cadmium, after the addition of the dilute AMD at 20°C. This could be due to the impact of metal removal mechanisms other than sorption, such as metal sulphide precipitation (Fig. 6-16b and 6-17b).

6.2.2.5 METAL MASS RETENTION

Upon completion of the sorption/desorption column experiment, a metal mass balance was performed on the peat material to identify any potential differences between the metal removal results obtained as a function of influent and effluent concentrations, and the metal retention obtained from the sequential extraction procedure. In theory, the difference between the metal mass entering and leaving the column should equal the metal mass retained by the peat as per:

$$\frac{\sum C_{in} \forall - \sum C_{out} \forall}{M_T} = \frac{\sum M_I S_I}{M_T} \quad (6-2)$$

where C_{in} and C_{out} were the influent and effluent metal concentrations (mg/m^3) measured through sampling, $\forall$ (m^3) was the volume of AMD added to the column, M_I was the oven-dried mass of the peat layer (kg), M_T is the total oven-dried mass of peat in the column (kg), and S_I was the metal mass removed in each fraction per unit mass of peat (mg/kg). The fixed metal composition of the peat (Table 4-1) was subtracted from the total metal mass retained during sequential extraction to account for metal removal as a function of metal loading in each of the columns. The results are summarized in Table 6-5, with metal mass values supplied and retained provided in Appendix D.

The results obtained from influent/effluent concentrations and metal mass retention demonstrated similar trends. Discrepancies between the column and sequential extraction results were attributed to one of two factors. The first pertains to the precision of the data reported as a result of the filtering process and the analytical equipment, which would have a greater impact on the results at lower metal concentrations (*i.e.* cadmium). Secondly, the sequential extraction procedure employed, although previously applied to peat materials (Wassay *et al.*, 1998), may not have accounted for all of the metals retained within a fraction. The use of sequential extraction for testing metal retention within peat would certainly merit further investigation.

Table 6-5: Metal Mass Balances for Experimental Columns (mmol of metal/kg of peat)

	Metal	LQ H[]			LQ L[]			HQ-H[]			HQ L[]		
		M _{I-o}	M _r	% Disc	M _{I-o}	M _r	% Disc	M _{I-o}	M _r	% Disc	M _{I-o}	M _r	% Disc
0°C	Al	10.5	11.2	107	22.9	32.9	144	21.4	15.5	72.4	44.0	58.6	133
	Cd	0.1	0.2	200	0.2	0.4	200	0.4	0.2	50.0	0.1	0.4	400
	Cu	8.9	5.0	56.2	2.5	1.3	52.0	10.6	5.7	53.8	5.6	3.1	55.4
	Fe	111	75.6	68.0	30.2	15.1	50.0	255	169	66.3	67.8	43.3	63.9
	Mn	1.0	0.7	70.0	2.1	2.1	100	2.7	0.5	18.5	0.8	1.3	163
	Ni	2.7	1.8	66.7	2.4	2.3	95.8	2.0	1.2	60.0	3.7	2.6	70.3
	Zn	5.1	3.9	76.5	9.3	10.1	109	26.2	23.7	90.5	7.0	6.2	88.6
20°C	Al	43.7	46.5	106	32.0	36.8	115	233	172	73.8	64.1	58.8	91.7
	Cd	0.06	0.4	667	0.2	0.4	200	1.3	2.5	192	0.2	0.6	300
	Cu	9.9	6.7	67.7	2.9	1.2	41.4	20.7	10.2	49.3	5.7	1.7	29.8
	Fe	99.4	53.1	53.4	32.2	13.6	42.2	244	141	57.8	64.7	34.4	53.2
	Mn	1.4	1.1	78.6	3.7	2.8	75.7	32.3	42.9	133	9.0	7.6	84.4
	Ni	3.7	3.0	81.1	3.0	2.4	80.0	24.2	13.6	56.2	5.5	3.5	63.6
	Zn	19.0	16.9	88.9	10.2	11.6	114	96.9	69.4	71.6	21.9	17.2	78.5

$$M_{I-o} = \Sigma M_r - \Sigma M_d$$

$$M_r = \Sigma M_r$$

$$\% \text{ Disc} = (\Sigma M_r) / (\Sigma M_r - \Sigma M_d) * 100$$

Under ideal single-constituent loading conditions, the total metal retention expected in the columns would have been HQ-H[] > LQ-H[] > HQ-L[] > LQ-L[] as was observed from the metal breakthrough curves. According to Table 6-5, only the metals that were consistently bound to the organic matter fraction, iron and copper, were found to follow this trend under both temperature regimes. A specific trend could not be determined for metals typically associated with the exchangeable fraction at 0°C. This was attributed to competitive adsorption and the preferential displacement of these more weakly bound metal ions, by other metal ions present in the AMD solution. At 20°C, however, aluminum, zinc, manganese, nickel and cadmium exhibited a higher total mass retention in the HQ-H[] than in the HQ-L[] columns. Sulphate reducing conditions were established under these loading conditions. As well, aluminum, zinc, manganese and nickel demonstrated a greater association with the organic matter and residual fractions (Fig. 6-15b and 6-17b), indicating that metal sorption onto microbiological surfaces, biological uptake and metal sulphide precipitation may have developed as possible removal mechanisms.

6.2.2.6 *IMPACT OF CONSTITUENT LOADING*

Under the lower temperature regime, the predicted and apparent sorption capacities of the peat column (Table 6-3) were greater at higher constituent loading. Generally, breakthrough based on metal mass retention occurred in the following order: LQ-L[] < HQ-L[] < LQ-H[] < HQ-H[]. Sulphate (Fig. 6-9a) utilization rates, effluent DO concentrations (Fig. 6-8a) and pH levels (Fig. 6-7a) were generally similar at the high and low constituent loadings. The breakthrough of all metals, with the exception of iron (removal = 96.7%, SD 0.83), was observed in the HQ-H[] column (Fig. 6-5a) in the following order (Table 6-4): manganese (17.1L), cadmium (17.8L), aluminum (24.7L), nickel (30.8L), zinc (35.6L) and copper (75.2L). In the LQ-H[] column (Fig. 6-3a). Breakthrough was reported for five metals: cadmium (5.5L), manganese (11.0L), zinc (16.1L), aluminum (18.1L) and nickel (27.4L). Comparatively, under low constituent loading conditions, the breakthrough of cadmium (13.6L), manganese (19.4L), zinc (33.1L), aluminum (35.6L) and nickel (78.0L), with 97.0% (SD 0.27) and 96.7% (SD 0.83) removals of copper and iron, respectively, were noted in the HQ-L[] column (Fig. 6-6a). In the LQ-L[] column (Fig. 6-4a), similar breakthroughs and removal efficiencies were reported: aluminum (3.4L), cadmium (8.1L), manganese (8.2L), zinc (18.9L) and nickel (64.6L), as well as 97.0% (SD 0.42) copper and 96.9% (SD 0.70) iron removals. Metal mass retention of aluminum, nickel, manganese, zinc and cadmium was generally found to be well distributed throughout the peat column at all mass loadings (Fig. 6-10, 6-12, 6-14 and 6-16). In general, the order of metal breakthrough at 0°C was Cd < Mn < Zn < Al < Ni < Cu < Fe.

At 20°C, the responses of the columns to constituent loading differed from that observed in the columns at 0°C. The impact of higher constituent loadings on the sorption capacity of the peat was dampened by the development of other metal removal mechanisms within the column.

Breakthrough (Table 6-4) was noted for cadmium (7.2L), manganese (20.2L), nickel (32.6L), zinc (33.9L) and aluminum (34.3L) in the LQ-H[] (Fig. 6-3b). However, with the exception of cadmium (5.6L), no breakthrough occurred in the HQ-H[] column. Similarly under lower constituent loading conditions, breakthrough was observed for cadmium (0.3L), iron (6.8L), manganese (13.9L) and zinc (14.4L) in the LQ-L[] column (Fig. 6-4b). Breakthrough was also observed in the HQ-L[] column (Fig. 6-6b): cadmium (0.3L), iron (10.8L), nickel (25.9L) and manganese (31.7L). However, in both cases of low constituent loading conditions at 20°C, the breakthrough curves exhibited a recovery in the cumulative metal retention curve with volumetric loading, which would suggest the establishment of other metal removal mechanisms with time.

6.2.2.7 *IMPACT OF HYDRAULIC LOADING*

At 0°C, the impact of high hydraulic loading was secondary to the effect of constituent loading. The volumetric breakthroughs of metals for each loading condition were presented in Section 6.2.2.6. In both the high and low constituent loading cases, metal breakthrough was consistently found to occur more rapidly at the lower volumetric loading (Table 6-4), which did not conform with the expected breakthrough behaviour. Generally, high-flow breakthrough would have been expected prior to low-flow breakthrough under similar constituent loading conditions and predicted sorption capacities (Table 6-3). This behaviour could be attributed to a poorer distribution of flow and the consequent establishment of preferential flow paths at lower volumetric loading conditions, which would lead to a smaller effective volume for metal mitigation within the low flow columns.

Under ambient temperature conditions, the highest removal efficiencies were also noted in the high-flow columns. This was attributed to the establishment of sulphate-reducing conditions in these columns where the peat would act as a carbon source and the moderate sulphate concentrations

would act as an electron acceptor for sulphate reducers in the column. The development of sulphate-reducing conditions in the high-flow columns was primarily due to the DO concentrations in the peat columns, where the final dissolved oxygen concentration in the column was a function of the influent DO concentrations, the rate of oxygen consumption in the columns and the rate of aeration in the column. Under this temperature regime, the solubility of oxygen in water was lower than at lower temperatures. Higher biological kinetics at higher temperatures led to a greater consumption of DO by microorganisms when compared to the low temperature columns under identical loading conditions. The opportunity for aeration in the column was lower than in the low-flow columns because of the higher volumetric loading and saturation of the peat.

The establishment of sulphate reducing conditions in the high-flow columns at 20°C was indicated by the relatively low effluent DO concentrations (Fig. 6-8b), the higher sulphate removal rates (Fig. 6-9b) and the significant increase in pH (Fig. 6-7b) noted for both of the high-flow columns. These conditions led to a decrease in effluent metal concentrations via metal sulphide precipitation reactions, resulting in the increased effluent solution pH as a result of alkalinity generation, as a product of biologically mediated sulphate reduction. The apparent recovery of the cumulative metal retention curves noted for iron, zinc and cadmium in the LQ-L[] column at 20°C (Fig. 6-4b) might also suggest the presence of a sulphate reducing environment. However, this was not supported by the increase in solution pH or increase in sulphate utilization rate as observed in the high-flow columns. It is believed that the low-flow systems would also eventually develop substantial bacterial growth, which will lead to higher sulphate and metal removal efficiencies.

The impact of the sulphate-reducing environment was noted more rapidly in the high-concentration column than in the low-concentration column. The HQ-H[] (Fig. 6-5b) system was established more rapidly (19 days) than the HQ-L[] (Fig 6-6b) system (43 d) due to the higher sulphate

concentrations in this column. It is surmised that once a substantial growth of the bacterial system will have taken place, higher sulphate utilization rates and greater metal retention would be apparent. It should be noted, however, that the establishment of sulphate-reducing conditions in the peat column might not be desirable. In the absence of an external readily biodegradable substrate, the microorganisms would employ the peat as a carbon source, which would lead to the deterioration of the physical matrix of the peat biofilter.

6.2.2.8 *IMPACT OF TEMPERATURE CONDITIONS*

In general, metal adsorption and retention were higher at warmer temperatures. However, the kinetic study indicated differing degrees of partitioning at different temperatures, which varied from metal to metal. These differences were attributed, in part, to higher reaction kinetics, increased solubility of some compounds at higher temperatures, as well as to competitive adsorption. Under the lower temperature regime, the strength of metal association with the exchangeable fraction of the peat (zinc, manganese, nickel and cadmium) appeared to decrease and, hence, metals typically retained within this fraction were retained to a lesser degree. Aluminum was also retained to a lesser degree at lower temperatures which was not consistent with the trend observed in the kinetic study, where adsorption was found to decrease with increasing temperature. This was attributed to the greater impact of other metal removal mechanisms at higher temperatures.

Iron and copper, on the other hand, demonstrated higher or comparable mass retentions at lower temperatures, under most loading conditions. These metals were primarily associated with the organic matter fraction, where adsorption reactions could generally be characterized as exothermic processes, thereby causing a weakening of sorptive forces between the peat binding sites and the

iron and copper ions (Viraraghavan and Dronamraju, 1995). However, as discussed in Section 5.2.2.1, the multi-ion composition of the AMD mixture would make it difficult to distinguish between competitive adsorption and the exothermic process response.

The higher temperature conditions also allowed for the development of sulphate-reducing conditions in the high-flow columns. This resulted in a noticeable pH increase (Fig. 6-7b) and the precipitation of dissolved metals ions as metal sulphides, as indicated by the increased retention of metals in the residual fraction under the HQ-H[] and HQ-L[] conditions (Fig. 6-15b and 6-17b). The establishment of sulphate-reducing bacteria consortiums is less likely to occur at lower temperatures because these are typically mesophilic organisms.

6.2.2.9 *IMPACT OF DESORPTION*

The flushing of the columns with dilute AMD generally had a low impact on copper and iron, which were largely associated with the organic matter fraction. Under LQ-H[] and LQ-L[] loading conditions at 0°C, decreases in cumulative metal retentions were noted for aluminum, zinc, manganese, nickel and cadmium which were primarily associated with the exchangeable fraction. This effect was generally less evident at 20°C. In the HQ-H[] and HQ-L[] columns, a decrease in the cumulative metal retention of aluminum, zinc, manganese, nickel and cadmium was also observed at 0°C during the desorption phase. At 20°C, desorption was negligible for all of the metals, with the exception of cadmium, which was attributed to the increased association of these metals with the organic matter and residual fractions. Cadmium did not show a strong affinity for the organic matter fraction, and thus, breakthrough and desorption were noted at 20°C.

6.2.3 SUBSTRATE/AMENDMENT MIXTURE FOR PEAT BIOFILTER

The impacts of temperature, water table and the addition of substrate/amendment mixtures on metal sorption onto peat were assessed in column experiments. Three substrate/amendment mixtures including sludge, sludge/limestone and sludge/lime mixtures were added at the top of duplicate peat columns at 0°C and 20°C, for a total of 12 columns. Constant hydraulic and constituent loadings were maintained throughout the experiment. The columns were subjected to different water table levels every 28 days. The effluent constituent concentrations from each column were monitored over the 84 days of testing. The complete effluent data arising from the substrate column experiments can be found in Appendix G, and the column volumetric water content and temperature profiles resulting from fluctuations in water level in Appendix H.

6.2.3.1 CONCEPTUAL MODEL

Each of the twelve columns in the substrate/amendment mixture study represented a metal mitigation vertical flow peat biofilter with a similar step influent concentration at the start of the experiment. The purpose of adding an organic substrate, such as pulp and paper sludge, was to provide a readily available carbon source for aerobic bacteria to prevent them from biodegrading the peat which could lead to a collapse of the physical biofilter matrix. The bacteria would also consume the dissolved oxygen present in the AMD solution, a necessary step for the establishment of sulphate reducing conditions in a latter stage of the combined passive treatment system. Finally, since the biodegradation reactions via aerobic bacteria are generally exothermic, a higher temperature profile would be expected to develop in zones of higher aerobic biological activity. If well established, these could prevent the peat biofilter system from freezing during the winter season in temperate climatic regions.

The columns supplied with pulp and paper sludge were intended to simulate the response of the peat biofilter system to the addition of an organic substrate under the operational design flow of 82 L/m²/d with the constituent concentrations listed in Table 3-2. The addition of alkalinity using limestone or lime was meant to raise the pH and lower the solution acidity in the top portion of the peat biofilter to provide conditions which could allow the growth of aerobic bacteria. Limestone would represent a gradual, long-term source of alkalinity, while lime could provide an immediate, short-term alkalinity source. Seasonal temperature effects were simulated by conducting the experiment with a set of three duplicate columns at 0°C and the other set of columns at 20°C.

With the addition of substrates and, in some cases, neutralizing amendments, adsorption and metal precipitation as metal hydroxides, metal carbonates and metal sulphides would be the primary removal mechanisms anticipated in the peat biofilter columns. In the sludge/lime and sludge/limestone columns, the neutralizing amendment will contribute alkalinity, which under appropriate pH conditions, would allow iron, aluminum and copper and zinc to precipitate out of solution and be physically retained within the peat matrix. During the batch studies, the adsorption of metal ions onto peat was shown to increase with increasing pH, which would also contribute to a higher metal retention in the sludge/lime and sludge/limestone columns. The total mono-layer saturation adsorption capacities for single-constituent metal ions under high-flow, high constituent loading conditions are presented in Table 6-3. As was demonstrated in the column loading experiment, the addition of a multi-component metal ion solution such as AMD resulted in competitive sorption conditions, which led to metal breakthroughs at much lower total mass loadings than predicted based on the isotherms evaluated for each of the metals. It was surmised that these became preferentially displaced by other metal ions in solution with higher affinities or binding capacities for the limited sorption sites on the peat.

Due to the organic nature of the peat material and the substrate, as well as the presence of moderate sulphate concentrations, the potential exists for metal mitigation via sulphate-reducing bacteria to become a significant. This was shown to occur in the peat column loading experiment, resulting in increases in effluent solution pH and alkalinity, as well as decreases in effluent metal, sulphate and DO concentrations as sulphate-reducing conditions developed. As was discussed previously, sulphate-reducing conditions would be expected to develop more quickly under warmer temperature conditions due to the lower solubility of oxygen and higher biological kinetics leading to oxygen consumption at higher temperatures.

The aim in changing water levels within the peat biofilter was primarily to assess the impact on metal retention. These fluctuations would be representative of seasonal field conditions, where rises in water level could occur as a result of spring runoff and lower water tables would be expected for the remainder of the year. Variations in water levels would displace aerobic and anaerobic zones previously established within the column. Increases in water level could potentially lead to changes in column temperature profiles. As such, the water level could represent a design parameter where the unsaturated zone would favour aerobic biodegradation and heat generation, while the saturated zone would lead to sulphate reduction and metal-sulphide precipitation. The design aspect would involve the situation of the water table at a level which optimizes activity in both regimes. Results obtained from this experiment will demonstrate the effect of substrate/amendment mixtures, varying water levels and temperature on the response of a peat biofilter to a moderate strength AMD influent.

6.2.3.2 COLUMN VOLUMETRIC WATER CONTENT AND TEMPERATURE PROFILES

To assess the impact of changing water levels on the volumetric water content within each of the peat biofilter columns, the dielectric constant (K_d) of the material was measured at 4.5 cm, 18 cm, 31.5 cm and 45 cm elevations from the bottom of each column with the help of a TDR probe. The dielectric constant was then used with Equation 4-13 to estimate the volumetric water content in the peat column at that depth. The mean volumetric water contents as a function of depth and effluent water level conditions at 0°C and 20°C are presented in Figures 6-18 to 6-20 for the sludge, sludge/limestone and sludge/lime amendment mixture columns, respectively. The complete data set is shown in Appendix H.

As expected, the volumetric water content generally increased with increasing depth. The volumetric water content also increased as the pressure head at the base of the column increased in each of the twelve columns. Duplicate columns indicated similar trends. No significant differences in the volumetric water content profiles could be observed, in comparing the profiles at 0°C and 20°C for each of the substrates. Likewise, the volumetric water content profiles did not appear to be affected significantly by the type of substrate/amendment mixture added to the peat columns.

Temperatures were recorded at 4.5 cm, 18 cm, 31.5 cm and 45 cm elevations from the bottom of the peat columns using thermocouples. The mean temperatures as a function of elevation and effluent water level conditions at 0°C and 20°C are presented in Figures 6-21 to 6-23 for the sludge, sludge/limestone and sludge/lime amendment mixture columns, respectively. Average daily temperature values as a function of column depth are reported in Appendix H.

Figure 6-18: Effect of Sludge Addition and Water Level on Volumetric Water Content Profiles in Peat Biofilter Columns at (a) 0°C and (b) 20°C

Figure 6-19: Effect of Sludge/Limestone Addition and Water Level on Volumetric Water Content Profiles in Peat Biofilter Columns at (a) 0°C and (b) 20°C

Figure 6-20: Effect of Sludge/Lime Addition and Water Level on Volumetric Water Content Profiles in Peat Biofilter Columns at (a) 0°C and (b) 20°C

Figure 6-21: Effect of Sludge Addition and Water Level on Temperature Profiles in Peat Biofilter Columns at (a) 0°C and (b) 20°C

Figure 6-22: Effect of Sludge/Limestone Addition and Water Level on Temperature Profiles in Peat Biofilter Columns at (a) 0°C and (b) 20°C

Figure 6-23: Effect of Sludge/Lime Addition and Water Level on Temperature Profiles in Peat Biofilter Columns at (a) 0°C and (b) 20°C

The temperature profiles between duplicate columns were fairly consistent. The mean ambient air temperatures were computed as 0.46°C (SD 1.66), 0.58°C (SD 1.85) and 1.23°C (SD 1.47) at 0°C and 21.9°C (SD 1.46), 21.7°C (SD 0.93) and 21.8°C (SD 0.76) at 20°C during the free draining, 15 cm and 30 cm water level stages of the experiment (Appendix D).

At 0°C, decreases in temperature with depth of 1.5°C and 1.8°C were noted between the top and bottom of the columns with sludge addition. Similarly, temperature differences of 1.4°C and 1.1°C, and 1.8°C and 1.5°C were observed in the sludge/limestone and sludge/lime columns, respectively. These were probably due to the influent AMD temperature which generally ranged from 8°C to 12°C.

The temperature profiles appeared to be significantly affected by the type of substrate/amendment mixture added to the column. Throughout the 84-day experiment, the mean temperature ranges between the top and bottom of the columns were found to be: 2.9°C (SD 1.29) to 1.4°C (SD 0.40) and 3.4°C (SD 1.24) to 1.6°C (SD 0.41) in the sludge columns; 2.7°C (SD 1.27) to 1.3°C (SD 0.34) and 2.1°C (SD 1.11) to 1.0°C (SD 0.46) in the sludge/limestone amendment columns; and 1.7°C (SD 1.35) to -0.1°C (SD 0.48) and 1.5°C (SD 1.46) to 0°C (SD 0.41) in the sludge/lime amendment columns. These can probably be attributed to the physical characteristics of the sludge/amendment mixtures added at the top of the columns. In general, the sludge material allowed AMD to percolate easily through this layer, such that pooling at the surface was rarely observed. Conversely, the sludge/lime mixture was relatively pasty and pooling was often observed at the surface. This may have caused the temperature of the pooled AMD to cool prior to entering the column, and hence, the lower temperatures.

The temperature profiles at 20°C did not appear to be significantly affected by the type of substrate/amendment mixture added to the column. Throughout the 84-day experiment, the mean temperature ranges between the top and bottom of the columns were found to be 20.7°C (SD 0.94) to 20.8°C (SD 0.94) and 20.5°C (SD 0.90) to 20.7°C (SD 0.93) in the sludge addition columns; 21.6°C (SD 0.91) to 21.5°C (SD 0.93) and 22.0°C (SD 0.97) to 21.7°C (SD 1.03) in the sludge/limestone addition columns; and 22.2°C (SD 0.89) to 21.8°C (SD 0.94) and 22.0°C (SD 0.88) to 21.7°C (SD 0.93) in the sludge/lime addition columns.

6.2.3.3 *INFLUENT CONCENTRATIONS*

Influent concentrations were monitored throughout the 84-day experiment. Mean influent concentrations and standard deviations are tabulated in Table 6-6. The raw influent data are presented in Appendix D. Influent variabilities of 4% to 9% were noted for constituent loadings at 0°C during the 84-day substrate/amendment experiment, while influent concentrations varied by 4% to 12% at 20°C.

Table 6-6: Average Influent Concentrations for the Substrate Experiments at 0°C and 20°C

Constituent	Observations	Experimental Temperature			
		20°C		0°C	
		Mean	St. Dev.	Mean	St. Dev.
pH	28	3.0	0.16	3.0	0.22
Acidity (mg/L CaCO ₃)	8	1120	70.0	1090	43.0
DO (mg/L)	26	5.1	0.63	6.9	0.58
SO ₄ (mg/L)	14	3190	129	3130	145
Fe (mg/L)	28	186	18.9	183	7.12
Al (mg/L)	28	81.2	5.29	80.8	6.95
Zn (mg/L)	28	93.3	6.32	90.2	6.98
Mn (mg/L)	28	25.1	1.24	24.4	1.53
Ni (mg/L)	28	19.1	1.04	19.6	0.97
Cu (mg/L)	28	18.1	0.96	17.9	0.69
Cd (mg/L)	28	6.0	0.29	5.6	0.40

6.2.3.4 EFFLUENT CONCENTRATIONS

The response of the peat biofilter columns was monitored throughout the 84-day experiment. The water level in each column was raised every 28 days. Cumulative metal retention curves for each of the experimental columns are presented in Figures 6-24 to 6-29 and effluent data can be found in Appendix G. The 10% cumulative breakthrough point was determined for each of the columns, and the impact of substrate/amendment addition on the time to reach 10% metal breakthrough from the peat column is summarized in Table 6-7.

Table 6-7: Time (Days) Required for Metal Ions to Reach 10% Cumulative Breakthrough with Various Substrate/Amendment Additions to a Peat Biofilter Column

	Column	Fe	Al	Zn	Mn	Ni	Cu	Cd
Sludge	4 (0°C)	76.3	17.2	16.1	10.3	19.8	78.2	18.3
	10 (0°C)	81.8	23.4	16.3	10.3	23.6	74.2	20.7
	3 (20°C)	35.0	26.6	17.2	14.2	18.4	NBT	54.2
	7 (20°C)	23.0	28.3	17.4	11.1	22.7	NBT	21.7
Sludge/ Limestone	5 (0°C)	NBT	15.9	12.1	3.5	15.6	NBT	13.5
	9 (0°C)	NBT	20.1	11.7	6.2	20.0	NBT	16.3
	8 (20°C)	43.4	35.7	15.6	6.7	23.1	NBT	20.2
	11 (20°C)	37.2	48.5	23.3	13.3	32.2	NBT	33.0
Sludge/ Lime	1 (0°C)	53.7	15.3	12.0	7.1	14.2	65.0	13.0
	2 (0°C)	72.5	50.5	36.1	22.1	45.6	NBT	42.6
	6 (20°C)	NBT	NBT	70.3	30.2	83.4	NBT	NBT
	12 (20°C)	NBT	NBT	82.4	56.4	NBT	NBT	NBT

The trends in preferential metal retention were similar in all columns at 0°C, with a 10% breakthrough order of Mn < Zn < Cd < Al = Ni < Cu = Fe reported for each of the columns (Fig. 6-24, 6-26, 6-28 and Table 6-7). With the exception of iron and copper, the addition of the sludge/limestone amendment did not appear to significantly improve metal retention at 0°C (Fig. 6-26), in comparison with the sludge mixture. Sludge/lime additions to the columns appeared to enhance metal retention through column 2 and column 1 to a lesser extent at 0°C (Fig. 6-28). The powdered lime addition allowed for a more readily available source of alkalinity, which would be manifested by higher metal retentions due to, it is assumed, the formation of metal precipitates as a

Figure 6-24: Effect of Sludge Addition on Cumulative Metal Retention in Peat Biofilter Columns at 0°C

Figure 6-25: Effect of Sludge Addition on Cumulative Metal Retention in Peat Biofilter Columns at 20°C

Figure 6-26: Effect of Sludge/Limestone Addition on Cumulative Metal Retention in Peat Biofilter Columns at 0°C

Figure 6-27: Effect of Sludge/Limestone Addition on Cumulative Metal Retention in Peat Biofilter Columns at 20°C

Figure 6-28: Effect of Sludge/Lime Addition on Cumulative Metal Retention in Peat Biofilter Columns at 0°C

Figure 6-29: Effect of Sludge/Lime Addition on Cumulative Metal Retention in Peat Biofilter Columns at 20°C

result of the higher local pH environment. Channeling was noted in Column 1 (difficulty in drawing samples with syringe, small sample yields compared to other columns) which may account for the discrepancies in the breakthrough curves between Columns 1 and 2.

The type of substrate/amendment mixture had a more significant impact on metal retention at 20°C than at 0°C. The average time required for 10% breakthrough in duplicate sludge columns occurred in the following order: Mn < Zn < Ni < Al < Fe < Cd < Cu (Fig. 6-25), while Mn < Zn < Cd < Ni < Fe < Al < Cu (Fig. 6-27) and Mn < Zn < Ni < Fe ≈ Cu ≈ Cd ≈ Al (Fig. 6-29) orders were noted in the sludge/limestone and sludge/lime columns. The times to reach 10% breakthrough were generally higher in the columns with neutralizing amendments, the highest being reported in the sludge/lime columns (Fig. 6-29). The availability of the alkaline material for neutralization and metal precipitation reactions as a result of the higher local pH environment were, again, responsible for the higher retention of metals in the sludge/lime columns.

Significant iron leaching was observed in the substrate/amendment columns at 20°C during the start of the study (Fig. 6-25, 6-27 and 6-29). This phenomenon was also noted in some columns during the sorption/desorption study (Fig. 6-4 and 6-6) and was attributed to the high content of iron in the peat material as determined in the characterization study (Table 4-1). The leaching of iron could have contributed to the early breakthrough of this metal in columns at 20°C when compared to the 0°C counterparts. Iron is typically bound to the organic matter fraction via adsorption processes. These adsorption reactions are generally exothermic in nature, which results in the weakening of the sorptive forces between the peat binding sites and the ion as temperature increases (Viraraghavan and Dronamraju, 1995).

The retention of cadmium was considerably higher in the substrate/amendment columns at 20°C than in the substrate/amendment columns at 0°C. Cadmium removal in the substrate/amendment study was also significantly higher than in the sorption/desorption study (Fig. 6-5). This was noted by a shift in the cadmium breakthrough curve from the sorption/desorption study (Fig. 6-5), where no substrate/amendment was added, to the substrate/amendment study (Fig. 6-24 to 6-29). The presence of the sludge and/or amendment may likely have affected solution chemistry, improved the potential for biological activity and/or contributed additional sites for adsorption.

The average pH, acidity, dissolved oxygen concentrations and cumulative sulphate removals under each of the water level conditions are presented in Tables 6-8 to 6-10 for the sludge/no amendment, sludge/limestone and sludge/lime mixtures. These data are presented as a function of time in Appendix G. With the exception of Columns 1 and 2 for the sludge/lime mixture addition, results from duplicate columns were fairly consistent. The variability observed in effluent constituent levels were consistent with influent constituent variability (Appendix D).

Table 6-8: Average Effluent pH, Acidity, Dissolved Oxygen and Sulphate Conditions as a Function of Water Level for Peat Biofilter Columns Using a Sludge/No Amendment Mixture

Column	Water Level	pH		Acidity (mg/L CaCO ₃)		Dissolved Oxygen (mg/L)		Sulphate (% Removal)	
		Mean	St.Dev.	Mean	St.Dev.	Mean	St.Dev.	Mean	St.Dev.
4 (0°C)	FD	2.9	0.23			6.3	0.66	5.8	0.27
	15 cm	3.1	0.24	1010	87.5	3.9	1.64	4.4	1.00
	30 cm	2.7	0.22	1050	27.7	3.7	0.38	4.6	0.10
10 (0°C)	FD	2.9	0.21			7.3	0.73	6.3	1.06
	15 cm	3.1	0.19	1010	59.1	4.8	1.33	5.3	0.90
	30 cm	2.7	0.26	1050	30.7	3.8	1.23	5.6	0.11
3 (20°C)	FD	3.1	0.16			2.3	1.09	10.4	1.01
	15 cm	3.0	0.17	956	47.3	2.1	0.53	8.2	1.13
	30 cm	2.7	0.21	1030	28.6	2.0	0.38	5.9	0.31
7 (20°C)	FD	3.0	0.14			1.9	1.10	7.6	1.17
	15 cm	3.2	0.32	881	142	1.6	0.49	6.1	0.70
	30 cm	2.7	0.18	1010	42.0	1.9	0.41	5.3	0.39

Table 6-9: Average Effluent pH, Acidity, Dissolved Oxygen and Sulphate Conditions as a Function of Water Level for Peat Biofilter Columns Using a Sludge/Limestone Mixture

Column	Water Level	pH		Acidity (mg/L CaCO ₃)		Dissolved Oxygen (mg/L)		Sulphate (% Removal)	
		Mean	St.Dev.	Mean	St.Dev.	Mean	St.Dev.	Mean	St.Dev.
5 (0°C)	FD	2.9	0.25			6.0	0.57	7.2	0.92
	15 cm	3.1	0.24	712.5	96.8	3.9	1.41	6.2	0.78
	30 cm	2.7	0.18	810.7	49.6	4.1	1.19	4.5	0.22
9 (0°C)	FD	2.9	0.24			7.0	0.58	7.3	1.06
	15 cm	3.0	0.22	743.8	55.4	5.9	1.13	5.3	0.90
	30 cm	2.7	0.20	760.7	38.9	4.4	0.93	3.6	0.11
8 (20°C)	FD	2.9	0.20			2.5	1.07	8.5	0.85
	15 cm	2.9	0.15	756.3	74.7	1.8	0.27	6.7	0.67
	30 cm	2.6	0.13	824.0	31.7	1.9	0.39	5.1	0.14
11 (20°C)	FD	3.1	0.16			2.3	0.88	9.1	1.04
	15 cm	3.1	0.20	675.0	64.5	2.0	0.69	7.5	0.92
	30 cm	3.1	0.21	794.8	71.4	2.2	0.38	5.5	0.46

Table 6-10: Average Effluent pH, Acidity, Dissolved Oxygen and Sulphate Conditions as a Function of Water Level for Peat Biofilter Columns Using a Sludge/Lime Mixture

		pH		Acidity (mg/L CaCO ₃)		Dissolved Oxygen (mg/L)		Sulphate (% Removal)	
		Mean	St.Dev.	Mean	St.Dev.	Mean	St.Dev.	Mean	St.Dev.
1 (0°C)	FD	2.9	0.27			7.4	0.54	5.4	0.42
	15 cm	3.1	0.19	718.8	62.5	3.9	1.42	4.6	0.57
	30 cm	2.8	0.25	810.5	43.5	4.1	1.05	3.5	0.05
2 (0°C)	FD	3.0	0.34			4.7	1.44	5.8	1.09
	15 cm	3.3	0.23	407.4	139.5	3.4	0.83	5.1	0.60
	30 cm	2.9	0.17	586.7	25.1	3.9	0.89	4.6	0.06
6 (20°C)	FD	3.1	0.25			2.59	1.30	7.2	0.77
	15 cm	3.2	0.22	156.3	12.5	1.95	0.37	6.8	0.27
	30 cm	3.0	0.21	242.1	79.8	1.98	0.33	6.9	0.53
12 (20°C)	FD	3.0	0.18			2.2	0.84	8.5	1.37
	15 cm	3.2	0.21	143.8	12.5	2.2	0.56	7.7	0.17
	30 cm	3.0	0.20	204.7	80.0	2.2	0.35	7.9	0.36

The type of substrate addition did not have a significant impact on effluent pH levels. As well, no noticeable trends were detected as a result of changes in water levels. Acidity was found to decrease with the availability of neutralizing materials, where the sludge/lime columns (Table 6-10) had the lowest acidity followed by the sludge/limestone columns (Table 6-9) and the sludge/no amendment columns (Table 6-8). Water levels did not appear to significantly affect the acidity

within the column. Finally, temperature only affected acidity levels in the sludge/lime column, in which acidity levels were significantly lower in the 20°C columns than in the 0°C columns, reflecting the lower metal concentrations.

At 20°C, dissolved oxygen concentrations were not significantly affected by the type of substrate. Effluent DO concentrations were generally in the order of 1 mg/L to 2 mg/L (Tables 6-8 to 6-10). At 0°C, the type of substrate also had little impact on effluent DO concentration but, free draining water level conditions generally resulted in significantly higher DO concentrations than at the 15 cm and 30 cm water level conditions. In fact, effluent DO concentrations were noted to decrease when the water level was changed to 15 cm (Appendix G).

Cumulative sulphate removal typically decreased with increasing water level, except in the sludge/lime columns at 20°C, where sulphate removals were maintained with changes in water level (Table 6-10). The warmer temperature regime generally yielded higher sulphate removal, especially at higher effluent water levels.

6.2.3.5 *IMPACT OF SUBSTRATE/AMENDMENT MIXTURE*

The trends observed in the HQ-H[] columns, which were operated under similar loading, but free draining conditions, were compared to the results obtained in the substrate/amendment mixture study. The order of 10% breakthrough, in terms of volumetric loading, in the HQ-H[] column at 0°C (Fig. 6-5a and Table 6-4) was generally found to be $Mn \approx Cd < Al < Ni < Zn < Cu < Fe$. Zn breakthrough occurred 8.8 days later in the HQ-H[] column (25.0 days) than in sludge/no amendment column (16.2 days), while cadmium (12.0 days vs. 19.5 days) and copper (54.9 vs. 76.2 days) breakthroughs occurred 7.5 days and 21.3 days earlier (Fig. 6-5a and 6-24). Thus, it

would appear that the addition of an organic substrate at 0°C would contribute to greater cadmium and copper retention at the expense of zinc retention. The substrate may have changed the solution chemistry and/or provided additional sorption sites for the removal of cadmium and copper. Zinc, however, remained mobile through this layer. Amendment additions in the form of alkalinity only improved metal retention when the alkalinity source was readily available, as in lime. Hence, better metal retentions were noted in the sludge/lime amendment columns at 0°C.

In comparing the results from the substrate/amendment mixture column study to those of the sorption/desorption column study (Fig. 6-5b) at 20°C, it would appear, at first glance, that substrate/amendment addition did not improve metal retention. However, it should be noted that sulphate reducing conditions had developed within the HQ-H[] column at this temperature as noted by the significant decrease in effluent sulphate concentration (Fig. 6-9) and consequent increase in pH (Fig. 6-7). These conditions did not develop in the peat biofilter columns during the substrate/amendment mixture study. In fact, the sulphate removal observed in the columns at 0°C and 20°C could probably be attributed to CaSO_4 precipitation. The high metal removals observed in the HQ-H[] column (Fig. 6-5b) were attributed, in part, to metal sulphide precipitation via sulphate reducing bacteria.

Effluent acidity concentrations and cumulative sulphate removal were also affected by the nature of the substrate amendment mixture. As would be expected, the acidity decreased with increasing availability of alkaline material, hence, the following order was observed with respect to ascending acidity concentrations: sludge/lime < sludge/limestone < sludge/no amendment at both 0°C and 20°C temperature regimes (Appendix G). Sulphate removal generally decreased as the effluent water level increased. This reduction in sulphate removal could be due to variations in flow

patterns and the resolubilization of CaSO_4 as a result of changing water chemistry. As an exception to the observed response in the other columns, sulphate reduction remained fairly consistent in the sludge/lime columns at 20°C. In fact, sulphate removal was found to increase in one of the columns (Column 6) with time.

The type of substrate/amendment mixture appeared to affect the surface temperature profile development in the sludge/limestone and sludge/lime columns at 0°C. This was attributed to the physical characteristics of the sludge/amendment mixtures added at the top of the peat biofilter columns which prevented the AMD from percolating quickly through the column, thereby resulting in the cooling of the AMD. The influent temperature of the AMD solution also had an impact on the temperature profile development with depth. The reaction of the AMD with limestone or lime would likely result in exothermic precipitation/neutralization reactions resulting in a slight increase in temperature throughout the lower layers of the peat column.

6.2.3.6 *IMPACT OF WATER LEVEL*

The water level appeared to have little impact on metal retention, but influenced effluent DO concentrations, acidity, and sulphate removal. At 0°C, DO concentrations were found to decrease when the effluent water level was raised to 15cm. Cumulative sulphate removal typically decreased with increasing water level under both temperature regimes, with the exception of the sludge/lime columns at 20°C, where sulphate removals were maintained with changes in water level.

Another significant impact which was noted as a result of changes in the effluent water level was the absence of sulphate reducing conditions in the peat biofilter columns, particularly at 20°C. A sulphate reducing environment was established in the HQ-H[] (Fig. 6-5b) peat column during the

sorption/desorption study at 20°C. These conditions also developed, to a lesser extent, in the peat column (Fig. 7-8) of the combined passive treatment system. Sulphate reducing conditions were indicated primarily through decreases in DO and sulphate concentrations, acidity and significant metal retention through the peat column. In the sorption/desorption study, a considerable rise in pH was also reported, and no metal breakthrough, with the exception of cadmium, was observed for the duration of the 85-day experiment.

It is plausible that changing water levels might have displaced the aerobic and anaerobic zones within the column, which hindered the establishment of a sulphate-reducing environment. The addition of the substrate at the top of the peat column could also have delayed the onset of sulphate reduction. The indicators for the development of such conditions occurred much later in the combined passive system than in the HQ-H[] study. Hence, it is also possible that the addition of a substrate might promote the growth of bacteria which may compete with sulphate-reducing bacteria in the peat column. In any case, the prevention of sulphate-reducing conditions in the peat column might be desirable, to preserve the physical matrix of the peat biofilter and allow for sulphate reduction to be established in the SRB stage where a more readily degradable substrate is provided.

6.2.3.7 *IMPACT OF AMBIENT TEMPERATURE*

With the exception of iron, metal retentions were higher at 20°C than at 0°C. The lower metal retention at 0°C can be explained in terms of chemical reaction kinetics which generally decrease with decreasing temperature. The warmer temperature regime generally yielded higher sulphate removal and DO utilization, as well as lower acidity possibly due to a combination of chemical and biological activity, which would be higher at higher temperatures.

CHAPTER 7

COMBINED PASSIVE TREATMENT SYSTEM STUDY

7.1 EXPERIMENTAL PROCEDURE

The performance of the overall combined passive treatment system and its individual system components was evaluated using a bench-scale experimental set-up. After some system adjustments based on preliminary results (Champagne *et al.*, 1999), the system was operated uninterrupted for a period of 10 months.

7.1.1 EXPERIMENTAL SET-UP

Laboratory investigations were conducted using the bench-scale experimental set-up illustrated in Figure 7.1. The columns and constant head apparatus were constructed using stainless steel. Teflon tubing was employed to connect each of the stages. Synthetic AMD was trickled from a 1/100 RPM peristaltic pump over an oxidation column (61 cm X 14.6 cm ID) filled with river washed rock. A 24 cm diameter sedimentation tank, 24 cm in depth, followed to settle any precipitates formed during the oxidation stage.

The AMD then passed through a peat biofilter column (61 cm X 14.6 cm ID). Prior to packing, milled New Brunswick *Sphagnum* peat was hand-sieved with a ¼" sieve and allowed to air-dry over a 72 hour period. The column was packed, in 10 cm lifts, with 45 cm of peat at a dry density of 191.5 kg/m³, which corresponded to a water holding capacity of 361.5% and a hydraulic conductivity of 1.12x10⁻² cm/s. A 15 cm layer of amendment mixture was added on top of the peat, as a source of carbon and alkalinity for the peat biofilter. The amendment mixture was composed

Figure 7-1: Combined Passive Treatment System Bench-scale Schematic

of dewatered sludge and limestone in a 70/30 v/v ratio. The sludge was obtained from the primary and secondary clarifiers of the MacLaren Pulp and Paper Plant in Masson, Quebec.

Next, the AMD flowed through two sulphate-reducing columns (63 cm X 14.6 cm OD). Sulphate reducing bacteria (SRB) were cultured using 1.0 L of primary clarifier effluent and 0.5 L of dewatered sludge from the MacLaren Pulp and Paper Plant, as well as 0.5 L of mixed liquor from the Robert O. Picard Environmental Center (ROPEC) wastewater treatment plant in Ottawa. A sulphate source was provided to the SRB in the form of Na_2SO_4 , with feed concentrations ranging from 100 mg/L to 300 mg/L during the culturing stage and the established culture stage, respectively. Once the culture was established, the SRB were inoculated by mixing the culture with spent mushroom compost supplied by Continental Mushroom in Metcalfe, Ontario. The column was filled and sealed to maintain anaerobic conditions throughout this stage. The system was maintained, prior to operating the bench-scale system, by providing a continuous feed/recycle of 500 mg/L SO_4 in the form of Na_2SO_4 .

From the SRB column, the AMD was directed to an anoxic limestone drain (ALD) column (91 cm X 4.5 ID). The ALD column was packed with 0.5 cm to 1.0 cm crushed limestone obtained from Peter Knippel Nursery Inc. at a bulk density of 1.9 g/cm³. The column was then sealed to maintain anoxic conditions throughout the ALD.

7.1.2 OPERATING CONDITIONS

The system was operated on a continuous basis under ambient laboratory temperature (18°C-21°C). Synthetic AMD, with the composition outlined in Table 3-2, was supplied to the system at a rate of 1.585 L/day, corresponding to a surface loading rate of 95 L/m²-d for the peat biofilter and

the SRB, and an overall empty bed hydraulic retention time (EBRT) of 25.7 days from the inlet of the sedimentation column to the outlet of the ALD. The EBRT through each of the sedimentation, peat biofilter, SRB and ALD components were estimated to be 6.9, 4.8, 13.1 and 0.9 days, respectively.

7.1.3 SAMPLING PROCEDURE AND ANALYSIS

Sampling began 1 day, after initial system start-up. The influent AMD and the effluent exiting each of the system components were collected and analyzed three times per week for pH, dissolved oxygen (DO) and metal concentrations. Samples were collected from each port using a 20 mL syringe. The DO concentration and pH were recorded immediately using a WWRbrand Dissolved Oxygen Meter Model 4000 and a WWRbrand pH/mV/Temperature Meter Model 3000, respectively. Next the samples were filtered using 0.45 μm Millipore filter paper. The filtrate was preserved by acidifying with 3 drops of concentrated HCl. Metal concentrations were determined via ICP performed in the Department of Chemistry at Carleton University.

To determine sulphate concentrations at each port, 15 mL samples were collected once a week and sent for analysis at Seprtech Laboratories in Ottawa. Acidity and/or alkalinity were also measured at each port on a weekly basis using a procedure specific for AMD as outlined in Standard Methods for Water and Wastewater Quality (1994). Sampling did not take place between day 78 and day 138 due to summer holidays and a lack of technical support to carry out these procedures. The regular sampling schedule was resumed on day 138 until the end of the experiment.

7.2 RESULTS AND DISCUSSION

The combined passive system was initiated on May 10th 1999 and was monitored over a 290 day period to evaluate the performance of the system. Results are discussed in the following sections and the complete data set arising from the experiment is presented in Appendix I.

7.2.1 CONSTITUENT LOADING

Influent concentrations were monitored throughout the 290-day combined system experiment. The mean constituent influent concentrations and standard deviations are tabulated in Table 7-1.

Constituent loading concentrations as a function of time can be found in Appendix I.

Table 7-1: Mean Influent Concentrations for the Combined Passive Treatment System

Constituent	Mean (mg/L)	Number of Observations	Standard Deviation (mg/L)
pH	3.2	62	0.39
Acidity	1750	30	183
DO	4.2	58	0.57
SO ₄	3030	27	226
Fe	189	57	17.0
Al	91.3	57	4.98
Zn	101	57	7.58
Mn	25.2	57	1.39
Ni	20.2	57	0.91
Cu	19.6	57	1.45
Cd	6.0	57	0.26

7.2.2 EFFLUENT CONCENTRATIONS

Variations in effluent pH, acidity/alkalinity, DO concentrations and sulphate concentrations as a function of time through each of the system components are presented in Figures 7-2 to 7-5. On average, the pH was found to remain relatively low through the oxidation (3.4, SD 0.41), sedimentation (3.3, SD 0.36) and peat biofilter (3.4, SD 0.30). The addition of the pulp and paper sludge/limestone amendment mixture at the top of the peat biofilter column did not appear to impact the effluent pH of this stage. A significant increase in pH was noted as the AMD passed through the first sulphate reducing stage (7.0, SD 0.19) with marginal increases recorded in the second sulphate reducing (7.1, SD 0.26) and ALD (7.2, SD 0.31) stages.

In terms of effluent concentrations, the combined system was found to have reached an equilibrium from day 243 onward, and hence, mean effluent values and their standard deviations were computed for that experimental period. From Figure 7-3, it can be seen that the solution acidity as CaCO_3 did not change significantly (1870 mg/L, SD 74.2 to 1910 mg/L, SD 45.3) as the AMD influent moved through the oxidation column. A 33% decrease in acidity to 1270 mg/L (SD 108) was noted as the AMD passed through the sedimentation column. This decrease in overall acidity was not found to coincide with a significant increase in pH (Fig. 7-2). It was thus attributed to a decrease in mineral acidity as oxidized metals were removed in the form of metal precipitates. Acidity decreased further moving through the peat biofilter column (671 mg/L, SD 79.6), as some of the metals were removed from solution through this stage, and the solution passed over limestone, a source of alkalinity. Once again, no significant change in pH was recorded.

Figure 7-2: pH as a Function of Time and System Component

Figure 7-3: Acidity/Alkalinity as a Function of Time and System Component

Figure 7-4: Dissolved Oxygen Concentrations as a Function of Time and System Component

Figure 7-5: Sulphate Concentrations as a Function of Time and System Components

Acidity was reduced completely through the first sulphate reducing stage and solution alkalinity as CaCO_3 increased significantly (1340 mg/L, SD 78.9). The increase in alkalinity was attributed to the generation of alkalinity as a product of sulphate reduction and metal sulphide precipitation. This phenomenon would be supported by low DO concentrations (Fig. 7-4), a significant increase in pH (Fig. 7-2) and decrease in sulphate concentrations (Fig. 7-5), as well as high metal retention (Fig. 7-9) as the AMD moved through the SRB1 column, all of which were observed in this stage. Alkalinity remained relatively high through the SRB2 (1440 mg/L, SD 74.6) and ALD (1350 mg/L, SD 63.6) stages of the combined system.

Dissolved oxygen concentrations remained fairly constant through the oxidation stage (4.1 mg/L, SD 0.51) and decreased slightly in the sedimentation stage (3.9 mg/L, SD 0.42). A significant decrease was noted as the AMD passed through the peat biofilter stage (1.5 mg/L, SD 0.56). This suggested some level of aerobic biological activity leading to the consumption of DO in the peat biofilter column. The reduction in DO concentration was an important element of the combined passive treatment system in order to establish anoxic conditions essential for the sulphate reducing stage of the system. Measured DO concentrations throughout the SRB1, SRB2 and ALD stages of the system were found to remain below 1 mg/L, with concentrations of 0.2 mg/L (SD 0.09), 0.2 mg/L (SD 0.09) and 0.3 mg/L (SD 0.11) reported, respectively.

Effluent sulphate concentrations through each of the system components did not appear to reach an equilibrium until day 277 (Fig. 7-5). From this time on, mean concentrations of 2870 mg/L (SD 10.0), 2900 mg/L (SD 20.8), 1900 mg/L (SD 30.6), 864 mg/L (SD 49.3), 811 mg/L (SD 5.8) and 815 mg/L (SD 5.8) were recorded in the oxidation, sedimentation, peat, SRB1, SRB2 and ALD stages of the combined system, respectively. As expected, sulphate concentrations did not change significantly in the oxidation and sedimentation columns. The observed decrease in the peat

biofilter column was probably due, in part, to the formation and precipitation of CaSO_4 as the AMD passed through the pulp and paper sludge/limestone amendment mixture at the top of the column. It could also be attributed to consumption by sulphate reducing bacteria in parts of the column where anoxic conditions were established, as indicated by the lower DO concentrations (Fig. 7-4). The establishment of sulphate reduction in the peat filter was observed in the previously described sorption/desorption study. The significant decrease in effluent sulphate concentrations in the SRB1 column were attributed to the consumption of sulphate via sulphate reducing bacteria. A slight decrease in sulphate concentration was noted through the second SRB, while no significant change was observed through the ALD.

Results illustrating percentage cumulative dissolved metal retention after each of the system components as a function of time are presented in Figures 7-6 to 7-11, as well as in Appendix H for individual metals. Measurements of system influent and effluent flow rates indicated a 14% reduction in flow. This was attributed to evaporative losses particularly in the oxidation stage which tended to increase the metal concentrations through these components. A 14% correction factor was applied to the volumetric inflow through the oxidation and subsequent stages of the combined passive system.

Slight aluminum, zinc, nickel and cadmium retentions appeared to take place within the oxidation and sedimentation columns. Respective cumulative removals of 7.4% (SD 0.13), 6.8% (SD 0.05), 6.5% (SD 0.08) and 6.9% (SD 0.08), 5.3% (SD 0.05) and 8.8% (SD 0.05), 6.1% (SD 0.09) and 9.8% (SD 0.16) were recorded from days 250 to 280, when the system had reached an equilibrium. The oxidation/sedimentation stage did not contribute significantly to the permanent immobilization of these metals through the system.

Figure 7-6: Cumulative Retention Through the Oxidation Stage

Figure 7-7: Cumulative Retention Through the Sedimentation Stage

Figure 7-8: Cumulative Retention Through the Peat Biofilter Stage

Figure 7-9: Cumulative Retention Through the First Sulphate Reducing (SRB1) Stage

Figure 7-10: Cumulative Retention Through the Second Sulphate Reducing (SRB2) Stage

Figure 7-11: Cumulative Retention Through the Anoxic Limestone Drain (ALD) Stage

Iron was significantly oxidized to form a precipitate in the oxidation column and then settled through the sedimentation stage. This was indicated by cumulative retention of 23.6% (SD 0.27) in the oxidation stage and 32.3% (SD 0.17) in the sedimentation stage. A fine orange precipitate accumulated in the sedimentation tank and was presumed to be oxidized iron hydroxide precipitate.

Significant reductions in iron (95.8%, SD 0.07), aluminum (87.7%, SD 0.37) and copper (99.2% SD 0.02) concentrations were found to occur through the peat biofilter (Figure 7-8). As was indicated previously in this study, iron was found to be leached out initially, due to the peat composition, followed by a notable increase in cumulative retention in the peat biofilter. Manganese, cadmium, zinc and nickel were found to be more mobile through this stage as indicated by the cumulative retention with time curves noted for each of these metals. However, relatively consistent metal retentions were observed in the peat biofilter from day 250 to the end of the experimentation period in which 26.3% (SD 0.10), 18.3%, (SD 0.10), 37.3% (SD 0.02) and 39.7% (SD 1.03) cumulative zinc, manganese, nickel and cadmium removals were recorded, respectively.

This behaviour was attributed to competitive adsorption occurring within the peat biofilter. Metal ions in the AMD solution compete for sorption sites in the peat, and those ions with tighter bonds are favoured, thereby releasing the more mobile ions back into solution. In this case, the adsorption of iron, aluminum and copper was preferred and these metal ions were retained within the peat column. These results are consistent with those found in the column loading (Fig. 6-3 to 6-6) and sequential extraction studies (Fig. 6-10 to 6-17). Iron and copper ion retentions were generally found to be greater than other metal ions which was attributed to their association with organic matter fraction of the peat. The other metal ions, with the exception of aluminum, were generally bound to the exchangeable fraction and were, therefore, more readily released back into solution

under competitive adsorption conditions. Aluminum removal through the peat biofilter component was probably primarily due to aluminum hydroxide precipitation as the AMD passed through the amendment mixture at the top of the column.

With the exception of cadmium, all of the metals remaining in solution after the peat biofilter stage were retained in the first SRB1 column (Fig. 7-9). 99.3% (SD 0.01), 99.6% (SD 0.01), 99.3% (SD 0.02), 97.8% (SD 0.02), 98.5% (SD 0.03) and 99.8% (SD 0.00) cumulative retentions were observed for iron, aluminum, zinc, manganese, nickel and copper through the first SRB stage, respectively. The cumulative metal retention was not found to change significantly through the second SRB (Fig. 7-10) stage with respective removals of 99.4% (SD 0.01), 99.8% (SD 0.00), 99.7% (SD 0.01), 97.6% (SD 0.03), 98.2% (SD 0.02) and 99.8% (SD 0.00) reported for iron, aluminum, zinc, manganese, nickel and copper. Cadmium retention increased from 39.7% (SD 1.03) in the peat biofilter to 64.2% (SD 1.4) and 65.7% (SD 1.14) in the SRB1 and SRB2 columns, respectively.

Metal mitigation through these two stages was attributed to the development of a sulphate-reducing environment in the SRB columns. The reduction of sulphate and consequent formation of metal sulphide precipitates via sulphate reducing bacteria process would be supported by an increase in alkalinity (Fig. 7-3), an increase in pH (Fig. 7-2), decrease in sulphate concentration (Fig. 7-5), the presence of an anoxic environment (Fig. 7-4), as well as high metal retention (Fig. 7-9 and 7-10) as the AMD moved through the SRB, all of which were observed in these two columns.

Cumulative metal retention trends did not change as the AMD solution flowed through the ALD (Fig. 7-11), which would indicate that this component did not contribute significantly to metal mitigation throughout the duration of this study. From day 250 to 277, metal removals after the

ALD stage were found to be 99.4% (SD 0.01), 99.6% (SD 0.01), 99.7% (SD 0.01), 98.0% (SD 0.02), 98.4% (SD 0.01), 99.6% (SD 0.01) and 66.5% (SD 1.16) for iron, aluminum, zinc, manganese, nickel, copper and cadmium, respectively.

7.2.3 INDIVIDUAL COMPONENT TREATMENT EFFICIENCY

The treatment efficiency of each component was examined for the 290 day experimental period. For most constituents, with the exception of sulphate, the system and individual components appeared to have reached a pseudo-steady state at day 250 of the test period. Relatively constant sulphate concentrations were obtained from day 277 until the end of the test period. The mean and standard deviation of the effluent constituent concentrations were computed, during the steady state period, for each of the system components and are summarized in Table 7-2.

As can be seen from Table 7-2, a slight increase in effluent metal and sulphate concentrations were observed after the oxidation and sedimentation stages for aluminum, manganese, nickel and cadmium. As discussed previously, this phenomenon was mainly attributed to evaporative losses through the oxidation column. Iron and manganese were the primary metals targeted for oxidation and, subsequently, sedimentation via these two system components. The ratios of cumulative metal retention to cumulative loading indicated that 32.3% and 9.5% of these two metals were respectively retained. Acidity was also found to decrease significantly through the sedimentation stage, which would support the removal of mineral acidity and, therefore, the removal of metals via oxidation reactions and precipitation.

Table 7-2: Effluent Constituent Concentrations as a Function of System Component

Constituent	Component											
	Oxidation		Sedimentation		Peat Biofilter		SRB1		SRB2		ALD	
	Mean	St. Dev.	Mean	St. Dev.	Mean	St. Dev.	Mean	St. Dev.	Mean	St. Dev.	Mean	St. Dev.
pH	3.4	0.41	3.3	0.36	3.4	0.30	7.0	0.19	7.1	0.26	7.2	0.31
Acidity (mg/L CaCO ₃)	1910	45.3	1270	108	671	79.6						
Alkalinity (mg/L CaCO ₃)							1340	78.9	1440	74.6	1350	63.6
DO												
(mg/L)	4.1	0.51	3.9	0.42	1.5	0.56	0.2	0.09	0.2	0.09	0.3	0.11
SO ₄												
(mg/L)	2870	10.0	2900	20.8	1900	30.6	864	49.3	811	5.8	815	5.8
Fe (mg/L)	167	24.1	145	25.1	2.6	0.68	0.6	0.06	0.6	0.22	0.4	0.07
(Cum Ret. %)	23.6	0.27	32.3	0.17	95.8	0.07	99.3	0.01	99.4	0.01	99.4	0.01
Al (mg/L)	97.7	3.62	96.4	3.57	25.7	4.88	0.1	0.04	0.1	0.04	0.1	0.05
(Cum Ret. %)	7.4	0.13	6.8	0.05	87.7	0.37	99.6	0.01	99.8	0.00	99.6	0.01
Zn (mg/L)	95.3	2.29	100	2.95	76.6	5.58	0.1	0.06	0.1	0.07	0.1	0.08
(Cum Ret. %)	6.5	0.08	6.9	0.08	26.3	0.10	99.3	0.02	99.7	0.01	99.7	0.01
Mn (mg/L)	26.7	1.55	27.8	1.46	24.7	2.67	0.4	0.09	0.4	0.09	0.4	0.07
(Cum Ret. %)	2.7	0.16	9.5	0.15	18.3	0.10	97.8	0.02	97.6	0.03	98.0	0.02
Ni (mg/L)	21.6	0.55	20.4	0.35	14.2	0.66	0.5	0.25	0.6	0.19	0.4	0.22
(Cum Ret. %)	5.3	0.05	8.8	0.05	37.3	0.02	98.5	0.03	98.2	0.02	98.4	0.01
Cu (mg/L)	20.5	0.76	20.2	0.59	<0.1	0.03	<0.1	0.00	<0.1	0.00	<0.1	0.01
(Cum Ret. %)	4.1	0.21	10.7	0.10	99.2	0.02	99.8	0.00	99.8	0.00	99.6	0.01
Cd (mg/L)	6.3	0.26	6.3	0.11	6.57	0.57	5.72	0.22	5.0	0.42	5.0	0.39
(Cum Ret. %)	6.1	0.09	9.8	0.16	39.7	1.03	64.2	1.40	65.7	1.14	66.5	1.16

The peat biofilter was primarily effective at removing iron, aluminum and copper ions with 1.4%, 27.9% and 0.2% of initial metal ion concentrations remaining in solution after this stage, respectively. The removal mechanisms would be sorption onto the peat surface, precipitation as the AMD solution passes through the pulp and paper sludge/limestone amendment mixture, and the formation and precipitation of metal sulphides via sulphate reducing bacteria. The limestone was responsible for raising the pH level in the top layers of this stage. However, pH levels returned to 3.4 which was the natural pH of the peat utilized in this experiment. The possible development of a sulphate reducing environment in the peat column was supported by the low DO concentrations (1.5 mg/L), the reductions in sulphate concentration (37.1%) and acidity (61.6%). It was assumed that dissolved oxygen concentration decreased through the peat biofilter mainly due to aerobic biodegradation of the carbon source provided in the amendment mixture. As was indicated in the previous column studies, cadmium, manganese, zinc and nickel demonstrated some initial retention, but were fairly mobile through this component.

With the exception of cadmium, all of the metal ions in the AMD solution fell below 1 mg/L concentrations after the SRB1 stage representing > 97.8% total influent metal mass retention and 64.2% cadmium retention (Table 7-2). The main removal mechanism in this system component was the formation and precipitation of metal sulphides via sulphate reducing bacteria. This was indicated by the low DO concentrations (0.2 mg/L), the reductions in sulphate concentration to 864 mg/L, the alkalinity (1340 mg/L) generated and significant increase in pH (7.0) at this stage. Sorption onto the surface of the mushroom compost could also have taken place as a secondary removal mechanism.

Effluent concentrations and cumulative retentions did not change significantly through the SRB2 and ALD components. This was attributed to the fact that AMD mitigation was efficiently achieved through the peat and SRB1 stages during the duration of this experiment. It is expected that, with time, metal removal due to sorption in the peat biofilter might become less significant as adsorption capacity of the peat will be reached. Mitigation in the SRB1 might also be reduced in time due to the consumption of the organic source (mushroom compost) by the microorganisms, at which point the mitigating sulphate reducing environment will move into the SRB2 stage.

The purpose of the ALD stage was to ensure adequate alkalinity and pH conditions as the mitigated AMD solution exited the combined passive treatment system. Any dissolved metal ions entering the ALD stage should be precipitated from solution as the effluent leaves this component and comes in contact with oxygen, provided adequate mitigating conditions exist. For this component to be effective, the conditions required are DO, iron and aluminum concentrations of less than 1 mg/L, and sulphate concentrations of less than 2000 mg/L. In this study, all of these conditions were met as the AMD exited both SRB stages of the combined passive treatment system. Under the experimental conditions of this bench-scale study, significant metal retention was not observed at this stage, as most of the metal removal occurred in the previous SRB stages. However, metal concentrations existing the ALD stage, and hence system, continued to show > 98.0% removal for all metals, with the exception of cadmium for which only 66.5% cumulative removal was demonstrated (Table 7-2).

7.2.4 PEAT BIOFILTER PERFORMANCE

In the combined system, the peat biofilter was provided with the same constituent and hydraulic loading, substrate/amendment mixture and ambient temperature as columns 8 and 11 in the substrate/amendment mixture study. The results obtained for the peat biofilter in the combined system were thus compared with the substrate/amendment mixture columns at 20°C. Although the order of breakthrough was consistent in both studies with $Mn < Zn < Cd < Ni < Al$ (Fig. 6-27, 7-8 and Table 6-7), in general, cumulative metal breakthroughs were found to occur earlier in the peat biofilter columns of the substrate/amendment mixture study. In the combined system, manganese, zinc, cadmium, nickel and aluminum breakthroughs were noted at 60 days, 67 days, 70 days, 75 days and 234 days, respectively. These were compared with average breakthrough times of 10 days, 19.5 days, 26.6 days, 27.7 days and 42.1 days, respectively, in the substrate/amendment mixture study (Table 6-7).

An average sulphate removal of 34.2% occurred in the peat biofilter column of the combined system (Table 7-2) compared to sulphate reductions $< 9.1\%$ in the two sludge/amendment mixture columns (Table 6-9). Acidity and DO levels were marginally lower in the peat biofilter column of the combined system with respective values of 671 mg/L (SD 79.6) and 1.5 mg/L (SD 0.56). The pH, on the other hand, was slightly higher with a value of 3.4 (SD 0.3) (Table 7-2). Comparatively, for columns 8 and 11, respectively, acidities of 756 mg/L (SD 74.7) to 824 mg/L (SD 31.7) and 675 mg/L (SD 64.5) to 824 mg/L (SD 71.4); DO concentrations of 1.9 mg/L (SD 0.39) to 2.5 mg/L (SD 1.09) and 2.0 mg/L (SD 0.69) to 2.3 mg/L (SD 0.88); and pH levels of 2.6 (SD 0.13) to 2.9 (SD 0.2) and 3.1 (SD 0.16) to 3.1 (SD 0.21) were reported in the substrate/amendment mixture study (Table 6-9).

The differences in breakthrough times could probably be attributed to the development of sulphate reducing zones in the peat biofilter of the combined system. This would appear to be supported by the slightly lower DO and acidity concentrations, higher pH and sulphate removal rates. Other contributing factors would include the significant removal of iron through the oxidation and sedimentation stages resulting in a decrease in competitive adsorption and change in water chemistry.

In comparing results from the sorption/desorption study, which was operated under similar loading conditions as the combined system and substrate/amendment mixture studies, it was found that the pH increased significantly after 19 days (Fig. 6-7b) in the HQ-H[] column at 20°C. This was attributed to the presence of anaerobic biological activity as indicated by the low DO concentrations of 1.6 mg/L (SD 0.36) (Fig. 6-8b) and higher sulphate utilization rate of 41.3 mg/L-d (SD 4.62 mg/L-d) (Fig. 6-9b) observed in this column. With peat acting as a carbon source, these conditions would have led to the establishment of a sulphate reducing environment, thereby resulting in the pH increase. However, it was noted that, although sulphate reducing conditions may have been established in the peat biofilter of the combined system, these conditions were not as active, as indicated by the metal breakthroughs with time and the lack of a significant increase in pH as was seen in the sorption/desorption study. It is possible that the addition of the substrate promoted the growth of bacteria and/or chemical reactions which competed with or inhibited sulphate reducing bacteria in the columns of the peat biofilters in both the combined system and the substrate/amendment mixture studies. The impact of substrate addition on the establishment of a sulphate reducing conditions would merit further investigation.

7.3 *ENGINEERING SIGNIFICANCE*

From the current design, the oxidation/sedimentation stages of the combined system will allow for the removal of approximately 30% of excess iron. Further considerations could be given to the oxidation and a precipitation of excess manganese, which could only effectively occur at a higher pH range.

The peat biofilter will be the limiting system component and should be designed to provide effective retention of metal ions generally bound to the organic matter fraction (Fe, Cu and Al). The breakthrough of copper and iron was not observed in this column after 10-month of operation at 20°C, however, 10% cumulative aluminum breakthrough was noted after approximately 8 months of operation. This breakthrough could have resulted from the exhaustion of sorption sites for aluminum adsorption and/or the depletion of the substrate/limestone mixture which provided a solution chemistry conducive to aluminum removal via precipitation reactions. In the former case, the depth of the peat biofilter could be increased to extend the theoretical time to breakthrough.

In the latter case, the frequency of substrate and/or amendment addition necessary to prevent aluminum breakthrough should be investigated. The presence of a readily available source of alkalinity (lime, limestone) is useful in that it may provide a solution chemistry that will enhance adsorption processes, precipitation reactions and aerobic biodegradation of the added substrate leading to the consumption of oxygen. Ultimately, the aim would be to limit the application of additional substrate and/or amendment to an annual basis. It is thought that substrate/amendment consumption would decrease during the winter months due to a typically lower flow of AMD during this season. Substrate/amendment consumption could also vary significantly on a larger scale compared to the bench scale.

The establishment of a sulphate reducing environment is highly desirable for the mitigation of the metal ions typically associated with the exchangeable fraction and that are relatively mobile through the peat biofilter (Zn, Mn and Ni). However, this condition should be limited to the SRB system. The presence of sulphate reducing conditions in the peat biofilter component would require a biodegradable carbon source. In the absence of an external carbon supply, as was seen in the sorption/desorption study, the peat would act as a carbon source which could lead to the deterioration of the peat biofilter matrix.

Although the development of a temperature profile was not observed in the columns during the substrate/amendment mixture study, it is thought that such a profile could develop in a system designed on a larger scale. A larger scale system would provide a much better insulation of the peat system than could be provided by 15 cm columns. Increased temperatures would result from the aerobic biodegradation of the substrate, reactions which are typically exothermic in nature. In order to increase the likelihood of temperature profile development during the winter months, operation of the combined system should commence in the spring or summer months. The establishment of higher temperatures within the peat biofilter and the provision of insulation of the biological components of the system will promote continued treatment and operation of the combined passive system throughout the winter season. This premise should be investigated further in a future study.

The effectiveness of the ALD component is limited by influent DO, iron and aluminum concentrations, which must fall below 1 mg/L, as well as sulphate concentrations and solution pH which should be under 2000 mg/L to minimize armouring. Under the operational conditions tested during this study, all of these conditions were met through removals via the oxidation/sedimentation, peat biofilter and SRB stages. The mitigation of the other metal

constituents was also provided prior to the ALD stage. However, the benefits of an ALD component should be considered on a long-term basis. Its purpose will be, after some years of operation or during the winter months, to ensure adequate effluent alkalinity and pH conditions as the treated AMD leaves the combined passive treatment system, and allow dissolved metal ions entering the ALD stage to be precipitated from solution as the effluent exits the ALD and comes in contact with oxygen.

The overall treatment efficiency of the system is given by the effluent concentrations observed after the ALD component. The results indicate that the combined passive treatment system was able to mitigate AMD and to provide total reductions of 99.7%, 99.9%, 99.9%, 98.6% 98.2% and 99.9% from influent concentrations for iron, aluminum, zinc, manganese, nickel and copper, respectively. Cadmium remained fairly mobile through the system with 66.5% total cumulative removal over the 10-month period. Concentrations of copper, nickel and zinc (Table 7-2) exiting the combined system were below MMLER discharge limits of 0.6 mg/L, 1.0 mg/L and 1.0 mg/L, respectively (Table 2-1). The initially low pH and highly acidic drainage was neutralized with an effluent pH of 7.2 and the alkalinity of 1350 mg/L as CaCO_3 . Sulphate concentrations were also reduced to 815 mg/L. Hence, the combined passive treatment system performed successfully at the bench-scale level of operation.

CHAPTER 8

CONCLUSIONS AND RECOMMENDATIONS

8.1 CONCLUSIONS

A combined passive treatment system was developed and evaluated for the mitigation of a moderate strength synthetic AMD. The system consists of four components with specific treatment functions: oxidation/sedimentation for excess metal removal; peat biofilter for heavy metal sorption and establishment of anoxic conditions; sulphate reducing bacteria for alkalinity generation and sulphate reduction; and anoxic limestone drain for alkalinity addition. The peat biofilter was considered to be the limiting component and presented the greatest degree of uncertainty in terms of combined passive treatment system performance, hence, efforts were focused on this component throughout this thesis.

Four studies were undertaken to characterize AMD mitigation throughout the peat biofilter and to evaluate the performance of the combined passive treatment system. (1) Physical/chemical characterization of the peat material. (2) Batch kinetic and equilibrium studies to determine the sorption capacity of the peat material under various pH and temperature conditions. (3) Peat column experiments aimed at assessing the impact of substrate/amendment addition, constituent loading, hydraulic loading, height of the water table and temperature on effluent constituent concentrations, the establishment of sulphate reducing conditions and the development of temperature profiles. (4) Design and evaluation of a bench-scale combined passive treatment system under continuous dosing conditions.

Since peat is a highly variable material, the physical/chemical characterization of the peat was necessary to provide a basis for the comparison of performance between systems using peat from different sources. The *Sphagnum* peat material utilized in this study was classified as hemic (33% < fiber content < 67%), high ash (ash content > 15%), highly acidic (pH < 4.5) and moderately absorbent (300% < water holding capacity < 800%).

A batch kinetic study was undertaken to determine the contact time required to reach equilibrium in the multi-component AMD solution as a function of temperature and pH. For Ni, Cu and Cd, the contact period required to reach equilibrium increased with increasing temperature, while the opposite trend was noted for Mn. The contact times necessary for Fe and Zn removal were relatively constant at all temperatures. Fe, Zn, Mn, Ni and Cd removal from a synthetic AMD mixture increased with increasing temperature, while Al and Cu removal decreased with increasing temperature. These responses were attributed to competitive adsorption, as well as increased solubility of some compounds and the inhibiting effects of exothermic adsorption processes at higher temperatures, which are difficult to distinguish in multi-component solutions. In general, equilibrium conditions were reached more rapidly at higher pH for Zn, Mn and Cu, more slowly for Al and Cd, while pH did not impact the required contact time for Fe and Ni.

The purpose of the batch equilibrium study was to determine the impact of pH on single-ion adsorption capacities. The Langmuir model was found to adequately represent single-constituent adsorption isotherms at pH levels of 3 to 5, but not at a pH of 2. Variations in pH observed during the equilibrium study conducted at a pH of 2, may partially account for why the data collected did not follow the Langmuir model. Adsorption capacities were relatively consistent at pH 3 to 5 where $\text{Cu} > \text{Ni} > \text{Zn} > \text{Cd}$. Metal removals from both single-ion and multi-component solutions were

generally found to increase with increasing pH. Multi-component metal ion adsorption capacities were also found to be significantly lower than single-component metal ion adsorption capacities.

The column sorption/desorption study conducted at 20°C and 0°C demonstrated the impact of hydraulic and constituent loadings, as well as temperature on metal retention in a packed peat column. At times, the multi-component nature of the AMD mixture made it difficult to distinguish between opposing effects such as competitive adsorption, and the impact of temperature on changes in solution chemistry, compound solubility, and the exothermic adsorption processes to explain trends in metal retention. At 0°C, it appeared as though the association of metals typically bound with the exchangeable fraction of the peat (Zn, Mn, Ni and Cd) weakened and the metals were retained to a lesser degree. Fe and Cu, which were primarily associated with the organic matter fraction, demonstrated higher or comparable mass retentions at lower temperatures under most loading conditions.

Predicted and actual sorption capacities of the peat column were greater at higher constituent loading. At 0°C, the breakthrough of metals generally occurred in the following order: LQ-L[] < HQ-L[] < LQ-H[] < HQ-H[] with an order of metal breakthrough of Cd < Mn < Zn < Al < Ni < Cu < Fe. At 20°C, the highest removal efficiencies were noted in the high-flow columns. This was attributed to the establishment of sulphate-reducing conditions in these columns with the peat acting as a carbon source and the moderate sulphate concentrations acting as an electron acceptor for sulphate reducers in the column. The establishment of sulphate reducing conditions in the high flow columns was indicated by relatively low effluent DO concentrations (~1 mg/L), higher sulphate removal rates and significant increases in pH demonstrated in both of the high flow columns. It was presumed that more rapid biological kinetics at higher temperatures led to a

greater consumption of DO by microorganisms. The opportunity for reaeration in the high flow columns was lower than in the low flow columns due to the higher volumetric loading and greater saturation of the peat. These conditions led to a decrease in effluent metal concentrations via metal sulphide precipitation, as was indicated by the increased retention of metals in the residual fraction, under the high flow conditions. This resulted in the increased effluent solution pH as a product of biologically mediated, alkalinity-generating sulphate reduction.

The impact of substrate/amendment mixture additions, water table fluctuations and temperature were assessed in the substrate/amendment mixture column study. At 0°C, the addition of an organic substrate contributed to the greater removal of Cd and Cu, and lower Zn retention. The substrate may have changed the solution chemistry and/or provided additional sorption sites for the removal of Cd and Cu. Amendment additions in the form of alkalinity improved metal retention to a greater extent when a more readily available alkaline source was provided. Hence, higher metal retentions were noted in the sludge/lime columns.

A bench-scale combined passive treatment system was designed and the mitigation potential of individual system components and the overall system were investigated. The overall treatment efficiency results indicated that the combined passive treatment system was able to mitigate AMD and to provide total reductions of 99.7%, 99.9%, 99.9%, 98.6% 98.2% and 99.9% for Fe, Al, Zn, Mn, Ni and Cu, respectively. Effluent concentrations of Cu, Ni and Zn complied with MMLER discharge limits of 0.6 mg/L, 1.0 mg/L and 1.0 mg/L, respectively. The initially low pH and highly acidic drainage was neutralized with an effluent pH of 7.2 and the alkalinity of 1350 mg/L as CaCO₃. Sulphate concentrations were also reduced to 815 mg/L. Hence, the bench-scale combined passive treatment system was successful in mitigating moderate strength AMD at a surface loading of 95 L/m²/d.

The oxidation/sedimentation stages of the combined system removed approximately 30% of excess Fe. The peat biofilter was expected to be the limiting system component and should be designed to provide effective retention of metal ions generally bound to the organic matter fraction (Fe, Cu and Al). The presence of a readily available source of alkalinity (lime, limestone) was found to be useful in that it provided a solution chemistry that enhanced adsorption processes, precipitation reactions and aerobic biodegradation of the added substrate leading to the consumption of oxygen. The cumulative breakthrough of all metals, with the exception of Cu and Fe, was shown to occur during the 10 months of operation at 20°C. Aluminum breakthrough was noted after approximately 8 months of operation. This breakthrough could have resulted from the exhaustion of sorption sites for aluminum adsorption and/or the depletion of the substrate/limestone mixture which provided a solution chemistry conducive to aluminum removal via precipitation reactions. In the former case, the depth of the peat biofilter could be increased to extend the theoretical time to breakthrough.

In comparing results from the peat biofilter of the combined passive treatment system to those from the sorption/desorption study, it was noted that sulphate reducing conditions were established in the peat biofilter of the combined system. However, these conditions were not as active, as indicated by the metal breakthroughs and the lack of increase in pH. A significant pH increase and no metal breakthrough, with the exception of Cd, were observed in the sorption/desorption study under similar experimental loading conditions. The order of breakthrough, $Mn < Zn < Cd < Ni < Al$, was consistent with the order obtained in the substrate/amendment mixture column study at 20°C. However, cumulative metal breakthroughs were found to occur earlier in the peat biofilter columns of the substrate/amendment mixture study than in the combined system which was probably due to the development of sulphate reducing conditions in the peat biofilter of the combined system.

The establishment of a sulphate reducing environment was found to be important for the removal of metal ions typically associated with the exchangeable fraction (Ni, Mn and Zn) and relatively mobile through the peat biofilter, with the exception of Cd which remained mobile through the system. However, sulphate reducing conditions should be limited to the SRB system, because the development of sulphate reducing conditions in the peat could lead to the deterioration of the peat biofilter matrix.

The purpose of the ALD component is to ensure adequate effluent alkalinity and pH conditions as the treated AMD exits the combined passive treatment system. For the ALD component to be efficient, influent DO, iron and aluminum concentrations, had to be < 1 mg/L, and sulphate concentrations and pH < 2000 mg/L and < 6 , respectively, all of which were achieved, along with significant mitigation of other constituents, in the previous components. Although the ALD did not significantly improve effluent quality during the 10-month testing period, the importance an ALD component should be considered on a long-term basis.

8.2 RECOMMENDATIONS

A vertical-flow combined passive treatment system was developed for the mitigation of AMD. A bench-scale version of the combined system was operated for a 10-month testing period using a synthetic AMD that reflects moderate strength AMD typical of Canadian-based metal mining sites. Much of this thesis work focused on the peat biofilter component of the system, because it was the least understood and considered to present the greatest uncertainty in terms of removal mechanisms and removal efficiencies. Further research is necessary to evaluate and characterize the combined passive treatment system and its individual components in the mitigation of AMD.

Specific short term work arising directly from this thesis research would include:

1. Bacterial characterization of peat biofilter and SRB system components.
2. Tracing of biologically-mediated processes in the sulphur cycle and biogenic alkalinity through the use of stable isotopes (^{13}C and ^{34}S)
3. Consideration of requirements for the oxidation and precipitation of excess manganese.
4. Investigation of solution chemistry and solution-solid interactions, leading to the incorporation of findings into the development of a biogeochemical model and a surface-ionization/complexation model to describe pH dependent behaviour.
5. Determination of the role of competitive adsorption, solution chemistry and exothermic process responses in removal of metals from a multi-component ion solution by peat.
6. Assessment of substrate addition on the establishment of a sulphate reducing conditions, as well as the frequency of substrate and/or amendment addition necessary to prevent metal breakthrough and the impact of temperature on substrate/amendment consumption.
7. Examination of removal mechanisms within the oxidation/sedimentation, peat biofilter and sulphate reducing bacteria and anoxic limestone drain components.
8. Performance evaluation of the overall combined passive system and individual system components under varying AMD strengths, flow conditions and temperature regimes.

Longer term research themes would consider:

9. Identification and testing of various substrates, natural amendments and neutralizing agents which could enhance the performance of individual components and maximize the useful life of the system.
10. Exploration of alternate combined passive system configurations to establish the optimal configuration for specific loading, operational, environmental and climatic conditions.
11. Field-scale design and testing of the combined passive treatment system

12. Field-scale investigation of temperature profile development, heat generation and system insulation resulting from aerobic biodegradation of the substrate within the peat biofilter .
13. Estimation of life expectancy of the combined system, frequency of component replacement
14. Determination of best remedial and/or disposal strategies for spent peat and compost, as well as process sludge resulting from AMD mitigation.

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APPENDIX A

CHARACTERISTICS OF SYNTHETIC ACID MINE DRAINAGE SOLUTION TESTED

Table A-1: Synthetic Acid Mine Drainage Solution

Element	AMD Elemental Concentration (mg/L)	Metal Salt	1 L Solution (g)
Fe	200	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	0.996
Zn	100	$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$	0.440
Al	90	$\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$	1.051
Mn	25	$\text{MnSO}_4 \cdot \text{H}_2\text{O}$	0.077
Ni	20	$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$	0.090
Cu	20	CuSO_4	0.050
Cd	6	$3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$	0.014
K	780	K_2SO_4	1.738
Na	460	Na_2SO_4	1.417

APPENDIX B

PHYSICAL/CHEMICAL CHARACTERIZATION RAW DATA

Table B-1: Extractable Ions

EXPERIMENTAL PROCEDURE															
100mL of 0.5 M HCl: Shake for 30 min - 0.5 g ground, oven-dried peat															
Filtered samples using Whatman No. 41 Filter Paper															
Collected filtrate for extractable ion analysis using ICP															
THEORY/RATIONALE															
Identifies which ions may be displaced by solution while elemental composition does not specify whether ions are mobile or not															
Extractable cations will provide a baseline to determine if ions are being retained or leached by AMD application at low pH															
REFERENCES															
NOTES															
ICP performed by Agriculture Canada Staff															
Use of oven-dried ground peat samples															
Some volume lost during filtration															
ID	Ca (ug/g)	P (ug/g)	K (ug/g)	Mg (ug/g)	Na (ug/g)	V (ug/g)	Cr (ug/g)	Co (ug/g)	Cu (ug/g)	Fe (ug/g)	Mn (ug/g)	Pb (ug/g)	Se (ug/g)	Zn (ug/g)	
1-1	2450	217	280	1320	491	33.5	0.0	7.85	0.0	123	1.61	0.00	0.0	65.4	
1-2	2260	193	222	1200	392	28.6	0.0	6.61	0.0	102	0.00	17.2	0.0	15.3	
1-3	2450	214	295	1370	474	28.1	0.0	7.80	0.0	111	0.92	0.00	0.0	16.4	
2-1	2210	239	236	1420	450	27.2	0.0	8.00	0.0	120	2.34	0.00	0.0	14.7	
2-2	2130	232	212	1320	437	26.5	0.0	7.81	0.0	127	2.72	3.07	0.0	17.2	
2-3	2070	232	241	1310	430	30.8	0.0	10.2	0.0	145	0.18	0.00	0.0	17.1	
3-1	2073	242	202	1360	445	35.8	0.0	5.37	0.0	98.3	0.47	18.0	0.0	12.9	
3-2	2120	278	212	1380	445	30.8	0.0	6.52	0.0	113	8.96	27.7	0.0	14.7	
3-3	2120	258	256	1350	448	32.3	0.0	8.44	0.0	120	0.91	0.00	0.0	14.7	
4-1	2220	278	271	1400	455	45.7	0.0	7.86	0.0	176	2.63	11.0	0.0	58.1	
4-2	2260	264	251	1410	445	45.4	0.0	7.18	0.0	159	2.30	10.9	0.0	55.0	
4-3	2200	286	241	1370	439	45.5	0.0	7.03	0.0	161	3.07	6.07	0.0	44.2	
5-1	2100	232	182	1330	463	38.8	0.0	3.39	0.0	79.2	2.88	18.7	0.0	14.4	
5-2	2060	223	295	1320	435	30.9	0.0	5.32	0.0	87.8	4.33	2.47	0.0	13.6	
5-3	2120	214	256	1340	469	32.8	0.0	3.39	0.0	87.0	0.00	9.58	0.0	14.4	
6-1	1930	252	227	1230	407	33.6	0.0	10.1	0.0	150	2.86	0.00	0.0	19.4	
6-2	1980	265	246	1260	409	35.3	0.0	7.88	0.0	137	3.04	0.41	0.0	18.4	
6-3	1970	259	251	1270	408	33.4	0.0	7.18	0.0	132	0.00	10.9	0.0	18.1	
7-1	2100	233	291	1400	461	32.4	0.0	0.94	0.0	83.2	0.01	42.0	0.0	26.4	
7-2	1850	229	246	1220	406	37.7	0.0	1.59	0.0	87.6	0.25	0.00	0.0	27.5	
7-3	2030	268	261	1350	452	38.0	0.0	2.40	0.0	84.8	2.96	26.0	0.0	26.6	
8-1	2110	248	222	1360	429	31.5	0.0	7.04	0.0	125	1.88	0.00	0.0	12.8	
8-2	2100	238	305	1340	436	37.6	0.0	5.81	0.0	113	0.33	0.00	0.0	13.5	
8-3	2000	236	207	1340	423	33.9	0.0	6.34	0.0	124	0.26	2.55	0.0	16.6	
C-1	14800	791	1886	3080	349	58.4	0.0	4.39	0.0	12.9	17.6	17.1	16.5	33.4	
C-2	15300	780	1969	2990	305	51.5	0.0	1.73	0.0	10.5	17.1	44.1	11.3	33.1	
C-3	15300	732	1891	2970	334	51.8	0.0	3.40	0.0	8.86	14.1	18.2	6.37	33.8	
2000 ug/g	2380	2428	2313	2260	2240	2410	2370	2290	2370	2200	2350	2410	2380	2270	
Dist. H ₂ O	0.0	17.6	15.5	11.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
Average	2120	243	246	1330	439	34.4	0.0	6.33	0.0	119	1.87	8.60	0.0	23.6	
St. Dev.	142	23.3	32.4	59.4	24.0	5.42	0.0	2.44	0.0	26.93	2.00	11.2	0.0	15.5	

Table B-2: Fixed Elemental Composition

EXPERIMENTAL PROCEDURE

100mL of 0.5 M HCl: Shake for 30 min - 0.5 g ground, oven-dried peat

Filtered samples using Whatman No. 41 Filter Paper

Collected filtrate for extractable ion analysis using ICP (analysis performed by Agriculture Canada staff)

THEORY/RATIONALE

Identifies which ions may be displaced by solution while elemental composition does not specify whether ions are mobile or not
Extractable cations will provide a baseline to determine if ions are being retained or leached by AMD application at low pH

REFERENCES

NOTES

ICP performed by Agriculture Canada Staff

Use of oven-dried ground peat samples

Some volume lost during filtration

[illegible]

Table B-3: Cation Exchange Capacity

EXPERIMENTAL PROCEDURE					
100 mL of 0.5 M HCl: Shake for 30 min - HCl displaces cations - 0.5 g oven-dried, ground sample					
Filtered samples using Whatman No. 41 Filter Paper: Washed to remove Cl ions					
100 mL of 0.5M Barium Acetate to fibers: Shake for 30 min; Filter samples using Whatman No. 41 filter paper					
Add 5 drops of phenolphthaleine indicator to filtrate: Titrate with NaOH until solution turns pink (endpoint)					
THEORY/RATIONALE					
HCl displaces cations					
Distilled water displaces Cl ions					
Barium acetate weak acid-Barium occupies sites					
NaOH neutralizes weak acid (acetic acid) formed from Barium dissociation					
REFERENCES					
McKeague (1978) Manuel de methodes d'echantillonnage et d'analyse des sols (p.99)					
NRC (1979) Peat testing Manual (p.109)					
NOTES					
$[\text{NaOH Volume (mL)}][0.09798][\text{Sample Volume (100mL)}]/[\text{Sample Weight (0.5g-peat, 1.0g-control)}]$					
Control ECSS 7 - ~33.1 meq/100g -> 1.0 g					
Sample	NaOH (mL)	CEC (meq/100g)	Sample	NaOH (mL)	CEC (meq/100g)
1-1	5.2	114.8	C-1	3.4	33.3
1-2	5.1	112.5	C-2	3.6	35.3
1-3	5.5	121.4	C-3	3.5	34.3
2-1	5.5	121.4	<p>Average CEC 119.3</p> <p>St. Dev. 4.44</p>		
2-2	5.3	117.0			
2-3	5.5	121.4			
3-1	5.3	117.0			
3-2	5.2	114.8			
3-3	5.3	117.0			
4-1	5.4	119.2			
4-2	5.2	114.8			
4-3	5.3	117.0			
5-1	5.6	123.6			
5-2	5.5	121.4			
5-3	5.4	119.2			
6-1	5	110.3			
6-2	5.3	117.0			
6-3	5.3	117.0			
7-1	5.8	128.0			
7-2	5.6	123.6			
7-3	5.4	119.2			
8-1	5.7	125.8			
8-2	5.7	125.8			
8-3	5.6	123.6			

Table B-4: Moisture Content

EXPERIMENTAL PROCEDURE						
Weighed dish: Weighed 10.0 g or 2.0 g of peat: Dried at 9°C for 48 hours: Recorded new sample weight						
THEORY/RATIONALE						
Dried at 90°C rather than 105°C to avoid loss of organic material						
REFERENCES						
ASTM Standards: D 2974-87: Standard Test Method for Moisture, Ash, and Organic Matter of Peat and Other Organic Soils Laboratory Methods for Testing Peat-Ontario Peatland Inventory Project: Ontario Geological Survey Misc. Paper 145						
NOTES						
Air-dried ground peat Sample Mill grinding to <0.5mm Air-dried peat, 1/4" sieve						
Air-Dried - 1/4" Sieved samples						
Sample	Dish + Foil (g)	Sample (g)	Initial Sample (g)	Final Sample (g)	Moisture (g)	Moisture (%)
1	62.18	10.08	72.26	71.24	1.02	11.20
2	61.00	10.07	71.07	70.17	0.90	9.87
3	60.25	10.07	70.32	69.45	0.87	9.51
4	60.46	10.08	70.54	69.63	0.91	9.96
5	59.57	10.03	69.60	68.69	0.91	9.93
6	59.67	10.07	69.74	68.17	1.57	18.53
7	61.02	10.04	71.06	70.12	0.94	10.34
8	63.67	10.04	73.71	72.78	0.93	10.17
Average					1.01	11.19
St. Dev.					0.23	3.01
Air-Dried - Finely Ground (<500 um) 1/4" Sieved samples						
Sample	Dish + Foil (g)	Sample (g)	Initial Sample (g)	Final Sample (g)	Moisture (g)	Moisture (%)
1	0.99	2.00	2.99	2.81	0.18	9.89
2	0.99	2.00	2.99	2.83	0.16	8.70
3	0.99	2.00	2.99	2.83	0.16	8.70
4	0.99	2.00	2.99	2.85	0.14	7.53
5	0.99	2.00	2.99	2.83	0.16	8.70
6	0.99	2.00	2.99	2.83	0.16	8.70
7	0.99	2.00	2.99	2.83	0.16	8.70
8	0.99	2.00	2.99	2.85	0.14	7.53
Average					0.16	8.55
St. Dev.					0.01	0.76

Table B-7: pH of Peat in Water and Calcium Chloride

EXPERIMENTAL PROCEDURE		
50 mL of distilled-deionized water or CaCl ₂ to 3.0 g oven-dried peat		
Shake for 30 min		
Measure pH with pH probe with temperature compensation		
THEORY/RATIONALE		
Expresses degree of acidity of peat suspended in solution		
pH readings in water modified by salts, while pH measured in CaCl ₂ influenced by salt concentration		
pH values in CaCl ₂ 0.5 to 0.8 units below pH in water because H ⁺ released due to cation exchange in CaCl ₂		
REFERENCES		
Levesque et al. 1980		
ASTM Standard D2976-71		
NOTES		
Sample No.	pH (CaCl ₂)	pH (Water)
1	2.96	3.80
2	3.02	3.83
3	3.01	3.81
4	3.02	3.80
5	3.00	3.75
6	3.01	3.77
7	3.00	3.81
8	3.02	3.84
Average	3.01	3.80
St. Dev.	0.02	0.03

Table B-8: Optical Density

EXPERIMENTAL PROCEDURE			
10mL of 0.025 M tetrasodium pyrophosphate to 1.0g of oven-dried peat (ground w/ cyclone sample Mill); Shake for 16 hrs			
Filtered samples with Whatman No. 42 Filter Paper			
2mL of filtrate + 8 mL of 0.025 M tetrasodium pyrophosphate (1:5)			
Tetrasodium pyrophosphate used to calibrate (zero) Perkin Elmer Lambda 3 UV/VIS Spectrophotometer			
Measured UV at 465, 550 and 665nm (280nm unstable)			
THEORY/RATIONALE			
280nm-Aromatic structures-Carbon quantity corresponding to aromatics			
465nm & 665nm-molecular dimensions-the higher the relative value the more stable (more humified) and vice versa			
Carbon in solution - can get interference due to Fe or Mg presence			
550nm (Kaila)-between 465nm and 665nm - can get interference due to pyrophosphate			
REFERENCES			
Manuel de methodes d'échantillonnage et d'analyse des sols - Agriculture Canada Library			
Les proprietes physiques, chimiques et morphologiques de quelques tourbes du Quebec et de l'Ontario			
NOTES			
Optical density-Physical state: state of decomposition; mesic to humic state			
CEC-Chemical state: state of oxidation and available functional sites moderate to low CEC mesic to fibric			
Indication of its chemical reactivity			
Use to compare with other peats			
Sample	465 (nm)	550 (nm)	665 (nm)
1-1	0.845	0.406	0.142
1-2	0.799	0.383	0.134
1-3	0.750	0.356	0.121
2-1	0.890	0.432	0.153
2-2	0.894	0.429	0.148
2-3	0.879	0.425	0.147
3-1	0.788	0.378	0.132
3-2	0.822	0.396	0.140
3-3	0.833	0.404	0.147
4-1	0.864	0.414	0.144
4-2	0.882	0.429	0.154
4-3	0.827	0.395	0.137
5-1	0.868	0.417	0.145
5-2	0.890	0.429	0.152
5-3	0.783	0.380	0.136
6-1	0.864	0.417	0.146
6-2	0.831	0.397	0.138
6-3	0.828	0.396	0.137
7-1	0.776	0.372	0.130
7-2	0.792	0.377	0.130
7-3	0.734	0.348	0.120
8-1	0.791	0.377	0.130
8-2	0.826	0.394	0.136
8-3	0.866	0.416	0.144

	465 nm	550 nm	665 nm
Average	0.830	0.399	0.139
St. Dev.	0.046	0.024	0.009
Kaila	39.863		
E ₄ :E ₆	5.959		

Table B-10: Constant Head (Column 2)

EXPERIMENTAL PROCEDURE										
Sieved air-dried peat using 1/4" sieve; Determined moisture content of peat										
Weighed columns: Packed columns in 4" lifts; Weighed columns + air-dried peat; Recorded ID, area and length of peat										
Flooded columns using constant head apparatus for 24 hours; Flow in = flow out										
For a constant head of 51.5 cm, collected water samples at 1 minute intervals in preweighed set of beakers										
Recorded weight of beaker and water; Determined weight of water; Computed cumulative volume of water collected over time										
Plotted cumulative volume of water Vs. time and calculated flow rate; Computed hydraulic conductivity										
Repeated procedure for constant heads of 28.5 and 69.0; Calculated average hydraulic conductivity										
THEORY/RATIONALE										
Assumed 1 g of water = 1 cm ³ of water										
REFERENCES										
ASTM Standard D 4511-93: Standard Test Method for Hydraulic Conductivity of Essentially Saturated Peat (Constant Head)										
Laboratory Methods for Testing Peat-Ontario Peatland Inventory Project: Ontario Geological Survey Misc. Paper 145										
NOTES										
Column 2										
Bulk Density = 251.1 (AD), 223.0 (OD)										
Modified ASTM Standards Method										
Time (min)	Beaker Weight (g)	Beaker+H ₂ O Weight (g)	H ₂ O (1) Weight (g)	Cum. H ₂ O (1) Vol. (cm ³)	Beaker+H ₂ O Weight (g)	H ₂ O (2) Weight (g)	Cum. H ₂ O (2) Vol. (cm ³)	Beaker+H ₂ O Weight (g)	H ₂ O (3) Weight (g)	Cum. H ₂ O (3) Vol. (cm ³)
1	81.66	95.38	13.72	13.72	89.46	7.80	7.80	100.92	19.26	19.26
2	84.71	98.65	13.94	27.66	92.09	7.38	15.18	104.14	19.43	38.69
3	82.34	96.11	13.77	41.43	89.23	6.89	22.07	101.69	19.35	58.04
4	86.10	100.13	14.03	55.45	93.43	7.33	29.39	105.22	19.12	77.15
5	82.16	96.31	14.15	69.61	89.37	7.21	36.61	101.21	19.05	96.21
6	81.42	95.38	13.96	83.56	88.69	7.27	43.87	100.69	19.27	115.47
7	66.33	80.52	14.19	97.76	73.54	7.21	51.09	85.22	18.89	134.37
8	81.31	95.36	14.05	111.81	88.65	7.34	58.43	100.82	19.51	153.88
9	67.41	80.98	13.57	125.38	74.81	7.40	65.83	86.64	19.23	173.11
10	81.01	95.25	14.24	139.62	88.75	7.74	73.57	100.40	19.39	192.50
11	87.40	101.51	14.12	153.73	95.10	7.71	81.27	107.33	19.94	212.43
12	81.92	96.09	14.17	167.90	89.71	7.79	89.06	100.82	18.90	231.33
13	83.55	98.20	14.65	182.55	91.32	7.77	96.83	102.78	19.23	250.56
14	86.27	100.50	14.23	196.78	93.77	7.50	104.33	105.30	19.03	269.59
15	87.05	101.67	14.62	211.40	94.36	7.31	111.64	105.87	18.82	288.41
16	81.46	95.61	14.15	225.55	88.60	7.14	118.78	100.42	18.96	307.37
17										
18										
19										
20										
D (cm)	L (cm)	Q (cm ³ /min)	K _D (cm/s)	Q ₁ (cm ³ /min)	K ₁ (cm/s)	Q ₂ (cm ³ /min)	K ₂ (cm/s)	Q ₃ (cm ³ /min)	K ₃ (cm/s)	
10.10	54.70	14.11	0.0031			7.44	0.0030	19.24	0.0032	
A (cm ²)	K _D (cm/s)	H ₁ (cm)	K ₁ (cm/s)	H ₂ (cm)	K ₂ (cm/s)	H ₃ (cm)	K ₃ (cm/s)			
80.12	0.0031	51.40	--			28.40	--	69.00	--	

Table B-11: Constant Head (Column 3)

EXPERIMENTAL PROCEDURE										
Sieved air-dried peat using 1/4" sieve; Determined moisture content of peat										
Weighed columns; Packed columns in 4" lifts; Weighed columns + air-dried peat; Recorded ID, area and length of peat										
Flooded columns using constant head apparatus for 24 hours; Flow in = flow out										
For a constant head of 51.5 cm, collected water samples at 1 minute intervals in preweighed set of beakers										
Recorded weight of beaker and water; Determined weight of water; Computed cumulative volume of water collected over time										
Plotted cumulative volume of water Vs. time and calculated flow rate; Computed hydraulic conductivity										
Repeated procedure for constant heads of 28.5 and 69.0; Calculated average hydraulic conductivity										
THEORY/RATIONALE										
Assumed 1 g of water = 1 cm ³ of water										
REFERENCES										
ASTM Standard D 4511-93: Standard Test Method for Hydraulic Conductivity of Essentially Saturated Peat (Constant Head)										
Laboratory Methods for Testing Peat-Ontario Peatland Inventory Project: Ontario Geological Survey Misc. Paper 145										
NOTES										
Column 3										
Bulk Density = 226.2 (AD), 200.9 (OD)										
Modified ASTM Standards Method										
Time (min)	Beaker Weight (g)	Beaker + H ₂ O Weight (g)	H ₂ O (l) Weight (g)	Flow (cm ³)	Flow (cm ³)	Flow (cm ³)	Flow (cm ³)	Flow (cm ³)	Flow (cm ³)	Flow (cm ³)
1	81.66	120.56	38.90	38.90	100.54	18.88	18.88	130.30	48.64	48.64
2	84.71	120.13	35.42	74.32	103.22	18.51	37.39	132.23	47.52	96.16
3	82.34	117.90	35.56	109.88	101.58	19.24	56.63	130.06	47.72	143.88
4	86.10	122.44	36.34	146.22	105.13	19.02	75.65	132.43	46.33	190.20
5	82.16	118.48	36.32	182.54	101.22	19.06	94.71	129.48	47.32	237.53
6	81.42	117.56	36.14	218.68	100.48	19.06	113.77	127.69	46.27	283.79
7	66.33	101.57	35.24	253.91	84.44	18.11	131.88	111.33	45.00	328.80
8	81.31	117.95	36.64	290.55	100.82	19.51	151.39	127.58	46.27	375.07
9	67.41	103.84	36.43	326.98	85.67	18.26	169.65	112.83	45.42	420.49
10	81.01	117.72	36.71	363.69	99.95	18.94	188.59	127.94	46.93	467.42
11	87.40	124.77	37.37	401.06	106.74	19.34	207.93	133.25	45.86	513.27
12	81.92	117.79	35.87	436.93	100.97	19.05	226.99	128.02	46.10	559.37
13	83.55	120.53	36.98	473.92	102.65	19.10	246.08	129.62	46.07	605.44
14	86.27	123.54	37.28	511.19	105.29	19.02	265.10	132.89	46.62	652.06
15	87.05	124.09	37.04	548.23	105.95	18.89	283.99	133.34	46.29	698.35
16	81.46	118.57	37.11	585.34	100.30	18.84	302.83	127.55	46.09	744.44
17										
18										
19										
20										
D (cm)	L (cm)	Q _t (cm ³ /min)	K ₁ (cm/s)	K ₂ (cm/s)	K ₃ (cm/s)	K ₄ (cm/s)	K ₅ (cm/s)	K ₆ (cm/s)	K ₇ (cm/s)	K ₈ (cm/s)
10.10	54.90	36.44	0.0081		18.94	0.0076		46.26	0.0077	
A (cm ²)	L _p (cm/s)	H (cm)	K ₁ (cm/s)	K ₂ (cm/s)	K ₃ (cm/s)	K ₄ (cm/s)	K ₅ (cm/s)	K ₆ (cm/s)	K ₇ (cm/s)	K ₈ (cm/s)
80.12	0.0078	51.40	--		28.50	--		69.00	--

Figure B-1: Constant Head Test – Column 2

Figure B-2: Constant Head Test – Column 3

Table B-12: Constant Head (Column 4)

EXPERIMENTAL PROCEDURE										
Sieved air-dried peat using 1/4" sieve; Determined moisture content of peat										
Weighed columns: Packed columns in 4" lifts; Weighed columns + air-dried peat; Recorded ID, area and length of peat										
Flooded columns using constant head apparatus for 24 hours; Flow in = flow out										
For a constant head of 51.5 cm, collected water samples at 1 minute intervals in preweighed set of beakers										
Recorded weight of beaker and water; Determined weight of water; Computed cumulative volume of water collected over time										
Plotted cumulative volume of water Vs. time and calculated flow rate; Computed hydraulic conductivity										
Repeated procedure for constant heads of 28.5 and 69.0; Calculated average hydraulic conductivity										
THEORY/RATIONALE										
Assumed 1 g of water = 1 cm ³ of water										
REFERENCES										
ASTM Standard D 4511-93: Standard Test Method for Hydraulic Conductivity of Essentially Saturated Peat (Constant Head)										
Laboratory Methods for Testing Peat-Ontario Peatland Inventory Project: Ontario Geological Survey Misc. Paper 145										
NOTES										
Column 4										
Bulk Density = 250.9 (AD), 222.8 (OD)										
Modified ASTM Standards Method										
Time (min)	Beaker Weight (g)	Beaker+H ₂ O Weight (1) (g)	H ₂ O (1) Weight (g)	Cumulative H ₂ O (1) Vol (cm ³)	Beaker+H ₂ O Weight (2) (g)	H ₂ O (2) Weight (g)	Cumulative H ₂ O (2) Vol (cm ³)	Beaker+H ₂ O Weight (3) (g)	H ₂ O (3) Weight (g)	Cumulative H ₂ O (3) Vol (cm ³)
1	81.66	96.72	15.06	15.06	89.29	7.63	7.63	102.26	20.60	20.60
2	84.71	99.02	14.31	29.37	92.41	7.70	15.33	105.56	20.85	41.45
3	82.34	96.62	14.28	43.65	90.00	7.66	22.99	102.18	19.84	61.29
4	86.10	100.03	13.93	57.57	93.74	7.64	30.62	106.78	20.68	81.96
5	82.16	96.30	14.14	71.72	89.95	7.79	38.42	102.43	20.27	102.24
6	81.42	96.01	14.59	86.30	89.15	7.73	46.14	101.27	19.85	122.08
7	66.33	80.43	14.10	100.41	74.23	7.90	54.05	86.41	20.08	142.17
8	81.31	95.79	14.48	114.89	89.30	7.99	62.04	101.76	20.45	162.62
9	67.41	81.71	14.30	129.19	75.40	7.99	70.03	87.67	20.26	182.88
10	81.01	95.75	14.74	143.93	88.85	7.84	77.87	101.45	20.44	203.32
11	87.40	101.76	14.37	158.29	95.14	7.75	85.61	108.05	20.66	223.97
12	81.92	96.47	14.55	172.84	89.99	8.07	93.68	101.94	20.02	243.99
13	83.55	97.75	14.20	187.04	91.79	8.24	101.92	103.97	20.42	264.41
14	86.27	100.68	14.41	201.45	93.88	7.61	109.53	107.15	20.88	285.29
15	87.05	101.82	14.77	216.22	95.04	7.99	117.52	107.32	20.27	305.56
16	81.46	95.54	14.08	230.30	89.54	8.08	125.60	101.72	20.26	325.82
17										
18										
19										
20										
ID (cm)	L (cm)	Q _t (cm ³ /min)	k _{xy} (cm/s)	Q _t (cm ³ /min)	k _{xy} (cm/s)	Q _t (cm ³ /min)	k _{xy} (cm/s)	Q _t (cm ³ /min)	k _{xy} (cm/s)	Q _t (cm ³ /min)
10.10	54.50	14.37	0.0032		7.88	0.0031		20.33	0.0033	
A (cm ²)	k _{xy} (cm/s)	h ₁ (cm)	k _{xy} (cm/s)	h ₂ (cm)	k _{xy} (cm/s)	h ₃ (cm)	k _{xy} (cm/s)	h ₄ (cm)	k _{xy} (cm/s)	h ₅ (cm)
80.12	0.0032	51.50	--		28.50	--		69.00	--	

Table B-13: Constant Head (Column 5)

EXPERIMENTAL PROCEDURE										
Sieved air-dried peat using 1/4" sieve; Determined moisture content of peat										
Weighed columns; Packed columns in 4" lifts; Weighed columns + air-dried peat; Recorded ID, area and length of peat										
Flooded columns using constant head apparatus for 24 hours; Flow in = flow out										
For a constant head of 51.5 cm, collected water samples at 1 minute intervals in preweighed set of beakers										
Recorded weight of beaker and water; Determined weight of water; Computed cumulative volume of water collected over time										
Plotted cumulative volume of water Vs. time and calculated flow rate; Computed hydraulic conductivity										
Repeated procedure for constant heads of 28.5 and 69.0; Calculated average hydraulic conductivity										
THEORY/RATIONALE										
Assumed 1 g of water = 1 cm ³ of water										
REFERENCES										
ASTM Standard D 4511-93: Standard Test Method for Hydraulic Conductivity of Essentially Saturated Peat (Constant Head)										
Laboratory Methods for Testing Peat-Ontario Peatland Inventory Project: Ontario Geological Survey Misc. Paper 145										
NOTES										
Column 5										
Bulk Density = 202.0 (AD), 179.4 (OD)										
Modified ASTM Standards Method										
Time (min)	Beaker Weight (g)	Beaker + H ₂ O Weight (g)	H ₂ O (1) Weight (g)	Cum. H ₂ O (1) Vol. (cm ³)	Beaker + H ₂ O Weight (g)	H ₂ O (2) Weight (g)	Cum. H ₂ O (2) Vol. (cm ³)	Beaker + H ₂ O Weight (g)	H ₂ O (3) Weight (g)	Cum. H ₂ O (3) Vol. (cm ³)
1	81.66	161.85	80.19	80.19	107.72	26.06	26.06	192.31	110.65	110.65
2	84.71	164.82	80.11	160.30	116.12	31.41	57.47	195.63	110.92	221.57
3	82.34	162.10	79.76	240.06	113.65	31.31	88.78	192.76	110.42	331.99
4	86.10	166.04	79.94	319.99	123.92	37.82	126.59	197.13	111.03	443.01
5	82.16	162.53	80.37	400.37	122.12	39.96	166.56	193.17	111.01	554.03
6	81.42	161.81	80.39	480.75	122.42	41.00	207.55	191.71	110.29	664.31
7	66.33	145.12	78.79	559.55	108.43	42.10	249.66	175.86	109.53	773.85
8	81.31	162.44	81.13	640.68	123.58	42.27	291.93	191.22	109.91	883.76
9	67.41	147.26	79.85	720.53	110.24	42.83	334.76	176.81	109.40	993.16
10	81.01	161.76	80.75	801.28	124.97	43.96	378.72	191.19	110.18	1103.34
11	87.40	167.33	79.94	881.21	130.39	43.00	421.71	198.32	110.93	1214.26
12	81.92	162.14	80.22	961.43	125.73	43.81	465.52	190.93	109.01	1323.27
13	83.55	164.43	80.88	1042.31	127.86	44.31	509.83	193.42	109.87	1433.14
14	86.27	167.08	80.81	1123.12	131.07	44.80	554.63	196.43	110.16	1543.30
15	87.05	166.83	79.78	1202.90	132.80	45.75	600.38	197.09	110.04	1653.34
16	81.46	161.73	80.27	1283.17	125.77	44.31	644.69	192.76	111.30	1764.64
17										
18										
19										
20										
ID (cm)	L (cm)	Q _t (cm ³ /min)	k _D (cm/s)	Q _t (cm ³ /min)	k _D (cm/s)	Q _t (cm ³ /min)	k _D (cm/s)	Q _t (cm ³ /min)	k _D (cm/s)	Q _t (cm ³ /min)
10.10	54.70	80.22	0.0177		43.76	0.0175		110.12	0.0182	
A (cm ²)	k _D (cm/s)	H (cm)	k _D (cm/s)	Q _t (cm ³ /min)	k _D (cm/s)	Q _t (cm ³ /min)	k _D (cm/s)	H (cm)	k _D (cm/s)	Q _t (cm ³ /min)
80.12	0.0178	51.50	--		28.50	--		69.00	--

Figure B-3: Constant Head Test – Column 4

Figure B-4: Constant Head Test – Column 5

Table B-14: Constant Head (Column 6)

EXPERIMENTAL PROCEDURE										
Sieved air-dried peat using 1/4" sieve; Determined moisture content of peat										
Weighed columns: Packed columns in 4" lifts; Weighed columns + air-dried peat; Recorded ID, area and length of peat										
Flooded columns using constant head apparatus for 24 hours; Flow in = flow out										
For a constant head of 51.5 cm, collected water samples at 1 minute intervals in preweighed set of beakers										
Recorded weight of beaker and water; Determined weight of water; Computed cumulative volume of water collected over time										
Plotted cumulative volume of water Vs. time and calculated flow rate; Computed hydraulic conductivity										
Repeated procedure for constant heads of 28.5 and 69.0; Calculated average hydraulic conductivity										
THEORY/RATIONALE										
Assumed 1 g of water = 1 cm ³ of water										
REFERENCES										
ASTM Standard D 4511-93: Standard Test Method for Hydraulic Conductivity of Essentially Saturated Peat (Constant Head)										
Laboratory Methods for Testing Peat-Ontario Peatland Inventory Project: Ontario Geological Survey Misc. Paper 145										
NOTES										
Column 6										
Bulk Density = 196.6 (AD), 174.6 (OD)										
Modified ASTM Standards Method										
Time (min)	Beaker Weight (g)	Beaker+H ₂ O Weight (g)	H ₂ O (3) Weight (g)	Cumulative H ₂ O (3) Vol. (cm ³)	Beaker+H ₂ O Weight (g)	H ₂ O (2) Weight (g)	Cumulative H ₂ O (2) Vol. (cm ³)	Beaker+H ₂ O Weight (g)	H ₂ O (3) Weight (g)	Cumulative H ₂ O (3) Vol. (cm ³)
1	81.66	187.62	105.96	105.96	121.19	39.53	39.53	225.33	143.67	143.67
2	84.71	188.61	103.90	209.86	134.10	49.39	88.92	226.93	142.22	285.89
3	82.34	187.06	104.72	314.58	130.68	48.34	137.26	223.33	140.99	426.88
4	86.10	190.59	104.49	419.06	139.65	53.55	190.80	228.76	142.66	569.53
5	82.16	184.02	101.86	520.93	136.78	54.62	245.43	225.32	143.16	712.70
6	81.42	186.42	105.00	625.92	136.76	55.34	300.76	221.63	140.21	852.90
7	66.33	168.14	101.81	727.74	119.78	53.45	354.22	206.55	140.22	993.13
8	81.31	184.72	103.41	831.15	139.17	57.86	412.08	223.86	142.55	1135.68
9	67.41	170.79	103.38	934.53	123.40	55.99	468.07	208.37	140.96	1276.64
10	81.01	184.96	103.95	1038.48	140.25	59.24	527.31	222.49	141.48	1418.12
11	87.40	191.93	104.54	1143.01	146.64	59.25	586.55	228.55	141.16	1559.27
12	81.92	185.50	103.58	1246.59	141.59	59.67	646.22	223.04	141.12	1700.39
13	83.55	186.57	103.02	1349.61	143.11	59.56	705.78	225.66	142.11	1842.50
14	86.27	189.95	103.68	1453.29	144.81	58.54	764.32	228.36	142.09	1984.59
15	87.05	191.75	104.70	1557.99	146.37	59.32	823.64	228.43	141.38	2125.97
16	81.46	185.70	104.24	1662.23	140.62	59.16	882.80	223.45	141.99	2267.96
17										
18										
19										
20										
ID (cm)	A (cm ²)	Q _t (cm ³ /min)	k _t (cm/s)	Q _t (cm ³ /min)	k _t (cm/s)	Q _t (cm ³ /min)	k _t (cm/s)	Q _t (cm ³ /min)	k _t (cm/s)	Q _t (cm ³ /min)
10.10	52.90	103.63	0.0221		59.05	0.0228		141.53	0.0226	
A (cm ²)	k _t (cm/s)	H (cm)	k _t (cm/s)	H (cm)	k _t (cm/s)	H (cm)	k _t (cm/s)	H (cm)	k _t (cm/s)	H (cm)
80.12	0.0225	51.50	--		28.50	--		69.00	--	

Table B-15: Constant Head (Column 8)

EXPERIMENTAL PROCEDURE										
Sieved air-dried peat using 1/4" sieve; Determined moisture content of peat										
Weighed columns: Packed columns in 4" lifts; Weighed columns + air-dried peat: Recorded ID, area and length of peat										
Flooded columns using constant head apparatus for 24 hours; Flow in = flow out										
For a constant head of 51.5 cm. collected water samples at 1 minute intervals in preweighed set of beakers										
Recorded weight of beaker and water; Determined weight of water; Computed cumulative volume of water collected over time										
Plotted cumulative volume of water Vs. time and calculated flow rate; Computed hydraulic conductivity										
Repeated procedure for constant heads of 28.5 and 69.0; Calculated average hydraulic conductivity										
THEORY/RATIONALE										
Assumed 1 g of water = 1 cm ³ of water										
REFERENCES										
ASTM Standard D 4511-93: Standard Test Method for Hydraulic Conductivity of Essentially Saturated Peat (Constant Head)										
Laboratory Methods for Testing Peat-Ontario Peatland Inventory Project: Ontario Geological Survey Misc. Paper 145										
NOTES										
Column 8										
Bulk Density = 216.3 (AD), 192.1 (OD)										
Modified ASTM Standards Method										
Time (min)	Beaker Weight (g)	Beaker+H ₂ O Weight (g)	H ₂ O (l) Weight (g)	Cum. H ₂ O Vol (cm ³)	Beaker+H ₂ O Weight (g)	H ₂ O (l) Weight (g)	Cum. H ₂ O Vol (cm ³)	Beaker+H ₂ O Weight (g)	H ₂ O (l) Weight (g)	Cum. H ₂ O Vol (cm ³)
1	81.66	130.49	48.83	48.83	110.26	28.60	28.60	152.41	70.75	70.75
2	84.71	132.72	48.01	96.84	112.81	28.10	56.70	156.19	71.48	142.23
3	82.34	131.64	49.30	146.14	111.48	29.14	85.84	153.17	70.83	213.06
4	86.10	135.35	49.25	195.38	114.33	28.23	114.06	157.52	71.42	284.47
5	82.16	131.57	49.41	244.80	110.61	28.45	142.52	154.19	72.03	356.51
6	81.42	130.34	48.92	293.71	109.81	28.39	170.90	152.83	71.41	427.91
7	66.33	114.65	48.32	342.04	94.03	27.70	198.61	137.71	71.38	499.30
8	81.31	130.79	49.48	391.52	109.64	28.33	226.94	153.10	71.79	571.09
9	67.41	116.62	49.21	440.73	95.77	28.36	255.30	138.70	71.29	642.38
10	81.01	130.49	49.48	490.21	110.08	29.07	284.37	152.67	71.66	714.04
11	87.40	136.98	49.59	539.79	116.41	29.02	313.38	158.77	71.38	785.41
12	81.92	131.27	49.35	589.14	110.65	28.73	342.11	154.11	72.19	857.60
13	83.55	133.39	49.84	638.98	113.98	30.43	372.54	155.92	72.37	929.97
14	86.27	136.18	49.91	688.89	115.25	28.98	401.52	157.20	70.93	1000.90
15	87.05	136.46	49.41	738.30	116.72	29.67	431.19	158.35	71.30	1072.20
16	81.46	132.65	51.19	789.49	110.17	28.71	459.90	153.60	72.14	1144.34
17										
18										
19										
20										
ID (cm)	L (cm)	Q _t (cm ³ /min)	k _m (cm/s)		Q _t (cm ³ /min)	k _m (cm/s)		Q _t (cm ³ /s)	k _m (cm/s)	
10.10	52.60	49.33	0.0105		28.72	0.0110		71.59	0.0113	
A (cm ²)	k _c (cm/s)	H (cm)	k _{avg} (cm/s)		H (cm)	k _{avg} (cm/s)		H (cm)	k _{avg} (cm/s)	
80.12	0.0109	51.50	--		28.50	--		69.10	--

Figure B-5: Constant Head Test – Column 6

Figure B-6: Constant Head Test – Column 8

Table B-16: Water Holding Capacity - Columns 2, 3 and 4

EXPERIMENTAL PROCEDURE							
Sieved air-dried peat using 1/4" sieve: Determined moisture content of peat							
Weighed columns: Packed columns in 4" lifts: Weighed columns + air-dried peat: Recorded volume of peat							
Flooded columns using constant head apparatus for 24 hours: Flow in = flow out							
Created suction equivalent to 15" of water and drained columns							
Re-wetted sample again and drained by suction: Repeated until consistent results were obtained							
THEORY/RATIONALE							
REFERENCES							
ASTM Standard D 2980-71							
Laboratory Methods for Testing Peat-Ontario Peatland Inventory Project: Ontario Geological Survey Misc. Paper 145							
NOTES							
Modified ASTM method							
Air-dried weight basis							
Trial	Column # (g)	Peat Volume (m)	Dry Peat (g)	Wet Peat Column (g)	Wet Peat (g)	Water Holding Capacity (Air) (%)	Water Holding Capacity (Oven) (%)
1	2	0.00438	(Air-dry)	6218.4	4842.6	340.1	395.5
2			1100.4	6241.8	4866.0	342.2	397.9
3			(Oven-dry)	6242.5	4866.7	342.3	398.0
4			977.3	6243.9	4868.1	342.4	398.1
					Average	342.3	397.4
					St. Dev.	0.1	0.1
1	3	0.00421	(Air-dry)	5419.4	4034.2	323.2	376.6
2			(Air-dry)	5375.4	3990.2	318.6	371.4
3			953.2	5352.2	3967.0	316.2	368.6
4			(Oven-dry)	5390.5	4005.3	320.2	373.1
5			846.5	5386.6	4001.4	319.8	372.7
6				5385.7	4000.5	319.7	372.6
					Average	319.0	372.5
					St. Dev.	1.9	2.1
1	4	0.00437	(Air-dry)	6194.3	4805.1	338.7	393.9
2			1095.4	6161.2	4772.0	335.6	390.5
3			(Oven-dry)	6152.9	4763.7	334.9	389.7
4			972.8	6188.9	4799.7	338.2	393.4
					Average	336.2	391.9
					St. Dev.	1.7	1.9

Table B-17: Water Holding Capacity - Columns 5, 6 and 8

EXPERIMENTAL PROCEDURE							
Sieved air-dried peat using 1/4" sieve; Determined moisture content of peat							
Weighed columns; Packed columns in 4" lifts; Weighed columns + air-dried peat; Recorded volume of peat							
Flooded columns using constant head apparatus for 24 hours; Flow in = flow out							
Created suction equivalent to 15" of water and drained columns							
Re-wetted sample again and drained by suction; Repeated until consistent results were obtained							
THEORY/RATIONALE							
REFERENCES							
ASTM Standard D 2980-71							
Laboratory Methods for Testing Peat-Ontario Peatland Inventory Project: Ontario Geological Survey Misc. Paper 145							
NOTES							
Modified ASTM method							
Oven-dried weight basis							
Column	Peat	Peat	Dry Peat	Wet Peat	Wet Peat	Wet Peat	Wet Peat
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
1	5	0.00424	(Air-dry)	4750.5	3381.6	295.0	344.8
2			856.0	4796.3	3427.4	300.4	350.8
3			(Oven-dry)	4802.6	3433.7	301.1	351.7
			760.2				
					Average	298.9	349.1
					St. Dev.	3.3	3.7
1	6	0.00434	(Air-dry)	4873.9	3504.6	310.5	362.2
2			853.8	4771.9	3402.6	298.5	348.7
3			(Oven-dry)	4763.0	3393.7	297.5	347.6
4			758.3	4744.9	3375.6	295.4	345.2
					Average	297.1	347.2
					St. Dev.	1.6	1.8
1	8	0.00440	(Air-dry)	5492.4	4123.1	333.4	388.0
2				5296.6	3927.3	312.8	364.8
3			951.4	5307.7	3938.4	314.0	366.1
4			(Oven-dry)	5278.6	3909.3	310.9	362.7
5			844.9	5221.7	3852.4	304.9	355.9
6				5227.6	3858.3	305.5	356.6
					Average	305.2	356.3
					St. Dev.	0.4	0.5

Table B-18: TDR Calibration**EXPERIMENTAL PROCEDURE**

A column was packed with peat; Determined initial dry mass of peat

Inserted two 15.0 cm (L) stainless steel probes into peat column; Moistened peat with known volume of distilled water

Determined apparent length (L_a) of TDR probe from oscilloscope reading connected to reflectometer using an x-y plotter

Computed apparent length of TDR probe using various volumes of water

Calculated dielectric constant (K_v) for each water volume; Plotted volumetric water content vs. dielectric constant

THEORY/RATIONALE**REFERENCES****NOTES**

Volume A	288.5 cm ³	Volume B	339.8 cm ³
cm/div	2 cm/division	time/div	0.833 ns/division
L	15 cm	c	30 ns/cm

Sample No.	Column	L (cm)	H ₂ O Volume (cm ³)	W.C. (volumetric)	W.C. (%)	K _v
1	B	7.8	281.59	0.8287	82.87	42.22
2	B	8.3	296.59	0.8728	87.28	47.80
3	B	8.5	299.99	0.8828	88.28	50.13
4	A	6.8	184.20	0.6385	63.85	32.09
5	A	7.3	220.40	0.7640	76.40	36.98
6	A	8.1	241.60	0.8374	83.74	45.53
7	A	8.3	253.80	0.8797	87.97	47.80
8	A	7.9	238.16	0.8255	82.55	43.31
9	B	7.3	264.44	0.7782	77.82	36.98
10	B	8.3	295.94	0.8709	87.09	47.80
11	B	8.7	320.94	0.9445	94.45	52.52
12	B	8.6	325.14	0.9569	95.69	51.32
13	B	8.5	304.49	0.8961	89.61	50.13
14	B	8.2	284.49	0.8372	83.72	46.66
15	B	7.5	264.49	0.7784	77.84	39.03
16	B	7.4	259.49	0.7637	76.37	38.00
17	B	5.8	197.75	0.5820	58.20	23.34

Table B-19: Peat Classification

EXPERIMENTAL PROCEDURE				
Classified peat on the basis of fiber content, ash content, acidity and water holding capacity Also included von Post classification				
THEORY/RATIONALE				
REFERENCES				
ASTM Standards: D 4427-92: Standard Classification of Peat Samples by Laboratory Testing				
NOTES				
Hemic (H ₄ -H ₆), high ash, highly acidic, moderately absorbent Sphagnum peat				
Test	Fiber	Hemic	Super	
Dry Weight	>1%	13-27%	<3%	
Fiber Content		65.88 (7.1)		
Test	H ₁ -H ₃	H ₄ -H ₆	H ₇ -H ₈	
Von Post	Fibric	Humic	Humic	
Degree of Humification		X		
Test	High Ash	Medium Ash	Low Ash	
Dry Weight	>1%	3-10%	<3%	
Ash Content	21.10 (4.51)			
Test	Highly Acidic	Highly Acidic	Highly Acidic	
pH in H ₂ O	<3.5	<3.5	<3.5	
Acidity	3.80 (0.03)			
Test	Extremely Absorbent	Highly Absorbent	Moderately Absorbent	Slightly Absorbent
Water Holding Capacity	>100%	100-1000%	50-100%	<50%
Absorbancy			X	

APPENDIX C

BATCH EXPERIMENTS

RAW DATA

Table C-4: Kinetic Study - pH 2.5, 30°C

EXPERIMENTAL PROCEDURE

Made up synthetic AMD solution; adjusted pH to 2.5; weighed 18-1.0 g specimens of pear

Added 150 mL of AMD solution: mixed on shaker at 180 rpm for specified time at 30°C

Filtered samples with 45um Millipore filters and acidified sample with 3 drops of concentrated HCl

Performed experiment in duplicate

Metal content analyzed via ICP in Department of Chemistry at Carleton University

THEORY/RATIONALE

Three controls mixed on shaker for 24 hour period along with other samples

C-1: 1.0 g of peat + 150 mL of distilled water

C-2: No pear + 150 mL of distilled water

C-3: No peat + 150 mL of AMD solution

REFERENCES

NOTES

Initial solution temperature 22.3°C

Incubator temperature 30°C

Initial solution pH 2.54

Sample	Time		P.L.		P.E.		T.M.		T.A.		T.B.		T.N.		T.C.		T.O.	
	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2
0.0 hr	22.3	22.3	2.5	2.5	200	200	92.7	91.9	104	105	26.7	26.6	19.7	20.3	20.6	20.5	6.18	6.28
0.25 hr	25.6	24.9	2.5	2.5	198	199	90.7	91.4	97.6	100	26.3	26.2	19.7	20.1	17.9	18.0	6.10	6.27
0.5 hr	26.1	26.1	2.5	2.5	197	197	90.9	91.2	97.7	98.6	26.3	26.2	19.5	19.8	17.7	17.8	6.02	6.24
0.75 hr	26.4	27.6	2.5	2.5	196	198	91.0	91.1	96.7	97.9	26.0	26.2	19.3	19.7	17.8	17.7	6.03	6.03
1.0 hr	27.7	28.5	2.5	2.5	195	193	90.6	89.9	96.3	97.7	26.2	26.1	19.5	19.3	17.6	17.6	6.05	5.86
1.25 hr	28.9	29.4	2.5	2.5	195	195	91.0	91.1	96.2	97.7	26.4	26.0	19.4	19.4	17.7	17.8	5.91	5.95
1.5 hr	28.4	28.8	2.5	2.5	193	194	90.4	90.6	96.5	95.5	26.1	26.3	19.4	19.5	17.6	17.9	5.92	5.85
1.75 hr	28.8	29.0	2.5	2.5	188	183	89.4	88.4	91.5	86.5	25.9	25.9	19.2	18.6	17.6	17.5	5.42	5.55
2.0 hr	29.2	29.7	2.5	2.5	183	182	89.0	88.5	89.5	86.7	26.2	25.7	17.9	18.7	17.5	17.5	5.43	5.17
2.25 hr	29.9	29.7	2.5	2.5	186	184	89.6	89.0	90.1	86.7	26.5	26.4	18.8	18.5	17.7	17.3	5.49	5.51
2.5 hr	29.3	30.3	2.5	2.5	186	176	89.2	87.2	91.1	85.4	25.7	24.3	18.7	17.4	17.5	17.2	5.43	5.16
2.75 hr	29.9	30.3	2.5	2.5	180	184	88.6	88.5	89.5	85.9	24.2	24.8	17.9	18.4	17.5	17.5	5.19	5.37
3.0 hr	29.6	30.3	2.5	2.5	183	179	88.3	87.6	90.6	86.6	24.7	25.0	18.5	17.8	17.5	17.2	5.32	5.25
3.5 hr	28.6	29.3	2.5	2.5	182	183	88.7	88.7	87.8	84.6	24.9	25.1	18.1	17.9	17.5	17.5	5.43	5.32
4.0 hr	29.0	29.8	2.5	2.5	176	176	86.7	87.1	85.1	84.2	24.7	24.7	17.2	17.0	17.0	17.3	5.26	5.02
6.0 hr	30.9	30.5	2.5	2.5	173	176	86.0	86.5	82.2	84.8	24.6	24.3	16.6	16.7	16.9	17.2	4.94	4.94
12.0 hr	29.6	30.7	2.4	2.4	171	172	86.0	86.5	82.5	83.9	23.6	23.9	16.5	16.6	17.1	17.1	4.83	4.77
24.0 hr	29.2	30.3	2.4	2.4	169	169	85.7	86.0	82.3	83.3	23.3	23.9	16.5	16.5	17.1	17.1	4.84	4.77
C-1	31.0	29.0	4.3	4.5	0.63	0.61	0.00	0.04	0.00	0.00	0.05	0.05	1.51	1.36	0.01	0.01	0.00	0.00
C-2	31.3	29.6	6.3	6.6	0.46	0.41	0.00	0.00	0.00	0.00	0.05	0.05	1.89	1.41	0.01	0.01	0.00	0.00
C-3	29.7	30.5	2.5	2.5	204	203	92.8	92.4	101	96.1	26.2	27.0	20.7	19.8	20.7	20.6	6.34	6.30
Det. Lim.		C-1	7.1	7.1	0.45	0.45	0.35	0.35	0.76	0.76	0.04	0.04	2.00	2.00	0.07	0.07	1.08	1.08
Precision		C-2	7.1	7.1	2.04	2.04	0.34	0.34	1.10	1.10	0.30	0.30	1.04	1.04	0.08	0.08	0.47	0.47
		C-3	2.5	2.5														

Table C-6: Equilibrium Study - Iron

EXPERIMENTAL PROCEDURE																	
Prepared 5L - 5 mM Fe solution using iron sulphate salt, adjusted pH to desired level using 1 N NaOH solution or 10% HCl solution																	
Weighed and placed 0.0g, 0.1g, 0.25g, 0.5g, 1.0g, 1.5, 2.0g and 4.0g of oven-dried peat sieved (No. 10) in 250mL serum bottles																	
Added 150mL of solution at specified pH to each of 8 serum bottles, allowed to mix using reciprocating shaker at 200 rpm for 24 hours																	
Allowed peat to settle for 20 min, recorded pH, filtered using 45 um Millipore filter, collected 50mL of filtrate and acidified																	
Tests performed in duplicate at ambient laboratory temperature (20°C)																	
THEORY/RATIONALE																	
Analysis of Freundlich and Langmuir isotherm to determine order of reaction and adsorption potential at each pH																	
REFERENCES																	
Amfalk <i>et al.</i> : 1996: <i>Water, Air, and Soil Pollution</i> : 87:131-148																	
Dissanayake and Weerassooriya: 1981: <i>International Journal of Environmental Studies</i> : 17:233-238																	
Gosset <i>et al.</i> : 1986: <i>Water Research</i> : 20(1):21-26																	
NOTES																	
Formation of yellowish fine precipitate at pH 4 and 5. Remains after shaking 24hrs.																	
pH may not group as much due to Fe(OH) ₃ precipitation which decreases pH																	
Formation of yellowish fine precipitate at pH 3. Clear after shaking 24hrs																	
Table A: Iron Adsorption Data (pH 3.0 to 5.0)																	
Sample	Fe C (mg/L)	pH = 3.0				pH = 4.0				pH = 5.0				pH = 6.0			
		wt/g	mg/g	pH	mg/g	wt/g	mg/g	pH	mg/g	wt/g	mg/g	pH	mg/g	wt/g	mg/g	pH	mg/g
A-1	287	0.000	5.0	3.9	275	0.000	4.0	3.9	273	0.000	3.0	3.0	280	0.000	2.0	2.0	287
A-2	287	0.100	5.0	3.9	253	0.102	4.0	4.0	254	0.104	3.0	3.2	263	0.102	2.0	2.0	284
A-3	287	0.251	5.0	3.9	222	0.251	4.0	3.8	229	0.252	3.0	3.4	241	0.250	2.0	2.0	279
A-4	287	0.501	5.0	3.9	180	0.504	4.0	4.0	192	0.501	3.0	3.8	211	0.501	2.0	2.1	270
A-5	287	1.003	5.0	3.9	109	1.004	4.0	3.9	135	1.002	3.0	3.8	156	1.001	2.0	2.3	252
A-6	287	1.504	5.0	4.1	52.6	1.500	4.0	4.0	85.6	1.502	3.0	3.9	100	1.503	2.0	2.5	225
A-7	287	2.004	5.0	4.3	31.6	2.002	4.0	4.1	54.6	2.005	3.0	4.1	53.6	2.005	2.0	2.9	183
A-8	287	4.003	5.0	4.1	11.5	4.005	4.0	3.9	18.2	4.000	3.0	4.4	25.1	4.002	2.0	3.2	78.1
Table B: Iron Adsorption Data (pH 3.0 to 5.0)																	
Sample	Fe C (mg/L)	pH = 3.0				pH = 4.0				pH = 5.0				pH = 6.0			
		wt/g	mg/g	pH	mg/g	wt/g	mg/g	pH	mg/g	wt/g	mg/g	pH	mg/g	wt/g	mg/g	pH	mg/g
B-1	285	0.000	5.0	3.9	269	0.000	4.0	3.8	280	0.000	3.0	3.0	280	0.000	2.0	2.1	282
B-2	285	0.101	5.0	3.9	248	0.101	4.0	3.9	261	0.103	3.0	3.3	262	0.103	2.0	2.1	279
B-3	285	0.251	5.0	4.0	218	0.251	4.0	3.8	234	0.251	3.0	3.5	239	0.255	2.0	2.1	274
B-4	285	0.503	5.0	3.9	171	0.502	4.0	3.9	196	0.500	3.0	3.6	211	0.501	2.0	2.1	266
B-5	285	1.004	5.0	4.0	101	1.002	4.0	3.9	129	1.002	3.0	3.8	148	1.004	2.0	2.4	244
B-6	285	1.504	5.0	4.1	50.3	1.500	4.0	4.0	81.7	1.501	3.0	3.9	98.3	1.504	2.0	2.7	213
B-7	285	2.005	5.0	4.2	30.3	2.004	4.0	4.2	52.4	2.003	3.0	3.9	69.7	2.003	2.0	2.9	182
B-8	285	4.004	4.9	3.9	11.5	4.004	4.0	4.3	15.8	4.004	3.0	4.2	27.1	4.001	2.0	3.3	72.4

Table C-7: Equilibrium Study - Aluminium

EXPERIMENTAL PROCEDURE																	
Prepared 5L - 5 mM Al solution using aluminum sulphate salt, adjusted pH to desired level using 1 N NaOH solution or 10% HCl solution																	
Weighed and placed 0.0g, 0.05g, 0.1g, 0.25g, 0.5g, 1.0g, 2.0g and 4.0g of oven-dried peat sieved (No. 10) in 250mL serum bottles																	
Added 150mL of solution at specified pH to each of 8 serum bottles, allowed to mix using reciprocating shaker at 200 rpm for 24 hours																	
Allowed peat to settle for 20 min, recorded pH, filtered using 45 um Millipore filter, collected 50mL of filtrate and acidified																	
Tests performed in duplicate at ambient laboratory temperature (20C)																	
THEORY/RATIONALE																	
Analysis of Freudlich and Langmuir isotherm to determine order of reaction and adsorption potential at each pH																	
REFERENCES																	
Arnfolk <i>et al.</i> : 1996: <i>Water, Air, and Soil Pollution</i> : 87:131-148																	
Dissanayake and Weerassooriya: 1981: <i>International Journal of Environmental Studies</i> : 17:233-238																	
Gosset <i>et al.</i> : 1986: <i>Water Research</i> : 20(1):21-26																	
NOTES																	
Difficult to stabilize pH at levels 4 and 5 which may explain some of the concentration results																	
pH decreases and rises again due to formation of Al(OH) ₃ precipitate and metal sorption																	
Cloudy white precipitate at pH 4 and 5																	
Clear at pH 3 and 2																	

Sample	In C (mg/L)	pH = 5.0				pH = 4.0				pH = 3.0				pH = 2.0			
		W(g)	Lang	Freud	Lang	W(g)	Lang	Freud	Lang	W(g)	Lang	Freud	Lang	W(g)	Lang	Freud	Lang
A-1	131	0.000	5.1	5.0	4.4	0.000	4.0	4.0	102	0.000	3.0	3.1	129	0.000	2.0	2.1	130
A-2	131	0.103	5.1	5.6	2.9	0.103	4.0	4.0	90.2	0.100	3.0	3.2	122	0.104	2.0	2.1	129
A-3	131	0.251	5.1	5.8	1.5	0.254	4.0	4.1	75.3	0.253	3.0	3.5	112	0.252	2.0	2.1	127
A-4	131	0.504	5.1	5.8	0.9	0.503	4.0	4.1	60.2	0.504	3.0	3.6	96.9	0.502	2.0	2.2	124
A-5	131	1.000	5.1	5.8	0.5	1.004	4.0	4.3	36.6	1.005	3.0	3.7	66.3	1.004	2.0	2.6	107
A-6	131	1.501	5.1	5.9	0.2	1.503	4.0	4.3	25.5	1.504	3.1	3.9	34.3	1.503	2.0	2.8	90.8
A-7	131	2.003	5.1	6.0	0.2	2.002	4.0	4.2	13.7	2.005	3.1	3.9	18.8	2.001	2.0	3.2	74.6
A-8	131	4.004	5.1	5.7	0.1	4.002	4.1	4.1	4.1	4.001	3.1	4.5	2.9	4.005	2.1	3.6	15.5

Sample	In C (mg/L)	pH = 5.0				pH = 4.0				pH = 3.0				pH = 2.0			
		W(g)	Lang	Freud	Lang	W(g)	Lang	Freud	Lang	W(g)	Lang	Freud	Lang	W(g)	Lang	Freud	Lang
B-1	133	0.000	5.0	4.8	4.3	0.000	4.0	4.0	112	0.000	3.0	3.2	130	0.000	2.0	2.1	133
B-2	133	0.101	5.0	5.2	2.8	0.105	4.0	4.0	100	0.101	3.0	3.3	123	0.102	2.0	2.1	132
B-3	133	0.250	5.0	5.5	1.2	0.253	4.0	4.0	83.7	0.254	3.0	3.4	114	0.253	2.0	2.2	130
B-4	133	0.502	5.0	5.6	0.5	0.504	4.0	4.0	67.8	0.500	3.0	3.6	99.4	0.501	2.0	2.3	123
B-5	133	1.000	5.0	5.6	0.3	1.000	4.0	4.0	38.1	1.002	3.0	3.6	71.0	1.004	2.0	2.6	111
B-6	133	1.502	5.0	5.8	0.3	1.503	4.0	4.1	30.4	1.504	3.0	3.7	45.9	1.504	2.0	2.8	97.1
B-7	133	2.003	5.0	5.8	0.2	2.004	4.0	4.3	10.3	2.003	3.0	3.9	22.2	2.002	2.0	3.1	84.4
B-8	133	4.000	5.1	5.6	0.1	4.002	4.0	4.2	4.7	4.005	3.0	4.4	2.8	4.003	2.0	3.8	17.1

Table C-8: Equilibrium Study - Zinc

EXPERIMENTAL PROCEDURE																	
Prepared 5L - 5 mM Zn solution using zinc sulphate salt, adjusted pH to desired level using 1 N NaOH solution or 10% HCl solution																	
Weighed and placed 0.0g, 0.05g, 0.1g, 0.25g, 0.5g, 1.0g, 2.0g and 4.0g of oven-dried peat sieved (No. 10) in 250mL serum bottles																	
Added 150mL of solution at specified pH to each of 8 serum bottles, allowed to mix using reciprocating shaker at 200 rpm for 24 hours																	
Allowed peat to settle for 20 min, recorded pH, filtered using 45 um Millipore filter, collected 50mL of filtrate sample and acidified																	
Tests performed in duplicate at ambient laboratory temperature (20°C)																	
THEORY/RATIONALE																	
Analysis of Freundlich and Langmuir isotherm to determine order of reaction and adsorption potential at each pH																	
REFERENCES																	
Armalk <i>et al.</i> : 1996: <i>Water, Air, and Soil Pollution</i> : 87:131-148																	
Dissanayake and Weerassooriya: 1981: <i>International Journal of Environmental Studies</i> : 17:233-238																	
Gosset <i>et al.</i> : 1986: <i>Water Research</i> : 20(1):21-26																	
NOTES																	
Sample	In C (mg/L)	pH=5.0				pH=5.5				pH=6.0				pH=7.0			
		Wt (g)	Initial pH	Final pH	Final C	Wt (g)	Initial pH	Final pH	Final C	Wt (g)	Initial pH	Final pH	Final C	Wt (g)	Initial pH	Final pH	Final C
A-1	331	0.000	5.0	5.3	330	0.000	4.0	4.2	328	0.000	3.0	3.0	331	0.000	2.0	2.1	331
A-2	331	0.101	5.0	4.5	317	0.102	4.0	4.0	315	0.103	3.0	3.1	322	0.102	2.0	2.1	326
A-3	331	0.252	5.0	4.2	297	0.254	4.0	4.0	298	0.253	3.0	3.1	310	0.254	2.0	2.1	321
A-4	331	0.505	5.0	4.3	273	0.504	4.0	4.0	272	0.504	3.0	3.4	292	0.502	2.0	2.1	319
A-5	331	1.005	5.0	4.3	220	1.003	4.0	3.9	221	1.002	3.0	3.6	263	1.005	2.0	2.2	313
A-6	331	1.502	5.0	4.1	185	1.504	4.0	3.8	190	1.504	3.0	3.8	232	1.503	2.0	2.3	306
A-7	331	2.002	5.0	4.0	160	2.005	4.0	3.9	165	2.004	3.0	3.8	199	2.002	2.0	2.5	299
A-8	331	4.000	5.1	3.8	86.0	4.005	4.0	3.8	94.0	4.004	3.0	3.9	135	4.004	2.0	2.8	275
Sample	In C (mg/L)	pH=5.0				pH=5.5				pH=6.0				pH=7.0			
		Wt (g)	Initial pH	Final pH	Final C	Wt (g)	Initial pH	Final pH	Final C	Wt (g)	Initial pH	Final pH	Final C	Wt (g)	Initial pH	Final pH	Final C
B-1	337	0.000	5.0	5.1	323	0.000	4.0	4.2	325	0.000	3.0	3.0	326	0.000	2.0	2.0	337
B-2	337	0.102	5.1	4.4	310	0.100	4.0	3.9	313	0.103	3.0	3.1	318	0.101	2.0	2.0	331
B-3	337	0.251	5.1	4.1	293	0.254	4.1	3.8	295	0.253	3.0	3.2	307	0.252	2.0	2.0	326
B-4	337	0.502	5.1	4.1	265	0.502	4.1	3.9	269	0.504	3.0	3.4	290	0.503	2.0	2.0	325
B-5	337	1.002	5.1	4.0	218	1.001	4.1	3.8	227	1.003	3.0	3.5	260	1.003	2.0	2.1	317
B-6	337	1.500	5.1	4.0	182	1.503	4.1	3.9	193	1.503	3.0	3.5	233	1.503	1.9	2.2	310
B-7	337	2.002	5.1	3.9	156	2.002	4.1	3.9	161	2.001	3.0	3.5	207	2.003	1.9	2.4	304
B-8	337	4.002	5.1	3.8	84.0	4.003	4.1	3.8	90.0	4.000	3.0	3.7	136	4.003	1.9	2.7	285

Table C-9: Equilibrium Study - Manganese

EXPERIMENTAL PROCEDURE																	
Prepared 5L - 5 mM Mn solution using manganese sulphate salt, adjusted pH to desired level using 1 N NaOH solution or 10% HCl solution																	
Weighed and placed 0.0g, 0.05g, 0.1g, 0.25g, 0.5g, 1.0g, 2.0g and 4.0g of oven-dried peat sieved (No. 10) in 250mL serum bottles																	
Added 150mL of solution at specified pH to each of 8 serum bottles, allowed to mix using reciprocating shaker at 200 rpm for 24 hours																	
Allowed peat to settle for 20 min, recorded pH, filtered using 45 um Millipore filter, collected 50mL of filtrate sample and acidified																	
Tests performed in duplicate at ambient laboratory temperature (20°C)																	
THEORY/RATIONALE																	
Analysis of Freundlich and Langmuir isotherm to determine order of reaction and adsorption potential at each pH																	
REFERENCES																	
Amfalk <i>et al.</i> : 1996: <i>Water, Air, and Soil Pollution</i> : 87:131-148																	
Dissanayake and Weerasooriya: 1981: <i>International Journal of Environmental Studies</i> : 17:233-238																	
Gosset <i>et al.</i> : 1986: <i>Water Research</i> : 20(1):21-26																	
NOTES																	
Sample	In C (mg/L)	pH = 5.0				pH = 6.0				pH = 7.0				pH = 8.0			
		Wt(g)	Initial pH	Final pH	In C	Wt(g)	Initial pH	Final pH	In C	Wt(g)	Initial pH	Final pH	In C	Wt(g)	Initial pH	Final pH	In C
A-1	312	0.000	5.0	5.3	308	0.000	4.0	4.5	302	0.000	3.0	2.9	308	0.000	2.0	1.9	312
A-2	312	0.102	5.0	4.8	296	0.102	4.0	4.5	290	0.101	3.0	3.4	299	0.105	2.0	1.9	310
A-3	312	0.250	5.0	4.7	281	0.250	4.0	4.7	276	0.251	3.0	3.8	284	0.254	2.0	2.0	309
A-4	312	0.504	5.0	4.7	258	0.503	4.0	4.8	254	0.502	3.0	4.3	262	0.500	2.0	2.0	306
A-5	312	1.005	5.0	4.7	214	1.002	4.0	4.8	210	1.004	3.0	4.3	221	1.003	2.0	2.2	290
A-6	312	1.503	5.0	4.7	175	1.504	4.0	4.8	178	1.502	3.0	4.6	188	1.504	2.0	2.7	286
A-7	312	2.003	5.0	4.7	137	2.004	4.0	4.7	139	2.002	3.0	4.7	151	2.002	2.0	3.2	262
A-8	312	4.001	5.0	4.5	88.0	4.000	4.0	4.5	98.0	4.003	3.0	4.7	104	4.002	2.0	3.6	192
Sample	In C (mg/L)	pH = 5.0				pH = 6.0				pH = 7.0				pH = 8.0			
		Wt(g)	Initial pH	Final pH	In C	Wt(g)	Initial pH	Final pH	In C	Wt(g)	Initial pH	Final pH	In C	Wt(g)	Initial pH	Final pH	In C
B-1	301	0.000	5.0	5.2	291	0.000	4.0	4.4	288	0.000	3.0	3.1	290	0.000	2.0	2.0	301
B-2	301	0.101	5.0	4.8	280	0.104	4.0	4.5	277	0.102	3.0	3.5	280	0.102	2.0	2.0	296
B-3	301	0.253	5.0	4.7	264	0.251	4.0	4.6	262	0.252	3.0	4.1	269	0.251	2.0	2.0	294
B-4	301	0.503	5.0	4.7	239	0.508	4.0	4.7	240	0.500	3.0	4.3	253	0.504	2.0	2.1	286
B-5	301	1.003	5.0	4.7	202	1.002	4.0	4.7	204	1.000	3.0	4.4	208	1.001	2.0	2.3	286
B-6	301	1.501	5.0	4.7	172	1.501	4.0	4.7	175	1.504	3.0	4.4	188	1.505	2.0	2.6	269
B-7	301	2.002	5.1	4.7	139	2.004	4.0	4.6	140	2.000	3.0	4.5	162	2.004	2.0	3.1	256
B-8	301	4.001	5.1	4.4	86.0	4.001	4.0	4.5	92.0	4.002	3.0	4.6	120	4.002	2.0	3.6	200

Table C-10: Equilibrium Study - Nickel

EXPERIMENTAL PROCEDURE																	
Prepared 5L - 5 mM Ni solution using nickel sulphate salt, adjusted pH to desired level using 1 N NaOH solution or 10% HCl solution																	
Weighed and placed 0.0g, 0.05g, 0.1g, 0.25g, 0.5g, 1.0g, 2.0g and 4.0g of oven-dried peat sieved (No. 10) in 250mL serum bottles																	
Added 150mL of solution at specified pH to each of 8 serum bottles, allowed to mix using reciprocating shaker at 200 rpm for 24 hours																	
Allowed peat to settle for 20 min, recorded pH, filtered using 45 um Millipore filter collected 50mL of filtrate sample and acidified																	
Tests performed in duplicate at ambient laboratory temperature (20C)																	
THEORY/RATIONALE																	
Analysis of Freundlich and Langmuir isotherm to determine order of reaction and adsorption potential at each pH																	
REFERENCES																	
Amfalk <i>et al.</i> : 1996: <i>Water, Air, and Soil Pollution</i> : 87:131-148																	
Dissanayake and Weerasooriya: 1981: <i>International Journal of Environmental Studies</i> : 17:233-238																	
Gosset <i>et al.</i> : 1986: <i>Water Research</i> : 20(1):21-26																	
NOTES																	
pH unstable at the pH 5 level																	
Run A did pH 5 last																	
Run B did pH 5 first																	
Sample	In C	pH = 5.0				pH = 4.0				pH = 3.0				pH = 2.0			
	(mg/L)	Wt(g)	pH	pH	pH	Wt(g)	pH	pH	pH	Wt(g)	pH	pH	pH	Wt(g)	pH	pH	pH
A-1	318	0.000	5.0	5.0	314	0.000	4.0	4.3	318	0.000	3.0	2.9	312	0.000	2.0	2.1	318
A-2	318	0.100	5.0	4.7	306	0.101	4.0	3.8	310	0.104	3.0	2.9	305	0.101	2.0	2.0	313
A-3	318	0.254	5.0	4.5	295	0.251	4.0	3.5	300	0.251	3.0	2.9	293	0.250	2.0	2.0	306
A-4	318	0.503	4.9	4.4	276	0.500	4.1	3.4	279	0.500	3.0	2.9	278	0.501	2.0	2.0	294
A-5	318	1.001	4.9	4.3	243	1.003	4.1	3.3	245	1.000	3.0	2.9	254	1.005	2.0	2.1	279
A-6	318	1.501	4.9	4.2	219	1.501	4.1	3.2	224	1.502	3.0	2.9	232	1.505	2.0	2.3	263
A-7	318	2.002	4.9	4.1	207	2.004	4.1	3.2	201	2.004	3.0	2.9	218	2.003	2.0	2.4	251
A-8	318	4.003	4.9	4.1	165	4.001	4.1	3.1	168	4.002	3.0	3.0	176	4.001	2.0	2.7	219
Sample	In C	pH = 5.0				pH = 4.0				pH = 3.0				pH = 2.0			
	(mg/L)	Wt(g)	pH	pH	pH	Wt(g)	pH	pH	pH	Wt(g)	pH	pH	pH	Wt(g)	pH	pH	pH
B-1	329	0.000	5.0	5.5	329	0.000	4.0	4.2	327	0.000	3.0	2.9	324	0.000	2.0	2.1	328
B-2	329	0.102	5.0	4.8	321	0.102	4.0	3.7	319	0.101	3.0	2.9	317	0.101	2.0	2.0	323
B-3	329	0.253	5.1	4.6	308	0.253	4.0	3.5	306	0.252	3.0	2.9	305	0.251	2.0	2.0	314
B-4	329	0.501	5.1	4.4	288	0.501	4.0	3.4	287	0.500	3.0	2.9	286	0.503	2.0	2.0	304
B-5	329	1.001	5.1	4.3	254	1.004	4.0	3.3	255	1.000	3.0	2.9	261	1.004	2.0	2.1	286
B-6	329	1.501	5.1	4.2	230	1.501	4.0	3.2	231	1.501	3.0	2.9	238	1.501	2.0	2.2	267
B-7	329	2.002	5.1	4.2	219	2.004	4.0	3.2	212	2.004	3.0	2.9	221	2.000	2.0	2.3	253
B-8	329	4.002	5.1	4.1	169	4.002	4.0	3.1	174	4.002	3.0	3.0	178	4.003	2.0	2.5	222

Table C-11: Equilibrium Study - Copper

EXPERIMENTAL PROCEDURE																	
Prepared 5L - 5 mM Cu solution using copper sulphate salt, adjusted pH to desired level using 1 N NaOH solution or 10% HCl solution																	
Weighed and placed 0.0g, 0.05g, 0.1g, 0.25g, 0.5g, 1.0g, 2.0g and 4.0g of oven-dried peat sieved (No. 10) in 250mL serum bottles																	
Added 150mL of solution at specified pH to each of 8 serum bottles, allowed to mix using reciprocating shaker at 200 rpm for 24 hours																	
Allowed peat to settle for 20 min, recorded pH, filtered using 45 um Millipore filter, collected 50mL of filtrate sample and acidified																	
Tests performed in duplicate at ambient laboratory temperature (20°C)																	
THEORY/RATIONALE																	
Analysis of Freundlich and Langmuir isotherm to determine order of reaction and adsorption potential at each pH																	
REFERENCES																	
Amfalk <i>et al.</i> : 1996; <i>Water, Air, and Soil Pollution</i> : 87:131-148																	
Dissanayake and Weerassooriya: 1981; <i>International Journal of Environmental Studies</i> : 17:233-238																	
Gosset <i>et al.</i> : 1986; <i>Water Research</i> : 20(1):21-26																	
NOTES																	
Sample	In C (mg/L)	pH = 5.0				pH = 4.0				pH = 3.0				pH = 2.0			
		Wt (g)	Initial pH	Final pH	Final C	Wt (g)	Initial pH	Final pH	Final C	Wt (g)	Initial pH	Final pH	Final C	Wt (g)	Initial pH	Final pH	Final C
A-1	322	0.000	5.0	4.7	320	0.000	4.0	4.1	320	0.000	3.0	2.8	318	0.000	2.0	2.0	322
A-2	322	0.104	5.1	4.7	294	0.104	4.1	3.6	296	0.101	3.0	2.9	300	0.101	2.0	1.9	317
A-3	322	0.252	5.1	4.4	267	0.250	4.1	3.4	266	0.255	3.0	3.0	276	0.255	2.0	1.9	310
A-4	322	0.504	5.1	4.3	208	0.502	4.1	3.2	220	0.504	3.0	2.9	231	0.501	2.0	1.9	300
A-5	322	1.004	5.1	4.3	147	1.005	4.1	3.3	163	1.005	3.0	3.0	173	1.005	2.0	2.0	281
A-6	322	1.502	5.1	4.2	100	1.503	4.1	3.2	112	1.505	3.0	3.0	124	1.504	2.0	2.5	268
A-7	322	2.001	5.1	4.2	56.3	2.003	4.1	3.3	62.0	2.004	3.0	3.1	73.0	2.001	2.0	3.0	252
A-8	322	4.003	5.1	4.3	14.0	4.004	4.1	3.4	19.0	4.005	3.0	3.3	24.3	4.000	2.0	3.2	185
Sample	In C (mg/L)	pH = 5.0				pH = 4.0				pH = 3.0				pH = 2.0			
		Wt (g)	Initial pH	Final pH	Final C	Wt (g)	Initial pH	Final pH	Final C	Wt (g)	Initial pH	Final pH	Final C	Wt (g)	Initial pH	Final pH	Final C
B-1	326	0.000	5.1	5.1	323	0.000	4.0	4.3	324	0.000	3.0	3.0	326	0.000	2.0	2.0	326
B-2	326	0.103	5.1	4.4	296	0.101	4.0	4.1	298	0.100	3.0	2.9	305	0.100	2.0	2.0	321
B-3	326	0.251	5.1	4.0	264	0.251	4.0	3.6	267	0.251	3.0	2.7	280	0.254	2.0	2.0	313
B-4	326	0.501	5.1	4.1	212	0.502	4.0	3.2	218	0.504	3.0	2.8	237	0.502	2.0	2.1	302
B-5	326	1.001	5.1	4.2	140	1.002	4.0	3.2	137	1.004	3.0	3.0	150	1.001	2.0	2.3	283
B-6	326	1.501	5.1	4.2	76.6	1.503	4.0	3.2	75.6	1.504	3.0	3.1	85.7	1.501	2.0	2.7	267
B-7	326	2.000	5.1	4.4	35.8	2.000	4.0	3.5	38.5	2.004	3.0	3.3	46.2	2.002	2.0	3.0	249
B-8	326	4.002	5.1	4.3	12.6	4.000	4.1	3.7	12.6	4.000	3.0	3.6	15.8	4.003	2.0	3.6	188

Table C-12: Equilibrium Study - Cadmium

EXPERIMENTAL PROCEDURE																	
Prepared 5L - 5 mM Cd solution using cadmium sulphate salt, adjusted pH to desired level using 1 N NaOH solution or 10% HCl solution																	
Weighed and placed 0.0g, 0.05g, 0.1g, 0.25g, 0.5g, 1.0g, 2.0g and 4.0g of oven-dried peat sieved (No. 10) in 250mL serum bottles																	
Added 150mL of solution at specified pH to each of 8 serum bottles, allowed to mix using reciprocating shaker at 200 rpm for 24 hours																	
Allowed peat to settle for 20 min, recorded pH, filtered using 45 um Millipore filter, collected 50mL of filtrate sample and acidified																	
Tests performed in duplicate at ambient laboratory temperature (20°C)																	
THEORY/RATIONALE																	
Analysis of Freundlich and Langmuir isotherm to determine order of reaction and adsorption potential at each pH																	
REFERENCES																	
Arnfolk <i>et al.</i> : 1996: <i>Water, Air, and Soil Pollution</i> : 87:131-148																	
Dissanayake and Weerassooriya: 1981: <i>International Journal of Environmental Studies</i> : 17:233-238																	
Gosset <i>et al.</i> : 1986: <i>Water Research</i> : 20(1):21-26																	
NOTES																	
Formation of yellowish fine precipitate at pH 4 and 5. Remains after shaking 24hrs.																	
pH may not group as much due to Fe(OH) ₃ precipitation which decreases pH																	
Formation of yellowish fine precipitate at pH 3. Clear after shaking 24hrs																	
Sample	Initial Cd (mg/L)	pH = 5.0				pH = 4.0				pH = 3.0				pH = 2.0			
		Wt(g)	Initial pH	Final pH	Final Cd (mg/L)	Wt(g)	Initial pH	Final pH	Final Cd (mg/L)	Wt(g)	Initial pH	Final pH	Final Cd (mg/L)	Wt(g)	Initial pH	Final pH	Final Cd (mg/L)
A-1	630	0.000	5.1	5.4	610	0.000	4.0	4.0	630	0.000	3.0	2.9	623	0.000	2.0	1.9	633
A-2	630	0.104	5.1	4.3	597	0.105	4.0	4.0	617	0.102	3.0	3.1	613	0.101	2.0	1.9	623
A-3	630	0.254	5.1	4.2	580	0.252	4.0	4.1	600	0.251	3.0	3.3	600	0.252	2.0	2.0	613
A-4	630	0.504	5.1	4.2	553	0.505	4.0	4.2	577	0.503	3.0	3.5	577	0.503	2.0	2.0	600
A-5	630	1.003	5.1	4.1	503	1.003	4.0	4.1	530	1.000	3.0	3.8	537	1.003	2.0	2.2	583
A-6	630	1.503	5.1	4.1	463	1.503	4.0	4.1	493	1.502	3.0	3.8	503	1.502	2.0	2.6	567
A-7	630	2.002	5.2	4.1	430	2.004	4.0	4.0	457	2.000	3.0	3.9	480	2.004	2.0	2.9	553
A-8	630	4.000	5.2	4.0	304	4.005	4.0	3.9	343	4.004	3.0	4.0	370	4.000	2.0	3.3	483
Sample	Initial Cd (mg/L)	pH = 5.0				pH = 4.0				pH = 3.0				pH = 2.0			
		Wt(g)	Initial pH	Final pH	Final Cd (mg/L)	Wt(g)	Initial pH	Final pH	Final Cd (mg/L)	Wt(g)	Initial pH	Final pH	Final Cd (mg/L)	Wt(g)	Initial pH	Final pH	Final Cd (mg/L)
B-1	623	0.000	5.1	5.2	623	0.000	4.0	4.2	623	0.000	3.0	3.1	623	0.000	2.0	2.2	610
B-2	623	0.103	5.1	4.3	610	0.104	4.0	4.2	610	0.103	3.0	3.4	613	0.100	2.0	2.3	603
B-3	623	0.254	5.1	4.0	593	0.254	4.0	4.0	593	0.253	3.0	3.6	600	0.252	2.0	2.3	593
B-4	623	0.503	5.1	4.0	567	0.501	4.0	4.0	567	0.502	3.0	3.8	580	0.500	2.0	2.4	580
B-5	623	1.002	5.1	4.0	517	1.000	4.0	4.0	520	1.001	3.0	3.9	543	1.002	2.0	2.7	567
B-6	623	1.503	5.1	3.9	470	1.502	4.0	4.0	483	1.500	3.0	3.9	507	1.504	2.0	3.2	547
B-7	623	2.004	5.1	3.9	437	2.003	4.0	3.9	450	2.001	3.0	4.0	473	2.002	2.0	3.3	530
B-8	623	4.004	5.1	3.7	311	4.002	4.0	3.9	326	4.002	3.0	3.9	360	4.005	2.0	3.4	477

APPENDIX D

COLUMN EXPERIMENT

RAW DATA & INFLUENT CONCENTRATIONS

Table D-1: Leaching/Sorption Column Study

EXPERIMENTAL PROCEDURE									
Added 3L of AMD at pH of 2.5 to stainless steel column, let stand covered for a period of 21 days									
Added 3L of distilled water at pH of 2.5 to stainless steel column, let stand covered for a period of 21 days									
Collected 40 mL samples of initial and final AMD and distilled water									
Analyzed for metal content using ICP in Chemistry Department at Carleton University									
THEORY/RATIONALE									
Determine metals leached from column at low pH using distilled water									
Determine metals sorbed onto column at low pH using AMD									
REFERENCES									
NOTES									
AMD initial sample broken during study, started again in January using new column									
Condition	Sample	pH	Al ³⁺ (ppm)	Co ²⁺ (ppm)	Ca ²⁺ (ppm)	Fe ²⁺ (ppm)	Mn ²⁺ (ppm)	Ni ²⁺ (ppm)	Zn ²⁺ (ppm)
	Detection Limit		0.07	0.18	0.02	0.09	0.02	0.15	0.49
	Precision		0.80	0.22	0.17	0.23	0.24	0.18	0.73
	Initial	2.5	87.79	6.30	19.67	203.13	25.57	20.68	104.58
	Final	2.5	87.41	6.50	19.59	206.74	25.98	21.06	106.37
AMD	Initial - Final		0.38	-0.20	0.08	-3.61	-0.41	-0.38	-1.79
	Sorption(+)/Desorption(-)		0.38	-0.20	0.08	-3.61	-0.41	-0.38	-1.79
	% Sorbed/Leached		0.43	3.17	0.41	1.78	1.60	1.84	1.71
	Initial	2.4	< D. L.	< D. L.	0.03	< D. L.	0.03	< D. L.	< D. L.
Distilled	Final	2.5	0.17	< D. L.	0.06	1.72	0.08	< D. L.	< D. L.
Water	Initial - Final		-0.17		-0.03	-1.72	-0.05		
	Sorption(+)/Desorption(-)		-0.17		-0.03	-1.72	-0.05		

Table D-2: Metal Mass Supplied
EXPERIMENTAL PROCEDURE

THEORY/RATIONALE															
Determine the total mass of metals supplied to each column															
REFERENCES															
NOTES															
	Sorp	Vol (L)						Desorp					Vol (L)		
Hi Q	1.37	L/day	102.8					Hi Q	2.74	L/day			27.4		
Lo Q	0.685	L/day	51.38					Lo Q	1.37	L/day			13.7		
	75	days							10	days					
Condition	Temp	Al (S)	Al (DS)	Co (S)	Co (DS)	Cu (S)	Cu (DS)	Pb (S)	Pb (DS)	Mn (S)	Mn (DS)	Ni (S)	Ni (DS)	Zn (S)	Zn (DS)
H[] (mg/L)	Cold	90.9	4.80	6.00	0.30	18.3	1.10	197	10.9	24.9	1.20	17.7	1.30	107	5.20
L[] (mg/L)	Cold	21.4	4.80	1.50	0.30	4.90	1.10	51.3	10.4	6.00	1.40	4.40	1.30	20.8	5.00
H[] (mg/L)	Warm	87.6	4.40	6.10	0.30	18.7	1.00	191	9.90	25.2	1.40	20.3	1.10	93.1	5.00
L[] (mg/L)	Warm	23.4	4.30	1.70	0.40	5.00	0.60	51.0	9.90	6.70	1.40	4.90	1.00	21.5	5.20
Cold	Rea WL (g)	mg		mg		mg		mg		mg		mg		mg	
LQ H[]	1644.5	4740		312		955		10300		1300		927		5580	
LQ L[]	1620.4	1170		81.2		267		2780		327		244		1140	
HQ H[]	1435.1	9470		625		1910		20600		2590		1850		11200	
HQ L[]	1479.9	2330		162		534		5560		655		488		2270	
Warm	Rea WL (g)	mg		mg		mg		mg		mg		mg		mg	
LQ H[]	1500.4	4560		317		974		9930		1310		1060		4850	
LQ L[]	1396.9	1260		92.8		265		2760		363		265		1180	
HQ H[]	1443.5	9120		635		1950		19900		2630		2120		9700	
HQ L[]	1425.1	2520		186		530		5510		727		531		2350	

Table D-3: Theoretical Total Column Adsorption Capacities
EXPERIMENTAL PROCEDURE

THEORY/RATIONALE

Determine the total mass of metals that could be removed in each column based on equilibrium isotherms at pH = 3

REFERENCES

NOTES

	Sorp		Vol (L)		Desorp		Vol (L)
Hi Q	1.37	L/day	102.8	Hi Q	2.74	L/day	27.4
Lo Q	0.685	L/day	51.38	Lo Q	1.37	L/day	13.7
	75	days			10	days	

Condition	Temp	Al (S)	Al (MW)	Ca (S)	Ca (MW)	Pb (S)	Pb (MW)	Fe (S)	Fe (MW)	Mn (S)	Mn (MW)	Ni (S)	Ni (MW)	Zn (S)	Zn (MW)
H[] (mg/L)	Cold	90.9	26.98	6.00	112.4	18.3	63.55	197	55.85	24.9	54.94	17.7	58.70	107	65.38
L[] (mg/L)	Cold	21.4	26.98	1.50	112.4	4.90	63.55	51.3	55.85	6.00	54.94	4.40	58.70	20.8	65.38
H[] (mg/L)	Warm	87.6	26.98	6.10	112.4	18.4	63.55	191	55.85	25.2	54.94	20.3	58.70	93.1	65.38
L[] (mg/L)	Warm	23.4	26.98	1.70	112.4	5.00	63.55	51.0	55.85	6.70	54.94	4.90	58.70	21.5	65.38
Cold	Desorp Vol (L)	Al (S)	Al (MW)	Ca (S)	Ca (MW)	Pb (S)	Pb (MW)	Fe (S)	Fe (MW)	Mn (S)	Mn (MW)	Ni (S)	Ni (MW)	Zn (S)	Zn (MW)
LQ H[]	1644.5	587		6.3		282		655		94.7		31.3		179	
LQ L[]	1620.4	518		1.6		102		409		25.6		8.0		51.7	
HQ H[]	1435.1	512		5.5		246		572		82.6		27.3		156	
HQ L[]	1479.9	473		1.4		93.3		374		23.4		7.3		47.2	
Warm	Desorp Vol (L)	Al (S)	Al (MW)	Ca (S)	Ca (MW)	Pb (S)	Pb (MW)	Fe (S)	Fe (MW)	Mn (S)	Mn (MW)	Ni (S)	Ni (MW)	Zn (S)	Zn (MW)
LQ H[]	1500.4	535		5.8		258		594		87.2		32.5		150	
LQ L[]	1396.9	452		1.5		89.6		352		24.5		7.7		45.9	
HQ H[]	1443.5	514		5.6		248		571		83.9		31.3		145	

Table D-4: Column Study Dry Densities

EXPERIMENTAL PROCEDURE									
Sieved air-dried peat using 1/4" sieve, determined moisture content									
Weighed empty columns: Compacted columns in 4" lifts									
Weighed columns + air-dried peat: Recorded column ID (14.6 cm) and peat height (46 cm)									
Computed bulk density on air-dried basis									
THEORY/RATIONALE									
REFERENCES									
NOTES									
As received peat contained 65% moisture (difficult to dry large volumes)									
This will allow comparison with physical characterization hydraulic conductivity and water holding capacity									
Second run of adsorption columns, 65% moisture									
Column	Column Height (cm)	Inside Diameter (cm)	Peat to Top (cm)	Peat Depth (cm)	Peat Volume (m ³)	Column Weight (g)	Dry Peat Column (g)	Dry Peat (Oven) (g)	Oven-Dried Density (kg/m ³)
1	61.0	14.6	15.0	46.0	0.00770	8658.6	12693.2	1412.1	183.4
2	61.0	14.6	15.5	45.5	0.00762	8586.5	13267.6	1638.4	215.1
3	61.0	14.6	15.0	46.0	0.00770	8843.2	13607.8	1667.6	216.5
4	61.0	14.6	14.0	47.0	0.00787	8597.1	13374.8	1672.2	212.5
5	61.0	14.6	14.5	46.5	0.00778	8875.1	13734.6	1700.8	218.5
6	61.0	14.6	15.0	46.0	0.00770	8813.6	12927.4	1439.8	187.0
7	61.0	14.6	15.0	46.0	0.00770	8418.4	12473.8	1419.4	184.3
8	61.0	14.6	14.5	46.5	0.00778	8884.2	12660.4	1321.7	169.8
9	61.0	14.6	14.0	47.0	0.00787	8597.2	12473.8	1356.8	172.4
10	61.0	14.6	13.5	47.5	0.00795	8599.5	12503.7	1366.5	171.8
11	61.0	14.6	14.5	46.5	0.00778	8451.8	12333.6	1358.6	174.5
12	61.0	14.6	15.0	46.0	0.00770	8606.5	12517.1	1368.7	177.7
13	61.0	14.6	15.0	46.0	0.00770	8585.6	12798.6	1474.6	191.5
14	61.0	14.6	15.0	46.0	0.00770	8609.1	13307.8	1644.5	213.5
15	61.0	14.6	15.0	46.0	0.00770	8604.9	13234.6	1620.4	210.4
16	61.0	14.6	15.0	46.0	0.00770	8619.0	12719.2	1435.1	186.3
17	61.0	14.6	15.0	46.0	0.00770	8845.5	13073.8	1479.9	192.2
Column	Column Height (cm)	Inside Diameter (cm)	Peat to Top (cm)	Peat Depth (cm)	Peat Volume (m ³)	Column Weight (g)	Dry Peat Column (g)	Dry Peat (Oven) (g)	Oven-Dried Density (kg/m ³)
14	61.0	14.6	15.0	46.0	0.00770	8609.1	12895.9	1500.4	194.8
15	61.0	14.6	15.0	46.0	0.00770	8604.9	12595.9	1396.9	181.4
16	61.0	14.6	15.0	46.0	0.00770	8619.0	12743.4	1443.5	187.4
17	61.0	14.6	15.0	46.0	0.00770	8845.5	12917.2	1425.1	185.1

Figure D-1: Sorption/Desorption Study Influent pH

Figure D-2: Sorption/Desorption Study Influent Dissolved Oxygen Concentrations

Figure D-3: Sorption/Desorption Study Influent Sulphate Concentrations

Figure D-4: Sorption/Desorption Study Influent Iron Concentrations

Figure D-5: Sorption/Desorption Study Influent Aluminum Concentrations

Figure D-6: Sorption/Desorption Study Influent Zinc Concentrations

Figure D-7: Sorption/Desorption Study Influent Manganese Concentrations

Figure D-8: Sorption/Desorption Study Influent Nickel Concentrations

Figure D-9: Sorption/Desorption Study Influent Copper Concentrations

Figure D-10: Sorption/Desorption Study Influent Cadmium Concentrations

Figure D-11: Substrate Study Influent pH

Figure D-12: Substrate Study Influent Acidity

Figure D-13: Substrate Study Influent Dissolved Oxygen Concentrations

Figure D-14: Substrate Study Influent Sulphate Concentrations

Figure D-15: Substrate Study Influent Metal Concentrations at 0°C

Figure D-16: Substrate Study Influent Metal Concentrations at 20°C

Figure D-17: Substrate Study Ambient Experimental Temperatures

APPENDIX E

COLUMN EXPERIMENT

METAL ADSORPTION/DESORPTION GRAPHS

Figure E-1: Iron Breakthrough at 0°C

Figure E-2: Iron Breakthrough at 20°C

Figure E-3: Aluminum Breakthrough at 0°C

Figure E-4: Aluminum Breakthrough at 20°C

Figure E-5: Zinc Breakthrough at 0°C

Figure E-6: Zinc Breakthrough at 20°C

Figure E-7: Manganese Breakthrough at 0°C

Figure E-8: Manganese Breakthrough at 20°C

Figure E-9: Nickel Breakthrough at 0°C

Figure E-10: Nickel Breakthrough at 20°C

Figure E-11: Copper Breakthrough at 0°C

Figure E-12: Copper Breakthrough at 20°C

Figure E-13: Cadmium Breakthrough at 0°C

Figure E-14: Cadmium Breakthrough at 20°C

APPENDIX F

COLUMN EXPERIMENT SEQUENTIAL EXTRACTION DATA

LQ - H[] C14 - 0 C**Layer 1**

Concentration mg/L								% Retained							
Sample ID	Al	Cd	Cu	Fe	Mn	Ni	Zn	Al	Cd	Cu	Fe	Mn	Ni	Zn	
W	2.98	0.12	0.91	52.8	0.38	0.37	1.45	2.62	17.9	5.14	4.83	16.3	16.3	24.1	
Ex	7.31	0.41	3.29	106	0.53	0.98	2.96	6.43	61.1	18.6	9.69	22.7	43.2	49.3	
Ox	4.87	0.08	0.15	223	0.14	0.24	0.78	4.29	11.9	0.85	20.4	6.01	10.6	13.0	
OM	72.6	0.06	17.3	912	0.84	0.70	0.94	43.4	6.08	66.4	56.7	24.5	21.0	10.6	
RM	49.1	0.02	1.59	91.5	0.71	0.20	0.18	43.2	2.98	8.98	8.37	30.5	8.83	3.00	

Layer 2

Concentration								% Retained							
Sample ID	Al	Cd	Cu	Fe	Mn	Ni	Zn	Al	Cd	Cu	Fe	Mn	Ni	Zn	
W	2.24	0.07	0.90	11.0	0.20	0.23	0.76	4.05	6.80	11.4	4.24	10.7	6.95	8.08	
Ex	8.54	0.67	4.21	51.7	0.92	1.85	5.74	15.4	65.0	53.5	19.9	49.1	55.9	61.0	
Ox	7.11	0.20	0.31	125	0.33	0.60	2.13	12.9	19.4	3.94	48.2	17.6	18.1	22.6	
OM	5.52	0.00	2.01	40.4	0.07	0.13	0.15	7.79	0.00	19.9	12.1	2.91	3.06	1.24	
RM	33.1	0.09	0.88	40.2	0.37	0.53	0.66	59.9	8.74	11.2	15.5	19.7	16.0	7.02	

Layer 3

Concentration								% Retained						
Sample ID	Al	Cd	Cu	Fe	Mn	Ni	Zn	Al	Cd	Cu	Fe	Mn	Ni	Zn
W	2.07	0.03	0.88	0.77	0.10	0.12	0.61	2.00	1.84	2.61	0.53	3.03	1.92	3.17
Ex	10.3	1.27	5.44	14.7	2.03	3.79	13.3	9.95	77.7	16.1	10.1	61.5	60.6	69.2
Ox	7.11	0.25	0.79	18.5	0.44	0.90	3.37	6.87	15.3	2.34	12.7	13.3	14.4	17.5
OM	75.7	0.06	36.7	110	0.54	1.79	2.28	42.4	2.13	63.1	43.9	9.48	16.6	6.88
RM	40.1	0.05	5.34	47.5	0.42	0.41	0.63	38.7	3.06	15.8	32.7	12.7	6.55	3.28

Layer 4

Concentration								% Retained						
Sample ID	Al	Cd	Cu	Fe	Mn	Ni	Zn	Al	Cd	Cu	Fe	Mn	Ni	Zn
W	0.95	0.00	0.27	0.62	0.00	0.00	0.08	1.05	0.00	1.40	0.55	0.00	0.00	0.70
Ex	6.95	0.77	2.90	2.80	1.27	3.04	7.90	7.65	76.8	15.1	2.50	54.9	59.3	69.2
Ox	4.82	0.18	0.40	10.8	0.31	0.75	2.17	5.30	18.0	2.08	9.65	13.4	14.6	19.0
OM	69.3	0.05	21.8	85.0	0.44	1.66	1.53	48.8	3.19	72.5	48.6	12.2	20.7	8.58
RM	33.8	0.02	1.72	43.3	0.45	0.27	0.29	37.2	2.00	8.94	38.7	19.5	5.27	2.54

Layer 5

Concentration								% Retained						
Sample ID	Al	Cd	Cu	Fe	Mn	Ni	Zn	Al	Cd	Cu	Fe	Mn	Ni	Zn
W	2.44	0.01	0.23	0.63	0.06	0.13	0.26	2.24	0.65	2.41	0.53	1.99	1.74	1.65
Ex	10.1	1.13	1.21	7.42	1.61	4.43	10.5	9.27	73.5	12.7	6.26	53.4	59.2	66.8
Ox	8.40	0.30	0.17	11.0	0.45	1.16	3.37	7.71	19.5	1.78	9.28	14.9	15.5	21.4
OM	61.6	0.09	10.3	45.1	0.41	2.27	1.71	36.2	3.75	69.1	24.4	8.71	19.4	6.96
RM	48.6	0.04	1.34	70.6	0.63	0.31	0.50	44.6	2.60	14.0	59.6	20.9	4.14	3.18

Total column

Layer	Mass Fraction			mg metal/kg peat				Total Fraction Bound (%)						
	Al	Cd	Cu	Fe	Mn	Ni	Zn	Al	Cd	Cu	Fe	Mn	Ni	Zn
1	2270	13.4	354	21900	46.6	45.3	120	2.26	3.91	3.62	3.81	5.77	3.48	5.11
2	1110	20.6	157	5190	37.5	66.2	188	9.15	72.3	19.4	10.6	49.6	57.6	65.4
3	2070	32.7	675	2910	66.1	125	385	6.84	17.2	2.07	22.5	13.0	14.9	19.1
4	1820	20.0	385	2240	46.2	102	228	38.4	2.81	62.6	46.2	11.6	16.9	6.72
5	2180	30.8	191	2370	60.2	150	314	43.3	3.74	12.3	17.0	20.1	7.04	3.66

LQ - L[] C15 - 0 C**Layer 1**

Concentration								% Retained						
Sample ID	Al	Cd	Cu	Fe	Mn	Ni	Zn	Al	Cd	Cu	Fe	Mn	Ni	Zn
W	4.18	0.14	0.84	8.69	0.46	0.48	1.82	2.38	7.09	2.84	1.80	11.0	6.37	9.33
Ex	21.5	1.37	4.81	48.4	1.96	4.05	11.9	12.2	69.4	16.3	10.0	46.8	53.7	61.0
Ox	13.3	0.33	0.45	84.9	0.50	1.07	3.54	7.57	16.7	1.52	17.5	11.9	14.2	18.1
OM	126	0.08	30.4	403	0.82	2.29	2.76	48.7	2.76	69.9	56.6	13.3	20.7	9.62
RM	51.1	0.08	2.79	68.0	0.71	0.38	0.38	29.1	4.05	9.44	14.0	17.0	5.04	1.95

Layer 2

Concentration								% Retained						
Sample ID	Al	Cd	Cu	Fe	Mn	Ni	Zn	Al	Cd	Cu	Fe	Mn	Ni	Zn
W	2.11	0.03	0.06	0.51	0.11	0.16	0.51	1.55	1.23	0.93	0.38	2.61	1.71	2.07
Ex	19.0	1.76	0.41	10.1	2.53	5.33	16.0	13.9	72.1	6.38	7.51	60.0	57.1	64.9
Ox	17.4	0.48	0.05	12.7	0.73	1.39	5.42	12.7	19.7	0.78	9.45	17.3	14.9	22.0
OM	80.4	0.18	5.15	63.5	0.46	2.96	3.18	45.9	5.75	62.5	36.8	8.50	24.7	10.1
RM	35.3	0.03	1.89	61.6	0.49	0.15	0.25	25.9	1.23	29.4	45.8	11.6	1.61	1.01

Layer 3

Concentration								% Retained						
Sample ID	Al	Cd	Cu	Fe	Mn	Ni	Zn	Al	Cd	Cu	Fe	Mn	Ni	Zn
W	2.82	0.07	0.04	0.82	0.23	0.22	1.41	2.47	2.00	9.91	0.69	4.20	2.56	3.24
Ex	12.7	2.64	0.02	12.1	3.48	5.02	29.5	11.1	75.3	4.96	10.2	63.6	58.3	67.8
Ox	12.1	0.63	0.01	12.5	0.88	1.22	9.15	10.6	18.0	2.48	10.5	16.1	14.2	21.0
OM	74.6	0.13	0.42	77.3	0.61	2.98	4.75	37.8	2.15	60.4	37.7	6.46	20.1	6.33
RM	43.5	0.09	0.09	48.7	0.53	0.42	0.69	38.0	2.57	22.3	40.9	9.68	4.88	1.59

Layer 4

Concentration								% Retained						
Sample ID	Al	Cd	Cu	Fe	Mn	Ni	Zn	Al	Cd	Cu	Fe	Mn	Ni	Zn
W	1.50	0.00	0.00	0.52	0.08	0.07	0.48	1.72	0.00	0.00	0.52	1.17	1.55	1.13
Ex	5.82	1.67	0.00	2.74	4.78	2.28	28.2	6.67	75.6	0.00	2.73	69.6	50.4	66.2
Ox	4.73	0.41	0.01	6.17	1.21	0.49	8.63	5.42	18.5	4.24	6.14	17.6	10.8	20.3
OM	83.3	0.11	0.29	105	0.96	2.35	7.35	61.1	3.18	78.8	66.8	8.95	33.2	11.0
RM	21.9	0.06	0.04	23.9	0.18	0.18	0.57	25.1	2.71	17.0	23.8	2.62	3.98	1.34

Layer 5

Concentration								% Retained						
Sample ID	Al	Cd	Cu	Fe	Mn	Ni	Zn	Al	Cd	Cu	Fe	Mn	Ni	Zn
W	2.63	0.00	0.01	0.68	0.27	0.03	0.49	2.98	0.00	5.20	0.65	2.67	3.22	2.36
Ex	4.82	0.44	0.01	4.32	6.81	0.38	13.6	5.46	77.2	5.20	4.12	67.4	40.8	65.5
Ox	4.74	0.11	0.01	7.85	1.81	0.09	4.50	5.37	19.3	5.20	7.49	17.9	9.67	21.7
OM	54.6	0.00	0.16	68.6	0.84	0.47	2.45	39.6	0.00	53.2	41.9	5.32	32.3	7.55
RM	41.2	0.02	0.06	48.1	0.67	0.13	0.61	46.6	3.51	31.2	45.9	6.64	14.0	2.94

Total Column Mass Fraction (mg/kg peat)								Fraction Bound (%)						
Layer	Al	Cd	Cu	Fe	Mn	Ni	Zn	Al	Cd	Cu	Fe	Mn	Ni	Zn
1	3520	39.5	591	9681	83.8	151	390	2.20	2.24	2.58	1.19	3.73	3.10	3.12
2	2730	48.8	129	2690	84.4	187	493	10.6	73.6	14.3	8.24	63.4	55.1	65.7
3	2290	70.1	8.07	2380	109	172	870	8.68	18.3	1.44	13.2	16.6	13.8	20.7
4	1750	44.2	4.71	2010	137	90.5	852	46.5	3.18	68.5	50.9	7.85	23.9	8.86
5	1770	11.4	3.85	2100	202	18.6	415	32.0	2.62	13.2	26.5	8.37	4.07	1.66

HQ - H[] C16 - 0 C**Layer 1**

Concentration								% Retained						
Sample ID	Al	Cd	Cu	Fe	Mn	Ni	Zn	Al	Cd	Cu	Fe	Mn	Ni	Zn
W	5.80	0.14	1.70	75.3	0.49	0.44	2.06	3.83	16.5	7.93	6.97	15.0	12.3	24.9
Ex	7.55	0.55	3.43	137	0.71	1.15	4.03	4.99	64.7	16.0	12.7	21.8	32.1	48.8
Ox	7.65	0.12	0.18	205	0.22	0.28	1.12	5.05	14.1	0.84	19.0	6.74	7.80	13.6
OM	97.6	0.00	22.1	865	0.91	2.33	1.32	40.6	0.00	64.9	50.4	17.6	40.9	10.1
RM	68.9	0.04	2.21	118	1.27	0.25	0.22	45.5	4.71	10.3	10.9	38.9	6.97	2.66

Layer 2

Concentration								% Retained						
Sample ID	Al	Cd	Cu	Fe	Mn	Ni	Zn	Al	Cd	Cu	Fe	Mn	Ni	Zn
W	2.69	0.06	0.97	42.9	0.22	0.16	0.87	3.35	9.51	5.35	4.59	12.8	9.50	16.1
Ex	5.83	0.39	3.16	106	0.53	0.77	2.83	7.26	61.8	17.4	11.3	30.8	45.7	52.4
Ox	5.47	0.10	0.13	212	0.20	0.20	0.94	6.81	15.9	0.72	22.7	11.6	11.9	17.4
OM	44.4	0.07	14.3	593	0.54	0.50	0.72	48.1	9.65	68.7	55.2	27.3	25.8	11.6
RM	27.7	0.02	1.42	57.8	0.30	0.12	0.13	34.5	3.17	7.84	6.18	17.4	7.12	2.41

Layer 3

Concentration								% Retained						
Sample ID	Al	Cd	Cu	Fe	Mn	Ni	Zn	Al	Cd	Cu	Fe	Mn	Ni	Zn
W	1.86	0.02	0.65	11.9	0.09	0.10	0.40	2.19	3.13	4.17	2.09	5.79	4.79	7.32
Ex	5.88	0.41	2.94	40.4	0.50	0.94	3.02	6.91	64.1	18.9	7.11	32.2	45.0	55.3
Ox	4.03	0.10	0.22	105	0.17	0.27	0.95	4.74	15.6	1.41	18.5	10.9	12.9	17.4
OM	46.1	0.10	13.0	435	0.48	0.81	1.07	43.4	12.5	66.7	61.2	24.7	31.0	15.7
RM	36.4	0.03	1.38	63.3	0.41	0.13	0.24	42.8	4.69	8.85	11.1	26.4	6.23	4.39

Layer 4

Concentration								% Retained						
Sample ID	Al	Cd	Cu	Fe	Mn	Ni	Zn	Al	Cd	Cu	Fe	Mn	Ni	Zn
W	2.66	0.03	0.84	4.15	0.10	0.13	0.52	3.21	2.76	4.28	1.66	4.51	2.91	4.21
Ex	7.60	0.78	3.44	17.3	1.16	2.48	8.01	9.18	71.7	17.5	6.93	52.3	55.4	64.8
Ox	4.70	0.20	0.36	44.9	0.32	0.69	2.41	5.68	18.4	1.84	18.0	14.4	15.4	19.5
OM	53.5	0.07	19.2	202	0.43	1.34	1.66	44.6	4.44	67.5	55.8	13.4	20.7	9.26
RM	30.9	0.03	1.73	43.9	0.34	0.25	0.28	37.3	2.76	8.82	17.6	15.3	5.59	2.26

Layer 5

Concentration								% Retained						
Sample ID	Al	Cd	Cu	Fe	Mn	Ni	Zn	Al	Cd	Cu	Fe	Mn	Ni	Zn
W	3.14	0.02	1.04	1.04	0.09	0.14	0.40	3.19	1.85	4.36	0.94	3.35	2.99	3.17
Ex	8.31	0.78	4.29	9.35	1.45	2.78	8.34	8.44	72.3	18.0	8.43	53.9	59.4	66.2
Ox	5.99	0.20	0.73	13.1	0.40	0.78	2.59	6.08	18.5	3.06	11.8	14.9	16.7	20.6
OM	47.6	0.07	22.0	52.9	0.34	1.17	1.33	33.8	4.54	64.6	33.4	8.85	17.5	7.39
RM	47.7	0.03	2.37	50.4	0.51	0.16	0.34	48.4	2.78	9.95	45.4	19.0	3.42	2.70

Total Column Mass Fraction (mg/kg peat)**Fraction Bound (%)**

Layer	Al	Cd	Cu	Fe	Mn	Ni	Zn	Al	Cd	Cu	Fe	Mn	Ni	Zn
1	3030	17.0	429	21600	65.3	71.8	165	3.24	6.30	5.27	4.60	8.65	5.87	9.64
2	1610	12.6	362	18700	34.4	33.7	108	7.06	67.9	17.5	10.5	38.0	49.2	59.5
3	1700	12.8	312	11400	31.1	41.8	109	5.59	16.8	1.64	19.7	11.4	13.4	18.2
4	1660	21.8	392	4990	44.3	89.5	247	41.6	5.55	66.3	53.8	17.1	26.0	9.96
5	1970	21.6	477	2220	53.8	93.6	252	42.5	3.50	9.24	11.3	24.7	5.51	2.74

HQ - L[] C17 - 0 C**Layer 1**

Concentration								% Retained							
Sample ID	Al	Cd	Cu	Fe	Mn	Ni	Zn	Al	Cd	Cu	Fe	Mn	Ni	Zn	
W	8.52	0.17	1.94	40.6	0.58	0.63	2.44	5.19	13.2	6.37	5.26	17.6	12.3	19.8	
Ex	14.3	0.81	4.71	94.3	1.07	2.04	6.39	8.71	62.9	15.5	12.2	32.4	39.9	51.8	
Ox	11.8	0.20	0.33	136	0.37	0.60	2.00	7.19	15.5	1.08	17.6	11.2	11.7	16.2	
OM	121	0.07	30.8	637	0.91	1.82	1.86	50.1	3.70	68.8	56.1	18.8	24.2	10.3	
RM	47.2	0.06	2.52	68.4	0.66	0.60	0.24	28.8	4.66	8.28	8.85	20.0	11.7	1.95	

Layer 2

Concentration								% Retained						
Sample ID	Al	Cd	Cu	Fe	Mn	Ni	Zn	Al	Cd	Cu	Fe	Mn	Ni	Zn
W	2.76	0.06	0.61	0.90	0.22	0.18	0.93	1.72	3.00	2.16	0.56	5.32	2.8	4.27
Ex	18.9	1.44	4.60	12.0	2.28	3.53	14.3	11.8	71.9	16.3	7.50	55.1	54.9	65.6
Ox	16.5	0.35	0.66	17.4	0.64	0.97	4.35	10.3	17.5	2.34	10.9	15.5	15.1	20.0
OM	92.4	0.13	25.1	87.2	0.61	1.76	2.37	44.8	5.07	69.5	42.5	11.5	21.3	8.48
RM	50.6	0.05	2.74	61.7	0.52	0.38	0.37	31.5	2.50	9.72	38.6	12.6	5.91	1.70

Layer 3

Concentration								% Retained						
Sample ID	Al	Cd	Cu	Fe	Mn	Ni	Zn	Al	Cd	Cu	Fe	Mn	Ni	Zn
W	1.98	0.02	0.04	0.60	0.08	0.13	0.40	1.39	1.08	1.85	0.46	2.29	1.87	2.14
Ex	16.9	1.42	0.17	6.25	2.00	4.04	13.0	11.8	76.6	7.87	4.75	57.2	58.1	69.5
Ox	12.5	0.32	0.02	10.7	0.51	0.86	3.60	8.76	17.3	0.93	8.13	14.6	12.4	19.3
OM	107	0.06	2.81	110	0.63	2.56	2.32	43.5	1.88	75.5	48.5	10.5	21.3	7.20
RM	49.2	0.06	0.30	50.3	0.54	0.44	0.35	34.5	3.23	13.9	38.2	15.4	6.33	1.87

Layer 4

Concentration								% Retained						
Sample ID	Al	Cd	Cu	Fe	Mn	Ni	Zn	Al	Cd	Cu	Fe	Mn	Ni	Zn
W	2.78	0.03	0.02	0.67	0.11	0.18	0.51	2.10	1.58	6.23	0.57	1.85	2.70	2.50
Ex	13.3	1.35	0.02	7.05	4.29	4.50	12.9	10.0	71.1	6.23	6.02	72.3	67.4	63.1
Ox	12.3	0.38	0.00	10.2	0.65	1.17	4.56	9.27	20.0	0.00	8.71	11.0	17.5	22.3
OM	96.9	0.09	0.33	86.6	0.60	0.35	3.13	46.7	3.04	65.8	47.3	6.47	3.36	9.80
RM	42.3	0.08	0.07	43.8	0.50	0.60	0.46	31.9	4.22	21.8	37.4	8.43	8.99	2.25

Layer 5

Concentration								% Retained							
Sample ID	Al	Cd	Cu	Fe	Mn	Ni	Zn	Al	Cd	Cu	Fe	Mn	Ni	Zn	
W	4.73	0.05	0.03	1.15	0.20	0.30	0.91	3.03	2.58	8.98	0.90	5.15	3.02	4.30	
Ex	15.2	1.37	0.01	11.7	2.11	5.01	13.3	9.73	70.7	2.99	9.18	54.3	50.5	62.8	
Ox	12.4	0.36	0.01	11.7	0.57	1.25	4.23	7.93	18.6	2.99	9.18	14.7	12.6	20.0	
OM	126	0.12	0.35	95.7	0.62	4.28	3.41	51.6	3.97	67.1	48.0	10.2	27.6	10.3	
RM	43.3	0.08	0.06	41.7	0.61	0.63	0.54	27.7	4.13	18.0	32.7	15.7	6.34	2.55	

Total Column Mass Fraction (mg/kg peat)**Fraction Bound (%)**

Layer	Al	Cd	Cu	Fe	Mn	Ni	Zn	Al	Cd	Cu	Fe	Mn	Ni	Zn
1	3280	25.8	609	15400	66.0	102	247	2.75	3.68	4.3	3.36	5.73	4.05	5.50
2	3220	40.0	564	3200	82.7	129	436	10.4	71.2	15.5	10.0	56.6	54.5	63.4
3	2850	37.1	43.2	2630	69.9	139	374	8.66	17.9	1.66	14.2	13.2	13.8	19.8
4	2650	38.0	6.42	2340	119	133	409	47.5	3.54	69.3	52.1	10.8	20.1	9.16
5	3130	38.7	6.68	2550	77.7	199	423	30.7	3.68	9.26	20.3	13.6	7.55	2.08

LQ - H[] H14 - 20 C**Layer 1**

Concentration mg/L								% Retained						
Sample ID	Al	Cd	Cu	Fe	Mn	Ni	Zn	Al	Cd	Cu	Fe	Mn	Ni	Zn
W	3.41	0.07	1.10	21.0	0.34	0.38	1.37	2.77	8.13	3.49	2.07	15.6	11.2	15.5
Ex	14.3	0.52	5.48	80.3	0.84	1.74	5.08	11.6	60.4	17.4	7.90	38.6	51.4	57.3
Ox	10.6	0.17	0.47	173	0.32	0.57	1.87	8.61	19.7	1.49	17.0	14.7	16.8	21.1
OM	88.3	0.06	28.8	885	0.42	0.73	0.24	48.8	4.74	62.2	59.2	13.1	14.7	1.84
RM	34.7	0.06	4.85	140	0.39	0.20	0.38	28.2	6.97	15.4	13.8	17.9	5.91	4.29

Layer 2

Concentration								% Retained						
Sample ID	Al	Cd	Cu	Fe	Mn	Ni	Zn	Al	Cd	Cu	Fe	Mn	Ni	Zn
W	1.40	0.05	0.68	0.40	0.15	0.19	0.73	0.91	1.95	1.24	0.28	3.17	1.77	2.53
Ex	17.9	1.90	7.95	9.56	2.86	6.05	19.3	11.7	74.1	14.5	6.62	60.5	56.2	66.8
Ox	11.4	0.42	1.28	13.9	0.67	1.49	5.19	7.42	16.4	2.33	9.62	14.2	13.8	18.0
OM	116	0.16	51.0	95.0	0.70	3.14	4.02	58.9	4.87	72.5	51.3	11.6	22.8	10.9
RM	32.4	0.07	5.16	46.5	0.50	0.58	0.54	21.1	2.73	9.41	32.2	10.6	5.39	1.87

Layer 3

Concentration								% Retained						
Sample ID	Al	Cd	Cu	Fe	Mn	Ni	Zn	Al	Cd	Cu	Fe	Mn	Ni	Zn
W	3.25	0.04	0.45	0.47	0.15	0.18	0.68	2.33	2.03	1.91	0.39	3.74	2.13	2.94
Ex	14.9	1.35	2.52	12.1	2.26	4.27	14.0	10.7	68.5	10.7	10.0	56.4	50.5	60.5
Ox	15.8	0.38	0.43	13.2	0.68	1.33	4.89	11.3	19.3	1.83	10.9	17.0	15.7	21.1
OM	129	0.21	30.2	107	0.93	3.91	5.21	53.6	6.18	74.4	51.3	13.5	26.8	13.1
RM	30.8	0.08	2.62	33.1	0.38	0.41	0.56	22.1	4.06	11.1	27.4	9.48	4.85	2.42

Layer 4

Concentration								% Retained						
Sample ID	Al	Cd	Cu	Fe	Mn	Ni	Zn	Al	Cd	Cu	Fe	Mn	Ni	Zn
W	1.81	0.02	0.04	0.17	0.05	0.10	0.29	1.06	0.93	1.62	0.15	1.31	1.06	1.25
Ex	15.8	1.50	0.15	5.01	2.05	4.81	14.4	9.25	69.6	6.09	4.39	53.9	51.1	61.9
Ox	15.7	0.46	0.02	7.57	0.65	1.38	5.39	9.19	21.3	0.81	6.63	17.1	14.7	23.2
OM	126	0.15	2.91	90.3	0.74	4.20	4.07	47.2	4.45	75.6	50.6	12.5	28.6	11.2
RM	56.9	0.08	0.39	43.6	0.58	0.43	0.58	33.3	3.71	15.8	38.2	15.2	4.57	2.49

Layer 5

Concentration								% Retained						
Sample ID	Al	Cd	Cu	Fe	Mn	Ni	Zn	Al	Cd	Cu	Fe	Mn	Ni	Zn
W	1.37	0.02	0.00	0.10	0.05	0.10	0.25	1.42	1.02	0.00	0.24	1.65	1.30	1.21
Ex	17.3	1.56	0.00	2.19	2.11	4.76	14.7	17.9	79.4	0.00	5.36	69.5	61.7	71.3
Ox	13.7	0.32	0.00	3.24	0.44	0.94	3.85	14.2	16.3	0.00	7.93	14.5	12.2	18.7
OM	64.9	0.07	0.13	23.0	0.37	2.53	2.28	42.9	2.28	45.4	36.0	7.80	21.0	7.07
RM	22.9	0.02	0.10	20.6	0.20	0.29	0.37	23.7	1.02	54.6	50.4	6.59	3.76	1.79

Total column

Layer	Mass Fraction mg metal/kg peat							Fraction Bound (%)						
	Al	Cd	Cu	Fe	Mn	Ni	Zn	Al	Cd	Cu	Fe	Mn	Ni	Zn
1	2460	17.2	630	####	43.5	67.7	177	1.64	2.10	2.02	1.54	4.17	2.39	3.17
2	3070	51.3	1100	2890	94.5	215	578	11.7	71.8	14.3	7.60	57.0	54.5	64.4
3	2790	39.4	471	2420	80.2	169	463	9.83	18.4	1.96	14.7	15.5	14.4	20.2
4	3420	43.1	49.2	2280	76.1	188	465	50.8	4.50	70.1	56.4	11.7	24.0	9.91
5	1940	39.3	3.66	817	60.7	154	413	26.0	3.26	11.7	19.8	11.5	4.81	2.32

LQ - L[] H15 - 20 C**Layer 1**

Concentration								% Retained							
Sample ID	Al	Cd	Cu	Fe	Mn	Ni	Zn	Al	Cd	Cu	Fe	Mn	Ni	Zn	
W	2.86	0.09	0.41	3.45	0.42	0.35	1.67	1.47	3.49	1.57	0.73	6.70	3.68	5.37	
Ex	19.2	1.68	2.57	26.0	3.01	4.51	17.6	9.87	65.1	9.84	5.47	48.1	47.4	56.6	
Ox	18.0	0.53	0.28	57.6	1.42	1.37	7.06	9.25	20.5	1.07	12.1	22.7	14.4	22.7	
OM	163	0.19	27.8	465	1.30	3.74	5.77	57.0	5.01	72.4	66.5	14.1	26.7	12.6	
RM	43.7	0.15	3.95	72.5	0.53	0.75	0.86	22.5	5.82	15.1	15.2	8.46	7.88	2.76	

Layer 2

Concentration								% Retained							
Sample ID	Al	Cd	Cu	Fe	Mn	Ni	Zn	Al	Cd	Cu	Fe	Mn	Ni	Zn	
W	1.05	0.02	0.08	0.30	0.08	0.10	0.38	0.78	0.64	1.13	0.27	1.07	0.93	0.92	
Ex	14.8	2.28	0.58	5.65	4.77	5.83	27.4	11.1	73.5	8.16	5.12	64.0	54.1	66.0	
Ox	11.7	0.58	0.07	8.7	1.36	1.38	8.50	8.74	18.7	0.99	7.89	18.3	12.8	20.5	
OM	97.5	0.17	7.34	81.5	1.04	3.88	5.87	56.8	4.27	80.6	57.6	10.9	28.1	11.0	
RM	30.3	0.09	0.65	32.1	0.43	0.43	0.67	22.6	2.90	9.15	29.1	5.77	3.99	1.61	

Layer 3

Concentration								% Retained						
Sample ID	Al	Cd	Cu	Fe	Mn	Ni	Zn	Al	Cd	Cu	Fe	Mn	Ni	Zn
W	2.74	0.03	0.02	0.40	0.28	0.41	1.19	2.94	1.10	5.68	0.35	3.33	5.01	2.65
Ex	6.69	1.98	0.02	7.19	5.52	4.01	28.2	7.18	72.3	5.68	6.29	65.7	49.0	62.8
Ox	7.62	0.53	0.00	9.99	1.55	1.06	9.77	8.18	19.4	0.00	8.74	18.4	13.0	21.8
OM	84.5	0.10	0.40	112	0.94	3.26	7.75	52.6	2.12	65.9	56.8	6.49	23.1	10.0
RM	27.1	0.14	0.08	31.8	0.51	0.81	1.22	29.1	5.11	22.7	27.8	6.07	9.90	2.72

Layer 4

Concentration								% Retained						
Sample ID	Al	Cd	Cu	Fe	Mn	Ni	Zn	Al	Cd	Cu	Fe	Mn	Ni	Zn
W	1.56	0.00	0.02	0.50	0.10	0.05	0.46	1.27	0.00	6.11	0.40	0.98	1.45	1.11
Ex	3.64	1.40	0.00	3.43	6.30	1.56	25.8	2.97	73.3	0.00	2.75	61.9	45.1	62.1
Ox	4.78	0.40	0.01	7.53	1.91	0.42	9.71	3.90	20.9	3.06	6.03	18.8	12.2	23.4
OM	72.1	0.14	0.23	99.6	1.44	1.93	8.09	37.7	4.69	45.0	51.1	9.05	35.7	12.5
RM	66.3	0.02	0.15	49.6	0.95	0.19	0.40	54.2	1.05	45.8	39.7	9.33	5.50	0.96

Layer 5

Concentration								% Retained						
Sample ID	Al	Cd	Cu	Fe	Mn	Ni	Zn	Al	Cd	Cu	Fe	Mn	Ni	Zn
W	2.39	0.00	0.00	0.38	0.14	0.03	0.27	2.92	0.00	0.00	0.39	2.08	4.54	1.97
Ex	3.72	0.56	0.00	4.18	4.41	0.24	8.44	4.55	75.0	0.00	4.24	65.5	36.3	61.7
Ox	4.28	0.14	0.00	5.85	1.13	0.05	2.81	5.23	18.8	0.00	5.93	16.8	7.56	20.5
OM	72.5	0.01	0.24	86.7	1.00	0.33	2.81	56.7	0.86	79.3	56.2	9.51	31.9	13.1
RM	25.0	0.04	0.04	32.8	0.41	0.13	0.37	30.6	5.36	20.7	33.2	6.09	19.7	2.70

Total Column Mass Fraction

Layer	Al	Cd	Cu	Fe	Mn	Ni	Zn	Al	Cd	Cu	Fe	Mn	Ni	Zn
1	3890	51.6	522	9520	125	190	622	1.69	1.26	1.55	0.54	2.61	2.88	2.30
2	2680	62.1	142	2210	149	215	831	7.68	71.3	9.30	5.03	61.5	49.6	62.2
3	1860	54.8	7.04	2290	168	164	898	7.41	19.7	1.06	9.71	18.9	13.1	21.9
4	2450	38.2	6.54	2500	204	69.1	831	52.5	3.75	73.8	61.0	9.74	27.3	11.6
5	1640	14.9	3.87	1970	135	13.2	274	30.7	3.97	14.3	23.7	7.25	7.09	2.04

HQ - H[] H16 - 20 C**Layer 1**

Concentration								% Retained						
Sample ID	Al	Cd	Cu	Fe	Mn	Ni	Zn	Al	Cd	Cu	Fe	Mn	Ni	Zn
W	5.02	1.54	1.67	16.7	4.47	3.78	16.8	0.79	10.4	1.60	0.98	15.2	15.7	18.4
Ex	13.9	6.88	4.39	27.0	5.29	7.07	30.4	2.19	46.5	4.20	1.59	18.0	29.4	33.4
Ox	15.2	3.05	0.62	136	11.9	3.09	17.7	2.39	20.6	0.59	8.01	40.4	12.9	19.4
OM	648	3.49	122	1570	8.82	12.3	31.7	69.3	16.0	79.4	62.9	20.4	34.8	23.7
RM	161	0.95	14.8	450	1.81	1.72	4.68	25.3	6.42	14.2	26.5	6.14	7.16	5.14

Layer 2

Concentration								% Retained						
Sample ID	Al	Cd	Cu	Fe	Mn	Ni	Zn	Al	Cd	Cu	Fe	Mn	Ni	Zn
W	0.86	0.53	0.3	0.13	3.48	3.60	17.2	0.23	1.36	0.54	0.05	3.40	3.73	3.70
Ex	0.00	20.0	0.31	0.00	29.7	28.1	182	0.00	51.4	0.56	0.00	29.0	29.1	39.2
Ox	0.54	6.00	0.08	1.30	35.1	5.52	70.6	0.15	15.4	0.14	0.55	34.3	5.72	15.2
OM	282	4.45	48.0	93.8	33.5	36.8	124	59.9	8.92	67.5	30.9	25.5	29.8	20.8
RM	146	8.89	17.3	162	7.88	30.5	98.1	39.7	22.9	31.2	68.5	7.70	31.6	21.1

Layer 3

Concentration								% Retained						
Sample ID	Al	Cd	Cu	Fe	Mn	Ni	Zn	Al	Cd	Cu	Fe	Mn	Ni	Zn
W	0.34	0.10	0.02	0.18	3.07	2.03	14.1	0.22	1.11	1.52	0.07	2.70	3.78	3.58
Ex	0.00	3.29	0.00	0.00	24.9	8.09	90.2	0.00	36.5	0.00	0.00	21.9	15.1	22.9
Ox	0.23	1.20	0.00	0.18	39.6	1.53	58.3	0.15	13.3	0.00	0.07	34.9	2.85	14.8
OM	89.5	2.30	1.30	222	61.2	57.5	316	33.4	14.8	57.4	49.7	31.3	62.2	46.5
RM	103	3.08	0.54	130	10.5	8.64	48.4	66.2	34.2	41.1	50.2	9.25	16.1	12.3

Layer 4

Concentration								% Retained						
Sample ID	Al	Cd	Cu	Fe	Mn	Ni	Zn	Al	Cd	Cu	Fe	Mn	Ni	Zn
W	0.33	0.00	0.01	0.18	0.60	0.11	1.16	0.20	0.00	2.39	0.08	0.22	3.35	2.06
Ex	0.00	0.15	0.00	0.00	8.27	0.25	8.10	0.00	34.6	0.00	0.00	3.00	7.61	14.4
Ox	0.37	0.05	0.00	0.09	6.92	0.05	5.90	0.23	11.5	0.00	0.04	2.51	1.52	10.5
OM	115	0.10	0.42	213	14.9	3.68	54.3	44.8	14.7	64.2	63.8	3.46	71.7	61.7
RM	90.1	0.17	0.14	77.2	250	0.52	6.39	54.8	39.2	33.4	36.1	90.8	15.8	11.3

Layer 5

Concentration								% Retained						
Sample ID	Al	Cd	Cu	Fe	Mn	Ni	Zn	Al	Cd	Cu	Fe	Mn	Ni	Zn
W	0.25	0.00	0.01	0.21	0.08	0.03	0.04	0.22	0.00	2.27	0.12	1.03	5.31	0.62
Ex	0.00	0.03	0.00	0.00	2.28	0.05	0.17	0.00	50.0	0.00	0.00	29.3	8.85	2.64
Ox	0.00	0.01	0.00	0.00	1.40	0.03	0.27	0.00	16.7	0.00	0.00	18.0	5.31	4.20
OM	87.4	0.00	0.50	152	4.60	0.43	7.64	49.6	0.00	72.7	56.9	37.9	48.7	76.0
RM	56.5	0.02	0.11	73.4	1.07	0.18	1.06	50.1	33.3	25.0	43.0	13.8	31.8	16.5

Total Column Mass Fraction (mg/kg peat)**Fraction Bound (%)**

Layer	Al	Cd	Cu	Fe	Mn	Ni	Zn	Al	Cd	Cu	Fe	Mn	Ni	Zn
1	####	296	2090	33900	589	480	1820	0.47	3.43	1.24	0.68	2.21	5.37	4.87
2	7350	778	1110	4730	2050	1930	9290	0.97	48.0	2.90	1.05	13.3	24.5	30.7
3	3110	180	26.3	5180	2270	1070	7890	1.14	16.3	0.43	5.34	18.0	5.74	15.1
4	3290	8.68	8.38	4280	5510	65.7	1130	58.7	11.5	75.1	58.3	15.2	41.1	33.7
5	2250	1.20	8.80	3420	155	11.3	129	38.8	20.7	20.3	34.6	51.3	23.4	15.7

HQ - L[] H17 - 20 C**Layer 1**

Concentration								% Retained							
Sample ID	Al	Cd	Cu	Fe	Mn	Ni	Zn	Al	Cd	Cu	Fe	Mn	Ni	Zn	
W	0.98	0.09	0.23	1.81	1.07	0.76	3.70	0.33	0.67	0.59	0.36	2.01	2.26	2.08	
Ex	0.00	5.08	0.15	0.14	11.4	6.58	45.9	0.00	38.0	0.38	0.03	21.4	19.6	25.8	
Ox	0.46	1.74	0.07	3.09	17.9	1.12	23.9	0.15	13.0	0.18	0.62	33.7	3.33	13.4	
OM	231	2.83	33.3	252	23.1	11.4	56.3	52.1	14.4	58.1	34.5	29.5	23.1	21.5	
RM	143	4.54	15.9	320	7.09	17.4	66.1	47.4	33.9	40.8	64.5	13.3	51.8	37.2	

Layer 2

Concentration								% Retained							
Sample ID	Al	Cd	Cu	Fe	Mn	Ni	Zn	Al	Cd	Cu	Fe	Mn	Ni	Zn	
W	1.00	0.06	0.10	0.88	0.71	0.44	2.02	0.88	2.63	4.89	0.47	2.52	3.88	2.85	
Ex	0.00	0.86	0.01	0.00	9.4	1.06	13.1	0.00	37.8	0.49	0.00	33.4	9.34	18.5	
Ox	0.12	0.28	0.01	0.22	6.64	0.13	6.89	0.11	12.3	0.49	0.12	23.6	1.14	9.74	
OM	86.7	0.33	1.84	167	11.4	10.3	51.5	59.3	11.3	70.2	69.2	31.6	70.8	56.8	
RM	45.2	0.82	0.49	56.9	2.53	1.69	8.59	39.7	36.0	24.0	30.2	8.98	14.9	12.1	

Layer 3

Concentration								% Retained						
Sample ID	Al	Cd	Cu	Fe	Mn	Ni	Zn	Al	Cd	Cu	Fe	Mn	Ni	Zn
W	0.10	0.00	0.00	0.10	0.11	0.00	0.04	0.10	0.00	0.00	0.06	1.40	0.00	1.18
Ex	0.00	0.04	0.00	0.00	1.56	0.07	0.20	0.00	42.9	0.00	0.00	19.8	9.18	5.90
Ox	0.15	0.00	0.00	0.00	1.52	0.02	0.16	0.14	0.00	0.00	0.00	19.3	2.62	4.72
OM	77.6	0.04	0.53	179	5.88	0.66	3.90	42.8	24.9	64.4	59.0	43.3	50.2	66.7
RM	59.9	0.03	0.17	71.9	1.28	0.29	0.73	57.0	32.2	35.6	40.9	16.2	38.0	21.5

Layer 4

Concentration								% Retained						
Sample ID	Al	Cd	Cu	Fe	Mn	Ni	Zn	Al	Cd	Cu	Fe	Mn	Ni	Zn
W	0.80	0.00	0.00	0.65	0.06	0.02	0.05	0.71	0.00	0.00	0.34	1.02	4.12	2.01
Ex	0.00	0.03	0.00	0.00	1.18	0.05	0.03	0.00	30.0	0.00	0.00	20.0	10.3	1.20
Ox	0.14	0.00	0.01	0.04	1.11	0.02	0.05	0.12	0.00	2.63	0.02	18.8	4.12	2.01
OM	114	0.00	0.50	234	4.56	0.29	2.41	64.4	0.00	84.2	78.6	49.5	38.2	61.9
RM	39.4	0.07	0.05	40.2	0.63	0.21	0.82	34.8	70.0	13.2	21.1	10.7	43.2	32.9

Layer 5

Concentration								% Retained						
Sample ID	Al	Cd	Cu	Fe	Mn	Ni	Zn	Al	Cd	Cu	Fe	Mn	Ni	Zn
W	0.96	0.00	0.01	0.42	0.03	0.00	0.00	0.78	0.00	2.02	0.29	1.55	0.00	0.00
Ex	0.00	0.04	0.00	0.00	0.55	0.06	0.03	0.00	70.9	0.00	0.00	28.4	16.1	3.87
Ox	1.03	0.01	0.00	0.26	0.25	0.03	0.05	0.83	17.7	0.00	0.18	12.9	8.07	6.45
OM	96.6	0.00	0.44	111	0.75	0.16	0.58	78.2	0.00	88.9	77.8	38.7	43.1	74.8
RM	39.0	0.01	0.07	48.5	0.56	0.19	0.18	20.2	11.3	9.05	21.7	18.5	32.7	14.9

Total Column Mass Fraction (mg/kg peat)**Fraction Bound (%)**

Layer	Al	Cd	Cu	Fe	Mn	Ni	Zn	Al	Cd	Cu	Fe	Mn	Ni	Zn
1	6030	267	780	9930	1060	672	3560	0.51	0.94	0.80	0.32	2.04	2.62	2.28
2	2280	45.5	40.9	3770	563	227	1420	0.00	38.0	0.38	0.01	24.8	16.8	23.2
3	2100	1.86	9.55	3520	158	15.3	67.8	0.25	12.8	0.21	0.30	28.3	2.83	12.2
4	2270	2.00	7.60	3810	118	9.71	49.8	58.0	13.9	59.3	55.8	32.6	35.4	32.4
5	2470	1.13	9.90	2850	38.8	7.43	15.5	41.3	34.4	39.3	43.6	12.2	42.3	29.9

APPENDIX G

COLUMN EXPERIMENT

SUBSTRATE/AMENDMENT MIXTURE GRAPHS

Figure G-1: pH Variation in Sludge/Lime Amended Columns

Figure G-2: pH Variation in Sludge Amended Columns

◆ Column 5 (0 C) ▲ Column 9 (0 C) ◆ Column 8 (20 C) ▲ Column 11 (20 C)
Figure G-3: pH Variation in Sludge/Limestone Amended Columns

◆ Column 1 (0 C) ▲ Column 2 (0 C) ◆ Column 6 (20 C) ▲ Column 12 (20 C)
Figure G-4: Acidity Variation in Sludge/Lime Amended Columns

Figure G-5: Acidity Variation in Sludge Amended Columns

Figure G-6: Acidity Variation in Sludge/Limestone Amended Columns

Figure G-7: Dissolved Oxygen Concentrations Variation in Sludge/Lime Amended Columns

Figure G-8: Dissolved Oxygen Concentrations Variation in Sludge Amended Columns

Figure G-9: Dissolved Oxygen Concentrations Variation in Sludge/Limestone Amended Columns

Figure G-10: Sulphate Removal Variation in Sludge/Lime Amended Columns

Figure G-11: Sulphate Removal Variation in Sludge Amended Columns

Figure G-12: Sulphate Removal Variation in Sludge/Limestone Amended Columns

Figure G-13: Metal Effluent Concentrations in Sludge/Lime Amended Columns at 0°C

Figure G-14: Metal Effluent Concentrations in Sludge/Lime Amended Columns at 20°C

Figure G-15: Metal Effluent Concentrations in Sludge Amended Columns at 0°C

Figure G-16: Metal Effluent Concentrations in Sludge Amended Columns at 20°C

Column 5 - 0°C

Column 9 - 0°C

Figure G-17: Metal Effluent Concentrations in Sludge/Limestone Amended Columns at 0°C

Figure G-18: Metal Effluent Concentrations in Sludge/Limestone Amended Columns at 0°C

APPENDIX H

COLUMN EXPERIMENT

SUBSTRATE/AMENDMENT MIXTURE

VOLUMETRIC WATER CONTENT & TEMPERATURE PROFILES

Figure H-1: Volumetric Water Content Profiles in Sludge/Lime Amended Columns at 0°C

Figure H-2: Volumetric Water Content Profiles in Sludge/Lime Amended Columns at 20°C

Figure H-3: Volumetric Water Content Profiles in Sludge Amended Columns at 0°C

Figure H-4: Volumetric Water Content Profiles in Sludge Amended Columns at 20°C

Figure H-5: Volumetric Water Content Profiles in Sludge/Limestone Amended Columns at 0°C

Figure H-6: Volumetric Water Content Profiles in Sludge/Limestone Amended Columns at 20°C

Figure H-7: Temperature Profiles in Sludge/Lime Amended Columns at 0°C

Figure H-8: Temperature Profiles in Sludge/Lime Amended Columns at 20°C

Figure H-9: Temperature Profiles in Sludge Amended Columns at 0°C

Figure H-10: Temperature Profiles in Sludge Amended Columns at 20°C

Figure H-11: Temperature Profiles in Sludge/Limestone Amended Columns at 0°C

Figure H-12: Temperature Profiles in Sludge/Limestone Amended Columns at 20°C

APPENDIX I

COMBINE PASSIVE SYSTEM EXPERIMENT INFLUENT/EFFLUENT GRAPHS

Figure I-1: Combined System Influent pH

Figure I-2: Combined System Influent Acidity

Figure I-3: Combined System Influent Dissolved Oxygen Concentrations

Figure I-4: Combined System Influent Sulphate Concentrations

Figure I-5: Combined System Influent Metal Concentrations

Figure I-6: Effluent Iron Concentrations at Various Stages Throughout Combined System

Figure I-7: Effluent Aluminum Concentrations at Various Stages Throughout Combined System

Figure I-8: Effluent Zinc Concentrations at Various Stages Throughout Combined System

Figure I-9: Effluent Manganese Concentrations at Various Stages Throughout Combined System

Figure I-10: Effluent Nickel Concentrations at Various Stages Throughout Combined System

Figure I-11: Effluent Copper Concentrations at Various Stages Throughout Combined System

Figure I-12: Effluent Iron Concentrations at Various Stages Throughout Combined System