UTILIZATION OF COAL/BIOMASS FLY ASH IN THE CONTROL AND TREATMENT OF ACID MINE DRAINAGE

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ABSTRACT

This study investigated the feasibility of using coal/biomass fly ash (CBFA) blended with various percentages of mine tailings, bentonite, and glacial till soil to control and treat acid mine drainage (AMD). Applications included their use as a cover (cap), liner, low permeability core for dams, and flow-through reactive barriers. These materials were chosen due to their availability and their potential to be a cost effective alternative to traditional technologies and materials. The study included: characterization of the CBFA, mine tailings, bentonite, and glacial till soil; laboratory fixed wall kinetic column permeation tests on the CBFA, mine tailings, glacial till soil, CBFA and mine tailings mixtures, CBFA and glacial till soil mixtures, and bentonite amended CBFA; and post-testing analysis of the materials involved in the laboratory tests. Distilled water and a synthetic AMD solution were used as the permeation fluids.

The results of the experiments indicated that the co-placement of CBFA with mine tailings, bentonite, and glacial till soil have potential applications in the geo-environmental field to prevent, contain, and/or treat AMD. A significant decrease in hydraulic conductivity was observed when AMD was permeated through CBFA only and the higher percentages (33% and 50%) of CBFA mixed with mine tailings. A minor decrease in hydraulic conductivity was observed in the lower CBFA / mine tailing mixtures and the CBFA / glacial till soil mixtures. The addition of bentonite to CBFA was effective in decreasing the hydraulic conductivity versus CBFA alone. CBFA alone could not meet the hydraulic conductivity of 1 x 10^{-7} cm/s or less required by USEPA regulations. Mixing 10% bentonite (by mass) with CBFA, however, decreased the hydraulic conductivity to 1 x 10^{-7} cm/s or less throughout the entire permeation both water and AMD. Results also indicate that the addition of CBFA was effective in neutralizing the AMD and reducing the concentrations of heavy metals to meet the regulatory requirements, except for aluminum which was found to leach from the CBFA at high pH.

Significant reductions in hydraulic conductivity of the CBFA and CBFA amended mine tailings can produce a low permeability barrier for the containment and subsequent prevention of AMD. This barrier can be used as a liner, cap, and low permeability dam core to contain acidic mine tailings and AMD. Applications as a cap and liner further prevent recharge of groundwater from rainfall and groundwater flow. Minor decreases in hydraulic conductivity of the CBFA and CBFA amended mine tailings and glacial till soil can serve as a flow through reactive barrier to treat AMD migration offsite and as an alkaline recharge medium up-gradient of ground water flow.

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1.0 INTRODUCTION

Acid mine drainage (AMD) is a major environmental challenge to the mining industry. Today's mine sites are often regulated by government agencies and require their approval prior to operation. Approval often includes a work plan, a mine waste and tailings disposal plan, an environmental control and monitoring plan, and a mine closure plan. The disposal of mine tailings and other mine waste in the past were often carried out in a manner that is not in compliance with today's regulations.

Improper disposal of mine tailings and waste rock from sulphide containing rock, results in the release of an acidic leachate, known as acid mine drainage (AMD) and sometimes called acid rock drainage (ARD). AMD in addition to having a low pH, often contains elevated concentrations of heavy metals. These concentrations generally exceed the governing mine effluent regulations and other guidelines, such as those set to protect aquatic life and drinking water quality. This release into the surface water regime (e.g. streams, rivers, ponds, lakes) has a potentially devastating effect on adjacent aquatic and terrestrial life. Contaminated surface water and infiltration into groundwater aquifers may also affect the drinking water quality of nearby towns.

The formation of AMD is often not immediate and may take several years. Once started, it is difficult to stop and may continue for many decades (BC-MEMPR 1989). This environmental impact may not be felt or noticed until long after the closure of the mine site. By then the mining companies may no longer be in existence and the mine sites may have been reverted back to the crown/state.

Current AMD prevention methods include, water covers; soil covers; and base neutralization. A water cover can provide an effective prevention method and in many cases it is the most economical option. Where a water cover is not practical (i.e due to a limited supply of surface water or the impoundment area is unable to effectively contain the water) soil covers are often used. Engineered soil covers substantially reduce the oxygen and water infiltration, however some oxidation may still occur over time. Base neutralization can take place either during the placement (co-placement) of the mine tailings or after the mine tailings final placement. Co-placement involves the addition of an alkaline material, such as lime, limestone, gypsum, and fly ash, with the acidic mine tailings during placement to provide alkalinity to balance the acid generating potential of the mine tailings. Base addition after the mine tailings final disposal involves placing a layer of alkaline material over the surface of the mine tailings, typically in the zone of oxidation (vadose zone). This alkaline layer also serves as an alkaline recharge medium to add alkalinity to the underlying mine tailings pore water during precipitation events. While these methods can be effective in preventing or decreasing the formation of AMD, the amount of additive required is often large, and in many cases impractical.

1.1 BACKGROUND

Traditional research on prevention and treatment of AMD has looked at water and soil covers, along with lime as a base additive. Recent research has investigated using coal fly ash for the prevention and treatment of AMD (Xenidis et al. 2002, Shang et al. 2006, Wang et al. 2006, Perez-Lopez et al. 2007, Yeheyis et al. 2007). Coal fly ash is a by-product from the burning of coal at thermal electric generating stations. While fly ash is used in the portland cement industry, it is often underutilized, requiring storage for future use or disposal as an industrial waste.

Coal fly ash has been researched by various researchers as a base additive for co-disposal with reactive mine tailings and in combination with bentonite as a containment barrier for AMD (Xenidis et al. 2002, Shang et al. 2006, Wang et al. 2006, Perez-Lopez et al. 2007, Yeheyis et al. 2007). The primary objectives of these studies were to monitor changes in the leachate pH and hydraulic conductivity, along with changes in the leachate chemistry, notably the heavy metals. Limited discussions regarding practical applications of the findings were provided. In addition, limited characterization of the fly ash was reported in the literature and no studies had examined coal/biomass fly ash from the burning of lignite coal with wood biomass. Finally, no studies were identified that looked at the addition of coal fly ash with native soil for applications of treating AMD.

1.2 RESEARCH OBJECTIVES

This research further expands on research carried out by others, with particular emphasis on using coal/biomass fly ash (CBFA) from a 16 % (by mass) biomass (softwood pellets) burn in combination with 84% lignite coal. The CBFA was obtained from the Atikokan coal generation station, owned by Ontario Power Generation, in Atikokan, Ontario.

The research was carried out in ten phases:

1) Characterization of the coal/biomass fly ash. This includes: neutralization potential; elemental composition; and geotechnical/geochemical properties when subjected to water and AMD permeation in a controlled laboratory environment.

2) Characterization of the reactive mine tailings used in this study from Sudbury,

Ontario. This includes: acid generating potential; elemental composition; and geotechnical/ geochemical properties when subjected to water and AMD permeation in a controlled laboratory environment.

3) Characterization of glacial till soil used in this study from Buchans, Newfoundland and Labrador. This includes: acid generating / neutralization potential; elemental composition; and geotechnical / geochemical properties when subjected to AMD permeation in a controlled laboratory environment.

4) Characterization of various percentages of CBFA amended reactive mine tailings, with particular emphasis on changes in leachate pH, elemental chemistry, and hydraulic conductivity when permeated with distilled water and AMD.

5) Characterization of various ratios of CBFA amended with bentonite, with particular emphasis on changes in leachate pH, elemental chemistry, and hydraulic conductivity when permeated with AMD.

6) Characterization of various ratios of glacial till soil amended with CBFA, with particular emphasis on changes in leachate pH, elemental chemistry, and hydraulic conductivity when permeated with AMD.

7) Performance of agitated static extraction tests on CBFA and mine tailings to investigate the leaching potential of metals with the increase of acidity.

8) Performance of agitated static extraction tests on 33% CBFA amended mine tailings to investigate the leaching potential of metals at different leachate pH values.

9) Investigation of the possible formation and/or dissolution of secondary minerals through the various AMD permeations tests by XRD and SEM analysis, and geochemical modelling of leachate chemistry.

10) Interpolation of the results to devise applicable applications for the findings.

The results of the research are used as a preliminary feasibility study for the use of Atikokan CBFA to treat, contain, and reduce the formation of AMD. Investigated is its use in conjunction with reactive mine tailings to treat, contain, and reduce the formation of AMD; amended with low percentages of bentonite to contain and treat AMD; and amended with glacial till soil to treat AMD.

1.3 METHODOLOGY

This research involved a number of steps. First, a literature review of previous studies investigating AMD prevention and treatment using coal fly ash and other alkaline materials was carried out. Also reviewed were papers that investigated the properties of fly ash, mine tailings, bentonite, and AMD. Next, characterization of fly ash, mine tailings, bentonite, glacial till soil, AMD, and combination thereof were conducted. This characterization involved a number of laboratory tests, including: acid based accounting (ABA), X-Ray Diffraction (XRD), X-Ray Florescence (XRF), Scanning electron microscopy and energy dispersive X-ray analysis (SEM-EDX), leachate extraction tests, and Inductively Coupled Plasma – Atomic Emission Spectrometry (ICP-AES).

Fixed wall kinetic columns were designed and constructed to carry out laboratory constant head permeability tests. Columns were constructed of either 50 mm or 75 mm ID clear acrylic tubing. Inert materials (nylon, vinyl, PVC, and stainless steel) were used as tubing, fasteners, collection containers, etc. The objective of these tests were to simulate the passage of effluent (water and/or AMD) through a pack made from the various concentrations of CBFA, mine tailings, bentonite, and soil investigated. Hydraulic conductivity and effluent pH were monitored, with select samples analyzed by ICP-AES to determine its elemental chemistry. Upon termination of the kinetic column tests, select samples were prepared and analysed for changes in mineralogy using XRD and SEM-EDX. Results from these tests were collaborated into four case studies (applications). At the time of writing, two of these case studies (Chapter 5 and 6) were submitted and accepted as conference papers.

1.4 THESIS OUTLINE

The thesis is presented in manuscript format. Chapter 1 is an introduction to the research which outlines the rational, objective, methodology, and structure of the research. Chapter 2 summarizes the literature review. Chapter 3 presents the geotechnical, chemical and mineralogical properties of the study materials (CBFA, mine tailings, bentonite, and glacial till) along with acid based accounting and characterization of the CBFA and mine tailings leachate at various acidity. Chapters 4, 5, 6 and 7 are case studies for the application of using CBFA for the treatment, containment and prevention of AMD. Chapter 8 summarizes the research conducted in this study, and presents conclusions and recommendations for future work.

Chapter 4 is a case study utilizing mine tailings amended with different percentages of CBFA. Five percentages (5, 10, 20, 33, and 50) of CBFA (by mass) were amended to mine tailings (mixed). Fixed wall, constant head permeation tests were carried out to study the effects of distilled water permeation on the leachate. Applications for these mixtures include within the vadose zone of mine tailings disposal facilities and as an alkalinity recharge medium up-gradient of reactive mine tailings disposal facilities.

Chapter 5 is a case study utilizing mine tailings amended with CBFA as a reactive barrier to treat and contain AMD. Five percentages (5, 10, 20, 33, and 50 percent) of CBFA (by mass) were mixed with reactive mine tailings (packs). Fixed wall, constant head permeation tests were carried out to study the effects of AMD permeation on the packs. Two reactive barrier scenarios are discussed: a flow through reactive barrier to treat AMD without influencing the groundwater flow; and, a low permeable barrier to treat and reduce AMD migration offsite.

Chapter 6 is a case study utilizing CBFA amended with bentonite as a low permeable barrier. Four percentages (2.5, 5, 7.5, and 10 percent) of bentonite (by mass) were mixed with CBFA. Also studied was the placement of a layer of CBFA upstream in two of the bentonite amended CBFA packs (10 and 20 percent). Fixed wall, constant head permeation tests were carried out to study the effects of AMD permeation on the packs. Discussed within Chapter 6 is its use as a low permeable containment barrier to treat and reduce AMD seepage, along with their possible application as a cap, liner, and low permeable core in containment dams.

Chapter 7 is a case study utilizing glacial till soil amended with CBFA as a reactive barrier. Four percentages (5, 10, 20, and 33 percent) of CBFA (by mass) were mixed with glacial till soil. Fixed wall, constant head permeation tests were carried out to study the effects of AMD permeation on the packs. Discussed within is its use as a flow through reactive barrier to treat AMD seepage.

1.5 REFERENCES

British Columbia Ministry of Energy Mines and Petroleum Resources (BC-MEMPR) 1989. Draft acid rock drainage technical guide. *British Columbia Acid Mine Drainage Task Force,* Victoria, BC.

Perez-Lopez, R., Nieto, J. and & Ruiz de Almodovar, G. 2007. Utilization of fly ash to improve the quality of the acid mine drainage generated by oxidation of a sulphide-rich mining waste. *Chemiosphere,* 67: 1637-1646.

Shang, J., Wang, H., Kovac, V. and Fyfe, J. 2006. Site specific study on stabilization of acid-generating mine tailings using coal fly ash. *Journal of Materials in Civil Engineering,* March/April: 140-151.

Wang, H., Shang, Kovac, V, and Ho, K. 2006. Utilization of Atikokan coal fly ash in acid rock drainage control from Musselwhite Mine tailings. *Canadian Geotechnical Journal,* 43: 229-243.

Xenidis, A., Mylona, E. and Paspaliaris, I. 2002. Potential use of lignite fly ash for the control of acid generation from sulphidic wastes. *Waste Management,* 22: 631-641.

Yeheyis, M., Shang, J. and Yanful, E. 2007. Beneficial utilization of coal fly ash as acid mine drainage barrier. *In* Proceedings of the 60th Canadian Geotechnical Conference & 8th Joint CGS/IAH-CNC Groundwater Conference, Ottawa, Canada, October 2007: pp 1494-1499.

2.0 LITERATURE REVIEW

2.1 INTRODUCTION

This research studied utilizing coal/biomass fly ash (CBFA) as an additive to prevent/retard the development of acid mine drainage (AMD), contain/reduce AMD seepage, and to treat AMD seepage. CBFA was studied by itself and amended with reactive mine tailings, bentonite, and glacial till soil. The primary research objective was to observe the reaction of AMD permeated through these materials by monitoring the changes in leachate pH and chemistry. A secondary research objective was to observe the reaction of AMD permeated through these materials on the leachate flow (hydraulic conductivity) and the formation of new compounds. Findings were compared with mine effluent regulations to determine the applicability of the study. To a lesser degree the findings were also compared with applicable guidelines for the protection of aquatic life and domestic drinking water quality.

If not properly managed and engineered, the disposal of coal fly ash and mine tailings may have severe environmental impacts. Leachate from coal fly ash has an alkaline pH, while mine tailings, when allowed to oxidize, has an acidic leachate with toxic concentrations of heavy metals. Research has shown that co-disposal of these two materials may be effective in producing a neutral to alkaline leachate with concentrations of heavy metals that are within applicable governing regulations and guidelines (Xenidis et al. 2002, Shang et al. 2006, Wang et al. 2006, Perez-Lopez et al. 2007).

Low permeability barriers are often used as a cap to reduce surface water infiltration (recharge), as a liner to reduce the egress of leachate, and as a low permeability core in containment dams and dykes. Current technologies include geosynthetic membranes, low permeability soil, low strength concrete, or combinations thereof. Due to the magnitude of many projects, these options are often not economically feasible. Low permeability soils are often the most economical when insitu and nearby deposits of soil can be utilized. Where the permeability of the soil is above the regulatory guidelines, sodium bentonite is often blended to achieve the required permeability. Previous studies have investigated the effects of AMD on bentonite and bentonite amended soil and coal fly ash. Bentonite was found to have a minimal buffering potential and observed an increase in the initial hydraulic conductivity and consolidation due to collapse of the bentonite double layer when the permeate was switched from water to AMD (Kashir et al. 2001).

Reactive barriers are a popular passive treatment technology to contain contamination plumes and to treat the effluent that may flow through (Blowes et al. 2003a, Gitari et al. 2006 and 2008a, Walton-Day 2003). Two types of reactive barriers are in use: 1) low permeability barrier to contain contamination and prevent the passage of effluent; and, 2) flow through barrier which allows the passage of groundwater while treating the contaminant. Flow through barriers can be of two configurations: 1) the groundwater flow regime is unaffected and the leachate flows through this barrier, while being treated; and, 2) the groundwater flow regime is redirected to flow within the reactive barrier to a controlled outlet, while being treated along the way (Potgieter-Vermaak et al. 2006).

An understanding of the geotechnical, chemical, physical, and mineralogical properties of the CBFA, mine tailings, bentonite, and soil assist in determining the application of each material to meet the study objectives. The formation process of AMD, its effects on the environment, and its interaction with the reactive barrier materials were studied.

2.2 COAL FLY ASH PROPERTIES

Coal fly ash is produced from the burning of pulverized coal in a coal-fired boiler. It is a fine grained, inorganic powdery incombustible particulate material that is carried off in the flue gas and collected by electrostatic precipitators, bag houses, or cyclones. The coal fly ash particles are fused during combustion into a glassy, spherical, amorphous structure. Coal fly ash for this study was from a 16% (by mass) wood biomass (softwood pellets from British Columbia) burn in combination with 84% western Canadian lignite coal at the Atikokan coal generation station, owned by Ontario Power Generation, in Atikokan, Ontario.

The chemical properties of fly ash are influenced by the coal burned and the techniques used for handling, burning and storage. There are four types of coal, anthracite, bituminous, subbituminous, and lignite. They vary in terms of heating value, chemical composition, ash content, and geological origin (ACAA 1997, USDOT 1995).

The largest portion of coal fly ash is used in the cement industry as an addition to Portland cement. It is divided into two classes based on its chemical properties: Class F and Class C. Class F originates from the burning of bituminous coal and Class C from lignite and subbituminous coal. The colour of fly ash can vary from tan to gray to black, depending on the amount of calcium and unburned carbon in the ash. The lighter the colour, the lower the carbon content and/or the higher the calcium content. Class C are usually light tan to buff in colour and Class F are usually a shade of grey (ACAA 1997, USDOT 1995).

2.2.1 Geotechnical Characteristics of Coal Fly Ash

Specific gravity is an important geotechnical characteristic which directly affects its bulk and relative densities. The specific gravity of fly ash usually ranges from 2.1 to 3.0. Test results on four representative samples of the fly ash used in this study had an average specific gravity of 2.42. Variation in specific gravity is dependent on many factors including gradation, particle shape, chemical composition, and entrapped air in porous particles.

Grain size distribution plays an important role in the material's geotechnical characterization when determining its strength, density, and hydraulic conductivity. Grain size distributions of the fly ash in this study show it to be predominantly silt with trace to some sand and trace of clay.

Fly ash is non-plastic in nature which directly affects the reliability of liquid and shrinkage limit tests. Pandian et al. (2004) reported that previous studies have shown that fly ash has a liquid limit ranging from 26% - 51%, which was not due to its plasticity characteristics but its fabric and carbon content. Pandian et al. (2004) reported that 70% of the coal ashes tested show negative free swell index which was due to flocculation. Potential swelling and shrinkage of fly ash is a concern when used as a liner/cap material.

Density is important in determining the strength of fly ash, compressibility (settlement), and permeability. The greater the density the higher the strength and the lower the compressibility and permeability of the fly ash. Compressibility characteristics of fly ash depend on its initial density, degree of saturation, self-hardening characteristics, and pozzolanic activity. Partially saturated fly ash is less compressible compared to those fully saturated (Pandian et al. 2004). Primary consolidation of fly ash is completed in a short period of time (typically during construction) compared to cohesive soils. The compressibility indices of fly ash are 10% - 20% of that of silt (Prashanth et al. 2001).

Permeability is an important parameter in the design of liners and dykes/dams to predict and manage leachate migration offsite. The permeability of coal fly ash depends on the grain size, degree of compaction and pozzolanic activity (Pandian et al. 2004). Void ratios and pore volumes are important in evaluating permeability and as a comparison basis when comparing results between different column tests and studies. Hydraulic conductivities of coal fly ash was found to vary significantly between previous studies and typically ranged from 1×10^{-7} cm/s to 1×10^{-4} cm/s when permeated with water. The hydraulic conductivities could be decreased by the addition of lime (Prashanth et al. 2001) and bentonite (Yeheyis et al. 2007). It has also been shown that permeating with AMD can decrease the hydraulic conductivities of the fly ash by up to 1000 times or greater within a short period of time (Xenidis et al. 2002, Shang et al. 2006, Wang et al. 2006, Yeheyis et al. 2007, Perez-Lopez et al. 2007).

2.2.2 Mineralogy and Geochemical Characteristics of Coal Fly Ash

The mineralogy of fly ash is dependent on the minerals found in the coal used for combustion. Typical minerals found in coal fly ash are: quartz, mullite, magnetite, hematite, periclase, cristobalite, tridymite, and spinel (Vuthaluru and French 2008). Fly ash consists mostly of silicon dioxide, aluminum oxide, iron oxide, and calcium oxide. Their percentages vary as per the coal source and type. Typical percentages (USDOT 1995) are:

Table 2.2.2 **Coal Fly Ash Specification**

Component	Class F (%wt)	Class C (%wt)
SiO_2	20-60	15-45
Al_2O_3	5-35	20-25
Fe_2O_3	10-40	4-15
CaO	1-12	15-40

The American Coal Ash Association (1997) identified other differences between Class F and Class C fly ashes such as the amount of alkalis (combined sodium and potassium) and sulfates (generally higher in Class C fly ashes than in Class F fly ashes) and the amount of unburned carbon remaining in the fly ash (higher in Class F fly ash (0-15%) than in Class C fly ash (0-5%)). The higher calcium and lower carbon contents of the Class C fly ash over Class F fly ash has resulted in Class C having a greater neutralizing potential in treating AMD (Xenidis et al. 2002).

Due to its high lime content, Class C fly ash has self cementing properties in the presence of water which allows it to harden and gain strength over time. Class F fly ash typically contains less lime and does not exhibit self cementing properties. The interaction of high calcium fly ash with water encourages the hydration of lime and gypsum to promote pozzolanic reactions which decrease the hydraulic conductivity and increase it compressive strength (Seal and Hammarstron 2003).

Coal fly ash has potential applications in acidic mine tailings management due to its chemical and mineralogical properties which make it a good binding agent and a possible substitute for gypsum, anhydrite, lime, or limestone currently used in the mining industry (Seal and Hammarstron 2003). The primary requirement for a material to be used as an alkaline (base) addition is if the material has significant neutralization potential (NP) which is based upon its calcium carbonate ($CaCO_3$) equivalency. Coal fly ash typically has between 15 to 30%, thus for every tonne of $CaCO_3$ that is needed approximately 5 tonnes of fly ash would be required to ensure sufficient alkalinity is present to neutralize AMD (Scheetz and Earle 1998).

Two metal leaching patterns were observed in the leachate of coal fly ash: early leaching and delayed leaching. Early leaching occurs when high concentrations of heavy metals are observed initially and decrease with subsequent pore volumes. Delayed leaching occurs when initial concentrations are initially low and increase to a maximum with subsequent pore volumes. Most metals show the early leaching pattern with the exception of barium, calcium, and strontium, which showed the delayed leaching behaviour (Creek and Shackelford 1992).

Field leachate tests by Mudd et al. (2004) showed that alkalinity is primarily due to the basic nature of the contained major minerals such as calcium and magnesium oxides found in the coal fly ash. These oxides, in addition to the low concentrations of acid generating minerals give the coal fly ash a substantial buffering capacity. Geochemical modelling of the leachate by Mudd et al. (2004) found: the sulphate minerals are often ubiquitous in coal fly ash, with gypsum, anhydrite ($CaSO_4$), and thenardite (Na_2SO_4) being possible mineral controlling species. Calcite, aragonite, and dolomite were the major carbonate minerals controlling carbon, calcium and magnesium. Aluminum and iron were present chiefly as oxides and/or hydroxides. The main aluminum mineral was alumina (Al_2O_3) and gibbsite ($Al(OH)_3$), which are controlling aluminum due to hydration and extended leaching in the ash. The dominant iron minerals are hematite and magnetite, with the iron activities in the leachate likely controlled by iron hydroxides.

Review of available leachate elemental chemistry results from previous research show coal fly ash to have a potential to leach trace elements into the environment. Some of these elements have concentrations that are too close to the analytical detection limits to allow interpretation to be conclusive. Many of the trace element concentrations may be due to the dissolution of $Fe(OH)_3$ or $Al(OH)_3$ and the subsequent release of any adsorbed metalloids (Mudd et al. 2004).

2.3 ACID GENERATING MINE TAILINGS

Mine tailings consist of crushed rock and process effluents that are generated in a mine processing plant. Mechanical and chemical processes are used to extract the metal from the ore, producing a waste known as mine tailings, which has no financial value to the mining company at the time of disposal. Extraction processes are not 100% efficient and trace amounts of metals remain in the tailings. Also, reagents and chemicals used in processing often remain in the tailings. Mine tailings are normally discharged as a slurry via a slurry pipeline to a final storage area commonly known as a Tailings Management Facility (TMF) or Tailings Storage Facility (TSF). Ponds, embankments and other types of surface impoundments are the most common storage methods used today (EC 2003).

Mine tailing are a major source of heavy metal contamination to surface and ground water, particularly when AMD is created. AMD can last for generations, posing a major concern to the mining industry. The weathering of mine tailings and its production of AMD, along with methods to control AMD, have been extensively researched.

The environment is the most crucial parameter constraining mine tailings storage which ultimately affects the way a facility is designed, built, operated and closed. The mine tailings physical and chemical characteristics determine the long term behaviour of the tailings and the potential short and long term liabilities and environmental impacts (EC 2003).

2.3.1 Geotechnical Characteristics of Mine Tailings

Tailings are a barren rock, crushed and ground to fine grain particles ranging in size from coarse sand to clay size particles. Grain size distributions of the mine tailings used in this study show it to be predominantly silt with trace to some sand and trace of clay. Grain size plays an important role in the generation of AMD as smaller sizes for example have an increased mineral surface area available for reactions (Jambor 2003, Smith and Beckie 2003).

Density is important in determining strength, compressibility (settlement), and permeability. The greater the density, the higher its strength and lower its compressibility and permeability. Mine tailings are non-plastic in nature with minimal shrinkage. Hydraulic conductivities of mine tailings were found to vary significantly in previous studies. Blowes et al. (2003b) reported that measurements of the hydraulic conductivity in mine tailings at several sites in Ontario ranged from 1×10^{-6} cm/s to 1×10^{-2} cm/s.

2.3.2 Mineralogy and Geochemical Characteristics of Mine Tailings

Common minerals in mine tailings include pyrite, marcasite, pyrrhotite, chalcopyrite, sphalerite, galena, arsenopyrite, tetrahedrite, and pentlandite, which constitute more than 95% of the sulphide mineral volume in most sulphide type ore deposits (Seal and Hammarstron 2003). Mine tailings may contain trace quantities of metals found in the host ore and compounds used in the extraction process. Elements are rarely found in their elemental form, but are typically found as complex compounds.

According to the European Commission (EC 2003), common additives found in tailings include:

- hydrocarbons from mining and processing activities,
- cyanide,
- sodium ethyl xanthate (SEX), potassium amyl xanthate (PEX), and methyl isobutyl carbinol (MIBC) used as frothing agents,
- sulfamic acid used as a cleaning / descaling agent,
- sulphuric acid used in the pressure acid leaching process,
- activated carbon used in carbon in pulp and carbon in leach processes, and
- calcium (typically as lime) to aid in pH control.

The oxidation of sulphide minerals occurs with either dissolved oxygen (O_2) in the water or dissolved ferric iron (Fe^{3+}) which through chemical reactions acts as the oxidizing agents. Dissolved ferric iron is more effective than dissolved oxygen in oxidizing sulphide minerals (Seal and Hammarstron 2003). This process in conjunction with a decrease in pH, results in the release of iron and other metals into the solution. Details of the weathering processes are presented in Section 2.6.1.

Mine tailings often contain carbonates which are effective in maintaining a neutral pH. These carbonates include calcite, siderite, ankerite, and dolomite; of which calcite is the most rapidly reacting carbonate (Blowes et al. 2003b). Research by Blowes et al. (2003b) has shown that in the early stages of weathering the dissolution of calcite can maintain the pH of the tailings pore water near neutral (pH 6.5 – 7.5). The dissolution of calcite ($CaCO_3$) is given by the following reaction:

$$CaCO_{3\,(s)} + H^{+}_{(aq)} \leftrightarrow Ca^{2+}_{(aq)} + HCO^{-}_{3\,(aq)} \qquad (2.1)$$

As calcite dissolution proceeds, sulphide mineral oxidation and dissolution of less soluble minerals occur. Oxidation of iron sulphides release high concentrations of Fe^{2+} that combine with HCO_3^- released by calcite dissolution to result in precipitation of siderite ($FeCO_3$). The precipitation of siderite is given by the following reaction:

$$Fe^{2+}_{(aq)} + HCO_3^{-}{}_{(aq)} \leftrightarrow FeCO_{3\,(s)} + H^{+}_{(aq)} \qquad (2.2)$$

As calcite becomes depleted the pH drops to where it is in equilibrium with siderite and siderite forms the primary pH buffer (pH 4.8 – 6.3). The dissolution of siderite is given by the following reaction:

$$FeCO_{3\,(s)} + H^{+}_{(aq)} \leftrightarrow Fe^{2+}_{(aq)} + HCO_3^{-}{}_{(aq)} \qquad (2.3)$$

Once dissolution of siderite reaches depletion and the pH drops, dissolution of gibbsite occurs, with a near constant pH of 4.0 – 4.3. Followed by dissolution of iron oxyhydroxides (pH 2.5 - 3.5). The dissolution of gibbsite and iron oxyhydroxides is given by the following reactions:

$$Al(OH)_{3\,(s)} \leftrightarrow Al^{3+}_{(aq)} + 3\ OH^{-}_{(aq)} \qquad (2.4)$$

$$Fe(OH)_{3\,(s)} \leftrightarrow Fe^{3+}_{(aq)} + 3\ OH^{-}_{(aq)} \qquad (2.5)$$

2.4 GLACIAL TILL SOIL

The glacial till soil used in this study was obtained from a pit near the town of Buchans, Newfoundland and Labrador. This soil was chosen due to its proximity to a decommissioned base metals (zinc, lead, and copper) mine, which provided practicality to its use.

Research on the effects of AMD on soil alone was limited. This may be due to the varying properties of insitu soil, which make the study site specific. Research on the use of soil amended with bentonite to reduce the migration of AMD by Kashir et al. (2000) found that the flow of AMD through soil could be reduced by amending the soil with bentonite. While the bentonite had limited neutralization, carbonate minerals in the soil were responsible for buffering the AMD pH and lowering the heavy metal concentrations.

2.5 BENTONITE

Bentonite used in this study was laboratory grade sodium montmorillonite from Wyoming, USA. Bentonite is formed naturally from the chemical weathering of volcanic materials such as volcanic tuff, volcanic ash, or other igneous and sedimentary rocks rich in the mineral montmorillonite. In addition to montmorillonite, bentonite can also contain other minerals such as quartz, feldspar, calcite and gypsum. Bentonite is chemically defined as $(Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})\cdot nH_2O$. Alternate formulas may exist, depending on the bentonite's origin and blending/alterations during processing (Minerals Zone 2005).

The geotechnical properties of bentonite are well known, due to its extensive use in the geotechnical and geoenvironmental fields. Two types of bentonite are often use: sodium bentonite and calcium bentonite. Sodium bentonite has a single water layer with particles containing Na^+ as the exchangeable ion, and calcium bentonite has a double water layer with particles containing Ca^{+2} as the exchangeable ion. The major difference between the two types is the potential to retain water and swell. Sodium bentonite swells in the presence of water while calcium bentonite does not. This swelling and retention of water makes sodium bentonite useful as a low permeability soil to contain water and contaminants (Minerals Zone 2005). Sodium bentonite is often used in liner and cap construction of landfills, in liners of containment ponds, and in low permeable cores of dams and dykes. Common practice is to amend native soils with bentonite to reduce its hydraulic conductivity to the magnitude of the governing regulation(s) or lower.

Limited study has been carried out on the effect of AMD on bentonite. This may be due in part to the bentonite's ability to reduce hydraulic conductivity below the regulatory guidelines. Kashir et al. (2001) showed that bentonite had a hydraulic conductivity of 2×10^{-9} cm/sec when permeated with water. Research by Kashir et al. (2000 and 2001) and Yeheyis et al. (2007) have shown switching the permeate from distilled water to AMD causes the hydraulic conductivity of the bentonite amended column packs to increase by up to one order of magnitude. Depending on the initial hydraulic conductivity, percentage of bentonite used, and overburden pressure, the increased hydraulic conductivity may subsequently exceed the regulatory guideline(s). These studies also showed that bentonite had little pH buffering potential and the majority of observed pH buffering was due to the neutralizing potential of the matrix the bentonite was amended with.

2.6 ACID MINE DRAINAGE (AMD)

Acid mine drainage (also known as Acid Rock Drainage – ARD) is the term for the leachate produced from oxidization of deposits of sulphide containing mine waste rock and tailings. This leachate is characterized by having a low pH, containing sulphuric acid, and elevated concentrations of heavy metals.

AMD typically refers to the outflow of acidic water from abandoned metal mines or coal mines. However, other areas where bedrock with elevated concentrations of sulphide and sulphate minerals has been disturbed may contribute AMD to the environment such as construction sites, subdivisions, transportation corridors, and power canals. AMD occurs naturally within some environments as part of the rock weathering process but is exacerbated by large-scale earth disturbances (mining, road rock cuts, water canals, etc.).

Skousen and Ziemkiewicz (1996) categorized mine drainage into five types:

Type 1 mine drainage has little or no alkalinity ($pH < 4.5$) and contains high concentrations of iron, aluminum, manganese, and other metals, acidity, and oxygen (typical AMD).

Type 2 mine drainage has high total dissolved solids containing high ferrous iron and manganese, low oxygen content, and a $pH > 6.0$. Upon oxidation however the pH of this water drops dramatically and becomes Type 1.

Type 3 mine drainage has moderate to high total dissolved solids, low to moderate ferrous iron and manganese, low oxygen content, a pH greater than 6.0, and alkalinity greater than acidity (commonly called alkaline mine drainage).

Type 4 mine drainage is neutralized AMD with a pH greater than 6.0 and high total suspended particulates, where the settling of metal hydroxides in the water has not yet occurred.

Type 5 mine drainage is also neutralized AMD, similar to Type 4, but where most metal hydroxides have precipitated in a settling pond and the main cations left in high concentrations are dissolved calcium and magnesium.

This study was performed using Type 1 mine drainage.

2.6.1 Acid Mine Drainage Formation

Pyrite and pyrrhotite are the main sulphides which contain both sulphur and iron. Their oxidation is a function of a number of physical, chemical, and biological processes. The reactions of these sulphides are presented below (Blowes et al. 2003b):

Pyrite (FeS_2)

Abiotic oxidation reaction

$$FeS_{2(s)} + {}^{7}/_{2}\, O_{2(aq)} + H_2O_{(l)} \rightarrow Fe^{2+}_{(aq)} + 2\, SO_4^{2-}{}_{(aq)} + 2\, H^{+}_{(aq)} \qquad (2.6)$$

At low pH Fe^{2+} oxidizes to Fe^{3+} through the reaction

$$Fe^{2+}_{(aq)} + {}^{1}/_{4}\, O_{2(aq)} + H^{+}_{(aq)} \rightarrow Fe^{3+}_{(aq)} + {}^{1}/_{2}\, H_2O_{(l)} \qquad (2.7)$$

The Fe^{3+} further reacts with the pyrite through the following reaction

$$FeS_{2(s)} + 14\ Fe^{3+}{}_{(aq)} + 8\ H_2O_{(l)} \rightarrow 15\ Fe^{2+}{}_{(aq)} + 2\ SO_4{}^{2-}{}_{(aq)} + 16\ H^+{}_{(aq)} \qquad (2.8)$$

The Fe^{3+} may hydrolyze and precipitate through the following reaction

$$Fe^{3+}{}_{(aq)} + 3H_2O_{(l)} \leftrightarrow Fe(OH)_{3(s)} + H^+{}_{(aq)} \qquad (2.9)$$

Summation of the above equation yields the following reaction

$$FeS_{2(s)} + {}^{15}/_4\ O_{2(aq)} + {}^{7}/_2\ H_2O_{(l)} \rightarrow Fe(OH)_{3(s)} + 2\ SO_4{}^{2-}{}_{(aq)} + 4\ H^+{}_{(aq)} \qquad (2.10)$$

Pyrrhotite (($Fe_{1-x}S$, $0<x<0.125$)

Oxidation reaction

$$Fe_{(1-X)}S_{(s)} + (2 - {}^{X}/_2)\ O_{2(aq)} + x\ H_2O_{(l)} \rightarrow (1 - x)\ Fe^{2+}{}_{(aq)} + SO_4{}^{2-}{}_{(aq)} + 2x\ H^+{}_{(aq)} \qquad (2.11)$$

The Fe^{3+} can further react with the pyrrhotite through the following reaction

$$Fe_{(1-X)}S_{(s)} + (8\text{-}2x)\ Fe^{3+}{}_{(aq)} + 4\ H_2O_{(l)} \rightarrow (9\text{-}3x)\ Fe^{2+}{}_{(aq)} + SO_4{}^{2-}{}_{(aq)} + 8\ H^+{}_{(aq)} \qquad (2.12)$$

It has been found that other minerals containing sulphides oxidize with ferric iron. These reactions include:

Galena (PbS)

$$PbS_{(s)} + 8\ Fe^{3+}{}_{(aq)} + 4\ H_2O_{(l)} \rightarrow Pb^{2+}{}_{(aq)} + 8\ Fe^{2+}{}_{(aq)} + SO_4{}^{2-}{}_{(aq)} + 8\ H^+{}_{(aq)} \qquad (2.13)$$

Chalcopyrite ($CuFeS_2$)

$$CuFeS_{2(s)} + 16Fe^{3+}_{(aq)} + 8H_2O_{(l)} \rightarrow Cu^{2+}_{(aq)} + 17Fe^{2+}_{(aq)} + 2SO_4{}^{2-}_{(aq)} + 16H^+_{(aq)} \quad (2.14)$$

Sphalerite (ZnS)

$$ZnS_{(s)} + 8\ Fe^{3+}_{(aq)} + 4\ H_2O_{(l)} \rightarrow Zn^{2+}_{(aq)} + 8\ Fe^{2+}_{(aq)} + SO_4{}^{2-}_{(aq)} + 8\ H^+_{(aq)} \qquad (2.15)$$

Arsenopyrite (FeAsS)

$$FeAsS_{(s)} + 13Fe^{3+}_{(aq)} + 8H_2O_{(l)} \rightarrow H_3AsO_{4(aq)} + 14Fe^{2+}_{(aq)} + SO_4{}^{2-}_{(aq)} + 13H^+_{(aq)} \quad (2.16)$$

Galena, chalcopyrite, sphalerite, and arsenopyrite are typically less abundant than pyrite and pyrrhotites. Therefore, their importance in generation of AMD is less significant, but are important as a potential source of metal and metalloids (USEPA 1994).

The oxidation by dissolved oxygen or oxidation by ferric iron ultimately depends on the pH of the water. Ferric iron has limited solubility at neutral pH therefore oxidation by dissolved oxygen dominates. At low pH, oxidation by ferric iron increases due in part to the catalytic activity of bacteria. Colonies of bacteria and archaea greatly accelerate the decomposition of metal ions. These microbes, called extremophiles, occur naturally in rock and survive in harsh conditions, but limited water and oxygen supplies usually keep their numbers low. The free ferric iron generated in pyrite weathering reactions further oxidizes the non-oxidized portion of pyrite establishing a cyclic and self-propagating series of reactions. Dissolved oxygen and ferric iron can also oxidize other sulphide minerals such as chalcopyrite, sphalerite, and galena (Seal and Hammarstron 2003).

Elevated concentrations of other metals, such as aluminum and magnesium, are also associated with AMD. This is not directly a result of pyrite oxidation, but is caused by AMD leaching these cations from other minerals within the tailings, as a secondary reaction (Scheetz and Earle 1998).

2.6.2 Prediction of Acid Mine Drainage Generation

Oxidization of mine tailings may be ongoing for hundreds of years and affect many generations. Therefore, techniques are required to predict the long term behaviour of AMD generation. Previous research has looked at both static and kinetic tests. Static tests are simple in nature and involve calculating the total acidity potential (AP) to the total neutralization potential (NP) to determine the net neutralizing potential (NNP) in a process called acid based accounting (ABA). A number of ABA techniques have been developed by various organizations around the world. Kinetic tests simulate the weathering process of mine tailings under an accelerated rate in the laboratory, and provide information on pH change and elemental chemistry (USEPA 1994, BC-MEMPR 1989).

Acid based accounting is a basic screening process, which provides no information on the speed of acid generation or neutralization. The potential for a given rock to generate and neutralize acid is determined by its mineralogical composition. This includes not only the quantitative mineralogical composition, but also individual mineral grain size, shape, texture and spatial relationship with other mineral grains. The term "potential" is used because even the most detailed analysis can give only a "worst case" value for potential acid production. Depending on the NP procedure used, a "worst case", "most likely case" or "best case" value for potential neutralization capability is calculated. The ABA technique used is typically a personal preference or the most commonly used in a geographical location or within an association.

According to USEPA (1994), components affecting the total capacity to generate acid are characterized by the amount of acid generating (sulphide) minerals present (assumes total reaction), the amount of acid neutralizing minerals present, and the amount and type of potential contaminants present. The rate of acid generation is dependent on the sulphide minerals, the carbonate and other neutralizing minerals, mineral surface area, and the presence of water, oxygen, and bacteria.

All ABA procedures involve the reaction of a sample with a mineral acid of measured quantity to determine the base equivalency of the acid consumed in g/kg or kg/tonne or tonne/1000 tonne calcium carbonate ($CaCO_3$). The USEPA (1994) identified five different test procedures, including Acid Base Accounting (Sobek), Modified Acid Based Accounting (Modified Sobek), BC Research Initial, Alkaline Production Potential – Sulphur, and Net Acid Production (NAP). This study used the Modified Acid Based Accounting (Modified Sobek) method. Details of this method are presented below (USEPA 1994, BC-MEMPR 1989):

The net neutralization potential (NNP) is calculated by the following equation:

$$NPP = NP - AP \tag{2.17}$$

where NP is the neutralization potential, calculated by the equation:

$$NP = \frac{50 \times [(0.1 \times A) - (0.1 \times B)]}{\text{weight of sample (g)}} \tag{2.18}$$

where A is the volume of HCl (ml) added to achieve a paste pH between pH 2.0 and 2.5 and

B is the volume of NaOH (ml) added to achieve a pH of 8.3.

AP is the acid potential, calculated by the equation:

$$AP = \%\ \text{sulphide sulphur} \times 31.25 \qquad (2.19)$$

The NNP is recorded as the equivalent amount of calcium carbonate. A negative NNP indicates that the material has the potential to be acid producing, whereas a positive NNP indicates the potential to neutralize.

2.6.3 Acid Mine Drainage Prevention and Treatment Techniques

Control of acid generation can be achieved by removing one or more of the three essential components in the acid-generating process (sulphide, air, or water).

Methods to prevent/control AMD include:

- water covers,
- soil covers and caps,
- alkaline recharge structures, and
- base additives to balance the AP and NP.

Methods to treat AMD include:

- reactive barriers to buffer the pH and treat AMD migration within the groundwater,
- alkaline addition,
- bactericides,

- collection and treatment of contaminants, and
- bioremediation.

At source prevention methods treat the acid-producing rock directly to stop or retard the production of acid, whereas treatment methods add alkalinity directly to AMD exiting the mine waste and tailings or direct the AMD through various passive systems for treatment. When properly designed and implemented, water and soil covers effectively prevent the formation of AMD, provided AMD has not already formed.

Water covers are considered the most effective method for preventing AMD formation. A water cover minimizes the atmospheric oxygen diffusion into the tailings and promotes the development of an anoxic environment. A disadvantage of a water cover is its ineffectiveness in treating AMD that has already generated within the mine tailings. The pH of this acidic water must be raised to neutral or greater to neutralize the AMD. Once neutralized, the water cover is then effective in preventing further oxidation of the mine tailings.

Soil covers are able to prevent the oxidation of mine tailings by creating an oxygen barrier. Soil covers are also effective in reducing the concentration of precipitation (rainfall) and surface water from reaching the mine tailings, thereby decreasing groundwater recharge and reducing the migration of AMD offsite. Often vegetation is planted on the soil cover to prevent erosion, reduce the oxygen diffusion into the soil, and depending on the plant species absorb metals (Yanful et al. 1999).

Alkaline recharge structures which collect and divert infiltrating water through porous alkaline zones, thereby inducing alkaline water into the tailings area, are sometimes used as a prevention and treatment technique. These structures can be as complicated as a series of mechanical devices and pumps (active treatment), to as simple as infiltrating water flowing through a bed of limestone or other alkaline material (passive treatment). This infiltrating alkaline water provides an alkaline front that migrates through the tailings spoil, neutralizing acidity and raising pH. This alkalinity addition can also displace bacteria and cause the acid-producing reaction to be slowed or completely stopped (EC 2003). A variation of this process was researched by Shang et al. (2006), who investigated the effects of permeating an alkaline coal fly ash leachate through mine tailings, which proved effective in maintaining an alkaline leachate.

Several categories for the use of alkaline additions include: 1) blending with potential acid-producing material to either neutralize the acid produced, or to retard and/or prevent the oxidation of oxidizing minerals; 2) incorporating in stratified layers at specific intervals within the spoil; 3) applying in trenches to create alkaline groundwater conduits to treat run off (flow through reactive barrier); 4) applying on or near the surface to create an alkaline wetting front that will migrate downward through the spoil; and, 5) applying as a cap/liner to create a low permeability barrier either on the surface of mine tailings or the floor of the mine tailings pond.

Base additives (when an alkaline material is blended or incorporated in stratified layers) usually rely on ABA to estimate the required amount of alkalinity for neutralization. While this does not take kinetics of release into account, it recognizes that if all of the minerals were to oxidize, then there would be sufficient alkaline material to neutralize the acid (BC-MEMPR 1989). Depending on the acid potential of the mine tailings a large quantity of alkaline material may be required, which may not be practical.

The addition of certain bactericides (e.g. gallionella) can immobilize heavy metals and others can reduce sulphate concentrations (Banks et al. 1997). Bioremediation technologies include the construction of wetlands to filter mine water runoff and removed concentrations of contaminants (Nyquist and Greger 2009). Wetlands in conjunction with select plant species may further reduce the concentration of certain heavy metals (Batty and Younger 2004).

2.6.4 Elemental Properties (AMD, mine tailings and coal fly ash)

Elements found in AMD are often dependent on the mineralogy of the mine tailings and the pH of the pore water. Heavy metals including iron, copper, nickel, lead, and zinc were investigated in this study. These metals have negative effects on the environment and have concentration limits that are governed by regulatory agencies. Alkali and alkaline earth metals were investigated due to their common occurrence as oxide and carbonate minerals and their potential to buffer pH. These elements, in addition to others found in high concentrations in AMD are presented below. Also included are their properties, health and environmental concerns, and applicable guidelines/regulations.

2.6.4.1 Aluminum (Al)

Aluminum is the most abundant metallic element in the Earth's crust (approximately 8% by weight) and the third most abundant of all elements (after oxygen and silicon). Because of its strong affinity to oxygen it is almost never found in the elemental state; instead it is found in oxides or silicates. This element is extensively mined and subsequently a source of mine tailings.

Aluminum has no known function in living cells and presents some toxic effects on humans in elevated concentrations. Although it is generally harmless to plant growth in pH-neutral soils, aluminum is a primary factor that reduces plant growth in acid soils, as the concentration of Al^{3+} cations disturbs root growth and function. Precipitated aluminum can also accumulate on fish gills and interfere with their breathing (Patnaik 2002, WHO 2008, International Aluminum Institute 2009).

The United States Environmental Protection Agency (USEPA 2003) sets the total concentration of aluminum in water at 1 mg/L as an average daily value for 30 consecutive days, with a maximum daily value of 2 mg/L. Canadian water quality guidelines for the protection of aquatic life developed by the Canadian Council of Ministers of the Environment (CCME 2007) provided guidelines for the protection of freshwater aquatic life only. This guideline is pH dependant with 5 µg/L at $pH < 6.5$ and 100 µg/L at $pH \geq 6.5$. Health Canada (2008) established a guideline value of 0.1 mg/L or 0.2 mg/L for drinking water quality depending on the treatment process. Environment Canada's metal mining effluent regulations (EC-MMER 2003) did not provide a regulatory value for aluminum in water.

Mudd et al. (2004) researched the leaching of aluminum from coal fly ash. Aluminum oxides and hydroxides, particularly gibbsite, amorphous $Al(OH)_3$, and alumina, were reported to be important in controlling aluminum concentrations due to hydration and extended leaching. Geochemical modelling indicated that gibbsite is controlling for pH above pH 8.5 while amorphous $Al(OH)_3$ controls for pH below 8.5. Gitari et al. (2008b) studied leaching from fly ash and found that the concentration of aluminum decreased with increased reaction time and with an increase in pH.

Kashir et al. (2001) continuously recorded the concentration of aluminum in the effluent of AMD permeated through pure bentonite column packs, where breakthrough was found to occur within two pore volumes of AMD. Blowes et al. (2003b) examined the pH buffering of mine tailings permeated with a low pH solution. Aluminum oxides and hydroxides in the mine tailings were found to dissolve at a pH of 4.0 to 4.5, providing minor pH buffering.

2.6.4.2 Arsenic (As)

Arsenic is widely distributed throughout the earth's crust and is typically introduced into groundwater through the dissolution of minerals and ores containing arsenic. Arsenic is a carcinogen that causes skin, lung, and bladder cancer as well as cardiovascular disease (Patnaik 2002, WHO 2008).

USEPA (2003) sets the total concentration of arsenic in water at 0.5 mg/L as an average daily value for 30 consecutive days, with a maximum daily value of 1 mg/L. EC-MMER (2003) sets the total concentration of arsenic in water at 0.5 mg/L as a maximum authorized monthly mean concentration, with a maximum grab sample value of 1 mg/L. CCME (2007) provided guidelines for both the protection of freshwater aquatic life and marine aquatic life of 5 µg/L and 12.5 µg/L, respectively. Health Canada (2008 established a guideline value of 0.01 mg/L for drinking water quality.

Mudd et al. (2004) researched the leaching of arsenic from coal fly ash, but the concentrations were too close to the analytical detection limits to allow interpretation to be conclusive. They attributed the observed concentrations to the release of sorbed metalloids during dissolution of iron and aluminum oxides under less oxidizing (more neutral or acidic) geochemical conditions. Perez-Lopez et al. (2007) examined arsenic in the AMD leachate permeated through layered and mixed column packs of mine tailings and coal fly ash. The amending of fly ash was shown to decrease the arsenic concentration in the leachate up to 100 times versus mine tailings alone.

2.6.4.3 Barium (Ba)

Barium is a soft silvery metallic alkaline earth metal which is not found in nature in its pure form due to its reactivity with air. While chemically similar to calcium and strontium, it is more reactive and oxidizes very easily when exposed to air and is highly reactive with water. All water or acid soluble compounds of barium are extremely poisonous. At low doses, barium acts as a muscle stimulant, while higher doses affect the nervous system, causing cardiac irregularities, tremors, weakness, anxiety, dyspnea and paralysis (Patnaik 2002, WHO 2008).

No guidelines/regulations for barium concentrations in water were available from USEPA (2003), EC-MMER (2003) or CCME (2007). Health Canada (2008) established a guideline value of 1 mg/L for drinking water quality.

Mudd et al. (2004) reported that barium may exist as pure sulphate or carbonate minerals in coal fly ash with a moderate to very low solubility. Barium may also exist as coprecipitates with strontium.

2.6.4.4 Calcium (Ca)

Calcium is a soft grey alkaline earth metal, and is the fifth most abundant element by mass in the Earth's crust. Calcium is not naturally found in its elemental state and is commonly found in sedimentary rocks (as the minerals calcite, dolomite and gypsum) and as silicate minerals in igneous and metamorphic rocks (plagioclase, amphiboles, pyroxenes and garnets). Calcium is an important component of a healthy diet and a mineral necessary for life. No guidelines/regulations for concentration in water were available from USEPA (2003), EC-MMER (2003), CCME (2007) or Health Canada (2008).

Geochemical modeling by Mudd et al. (2004) indicated that calcium in the fly ash leachate may be due to the dissolution of sulphate (gypsum and anhydrite) and carbonate (calcite, aragonite, and dolomite) minerals. Perez-Lopez et al. (2007) determined that coal fly ash controlled the concentration of calcium in mine tailing packs amended with coal fly ash. A high concentration of calcium was initially found in the mine tailings leachate, decreasing rapidly with continued permeation due to the depletion of carbonate minerals. Gitari et al. (2008b) found that the leachate concentration of calcium increased to a maximum within 10 minutes of contact, after which it slightly decreased due to possible development of gypsum and anhydrite, which was reported to possibly control solubility. Kashir et al. (2001) recorded the continuous calcium concentration in the effluent of AMD permeated through a bentonite column pack, where breakthrough was found to occur within two pore volumes of AMD.

2.6.4.5 Chromium (Cr)

Chromium is the 21st most abundant element in the Earth's crust. Chromium compounds are found in the environment, due to erosion of chromium containing rocks. The relation between Cr(III) and Cr(VI) is strongly dependant on pH and oxidative properties, but in most cases Cr(III) is dominant (Patnaik 2002, WHO 2008).

Low concentrations of chromium as Cr(III) are not usually considered a health hazard as chromium is an essential trace mineral required for good health. However, Cr(VI) compounds can be toxic if ingested or inhaled and is an established human carcinogen (Patnaik 2002, WHO 2008).

Neither USEPA (2003) nor EC-MMER (2003) has metal mining regulatory guidelines for chromium in water. CCME (2007) has guidelines which are dependent on the chromium oxidization state for both the protection of freshwater aquatic life (8.9 µg/L for Cr(III) and 1 µg/L for Cr(IV)) and marine aquatic life (56 µg/L for Cr(III) and 1.5 µg/L for Cr(IV)). Health Canada (2008) established a guideline value of 0.05 mg/L for drinking water quality.

Cornelis et al. (2008) studied leaching of chromium from alkaline solid waste and reported that chromium is almost always found in the hexavalant phase (Cr(IV)), and only its oxidation can cause chromium to leach. Shang et al. (2006) investigated the concentrations of chromium in the leachate of water and AMD permeated through coal fly ash in kinetic column tests, and found concentrations to be lower when permeated with water, which further decreased with continued permeation. Wang et al. (2006) conducted similar tests on coal fly ash along with mixtures of coal fly ash and mine tailings column pack, where chromium concentrations were found to decrease with continued permeation.

2.6.4.6 Copper (Cu)

Copper is a transition (heavy) metal. This element is extensively mined and subsequently a source of mine tailings. Copper is often found in other metal ore deposits in lower concentrations. Trace amounts of copper are found in the Earth's crust and are usually found as sulphides (chalcopyrite, bornite, covellite, chalcocite), carbonates (azurite and malachite), and oxides (cuprite).

Copper is essential for plants and animals, but certain copper compounds and concentrations can be toxic. Copper has been found to accumulate in the liver and can lead to liver and brain damage. Dissolved copper in the water can affect marine life by damaging their gills, liver, kidneys, and the nervous system (Patnaik 2002, WHO 2008).

USEPA (2003) regulated the total concentration of copper in water at 0.15 mg/L as an average daily value for 30 consecutive days, with a maximum daily value of 0.3 mg/L. EC-MMER (2003) regulated the total concentration of copper in water at 0.3 mg/L as a maximum authorized monthly mean concentration, with a maximum grab sample value of 0.6 mg/L. CCME (2007) provided guidelines for the protection of freshwater aquatic life only, which ranged from 2 μg/L to 4 μg/L, depending on the water hardness. Health Canada (2008) established an operational guideline value of ≤1 mg/L for drinking water quality.

Geochemical modeling by Gitari et al. (2008b) found that the concentration of copper in the leachate was under-saturated for $Cu(OH)_2$ for the duration of the test but concentrations remained low due to adsorption and co-precipitation with iron and aluminum. Solubility of CuO in coal fly ash was investigated by Pendian et al. (2004), who found that at pH 9.5 the concentrations were lowest. Perez-Lopez et al. (2007) and Yeheyis et al. (2007) found a 100 times and greater reduction in copper concentration of AMD effluent permeated through coal fly ash amended mine tailings versus AMD permeated through mine tailings alone. Kashir et al. (2001) continuously recorded the concentration of copper in the effluent of AMD permeated through bentonite column packs, where breakthrough was found to occur within eight pore volumes of AMD.

2.6.4.7 Iron (Fe)

Iron and iron alloys (steels) are the most common metals in everyday use. It is extensively mined and subsequently a source of mine tailings. Iron is the fourth most abundant element in the Earth's crust. Pure iron is rarely found in this form because it oxidizes readily in the presence of oxygen and moisture. Most of the iron is found combined with oxygen as iron oxide minerals such as hematite and magnetite.

Iron is an essential element for maintaining good health in most living organisms. Excessive iron can be toxic because free ferrous iron reacts with peroxides to produce free radicals. These free radicals are highly reactive and can damage DNA, proteins, lipids, and other cellular components, thereby causing long-term organ damage and possible death (Patnaik 2002, WHO 2008)..

USEPA (2003) regulated the total concentration of iron in water at 1 mg/L as an average daily value for 30 consecutive days, with a maximum daily value of 2 mg/L. CCME (2007) provided guidelines for the protection of freshwater aquatic life only, with a concentration of 0.3 mg/L. Health Canada (2008) established an operational guideline value of ≤ 0.3 mg/L for drinking water quality. No concentration values were provided by EC-MMER (2003) for water.

Mudd et al. (2004) researched the leaching of iron from coal fly ash and found that iron oxide and hydroxide phases in the leachate were controlling the iron concentration, particularly hematite and magnetite. Gitari et al. (2008b) found that the concentration of iron decreased with increased reaction time and with an increase in pH. Solubility of $Fe(OH)_3$ in coal fly ash was investigated by Pendian et al. (2004), who found that at pH 8.5 the concentrations were lowest. Perez-Lopez et al. (2007) examined iron in the AMD leachate permeated through layered and mixed column packs of mine tailings and coal fly ash, where amending mine tailings with fly ash decreased the iron concentration to trace values. Kashir et al. (2001) continuously recorded the concentration of iron in the effluent of AMD permeated through bentonite column packs, where iron concentrations consistently remained at trace amounts.

2.6.4.8 Lead (Pb)

Lead is a metallic element (heavy metal). Lead does occur in nature, but is rare and usually found in ore with zinc, silver and copper. The main lead minerals are galena, cerussite and anglesite. This element is extensively mined and subsequently a source of mine tailings.

Lead is poisonous and can damage nervous connections, causing blood and brain disorders. The effects of lead are the same whether it enters the body through breathing or swallowing. Because of its low reactivity and solubility, poisoning occurs when the lead is dispersed or with long term exposure (Patnaik 2002, WHO 2008).

USEPA (2003) regulated the total concentration of lead in water at 0.3 mg/L as an average daily value for 30 consecutive days, with a maximum daily value of 0.6 mg/L. EC-MMER (2003) regulated the total concentration of lead in water at 0.2 mg/L as a maximum authorized monthly mean concentration, with a maximum grab sample value of 0.4 mg/L. CCME (2007) provided guidelines for the protection of freshwater aquatic life only, which ranges from 1 µg/L to 7 µg/L, depending on the water hardness. Health Canada (2008) established a guideline value of 0.01 mg/L for drinking water quality.

Perez-Lopez et al. (2007) found a minimum of 1000 times reduction in lead concentration of AMD effluent permeated through coal fly ash amended mine tailings versus AMD permeated through mine tailings alone. Yeheyis et al. (2007) recorded a minimum of 100 times reduction of the concentration of lead in the AMD permeated through coal fly ash packs. Leachability extraction tests by Stouraiti et al. (2001) of various percentages of coal fly ash amended mine tailings found that lead was highest in the mine tailings control (i.e. mine tailings only) with only trace values in 10 wt% fly ash.

2.6.4.9 Magnesium (Mg)

Magnesium is an alkaline earth metal and constitutes about 2% of the Earth's crust by mass (8th most abundant element). The free element (metal) is not found naturally on Earth, since it is highly reactive and soluble but is often found in large deposits of magnesite, dolomite, and other minerals, and in mineral waters, where magnesium ion is soluble.

Due to the important interaction between phosphate and magnesium ions, magnesium ions are essential to the basic nucleic acid chemistry of life. Excess magnesium in the blood is freely filtered at the kidneys, and for this reason it is difficult to overdose on magnesium from dietary sources alone (Patnaik 2002, WHO 2008). No guidelines/regulations for concentrations in water were available from USEPA (2003), EC-MMER (2003), CCME (2007) or Health Canada(2008).

Geochemical modeling by Mudd et al. (2004) on coal fly ash leachate showed that carbonate minerals were controlling the magnesium concentration, particularly dolomite. Gitari et al. (2008b) found that for mixtures of fly ash and mine tailings, the fly ash controlled the concentration of magnesium. The magnesium concentration was found to increase with increasing fly ash concentration. Kashir et al. (2001) continuously recorded the concentration of magnesium in the effluent of AMD permeated through bentonite column packs, where breakthrough was found to occur within five pore volumes of AMD.

2.6.4.10 Nickel (Ni)

Nickel is a transition (heavy) metal which is often used with other metals to form alloys. This element is extensively mined and subsequently a source of mine tailings. Nickel is often found in other metal ore deposits in lower concentrations. The main nickel minerals are pentlandite, millerite, nickeliferous limonite and garnierite.

Nickel plays numerous roles in the biology of microorganisms and plants. Nickel is carcinogenic to humans in high and continued exposure limits when injected. It is also believed that inhalation may also be carcinogenic (Patnaik 2002, WHO 2008).

USEPA (2003) regulated the total concentration of nickel in water at 1 mg/L as an average daily value for 30 consecutive days, with a maximum daily value of 2 mg/L. EC-MMER (2003) regulated the total concentration of nickel in water at 0.5 mg/L as a maximum authorized monthly mean concentration, with a maximum grab sample value of 1 mg/L. CCME (2007) provided guidelines for the protection of freshwater aquatic life only, which ranges from 25 µg/L to 150 µg/L, depending on the water hardness. Health Canada (2008) provided no guideline value for drinking water quality.

Research by Shang et al. (2006) found a 1000 times decrease of nickel in solution leached from mine tailings when an alkaline fly ash leachate was used versus distilled water.

2.6.4.11 Potassium (K)

Potassium is an alkali metal that oxidizes rapidly in air and is very reactive and soluble with water. Potassium in nature occurs as ionic salt and makes up about 2.4% of the Earth's crust by mass (7th most abundant element). Potassium is necessary for the function of all living cells, and is naturally present in all plant and animal tissues. No guidelines/regulations for concentration in water were available from USEPA (2003), EC-MMER (2003), CCME (2007) or Health Canada (2008).

Research by Kashir et al. (2001) continuously recorded the concentration of potassium in the effluent of AMD permeated through bentonite. It was found that the when permeated with AMD, the concentration of potassium in the effluent increased 1.5 times versus the AMD concentration. This indicated the possible release of potassium from the bentonite due to ion exchange and the collapse of the bentonite double layer..

2.6.4.12 Silicon (Si)

Silicon makes up 25.7% of the Earth's crust by mass (2nd most abundant element after oxygen) and is mostly found as silicon dioxide (SiO_2), also known as silica or quartz. Silicon dioxide is inert and harmless, expect when finely divided crystalline silica dust or fumed silica is inhaled, which can lead to silicosis, bronchitis or cancer (Patnaik 2002). No guidelines/regulations for concentrations in water were available from USEPA (2003), EC-MMER (2003), CCME (2007) or Health Canada (2008).

Geochemical modelling by Mudd et al. (2004) identified a number of probable silica and mixed alumina-silicate phases in coal fly ash. They concluded that quartz was most likely the controlling dissolution phase, but other phases were responsible for precipitation due to the high temperature required for the formation of quartz.

2.6.4.13 Sodium (Na)

Sodium is an alkali metal that is reactive and soluble in water. Sodium in nature occurs as ionic salt and makes up about 2.6% of the Earth's crust by mass (6th most abundant element). Sodium is necessary for the function of all living cells, and is naturally present in all plant and animal tissues (Patnaik 2002). No guidelines/regulations for concentrations in water were available from USEPA (2003), EC-MMER (2003), or CCME (2007). Health Canada (2008) provided an operational guideline value of ≤ 200 mg/L.

Kashir et al. (2001) continuously recorded the concentration of sodium in the effluent of AMD permeated through bentonite and found that the concentration of sodium was initially high (2.5 times AMD concentration) when first permeated with AMD, decreasing to the AMD concentration in eight pore volumes.

2.6.4.14 Strontium (Sr)

Strontium is an alkaline earth metal that is highly reactive in water. Strontium commonly occurs in nature and is the 15th most abundant element on earth. Due to strontium's similarity to calcium, the human body absorbs strontium as if it were calcium. While stable forms of strontium might not pose a significant health threat, the radioactive forms of strontium can lead to various bone disorders and diseases, including bone cancer (Patnaik 2002).. No guidelines/regulations for concentrations in water were available from USEPA (2003), EC-MMER (2003), CCME (2007) or Health Canada (2008).

Mudd et al. (2004) reported that strontium may exist as pure sulphate or carbonate minerals in coal fly ash with a moderate to very low solubility, and that strontium may also exist as coprecipitates with barium. Leaching tests on coal fly ash by Gitari et al. (2008b) found that the concentration of strontium increased with increased reaction time and with an increase in pH.

2.6.4.15 Sulphur (S)

Sulphur is an abundant multivalent non-metal found in nature as a pure element and as sulphide (S) and sulphate (SO_4) minerals. These sulphide and sulphate minerals are often exploited for their valuable metals (i.e. iron, copper, nickel, zinc), while the sulphur fractions are considered waste and discharged as mine tailings. As described earlier in Section 2.6.1, sulphur is a major contributor to AMD. No guidelines/regulations for concentration in water were available from USEPA (2003), EC-MMER (2003), and CCME (2007). Health Canada (2008) provided an operational guideline value of ≤ 500 mg/L as sulphate.

The sulphur concentration is important in determining the formation of secondary minerals. Gypsum and ettringite are two secondary minerals that both require sulphur to form. These minerals were both reported to form due to the permeation of AMD through fly ash, resulting in a decrease in hydraulic conductivity. Geochemical modelling by Mudd et al. (2004) identified gypsum, anhydrite, and thenardite as possible minerals entering solution. Gitari et al. (2008b) also identified the formation and dissolution of gypsum using geochemical modeling. Comparison of SO_4 concentrations with the saturation index for gypsum for column tests by Perez-Lopez et al. (2007), show a substantial decrease in SO_4 when gypsum became over saturated in solution. Kashir et al. (2001) continuously recorded the concentration of sulphur in the effluent of AMD permeated through bentonite column packs, where breakthrough was found to occur within eight pore volumes of AMD.

2.6.4.16 Zinc (Zn)

Zinc is a transition (heavy) metal which is often used with other metals to form alloys. This element is extensively mined and subsequently a source of mine tailings. Zinc is often found in other metal ore deposits in lower concentrations. The main zinc minerals are smithsonite, hemimorphite, wurtzite, and hydrozincite.

Zinc plays numerous roles in the biology of micro organisms and plants and is an essential element for proper health. Symptoms of chronic zinc deficiency are stunted growth and retarded sexual development. Excessive zinc can suppress copper and iron absorption (Patnaik 2002, WHO 2008).

USEPA (2003) regulated the total concentration of zinc in water at 0.5 mg/L as an average daily value for 30 consecutive days, with a maximum daily value of 1 mg/L. EC-MMER (2003) regulated the total concentration of zinc in water at 0.5 mg/L as a maximum authorized monthly mean concentration, with a maximum grab sample value of 1 mg/L. CCME (2007) provided a guideline of 30 µg/L for the protection of freshwater aquatic life, only. Health Canada (2008) established an operational guideline value of ≤ 5 mg/L for drinking water quality.

Solubility of ZnO in coal fly ash was investigated by Pendian et al. (2004), who found that the concentrations were lowest at a pH of 9.5. Gitari et al. (2008b) found that the concentration of zinc was under-saturated for $Zn(OH)_2$ for the duration of the test but concentrations remained low due to adsorption and co-precipitation with iron and aluminum. Leachability extraction tests by Stouraiti et al. (2001) of various percentages of coal fly ash amended mine tailings found that zinc was highest in the mine tailings control (i.e. mine tailings only), which decreased linearly with increased fly ash content (trace values recorded in 10 wt% fly ash). Kashir et al. (2001) continuously recorded the concentration of zinc in the effluent of AMD permeated through bentonite column packs, where breakthrough was found to occur within eight pore volumes of AMD.

2.7 applications of coal/biomass fly ash in mine tailings management

The net neutralizing potential of CBFA along with its relatively low cost and availability make CBFA a viable option to contain and treat AMD. Prevention of AMD by co-placement of CBFA with reactive mine tailings may require a high percentage of CBFA to offset the acid generating potential of the reactive mine tailings (see Section 3.2). This percentage may not be practical for co-placement for the entire volume of mine tailings, therefore co-placement may be limited to the zone of oxidation (vadose zone). Misra et al. (1996) and Scheetz et al. (1998) reported that although ABA indicated that mixtures of mine tailings and CBFA with a negative net neutralizing potential may form AMD, the addition of coal fly ash created an impervious coating of fly ash over the mine tailing particles and significantly slow down oxidation.

Co-placement of CBFA with representative onsite materials (reactive mine tailings and glacial till soil) were investigated. Applications included a flow through reactive barrier, where minimal changes in hydraulic conductivity were observed, to treat AMD plumes migrating offsite, and as a low permeability barrier (liner, cap, dam core) when a substantial decrease in hydraulic conductivity occur. Bayat (1998) reported that the chemical and mineralogical properties of coal fly ash make it a good alkaline binding agent and a substitute for gypsum, anhydrite, lime, and limestone commonly used in the mining industry to treat AMD.

2.7.1 Reaction Between Coal Fly Ash and Acid Mine Drainage

The hindrance of AMD flowing through coal fly ash is mainly attributed to free lime, which has the following chemicial reactions with water (Seal and Hammarstron 2003).

$CaO + H_2O \rightarrow Ca(OH)_2$ (2.20)

$Ca(OH)_2 \rightarrow Ca^{2+} + 2[OH]^-$ (2.21)

$Ca^{2+} + 2[OH]^- + SiO_2 \rightarrow CSH$ (gel) Calcium Silicate Gel (2.22)

$Ca^{2+} + 2[OH]^- + Al_2O_2 \rightarrow CAH$ (gel) Calcium Aluminate Gel (2.23)

The formation of these cementitious materials (CSH and CAH) is reported by Seal and Hammarstron (2003) to be capable of binding inert materials together. Upon contact with a low pH AMD that contain significant sulphate there is a resulting increase in dissolved calcium that reacts with the sulphate to form calcium sulphate that further hydrate to form gypsum as shown in the following reaction:

$Ca^{2+} + SO_4^{2-} + 2\ H_2O \rightarrow CaSO_4 \bullet 2\ H_2O$ (2.24)

The hydrogen ions in the AMD are further neutralized by the hydroxyl ions generated in the reaction of calcium hydroxide to calcium as shown in the following reaction:

$Ca(OH)_2 + 2H^+ \rightarrow Ca^{2+} + 2\ H_2O$ (2.25)

The increased pH leads to precipitation of dissolved metals and the formation of secondary minerals through the reactions of the cementitious materials derived from the coal fly ash and gypsum (Yeheyis et al. 2007). Gypsum can further react with aluminum to form the secondary mineral ettringite. Ettringite is a result of the reaction of calcium aluminate with calcium sulfate. Both gypsum and ettringite are products of hydration which result in swelling during mineral formation. This swelling reduces the presence of large pores in the medium resulting in a decrease in the hydraulic conductivity (Mohamed et al. 2002). Ettringite was identified by XRD on a field study of landfilled Atikokan coal fly ash by Yeheyis et al. (2008).

The blending of coal fly ash with reactive mine tailings was reported by Misra et al. (1996) and Scheetz et al. (1998) to form a low strength cement which encapsulated some of the pyrite and rendered it unavailable to oxidize to form AMD. In addition, the neutralizing potential of coal fly ash consumes the acidic potential of the tailings and increased the pH, causing the metals in the solution to precipitate and lose their mobility (Eaker 1997). The precipitation of metals and the formation of secondary minerals have the potential to clog voids between solid particles, resulting in a further decrease in the hydraulic conductivity (Potgieter-Vermaak et al. 2006).

2.7.2 Case Studies on the Treatment and Containment of Acid Mine Drainage

Case studies have been reported in the literature on the reaction of AMD and coal fly ash. Most studies investigated the utilization of coal fly ash in combination with reactive mine tailings. Limited studies were found on the use of coal fly ash solely or amended with bentonite (to lower its initial hydraulic conductivity). The literature review was unable to identify studies that examined the utilization of coal fly ash blended with soil to treat AMD, although a study on the effects of AMD on two different soil types amended with bentonite was reviewed. None of these studies utilized fly ash from the combined burning of lignite coal and biomass.

In kinetic laboratory column tests by Wang et al. (2006), mine tailings from Musselwhite Mine in northern Ontario were mixed with coal fly ash from the Atikokan power generation plant (burning of lignite coal only) to study its suitability to control and mitigate the generation of AMD. The physical, chemical and mineralogical properties of the fly ash and mine tailings were determined and six column tests performed. One column test was performed with pure fly ash permeated with water. A second column was pure fly ash permeated with AMD. Four other column tests were performed with mine tailings / fly ash ratios of 1:1, 2:1, 3:1 and 4:1. These four tests were permeated with AMD. Tests were conducted to monitor the leaching properties (hydraulic conductivity, pH, and elemental composition) of the packs. A decrease in hydraulic conductivity of three orders of magnitude was observed in the fly ash pack when permeated with AMD, while negligible change was observed when permeated with water. The hydraulic conductivity of the mine tailings permeated with AMD also decreased with the addition of fly ash. The effluent leachate from all tests maintained an alkaline pH with concentrations of examined elements below the environmental regulatory limits.

A study by Xenidis et al. (2002) examined the potential use of lignite coal fly ash in the control of acid generation from sulphidic mine tailings containing 27% sulphur. Samples were homogeneously mixed with various amounts of fly ash, ranging from 10% to 63% and placed in kinetic laboratory columns. The drainage quality of the columns was monitored over a test period of 600 days. The hydraulic conductivity of the mixtures were measured to evaluate the potential of fly ash to form a low permeability layer. Based on the results, the addition of fly ash to sulphidic tailings, even at the lower amount, increased the leachate pH from a pH of 8.6 to 10.0 and decreased the dissolved concentrations of contaminants, mainly Zn and Mn, to values that meet the European regulatory limits for potable water. Higher fly ash concentrations (31% and 63%) reduced the hydraulic conductivity by 2 to 3 orders of magnitude. The study concluded that the optimum amount of fly ash addition (for the study materials), with respect to neutralization and hydraulic conductivity, was between 20% and 30%.

A site specific case study by Shang et al. (2006) examined the potential of stabilizing acid generating mine tailings from a Sudbury, Ontario, mine by codisposal with coal fly ash from the Nanticoke power generation station in Ontario. The study included characterization of the mine tailings and fly ash, oxidation tests on the mine tailings, and laboratory kinetic column permeation tests. Results showed that when permeated with AMD the hydraulic conductivity of the fly ash decreased more than 3 orders of magnitude. It was also shown that the fly ash leachate (i.e. water permeated through the fly ash) when permeated through the mine tailings neutralized the acidic pore fluid of the mine tailings. The effluent pH was found to be alkaline and heavy metal concentrations decreased.

Yeheyis et al. (2007) examined the potential of using coal fly ash and bentonite/fly ash mixtures as a barrier material for mine waste and AMD by conducting laboratory kinetic column test. Because of the high permeability (above the regulatory guideline) of fly ash permeated with water, bentonite was added to achieve the required regulatory permeability. The addition of 5% and 10% by mass of bentonite to coal fly was successful in lowering the hydraulic conductivity when permeated with water. However a slight increase in hydraulic conductivity was observed when permeated with AMD. The 5% bentonite addition had an initial permeability above the regulatory guideline, but a decrease in hydraulic conductivity was observed with continued AMD permeation. The 10% bentonite met the regulatory guideline but no further decrease in hydraulic conductivity was observed with continued AMD permeation. Fly ash when permeated with AMD observed a 2 order of magnitude decrease (to less than 10^{-8} cm/sec) in hydraulic conductivity upon termination of the test. Effluent pH was found to be alkaline throughout the tests and heavy metal concentrations were below the leachate criteria set by the Ontario government.

The effects of AMD permeation on soil amended with bentonite were investigated by Kashir and Yanful (2000) using laboratory kinetic column tests. The objective of the study was to examine the long term environmental degradation of these materials from continued permeation of AMD. Six percent bentonite (by mass) was added to two natural soils to represent slurry wall backfill materials, and permeated with AMD. One was a carbonate rich (32%) soil from London, Ontario, and the other was a carbonate free soil from the Heath Steele mine in New Brunswick. An increase in permeability was not observed in either test upon switching to AMD. The carbonate free soil (Heath Steele) showed nearly constant hydraulic conductivity with continued AMD permeation while the carbonate rich soil (London) showed a continuous decrease until termination of the test. The carbonate rich soil was effective in maintaining a near neutral pH for the duration of the test, while the carbonate free soil quickly became acidic. The carbonate rich soil was also effective in reducing the concentrations of many of the heavy metals, while the carbonate free soil was ineffective in reducing concentrations.

Kashir and Yanful (2001) in another study examined the effects of AMD permeation on bentonite alone using kinetic laboratory column tests. This study showed that the hydraulic conductivity increased by up to one order when permeated with AMD. The pH buffering potential of bentonite was minimal (consumed within 5 pore volumes) and was ineffective in treating most heavy metals. The increase in hydraulic conductivity was attributed to the collapse of the diffuse double layer surrounding the clay particles.

2.8 SUMMARY

This chapter reviewed the physical, geotechnical, chemical, and mineralogical properties of the different materials used in this study (coal fly ash, reactive mine tailings, soil, and bentonite). Also investigated were the properties of AMD, including its formation, control and treatment, health and environmental concerns, and reactions with the study materials (coal fly ash, mine tailings, soil, and bentonite).

Recent studies on the interaction of AMD with coal fly ash and combinations of coal fly ash with mine tailings and bentonite were reviewed to determine their potential engineering applications for the treatment and containment of AMD when used as a reactive barrier. Of particular interest were changes in hydraulic conductivity, leachate pH, and leachate chemistry. While most studies looked at the pH and heavy metal buffering potential of coal fly ash, limited research has been conducted on the effects of AMD on the permeability of coal fly ash, either by itself or in combination with other materials. This research further focuses on hydraulic conductivity and AMD treatment properties of AMD permeated through kinetic laboratory columns of coal/biomass fly ash by itself and amended with various ratios of mine tailings, glacial till soil, and bentonite. Findings were used to determine their application in reactive barriers to treat and/or contain reactive mine tailings and the associated AMD.

2.9 REFERENCES

American Coal Ash Association (ACAA) 1997. *1996 Coal Combustion Product-Production and Use*. Alexandria, Virginia.

Banks, D., Younger, P., Arnesen, R., Iversen, E., and Banks, S. 1997. Mine-water chemistry: the good, the bad and the ugly. *Environmental Geology,* 32(3): 157-174.

Batty, L. and Younger, P. 2004. Growth of phragmites australis (Cav.) trin ex. steudel in mine water treatment wetlands: effects of metal and nutrient uptake. *Environmental Pollution,* 132: 85-93.

Bayat, O. 1998. Characterization of Turkish Fly Ashes. *Fuel,* 77, No. 9/10: 1059-1066.

British Columbia Ministry of Energy Mines and Petroleum Resources (BC-MEMPR) 1989. Draft acid rock drainage technical guide. *British Columbia Acid Mine Drainage Task Force,* Victoria, BC.

Blowes, D., Bain, J., Smyth, D., and Ptacek, C. 2003a. Treatment of mine drainage using permeable reactive materials. *Environmental Aspects of Mine Wastes, Volume 31 (Chapter 17):* Mineralogical Association of Canada, Vancouver, BC.

Blowes, D., Ptacek, C., and Jurjovec, J. 2003b. Mill tailings: hydrogeology and geochemistry. *Environmental Aspects of Mine Wastes, Volume 31 (Chapter 5)*: Mineralogical Association of Canada, Vancouver, BC.

Canadian Council of Ministers of the Environment (CCME) 2007. Canadian Water Quality Guidelines for the Protection of Aquatic Life. Winnipeg. http://ceqg-rcqe.ccme.ca/download/en/134/ (accessed April 2009).

Cornelis, G., Johnson, A., Van Gerven, T., and Vancasteele, C. 2008. Leaching mechanisms of oxyanionic metalloid and metal species in alkaline solid wastes: A review. *Applied Geochemistry,* 23: 955-976.

Creek, D. and Shackelford, C. 1992. Permeability and leaching characteristics of fly ash liner materials. Transportation research record 1345 TRB, *National Research Council*, pp 74-83.

Eaker, C. 1997. The use of alkali-activated fly ash grouts for the remediation of AMD from underground mines. *Fuel and Energy Abstracts,* 38: 405.

European Commission (EC) 2004. Draft reference document on best available techniques for management of tailings and waste-rock in mining activities. *European Commission,* Seville, Spain.

Environment Canada Metal Mining Effluent Regulations (EC-MMER) 2003. Status report on water pollution prevention and control under the metal mining effluent regulations, Ottawa. http://www. ec.gc.ca/nopp/docs/rpt/waterpollution/mining2003/en/c2.cfm (accessed Feb. 2009).

Gitari, M., Petrik, L., Etchebers, O., Key, D., Iwuoha, E., and Okvjeni, C. 2006. Treatment of acid mine drainage with fly ash: Removal of major contaminants and trace elements. *Journal of Environmental Science and Health,* 41.8: 1729-1747.

Gitari, M., Petrik, L., Etchebers, O., Key, D., Iwuoha, E., and Okvjeni, C. 2008a. Passive neutralisation of acid mine drainage by fly ash and its derivatives: A column leaching study. *Fuel,* 87: 1637-1650.

Gitari, M., Petrik, L., Etchebers, O., Key, D., and Okvjeni, C. 2008b. Utilization of fly ash for treatment of coal mines wastewater: Solubility controls on major inorganic contaminants. *Fuel,* 87: 2450-2462.

Health Canada 2008. Guidelines for Canadian drinking water quality. Federal-provincial-territorial committee on drinking water of the federal-provincial-territorial committee on health and the environment, Ottawa, May 2008.

International Aluminum Institute 2009. Health in the Aluminum Industry, http://www.world-aluminium.org/?pg=/Downloads/Publications/Full%20Publication&path=278 (accessed April 2009).

Jambor, J. 2003. Mine waste mineralogy and mineralogical perspectives of acid base accounting. *Environmental Aspects of Mine Wastes, Volume 31 (Chapter 6):* Mineralogy Association of Canada, Vancouver, BC.

Kashir, M. and Yanful, E. 2001. Hydraulic conductivity of bentonite permeated with acid mine drainage. *Canadian Geotechnical Journal,* 38: 1034-1048.

Kashir, M. and Yanful, E. 2000. Compatibility of slurry wall backfill soils with acid mine drainage. *Advances in Environmental Research,* 4: 251-268.

Minerals Zone 2005. Bentonite and Fuller's Earth, http://www.mineralszone.com/minerals/bentonite.html, (accessed April 2009).

Misra, M., Yang, K., and Mehta, R. 1996. Application of fly ash in the agglomeration of reactive mine tailings. *Journal of Hazardous Materials*, 51: 181-192.

Mudd, G., Weaver, T., and Kodikara, J. 2004. Environmental geochemistry of leachate from leached brown coal ash. *Journal of Environmental Engineering,* December: 1514 – 1526.

Nyquist, J. and Greger, M. 2009. A field study of constructed wetlands for preventing and treating acid mine drainage. *Ecological Engineering,* 35: 630-642.

Pandian, N. 2004. Fly ash characterization with reference to geotechnical applications. *Journal Indian Institute Science,* 84: 189-216.

Patnaik, P. 2002. Handbook of inorganic chemicals. McGraw-Hill, Toronto.

Perez-Lopez, R., Nieto, J. and & Ruiz de Almodovar, G. 2007. Utilization of fly ash to improve the quality of the acid mine drainage generated by oxidation of a sulphide-rich mining waste. *Chemiosphere,* 67: 1637-1646.

Potgieter-Vermaak, S., Potgieter, J., Monama, P., and Van Gricken, R. 2006. Comparison of limestone, dolomite and fly ash as pre-treatment agents for acid mine drainage. *Minerals Engineering*, 19: 454-462.

Prashanth, J., Sivapullaiah, P., and Srdharan, A. 2001. Pozzolanic fly ash as a hydraulic barrier in land fills. *Engineering Geology,* 60: 245-252.

Scheetz, B. and Earle, R. 1998. Utilization of fly ash. *Current opinion in solid state & materials science,* 3.5: 510-520.

Seal, R. and Hammarstron, J. 2003. Geoenvironmental models of mineral deposits: Examples from massive sulfide and gold deposits. *Environmental Aspects of Mine Wastes, Volume 31 (Chapter 2)*: Mineralogy Association of Canada, Vancouver, BC.

Shang, J., Wang, H., Kovac, V. and Fyfe, J. 2006. Site specific study on stabilization of acid-generating mine tailings using coal fly ash. *Journal of Materials in Civil Engineering,* March/April: 140-151.

Skousen, J.G., and Ziemkiewicz, P.F. 1996. Acid mine drainage control and treatment. National Research Center for Coal and Energy, *West Virginia University,* Morgantown, WV.

Smith, L. and Beckie, R. 2003. Hydrologic and geochemical transport processes in mine waste rock. *Environmental Aspects of Mine Wastes, Volume 31 (Chapter 3)*: Mineralogy Association of Canada, Vancouver, BC.

Stouraiti, C., Xenidis, A., and Paspaliaris, I. 2001. Reduction of Pb, Zn, and Cd availability from tailings and contaminated soils by the application of lignite fly ash. *Water, Air, and Soil Pollution* 137: 247-265.

United States Department of Transportation (USDOT) 1995. Federal Highway Administration and American Coal Ash Association, *Fly Ash Facts for Highway Engineers.* Report No. FHWA-SA-94-081, Washington, DC.

United States Environmental Protection Agency (USEPA) 1994. Technical Document: Acid Mine Drainage Prediction. *Office of Solid Waste, Special Waste Branch*, EPA 530-R-94-036.

United States Environmental Protection Agency (USEPA) 2003. Ore mining and dressing point source category. 40-CRF-440.

Vuthaluru, H. and French, D. 2008. Ash chemistry and mineralogy of an Indonesian coal during combustion, Part 1 drop-tube observations. *Fuel Processing Technology,* 89: 595-607.

Walton-Day, K. 2003. Passive and active treatment of mine drainage. *Environmental Aspects of Mine Wastes, Volume 31 (Chapter 16)*: Mineralogical Association of Canada, Vancouver, BC.

Wang, H., Shang, Kovac, V, and Ho, K. 2006. Utilization of Atikokan coal fly ash in acid rock drainage control from Musselwhite Mine tailings. *Canadian Geotechnical Journal,* 43: 229-243.

World Health Organization (WHO) 2008. Guidelines for drinking water quality. Geneva, http://www.who.int/entity/water_sanitation_health/dwq/fulltext.pdf (accessed June 2009).

Xenidis, A., Mylona, E. and Paspaliaris, I. 2002. Potential use of lignite fly ash for the control of acid generation from sulphidic wastes. *Waste Management,* 22: 631-641.

Yanful, E., Simms, P., and Payant, S. 1999. Soil covers for controlling acid generation in mine tailings: a laboratory evaluation of the physics and geochemistry. *Water, Air, and Soil Pollution*, 114: 347-375.

Yeheyis, M., Shang, J. and Yanful, E. 2007. Beneficial utilization of coal fly ash as acid mine drainage barrier. *In* Proceedings of the 60th Canadian Geotechnical Conference & 8th Joint CGS/IAH-CNC Groundwater Conference, Ottawa, Canada, October 2007: pp 1494-1499.

Yeheyis, M., Shang, J. and Yanful, E. 2008. Characterization and environmental evaluation of Atikokan coal fly ash for environmental applications. *Journal of Environmental Engineering Science,* 7: 481-498.

3.0 MATERIAL PROPERITES AND CHARACTERIZATION

Geotechnical and geo-chemical characterization was conducted on all materials used in the study. Particle size analysis, specific gravity, and Atterberg limits tests were conducted on the coal/biomass fly ash (CBFA), mine tailings, glacial till soil, and bentonite amended CBFA mixtures. Representative samples of the CBFA, mine tailings, and soil were sent to a third party laboratory for acid based accounting (ABA) and determination of their oxides and elemental composition by X-Ray fluorescence (XRF). Oxides and elemental composition of the bentonite was also determined by XRF.

Selected samples were collected prior to and upon completion of kinetic column tests for qualitative analysis of mineralogy changes by X-Ray diffraction (XRD). Scanning electron microscopy and energy dispersive X-ray analysis (SEM-EDX) were conducted to further investigate the mineralogy.

3.1 GEOTECHNICAL PROPERTIES

3.1.1 Particle Size Analysis

The distribution of particle sizes was determined by the hydrometer method in accordance with the American Society for Testing and Materials standard D422 (ASTM 2007). Particle size analysis is important in determining the material's strength, density, and hydraulic conductivity. Details on specifics of each material is presented in subsequent chapters and summarized in Table 3.1.1.

Table 3.1.1 Geotechnical properties of study materials

Parameter	Coal/ Biomass Fly Ash (CBFA)	Mine Tailings (MT)	Glacial Till Soil[1] (GT)	Bentonite (2.5% to 10% bentonite amended with CBFA[2]
% Sand	10	10	55	9.8 – 8.1
% Silt	84	80	37	82.6 – 75.7
% Clay	6	10	8	7.6 – 12.4
Specific Gravity	2.42	3.58	2.41	2.42 – 2.59
Liquid Limit[3]	-	-	-	27 – 105
Plastic Limit[3]	-	-	-	20 – 37

[1] Grain size represent particles passing 425μm sieve (~50% of total sample >425μm)
[2] Tests conducted on bentonite/CBFA mixtures, values show range between 2.5% and 10% bentonite.
[3] Liquid and plastic limit tests could not be performed on CBFA, mine tailings and glacial till soil.

3.1.2 Specific Gravity

The specific gravity was measured in accordance with ASTM standard D854 (ASTM 2006a) on representative samples of CBFA, mine tailings and glacial till soil. The various percentages of bentonite amended CBFA used in the study were determined individually after mixing. Specific gravity is required to determine the materials bulk and relative densities, along with calculating the materials void ratio and porosity. Details on specifics of each material is presented in subsequent chapters and summarized in Table 3.1.1.

3.1.3 Atterberg Limits

Atterberg limits (liquid and plastic) were conducted in accordance with ASTM standard D4318 (ASTM 2005) on samples of CBFA, mine tailings and glacial till soil. The various percentages of bentonite amended CBFA used in the study were determined individually after mixing. Details on specifics of each material is presented in subsequent chapters and summarized in Table 3.1.1. Tests could not be carried out on particles smaller than 75 µm for the CBFA, mine tailings and glacial till soil samples, indicating that these materials are non plastic. Atterberg limits are important in determining the materials workability, strength, and settlement characteristics.

3.1.4 Hydraulic Conductivity

Hydraulic conductivity tests were conducted in fixed wall permeameters constructed for the study from inert (nonreactive) materials. Test procedures were in general agreement with ASTM standards D5084-03 (ASTM 2003) and D2434-68 (ASTM 2006b). Hydraulic conductivity is important in the design of caps, liners, dams, and flow-through reactive barriers to predict and manage AMD migration offsite and in determining the rate of groundwater recharge.

3.2 ACID BASED ACCOUNTING (ABA)

Samples of CBFA, mine tailings, glacial till soil and mixtures of CBFA amended mine tailings were sent to a third party laboratory for ABA in accordance with the Modified Sobek Method (BC-MEMPR 1989). Details on the ABA methods and calculations are provided in Section 2.6.2. Results for the CBFA and mine tailings along with the various mixtures of CBFA amended mine tailings are presented in Table 3.2. ABA was not conducted on the bentonite or bentonite amended CBFA samples. Upon reviewing the chemical composition of bentonite, it is expected to be non-acid producing due to its low sulphur content.

Table 3.2 **Net neutralizing potential (NNP)of CBFA and mine tailings mixtures**

Parameter	100% MT (control)	95% MT 5% CBFA	90% MT 10% CBFA	80% MT 20% CBFA	67% MT 33% CBFA	50% MT 50% CBFA	100% CBFA
NNP[1]	-416	-387	-375	-305	-197	-68.6	298

[1] Net Neutralizing Potential (t $CaCO_3$/1000 t)

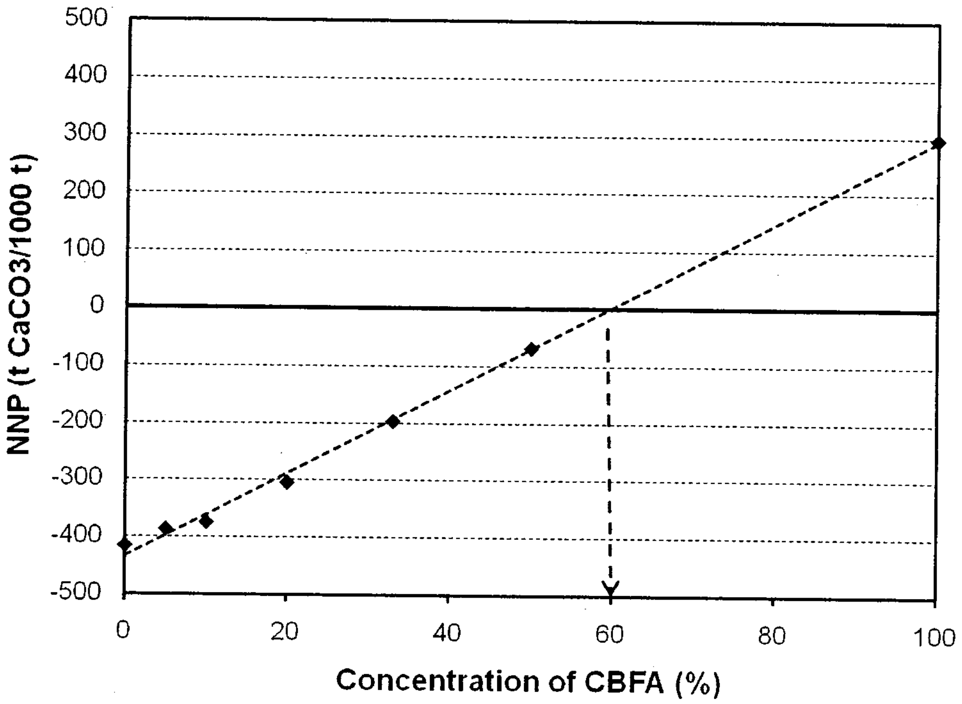

Figure 3.2 **Acid based accounting results (NNP versus CBFA percentage)**

The NNP is recorded as the equivalent amount of calcium carbonate ($CaCO_3$) in tonnes per 1000 tonnes of material or in kilograms per tonne of material. A negative NNP indicates that the material has the potential to be acid producing, whereas a positive NNP means the acid potential is offset by the neutralizing potential for a positive NNP. Figure 3.2 shows the NNP with respect to the percentage by mass of CBFA. The relationship of the NNP is shown to be linear with respect to the percentage of CBFA added. Interpolation of this data indicated that approximately 60 percent CBFA was required to reach a NNP of zero tonnes $CaCO_3$/1000 tonnes of mixture (i.e. neutralize the acid generating potential of the mine tailings). All column packs (except the 100% CBFA control) had a net acid generating capacity (negative NNP).

3.3 OXIDES AND ELEMENTAL CHEMISTRY (XRF)

Representative samples of the CBFA, mine tailings, bentonite, and soil were sent to a third party laboratory for determination of their oxides and elemental composition by X-Ray fluorescence (XRF). XRF is the emission of fluorescent X-rays from a material that has been excited by bombarding with high-energy X-rays or gamma rays. Results were reported as a percentage for oxides as the major constituents and as grams/tonne (i.e. ppm) for the major elements. Results are shown in Table 3.3a and 3.3b.

Table 3.3a Composition of study materials as major oxides

Component	Mine Tailings (%)	CBFA (%)	Glacial Till (%)	Bentonite (%)
SiO_2	31.7	45.2	74.4	58.4
Al_2O_3	8.06	21.5	11.3	15.6
Fe_2O_3	42.3	4.04	3.41	5.38
MgO	2.97	2.51	0.45	1.80
CaO	3.58	13.6	0.80	2.11
Na_2O	1.31	7.33	3.52	2.40
K_2O	0.97	0.73	3.11	0.52
TiO_2	0.59	0.95	0.39	0.14
P_2O_5	0.11	0.62	0.06	0.07
MnO	0.11	0.02	0.05	0.32
Cr_2O_3	0.04	0.01	0.07	<0.01
V_2O_5	0.03	0.03	<0.01	<0.01
SO_4	1.22	0.2	<0.01	0.21
LOI[1]	6.53	0.36	1.99	13.1

Note: [1] Loss on ignition

Table 3.3b Composition of study materials as major elements

Component	Mine Tailings (g/t)	CBFA (g/t)	Glacial Till (g/t)	Bentonite (g/t)
Ag	<2	<2	<2	<2
As	<30	<30	<30	<30
Ba	300	3900	420	430
Be	0.64	4.2	1.6	1.5
Cd	<2	<2	<10	<10
Co	190	16	9	5
Cu	1200	41	98	26
Li	<5	16	<10	<10
Mo	<5	10	<5	<5
Ni	4900	27	<20	<20
Pb	<100	48	<40	<40
Sr	130	3300	70	170
S	136000	<100	6	<100
Zn	180	53	68	64

3.4 SYNTHETIC ACID MINE DRAINAGE

A synthetic AMD was prepared in the laboratory by mixing distilled water with metal sulphates, chlorides, and nitrates to a concentration that is typical of field AMD concentrations provided by Vale Inco. Solutions were periodically mixed during the first 24 hour period to assist dissolution, after which the solution was filtered through a 1 μm domestic drinking water filter to remove any suspended particles. Details of the AMD solutions used in the study are presented in Chapters 5, 6 and 7.

3.5 EXTRACTION TESTS

Agitated static extraction tests (also known as leaching tests) were conducted on CBFA, mine tailings, and CBFA/mine tailings mixed samples. This test involved placing 10 g (dry) of

CBFA, mine tailings, or CBFA/mine tailings mixtures and 200 ml of leaching fluid (pH adjusted distilled water), in a 500 ml glass jar with a plastic lid. The pH was adjusted by the addition of nitric acid to the distilled water prior to addition of the CBFA, mine tailings, or CBFA/mine tailings mixtures. Samples were rotated and allowed to freely mix with the leachate at 30 to 40 revolutions per minute for 16 to 24 hours. The agitating of the samples assists the tests to reach steady-state conditions as quickly as possible. The drawback with agitated extraction tests is that they measure the chemical properties of a soil/leachate system rather than the physical, rate-limiting mechanisms. Therefore, the test may over-estimate the short-term release of constituents (USEPA 1999). Three sets of extraction tests were conducted.

1) Mine tailings in a distilled water medium at varying acidity addition (as moles of HNO_3),

2) CBFA in a distilled water medium at varying acidity addition (as moles of HNO_3), and

3) 33% CBFA mixed with 67% mine tailings in a distilled water medium at varying final pH values.

Prior to conducting the test, the pH and elemental chemistry of the leachate solution (distilled water) was analyzed (Table 3.5). Upon termination of the tests the samples were allowed to clear and then sampled and its pH determined. Representative samples were further filtered using a 0.45 μm filter to remove suspended solids. The samples were stored in a 15 ml sample test tube, acidified to pH 3 or less with nitric acid, and analyzed for elemental composition by inductively coupled plasma – atomic emission spectrometry (ICP-AES).

Table 3.5 **Distilled water properties**

Element/Parameter	Concentration[1]	Element/Parameter	Concentration[1]
pH	6.8 - 7.5		
Aluminum	0.01	Sodium	0.32
Arsenic	nd	Magnesium	0.032
Barium	0.005	Nickel	nd
Calcium	0.3	Sulphur	0.12
Chromium	nd	Silica	nd
Copper	nd	Strontium	0.02
Iron	nd	Lead	nd
Potassium	0.06	Zinc	0.007

Note: [1] in mg/L unless specified,
shown values were highest concentrations encountered
nd - less than icp detection limits

Extraction tests were first conducted on mine tailings and CBFA samples. The ICP-AES results were plotted with respect to acidity addition (i.e. moles of nitric acid) for the mine tailings and CBFA tests. The results were used to determine the effects of acidity on the leachability of heavy metals and other elements from the CBFA and mine tailings. Figures 3.5a-e show the concentration of copper, nickel, iron, zinc and lead versus moles of HNO_3 (i.e. acidity). The figures show the concentration of each of the five metals in the mine tailing leachate to be greater than that in the CBFA leachate. Copper was found to be 1 to 2 orders of magnitude greater in the range of HNO_3 used, while nickel and iron were both 2 to 3 orders of magnitude greater. For zinc the concentrations appeared to be dependant on the HNO_3 concentration. As shown in Figure 3.5d, while 2 orders of magnitude were reported in the mine tailings leachate for ≤ 0.01 M of HNO_3, at $HNO_3 > 0.01$ M the concentration of zinc in the leachate is only slightly higher than that of the CBFA leachate. As shown in Figure 3.5e, only lead concentrations from the mine tailings were reported (CBFA leachate concentrations were below the detection limits), and increased linearly with increased HNO_3. Results showed that the leaching of the heavy metals (copper, nickel, iron, lead, and zinc) were predominantly controlled by the addition of acidity to the mine tailings.

Figure 3.5f shows the concentration of calcium versus concentration of HNO_3. Calcium concentrations were found to increase with increased acidity in the CBFA tests, while the mine tailings tests remained relatively unchanged after a concentration of 0.003 M of HNO_3. The increased calcium concentrations were due to the dissolution of calcium minerals within the CBFA. The dissolution of calcium oxide and calcium carbonate minerals resulted in an increase in pH which was observed in the leachate at termination of the tests. Similar trends were observed in the other alkaline metals: barium, magnesium, and strontium. These alkaline metals also have a potential to buffer the acidity.

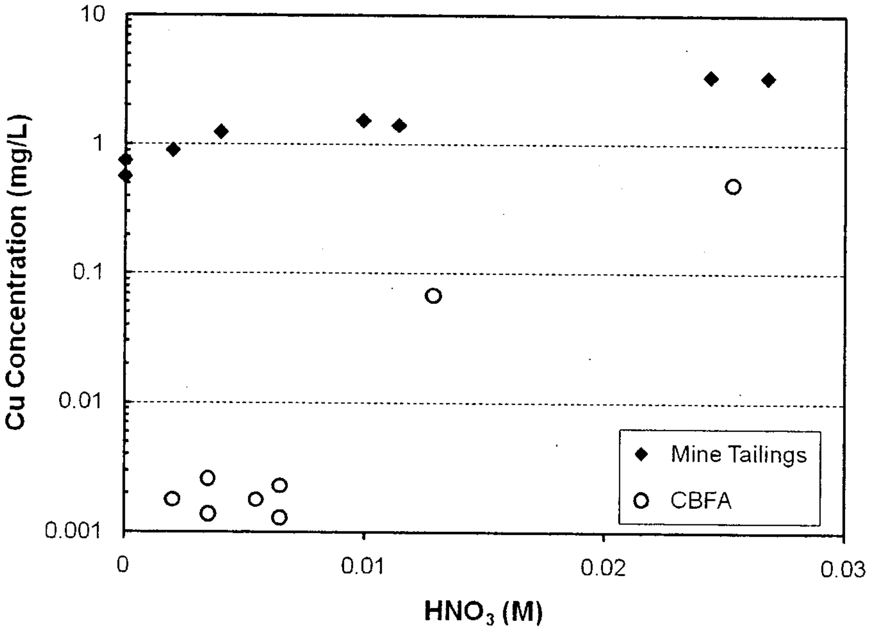

Figure 3.5a **Concentration of copper versus concentration of HNO_3 (mine tailings and CBFA)**

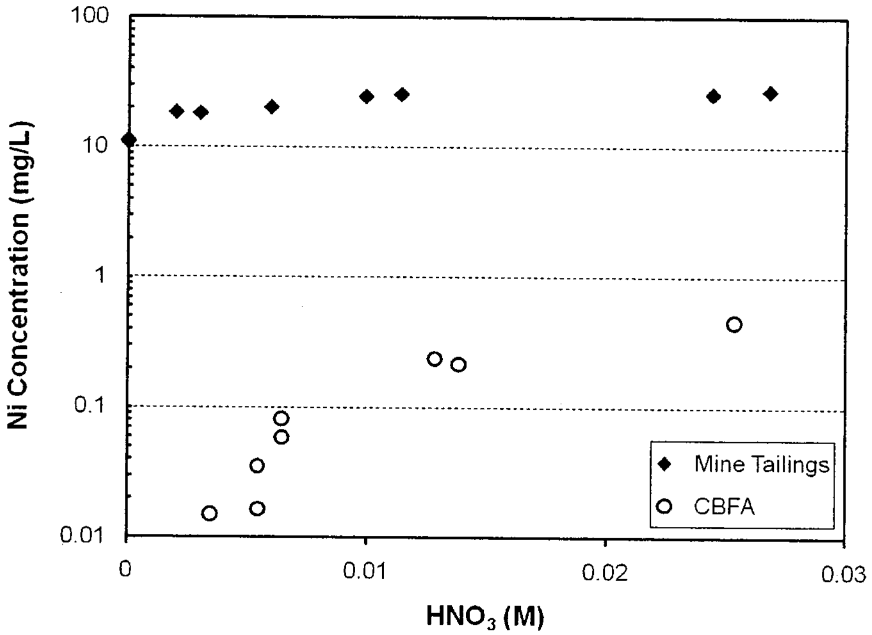

Figure 3.5b Concentration of nickel versus concentration of HNO$_3$ (mine tailings and CBFA)

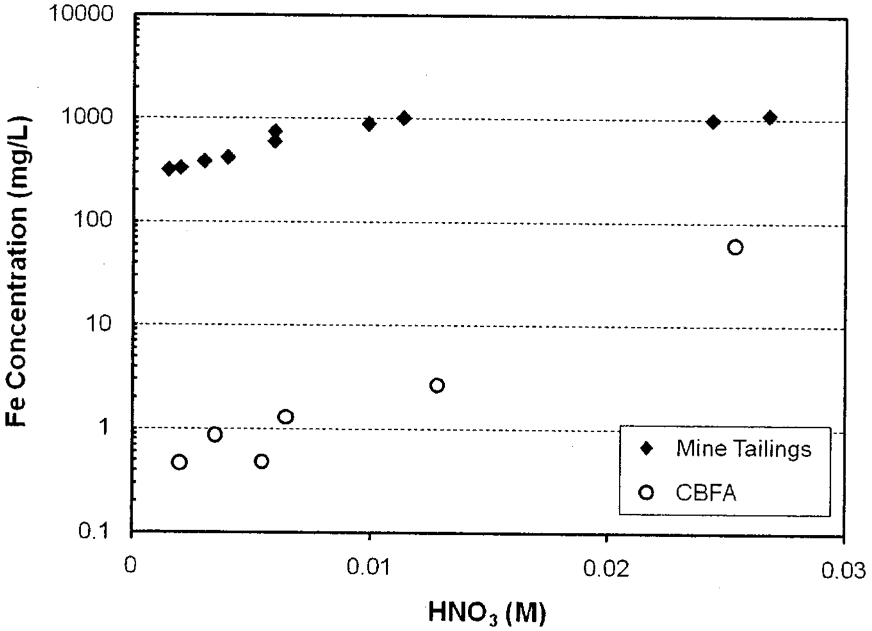

Figure 3.5c Concentration of iron versus concentration of HNO$_3$ (mine tailings and CBFA)

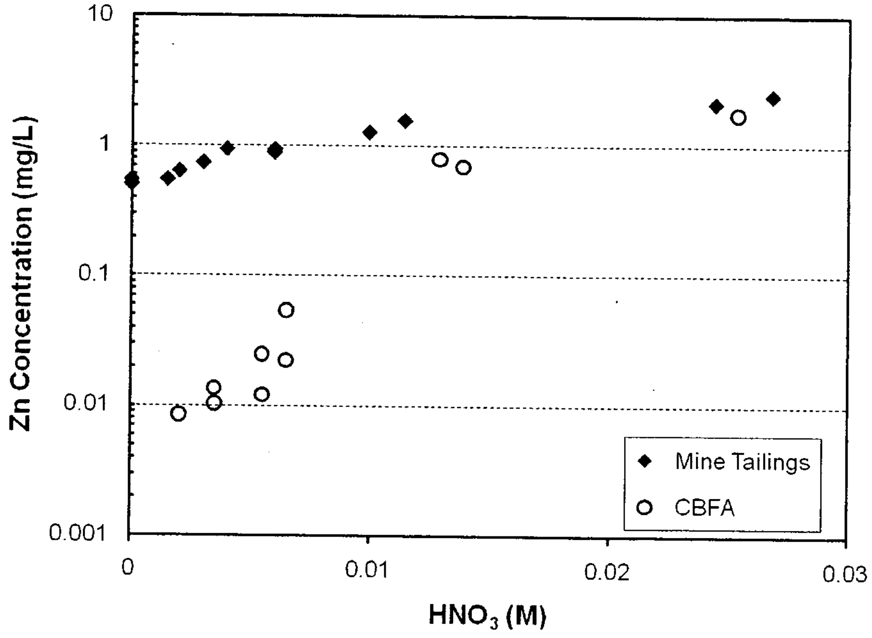

Figure 3.5d Concentration of zinc versus concentration of HNO_3 (mine tailings and CBFA)

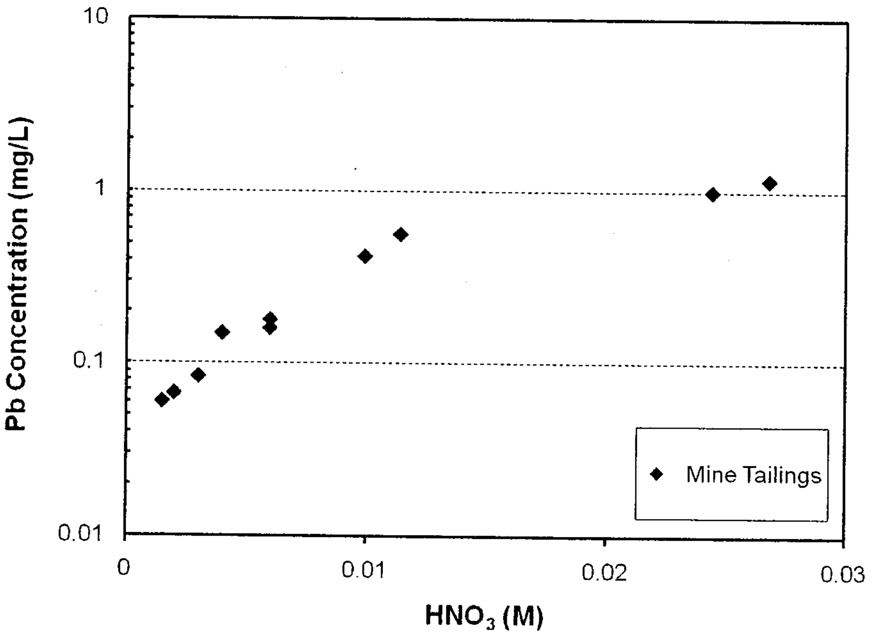

Figure 3.5e Concentration of lead versus concentration of HNO_3 (mine tailings)

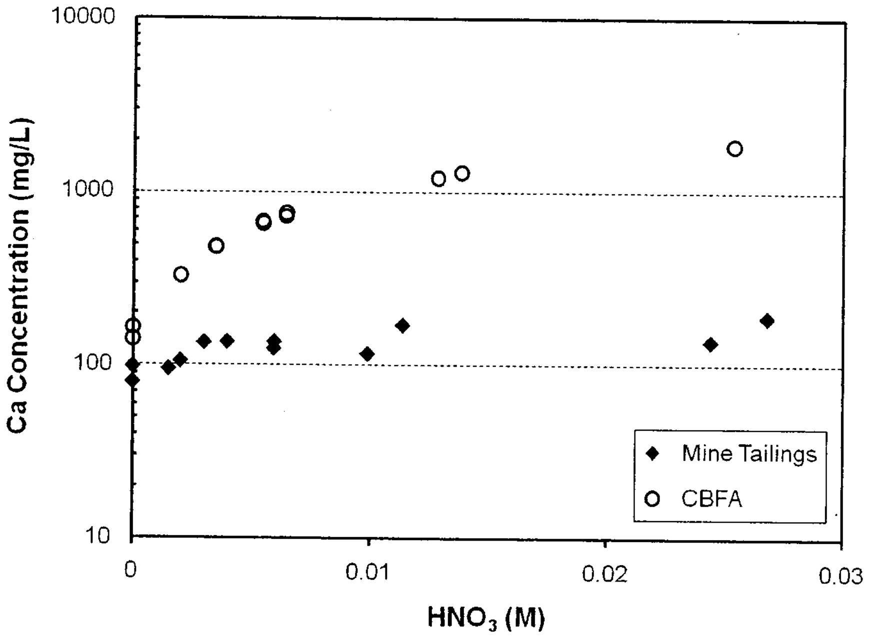

Figure 3.5f **Concentration of calcium versus concentration of HNO_3 (mine tailings and CBFA)**

Samples of 33% CBFA amended with 67% mine tailings were used in subsequent extraction tests to examine the elemental composition of the leachate versus the leachate pH. The pH was adjusted by the addition of nitric acid to the distilled water prior to conducting the tests. The ICP-AES results were plotted with respect to the leachate pH at termination of the tests. Figure 3.5g show the concentrations of copper, nickel, and zinc.

As seen in Figure 3.5g, the concentration of copper was the lowest between pH 6 and 11 (generally constant within this pH range) and increased exponentially at pH < 6. Research by Pandian et al. (2004) on the solubility of amorphous CuO in coal fly ash with respect to pH showed dissolved copper concentrations to be lowest at a pH of 9 to 10. Figure 3.5g shows the concentration of nickel lowest and relatively unchanged at pH > 8.0. Below a pH of 8 however nickel concentrations increased exponentially with decreasing pH and plateaued to a maximum concentration of 10 mg/L at a pH ≤ 6. Zinc was at its lowest concentration at a pH of 9.5 and increased exponentially with decreasing pH. The concentration of zinc also increased at a pH > 9.5. Research by Pandian et al. (2004) on the solubility of amorphous ZnO in coal fly ash with respect to pH showed dissolved zinc concentrations to be lowest at a pH of 9.5 which is in agreement with this study. Lead concentrations in the leachate were below the analytical detection limit in most of the analyzed samples.

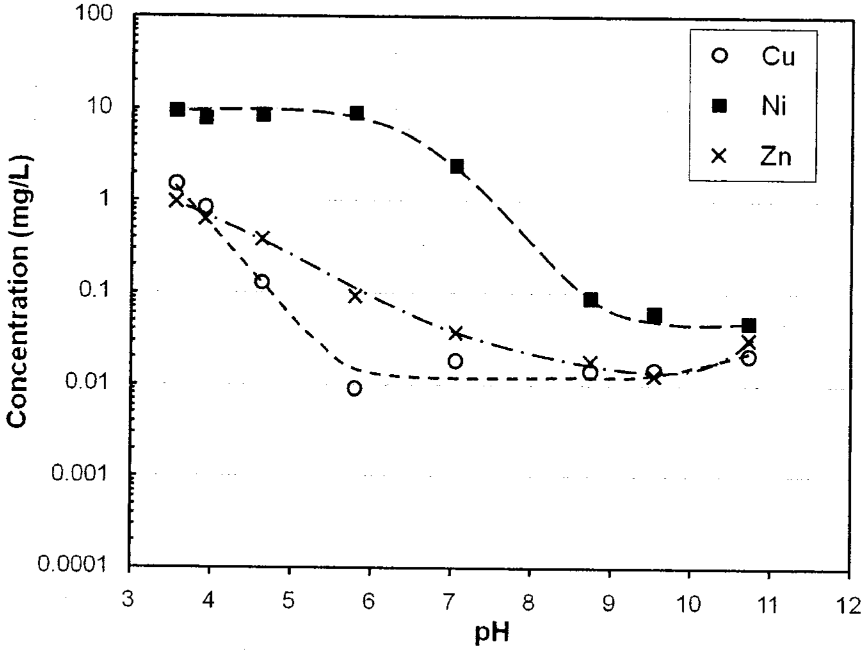

Figure 3.5g **Concentration of Cu, Ni, and Zn versus leachate pH (33% CBFA amended mine tailings)**

The curves of the alkaline earth metal elements (barium, calcium, strontium, and magnesium) concentrations versus pH are plotted on the same figure (Figure 3.5h). Barium and strontium are of interest due to their high concentrations in the CBFA (3900 g/t and 3300 g/t, respectively). As shown in Figure 3.5h the barium concentration was lowest at pH 7 and increased exponentially with higher and lower pH. Calcium and strontium showed an exponential increase in concentration with decreasing pH below a pH of 8. The concentrations were predominantly constant at a pH ≥ 8. Magnesium also had an exponential increase in concentration with decreasing pH below a pH of 10. Above a pH of

10 the concentration decreased rapidly by more than one order of magnitude.

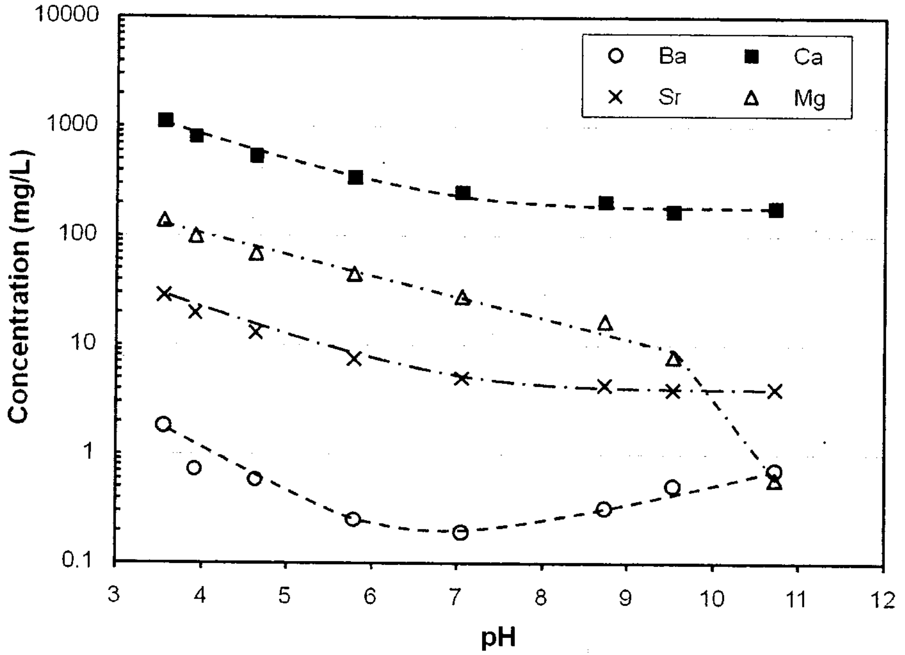

Figure 3.5h Concentration of Ba, Ca, Sr, and versus leachate pH (33% CBFA amended mine tailings)

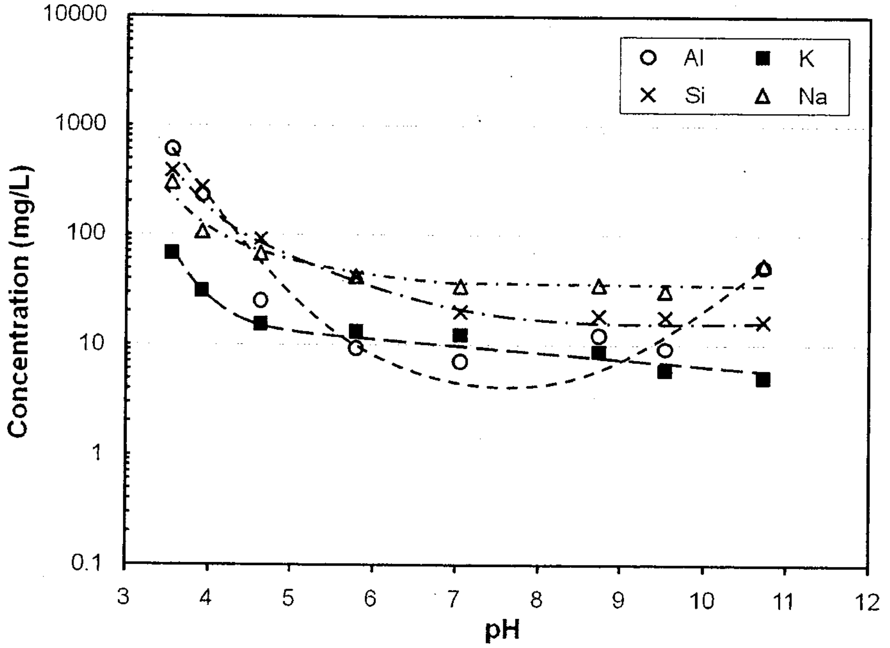

Figure 3.5i Concentration of Al, K, Si, and Na versus leachate pH (33% CBFA amended with mine tailings)

The concentration curves for elements commonly found in rock and soil (aluminum, potassium, silicon, and sodium) are grouped together and plotted on the same figure (Figure 3.5i). As seen in the figure, aluminum concentrations were lowest between a pH of 6 to 10 (generally constant within this range) but increased exponentially at a pH < 6 and pH >10. Potassium and sodium have a slight increase in concentration with decreasing pH until a pH of 5, at which point concentrations increased substantially in an exponential manner with continued decrease in pH. Silicon concentrations are predominantly unchanged above a pH of 7. Below pH 7 the concentrations increased in an exponential manner.

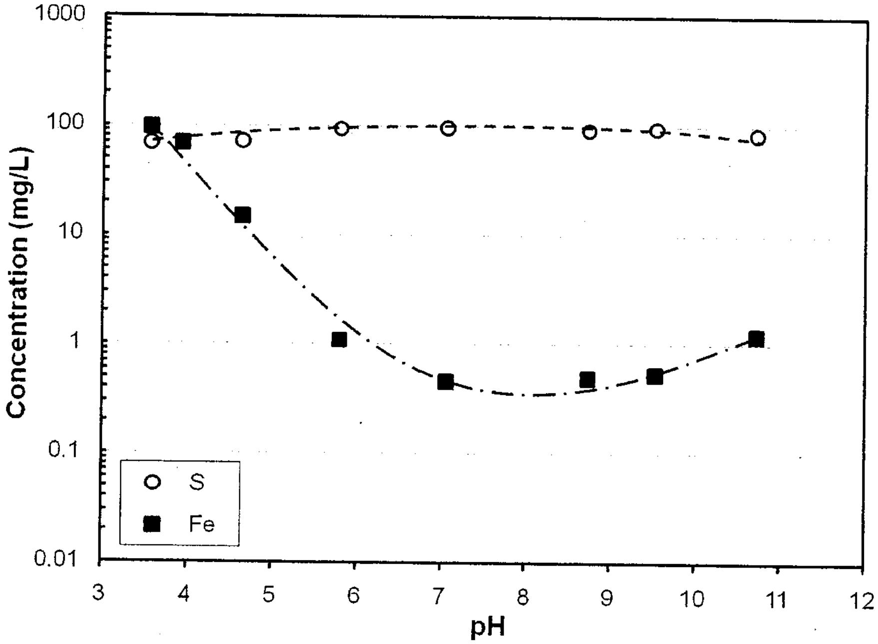

Figure 3.5j **Concentration of Fe and S versus leachate pH (33% CBFA amended with mine tailings)**

Figure 3.5j shows the concentrations of sulphur and iron, two major elements found in iron sulphide minerals (pyrite and pyrrhotite) and a major contributor to the formation of AMD. As shown in the figure, iron concentrations were lowest at a pH of 8 and increase exponentially with decreasing pH. The concentration also increased above a pH of 8. Research by Pandian et al. (2004) on the solubility of amorphous $Fe(OH)_3$ in coal fly ash with respect to pH show dissolved iron concentrations to be lowest at a pH of 8.5. As shown in Figure 3.5j, the concentration of sulphur was highest at a pH of 8. A slight decrease in concentration was observed at pH values higher and lower than a pH of 8. The main iron sulphide mineral present in the mine tailings identified by XRD was pyrrhotite ($Fe_{1-x}S$ where x=0 to 0.2). This mineral was also identified by Shang et al. (2006) on mine tailings from the area used in their study.

3.6 GEOCHEMICAL COMPUTER MODELING

Geochemical computer modeling was conducted to determine the saturation indices of possible minerals that may be present in the leachate of the extraction tests. The chemical equilibrium software VMinteq v.2.53 (KTH 2007) was used for the modelling. VMinteq is a Windows based Visual Basic version of USEPA's (2008) MinteqA2 geochemical computer modelling software. The elemental concentrations in solution and the solution pH were entered for each extraction test and modelled. The aqueous geochemical modelling allowed for the calculation of the equilibrium among the aqueous species of the effluent solutions which includes mineral saturation indices and suggests mineral phases that may control the pore water quality.

Saturation index (SI) is defined as (Bussiere et al. 2004):

$$SI = \log \frac{IAP}{K_{sp}} \qquad (3.1)$$

Where IAP is the ion activity product and K_{sp} is the solubility product constant of the mineral of interest. A SI value of zero indicates equilibrium conditions. A SI greater than zero (i.e. $IAP>K_{sp}$) indicates that the mineral has the potential to precipitate, and a SI less than zero (i.e. $IAP<K_{sp}$) indicates that the mineral has the potential to dissolve (Bussiere et al. 2004).

Minerals of interest included aluminum and iron species, carbonates (calcite and dolomite), and minerals identified in the fly ash hydration process (gypsum and ettringite). Figure 3.6a shows the saturation indices of common aluminum species with respect to the leachate pH. All of the four identified minerals ($Al(OH)_3$, gibbsite, Al_2O_3, diaspore) had a maximum saturation index at pH 6.5. The low aluminum concentrations between pH of 6 and 10 shown in Figure 3.5i were in agreement with the aluminum species saturation index of zero or greater in Figure 3.6a within this pH range. Research by Mudd et al. (2004) indicated that gibbsite was controlling the aluminum concentration for pH above pH 8.5 and amorphous $Al(OH)_3$ controlled below pH 8.5.

Figure 3.6b shows the saturation indices of common iron species (ferrihydrite, goethite, hematite, and K-jarosite) with respect to the leachate pH. Ferrihydrite, goethite and hematite (iron oxides) were over saturated throughout the pH range tested with a maximum saturation index at pH ~ 8.4. The low iron concentrations shown in Figure 3.5j at a pH of 8 is in agreement with the peaks in iron species saturation indices in Figure 3.6b. Iron concentrations and saturation indices correspond with research by Mudd et al. (2004) and Pendian et al. (2004). Potassium jarosite was found to be at equilibrium at a pH of approximately 8.4 (corresponding to the peaks for the other iron minerals). Below this pH potassium jarosite was over saturated and under saturated above this pH.

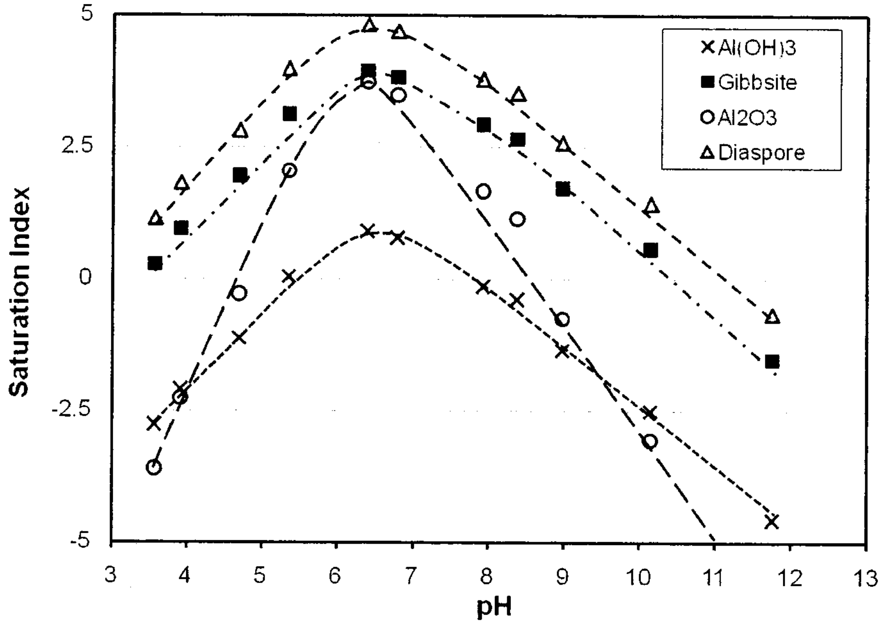

Figure 3.6a Aluminum species minerals – saturation index versus leachate pH

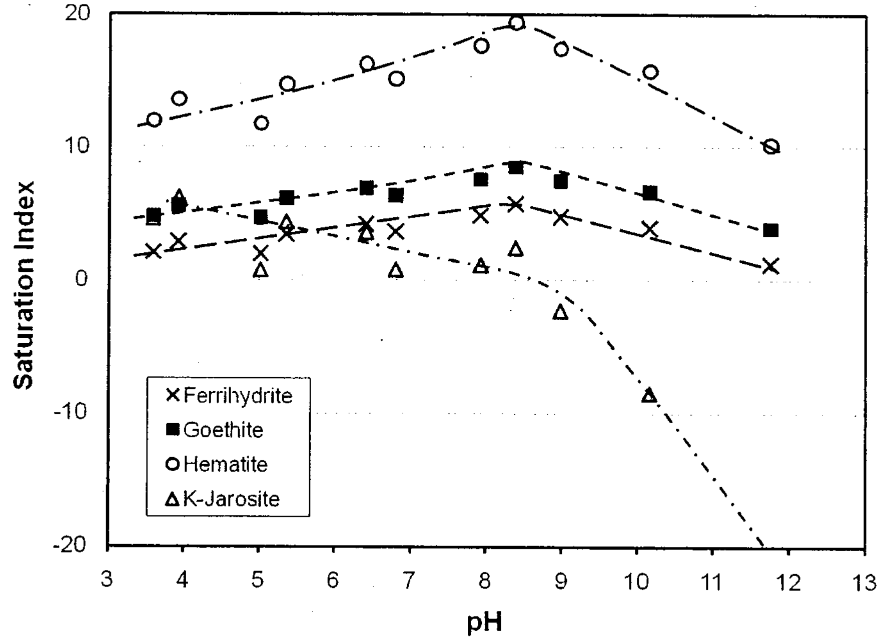

Figure 3.6b Iron species minerals – saturation index versus leachate pH

Figure 3.6c shows the saturation indices of calcite, dolomite, gypsum, and ettringite with respect to leachate pH. Calcite and dolomite are common carbonates found in mine tailings. Gypsum and ettringite were identified by Yeheyis et al. (2007) and by XRD as being formed from the reaction of AMD with coal fly ash (see Section 6.3.4). The formation of ettringite from the reaction of calcium aluminates with calcium sulphate in the early stages of hydration was also reported by Shang et al. (2007) and Lu et al. (2008). Yeheyis et al. (2008) also identified by XRD the formation of ettringite in landfilled coal fly ash at the Atikokan power generating plant. Gypsum and ettringite were not identified by XRD prior to permeation in either the CBFA or mine tailings samples.

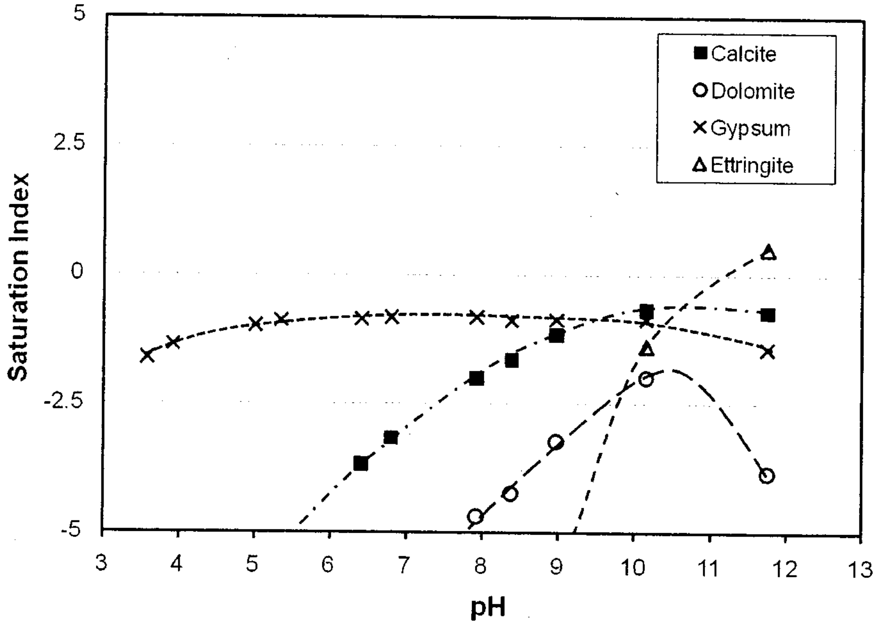

Figure 3.6c **Calcite, dolomite, gypsum, and ettringite – saturation index versus leachate pH**

Figure 3.6c shows that calcite is under-saturated for the entire pH range studied, plateauing at a SI of -1 at a pH ≥ 10. This plateau corresponds to the constant calcium concentration at a pH ≥ 9 in Figure 3.5h, indicating that calcite has possibly reached equilibrium at pH ≥ 9. The figure also shows that dolomite is also under-saturated for the entire pH range studied, reaching a maximum SI of -1.5 at a pH of approximately 10.5. The one fold decrease in concentration observed in Figure 3.5h indicates the possibility of dolomite reaching equilibrium at pH ~ 10.5. Gypsum is shown to be slightly under-saturated for the entire pH range. Ettringite became over-saturated at a pH ≥ 11. This over-saturation corresponds with a high concentration of available aluminum needed for its formation (see Figure 3.5i).

3.7 CONCLUSIONS

Acid based accounting conducted on mixed proportions of CBFA and mine tailings show that the net neutralizing potential (NNP) was a linear relationship between the amount of positive NNP material (CBFA) and negative NNP material (mine tailings). For the study materials a mixture of approximately 60% CBFA and 40% mine tailings would result in a NNP of zero.

Extraction tests showed that heavy metal concentrations in the leachate from mine tailings were higher than CBFA when a equal amount of HNO_3 (M) was added to the leachate solution. This indicated that the mine tailings are possibly controlling the concentrations of heavy metals in solution. With the continued addition of alkalinity the heavy metal concentrations in the CBFA leachate did observe a greater rate of increase than observed in the mine tailings. The increased acidity resulted in a decrease in concentration differences.

Extraction tests conducted on mixtures of 33% CBFA and 67% mine tailings, which reported the concentration of metals versus the leachate pH show the lowest concentrations for most metals to be in the pH range of pH 7 to pH 9.5. Below a pH of 7 most heavy metals, iron, and aluminum concentrations increased rapidly in an exponential manner. Above a pH of 9.5 iron and aluminum concentrations once again increase exponentially, while most of the heavy metals only showed a slight increase. This pH range corresponded with the Environment Canada (EC-MMER 2003) and US EPA (USEPA 2003) metal mining effluent regulations of pH 6 to 9.5 and pH 6 to 9, respectively.

3.8 REFERENCES

American Society for Testing and Materials (ASTM) D422 – 63, 2007. Standard Test Method for Particle-Size Analysis of Soils. ASTM International, West Conshohocken, PA.

American Society for Testing and Materials (ASTM) D854 – 06, 2006a. Standard Test Methods for Specific Gravity of Soil Solids by Water Pycnometer. ASTM International, West Conshohocken, PA.

American Society for Testing and Materials (ASTM) D2434 – 68, 2006b. Standard Test Method for Permeability of Granular Soils (Constant Head). ASTM International, West Conshohocken, PA.

American Society for Testing and Materials (ASTM) D4318 – 05, 2005. Standard Test Methods for Liquid Limit, Plastic Limit, and Plasticity Index of Soils. ASTM International, West Conshohocken, PA.

American Society for Testing and Materials (ASTM) D5084 – 03, 2003. Standard Test Methods for Measurement of Hydraulic Conductivity of Saturated Porous Materials Using a Flexible Wall Permeameter. ASTM International, West Conshohocken, PA.

British Columbia Ministry of Energy Mines and Petroleum Resources (BC-MEMPR) 1989. Draft acid rock drainage technical guide. *British Columbia Acid Mine Drainage Task Force,* Victoria, BC.

Bussiere, B., Benzaazoua, M., Aubertin, M., and Mbonimpa, M. 2004. A laboratory study of covers made of low sulphide tailings to prevent acid mine drainage. *Environmental Geology,* 45: 609-622.

Environment Canada Metal Mining Effluent Regulations (EC-MMER) 2003. Status report on water pollution prevention and control under the metal mining effluent regulations, Ottawa. http://www.ec.gc.ca/nopp/docs/rpt/waterpollution/mining2003/en/c2.cfm (accessed February 2009)

KTH 2007. Department of Land and Water Resources Engineering, Stockholm, Sweden, http://www.lwr.kth.se/English/OurSoftware/vminteq (accessed January 2008).

Lu, P., Li, Q., and Zhai, J. 2008. Mineralogical characterization and reaction path modeling of the pozzolanic reaction of fly ash-lime systems. *Journal of the American Ceramic Society,* 91: 955-964.

Mindat.org 2009. Fairchildite, http://www.mindat.org/min-1442.html (accessed May 2009).

Mudd, G., Weaver, T., and Kodikara, J. 2004. Environmental geochemistry of leachate from leached brown coal ash. *Journal of Environmental Engineering,* December: 1514 – 1526.

Pandian, N. 2004. Fly ash characterization with reference to geotechnical applications. *Journal Indian Institute Science,* 84: 189-216.

Scheetz, B. and Earle, R. 1998. Utilization of fly ash. *Current opinion in solid state & materials science,* 3.5: 510-520.

Shang, J., Wang, H., Kovac, V. and Fyfe, J. 2006. Site specific study on stabilization of acid-generating mine tailings using coal fly ash. *Journal of Materials in Civil Engineering,* March/April: 140-151.

Sheng, G., Li, Q., Zhai, J. and Li, F. 2007. Self-cementitious properties of fly ashes from CFBC boilers co-firing coal and high-sulphur petroleum coke. *Cement and Concrete Research,* 37: 871-876.

United States Environmental Protection Agency (USEPA) 1999. Public Meeting on the Development of New Waste Leaching Procedures, http://www.epa.gov/epawaste/hazard/testmethods/leaching.htm (accessed June 2009).

United States Environmental Protection Agency (USEPA) 2003. Ore mining and dressing point source category, 40-CRF-440.

United States Environmental Protection Agency (USEPA) 2008. Exposure assessment models, http://epa.gov/ceampubl/mmedia/minteq/ index.html (accessed April 2009).

Yeheyis, M., Shang, J. and Yanful, E. 2007. Beneficial utilization of coal fly ash as acid mine drainage barrier. *In* Proceedings of the 60th Canadian Geotechnical Conference & 8th Joint CGS/IAH-CNC Groundwater Conference, Ottawa, Canada, October 2007, pp 1494-1499.

Yeheyis, M., Shang, J. and Yanful, E. 2008. Characterization and environmental evaluation of Atikokan coal fly ash for environmental applications. *Journal of Environmental Engineering Science*, 7: 481-498.

4.0 CO-PLACEMENT OF COAL/BIOMASS FLY ASH WITH REACTIVE MINE TAILINGS FOR THE PREVENTION AND TREATMENT OF ACID MINE DRAINAGE

4.1 INTRODUCTION

This study investigated the co-placement of coal/biomass fly ash (CBFA) with reactive mine tailings for the prevention of acid mine drainage (AMD). Investigated were the effects of groundwater flow under non-oxidizing conditions on leachate chemistry, pH, and hydraulic conductivity. Two co-placement applications were considered: 1) in the vadose zone of existing mine tailings spoils; and 2) as an alkaline recharge medium up-gradient of existing reactive mine tailings spoils.

4.2 MATERIALS AND METHODS

4.2.1 Coal/Biomass Fly Ash

CBFA was obtained from the Atikokan Thermal Generating Station, in Atikokan, Ontario, during a 16 % (by mass) softwood biomass burn with 84 % western Canadian lignite coal. Major CBFA constituents reported as oxides are silica (SiO_2), aluminum oxide (Al_2O_3), calcium oxide (CaO), sodium oxide (Na_2O), and iron oxide (Fe_2O_3) (see Table 3.3a). Acid based accounting (ABA) by the Modified Sobek Method (BC-MEMPR 1989) indicates a net neutralizing potential (NNP) of 298 tonnes $CaCO_3$/1000 tonnes.

Grain size analysis conducted in accordance with American Society for Testing and Materials

(ASTM) standard D422 (ASTM 2007), on three representative CBFA samples, showed that CBFA consists predominantly of particles in the silt size range (~84%) with traces of sand (~10%) and clay (~6%) sized particles. The specific gravity measured by ASTM standard D854 (ASTM 2006) was 2.42. The liquid and plastic limits in accordance with ASTM standard D4318 (ASTM 2005) could not be measured on particles smaller than 75 µm, indicating that the CBFA is non plastic.

4.2.2 Mine Tailings

Fresh mine tailings were obtained from Vale-Inco, in Sudbury, Ontario. The tailings were kept in plastic buckets under a layer of water and below 4°C until their use in the column tests. Major constituents reported as oxides were Fe_2O_3, SiO_2, Al_2O_3, CaO, and MgO. A large concentration of sulphur in the mine tailings (136,000 g/t) was associated with sulfide and sulfate minerals. The most abundant heavy metals are nickel and copper with concentrations in the thousands of grams per tonne (Table 3.3b). ABA indicated a NNP of -416 tonnes $CaCO_3$/1000 tonnes, which corresponds to a strong acid generating potential.

Grain size analysis on two representative samples showed that the mine tailings predominantly contained particles in the silt size range (~80%) with traces of sand (~10%) and clay (~10%) sized particles. The tailings specific gravity was 3.58. Liquid and plastic limits could not be measured on particles smaller than 75 µm, which indicated that the mine tailings are non plastic.

4.2.3 Kinetic Column Tests

Laboratory kinetic column tests were carried out to study the effects of groundwater flow on the hydraulic conductivity and leachate pH and elemental composition for various percentages of mixed mine tailings and CBFA. The physical properties of the kinetic column packs are summarized in Table 4.2.3. Percentages of CBFA amended with mine tailings investigated included 5%, 10%, 20%, 33%, and 50% by mass. Also investigated were a 100% mine tailings control and 100% CBFA. These mixtures are identified on the figures as 5/95, 10/90, 20/80, 33/67, 50/50, MT, and CBFA, respectively.

Table 4.2.3 Properties of kinetic column tests (CBFA and mine tailings mixtures permeated with distilled water)

Parameter	100% MT (control)	95% MT 5% CBFA	90% MT 10% CBFA	80% MT 20% CBFA	67% MT 33% CBFA	50% MT 50% CBFA	100% CBFA
NNP[1]	-416	-387	-375	-305	-197	-68.6	298
Specific Gravity	3.58	3.52	3.46	3.35	3.19	3.00	2.42
Initial Dry Mass (g)	1314.4	1317.6	1179.6	1242.8	984.5	1034.9	726.8
Final Dry Mass (g)	1299.9	1305.5	1208.6	1281	1004.6	1040.2	736.7
Initial Dry Density (g/cc)	2.17	2.2	2.11	1.98	1.85	1.83	1.79
Final Dry Density (g/cc)	2.29	2.22	2.17	2.06	1.94	1.91	1.82
Initial Sample Height (mm)	145	143	134	150	127	135	97
Final Sample Height (mm)	136	141	133	149	123	130	97
Initial Porosity	0.394	0.373	0.391	0.408	0.422	0.389	0.259
Final Porosity	0.350	0.371	0.382	0.406	0.395	0.362	0.249

[1] Net Neutralizing Potential (t $CaCO_3$/1000 t)

Seven columns were manufactured for this study. The columns were constructed of 75-mm ID clear acrylic tubing. Inert materials (nylon, vinyl, PVC, and stainless steel) were used as tubing, fasteners, collection containers, etc. Mine tailings and CBFA were thoroughly mixed in a bowl to ensure homogeneity. They were prepared just wet of optimum (~2%) by adding distilled water and placed in the column in three equal layers. This moisture content was used to achieve the minimal hydraulic conductivity while maximizing the density. Each layer was rodded 25 times with a 10 mm diameter plastic rod. After rodding, the sides of the column were tapped to remove air bubbles. Next, the top surface of the pack was trimmed and covered with a porous fabric and stone. Upon final assembly, the pack was confined by applying a surcharge load of 7 kPa to the sample pack via a load piston for a minimum of 16 hours. This allowed initial consolidation of the packs prior to permeation. Upon permeation the load was set to just greater (approximately 5 kPa) than the permeate head to prevent piping and swelling of the packs, and to reduce the potential of additional surcharge causing consolidation. A schematic of the column test setup is presented in Figure 4.2.3.

All of the seven columns were permeated with distilled water with a hydraulic gradient between 4 and 10 that resulted in a flow rate of 0.5 nPV/day to 1.0 nPV/day. The hydraulic gradient was controlled by adjusting the height (head) of the reservoir. Properties of the distilled water are presented in Table 3.5. Column tests were run for a minimum of 80 nPV. The concept of progressive pore volumes (nPV), which is the total of quantity of leachate (Q) flowing through the sample divided by the initial pore volume (PV_0) of the sample, allows comparing results from test columns having different initial pore volumes.

$$nPV = Q / PV_0 \tag{4.1}$$

At the observed permeability and a field hydraulic gradient of 1, 80 nPV simulates the groundwater flow in 10 years per metre of thickness.

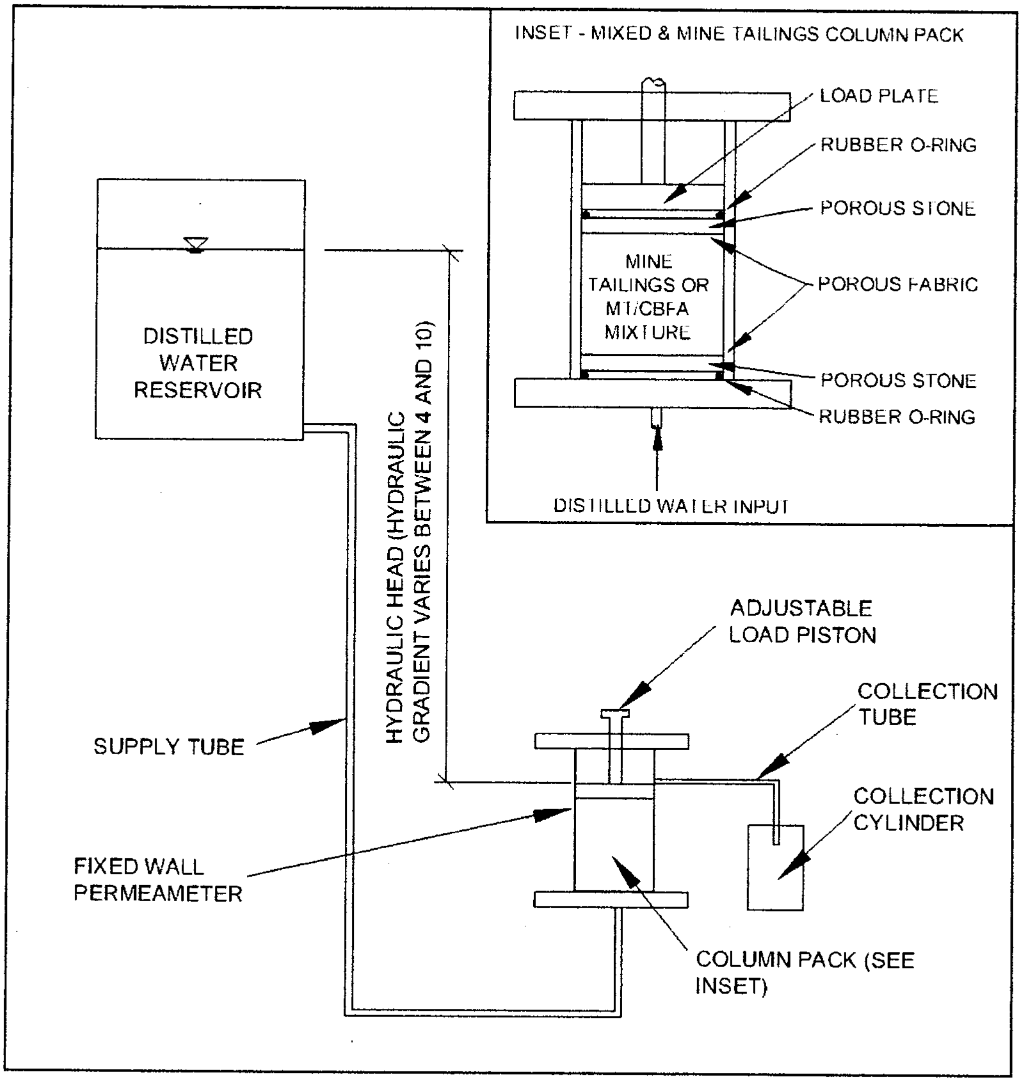

Figure 4.2.3 Schematic of distilled water kinetic column test setup

Effluent metal concentrations were compared to the EC-MMER (2003) and the USEPA (2003) mine effluent regulations. The CCME (2007) water quality guidelines for the protection of freshwater aquatic life and Health Canada (2008) fresh water drinking guidelines were also compared.

During the tests, effluent samples were collected, weighed, time recorded, and the hydraulic head measured. The hydraulic gradient, hydraulic conductivity, flow rate, and progressive pore volumes were calculated. All leachate samples were analyzed for pH. Select leachate samples were acidified to a pH of 3 or less with nitric acid and analyzed for elemental composition by ICP-AES. Upon termination of the tests, the weight, height and moisture contents of the column packs were measured, and the final dry density and porosity calculated. Details are presented in Table 4.2.3.

4.3 RESULTS AND DISCUSSION

4.3.1 Acid Based Accounting

Samples were sent to a third party laboratory for acid based accounting (ABA) in accordance with the Modified Sobek Method (see Table 4.2.3 for mixture specific results). Details on the ABA methods and calculations are provided in Section 2.6.2. Results (see Section 3.2) indicate that approximately 60% CBFA (by mass) would be required to obtain a net neutralizing potential (NNP) of zero (i.e. non acid producing) when mixed with the mine tailings. This percentage of required CBFA for co-disposal within the full depth (thickness) of disposal is not practical for large volumes of mine tailings. This quantity can be reduced by utilizing the CBFA in the vadose zone of the upper section of mine tailing spoils, as the majority of the oxidation occur within this zone. In addition, this vadose zone layer can be further utilized to create an alkaline recharge medium to buffer the pH of rainwater (groundwater) flowing from the surface into the underlying mine tailings.

4.3.2 Hydraulic Conductivity

Hydraulic conductivity results for the five mixed CBFA / mine tailings, 100% CBFA, and 100% mine tailings control packs are presented in Figure 4.3.2. Hydraulic conductivity ranged from

4.5×10^{-6} cm/s to 1.1×10^{-5} cm/s initially and from 3.0×10^{-6} cm/s to 1.3×10^{-5} cm/s at termination of the test (80 nPV). The hydraulic conductivity was predominantly constant for all columns with the exception of a slight reduction in hydraulic conductivity observed in the CBFA control from the start of the test to 20 nPV (4.5×10^{-6} cm/s to 3.0×10^{-6}). This reduction was possibly due to pozzolanic and hydration activities of the CBFA (Pandian et al. 2004). The hard brittle consistency of the CBFA pack during removal from the column at termination of the test supports this assumption.

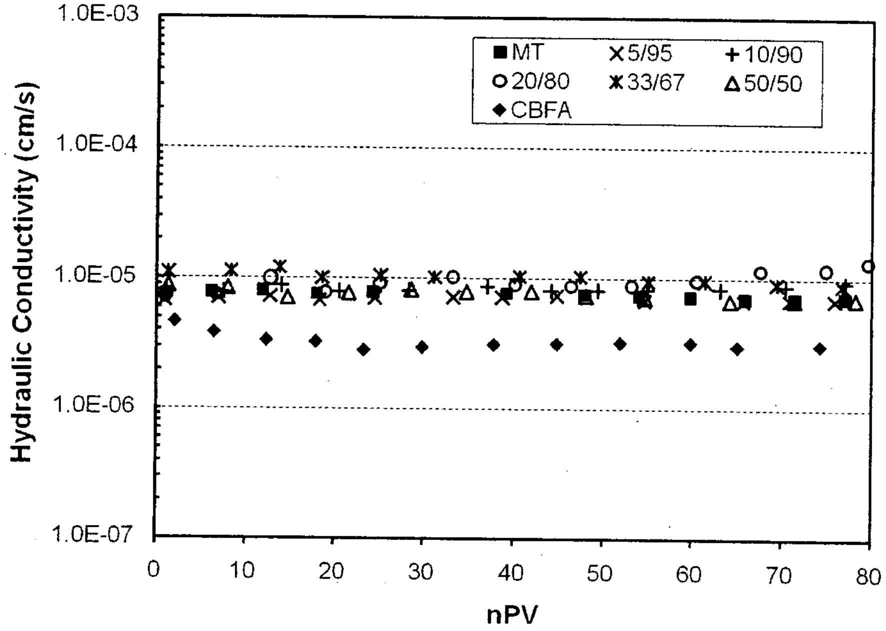

Figure 4.3.2 **Hydraulic conductivity versus nPV (mine tailings/CBFA mixtures permeated with distilled water)**

4.3.3 Effluent pH

Effluent pH results for the five mixed CBFA / mine tailings along with the 100% CBFA, and 100% mine tailings control packs are presented in Figure 4.3.3. As shown in the figure an increased in pH was observed with the increase in CBFA content. The effluent of all the

CBFA/mine tailings mixtures and the 100% CBFA columns remained alkaline (8.5 > pH > 11.9) throughout the tests, while the pH of the mine tailings control was predominantly neutral (6.5 > pH > 7.5). The optimum pH buffering was observed with the addition of as low as 20% CBFA (i.e. similar pH values for 20% to 100% CBFA). A study by Shang et al. (2006) found that the alkaline leachate from coal fly ash was effective in buffering the pH of the underlying acidic mine tailings pore water.

The 5%, 10%, 20%, and 33% CBFA packs had a lower initial pH (8.5 > pH > 9.6) before reaching a maximum pH (10.7 > pH > 11.2). This lower initial pH was likely due to the reaction of the lower percentages of CBFA with the mine tailings during mixing. An odour and discolouration (yellow tint) was observed in the leachate collected during the initial 5 nPV of permeation. The odour and discolouration corresponded with elevated sulphur and potassium concentrations in the leachate and the recorded low dissolved oxygen values in the leachate. The 50% CBFA amended mine tailings pack behaved similarly to the 100% CBFA pack, with an initial maximum pH (pH 11.2 and 11.9, respectively) which decreased linearly with continued permeation (pH > 10.3 at termination of the test).

The mine tailings control fluctuated between pH 6.5 and pH 7.5 throughout the test which was similar to the pH of the distilled water used as permeation which had a pH between 6.8 and 7.5. The similarity between the pH of the mine tailings effluent and the distilled water permeate is likely due to the non-oxidizing conditions within the column test (i.e. continuously submerged in water) and low concentrations of soluble minerals in the mine tailings at neutral pH.

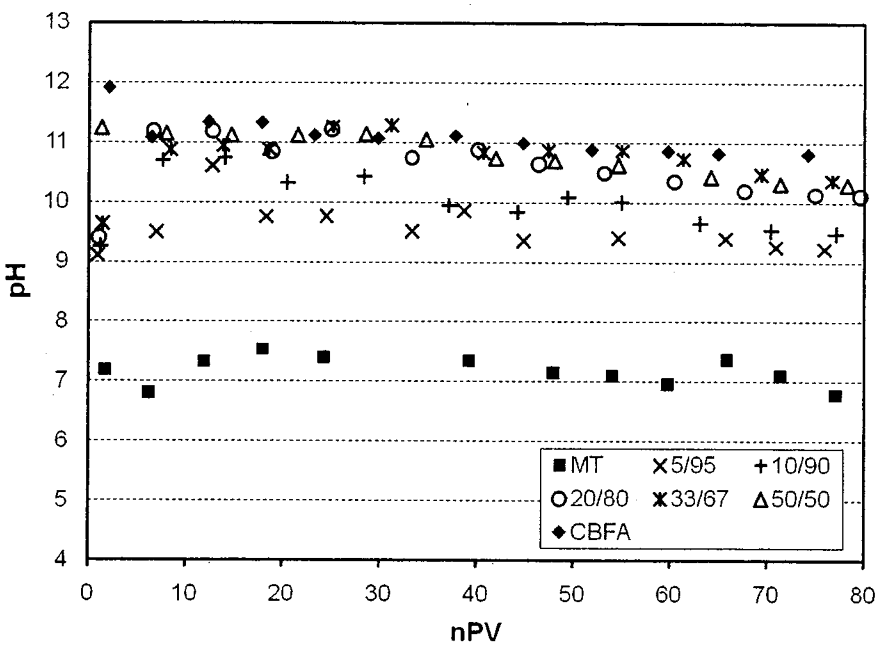

Figure 4.3.3 Effluent pH versus nPV (mine tailings/CBFA mixtures permeated with distilled water)

4.3.4 Effluent Composition

The range of dissolved concentrations of major elements in the columns effluent is shown in Tables 4.3.4a and 4.3.4b. Where applicable, these elements are compared to the EC-MMER (2003) and USEPA (2003) mine effluent regulations (shown in Table 4.3.4a). The CCME (2007) freshwater aquatic life guidelines and the Health Canada (2008) drinking water guidelines (shown in Table 4.3.4a) are presented for reference only. Many of the elevated concentrations were likely due to chemical reactions between the CBFA and mine tailings during mixing.

Table 4.3.4a Effluent analyses of CBFA and mine tailings kinetic column tests permeated with distilled water, including regulatory guidelines

Element	EC-MMER Guideline	USEPA Guideline	CCME-FAL Guideline	Health Canada Guideline	100% Mine Tailings	100% CBFA
Aluminum	na	1	0.1	0.1/0.2	0.02 – 0.11	12.56 – 361.10
Arsenic	0.5	0.5	0.001	0.01	nd – 0.132	nd – 0.023
Barium	na	na	na	1	0.016 – 0.092	0.611 – 35.530
Calcium	na	na	na	na	10.2 – 547.7	14.9 – 149.8
Chromium	na	na	0.001	0.05	nd – 0.002	0.011 – 0.420
Copper	0.3	0.15	0.002	1	nd – 0.008	nd – 0.007
Iron	na	1	0.3	0.3	0.011 – 0.552	0.001 – 0.253
Potassium	na	na	na	na	3.5 – 121.0	0.4 – 26.7
Magnesium	na	na	na	na	0.303 – 89.600	0.001 – 0.198
Sodium	na	na	na	200	2.5 – 145.4	10.1 – 292.4
Nickel	0.5	0.1	0.025	na	0.001 – 0.559	nd – 0.016
Lead	0.2	0.3	0.001	0.01	nd – 0.028	nd – 0.010
Sulphur	na	na	na	500	4.7 – 943.9	1.1 – 508.1
Silica	na	na	na	na	2.19 – 2.84	0.11 – 6.53
Strontium	na	na	na	na	0.03 – 1.21	5.77 – 37.1
Zinc	0.5	0.5	0.03	5	0.003 – 0.058	0.009 – 0.065
pH	6.0 - 9.5	6.0 - 9.0	6.5 - 9.0	6.5 - 8.5	6.5 – 8.5	10.6 – 11.9

Notes: Concentration in mg/L unless otherwise specified
na - no guideline provided.
nd - readings were below the minimum detection concentration of the icp standard.

Table 4.3.4b Effluent analyses for CBFA / mine tailings mixed kinetic column tests permeated with distilled water

Element	5% CBFA / 95% Mine Tailings (Mixed)	10% CBFA / 90% Mine Tailings (Mixed)	20% CBFA / 80% Mine Tailings (Mixed)	33% CBFA / 67% Mine Tailings (Mixed)	50% CBFA / 50% Mine Tailings (Mixed)
Aluminum	2.29 – 12.08	2.50 – 14.75	9.12 – 18.88	3.06 – 20.07	13.25 – 33.87
Arsenic	nd – 0.019	nd – 0.020	nd – 0.014	nd – 0.023	0.009 – 0.023
Barium	0.111 – 0.305	0.270 – 0.773	0.252 – 2.149	0.151 – 1.575	0.230 – 7.046
Calcium	13.6 – 636.6	20.2 – 486.9	38.3 – 118.3	53.4 – 592.7	38.6 – 144.3
Chromium	nd – 0.002	nd	nd – 0.001	nd – 0.004	0.001 – 0.002
Copper	nd – 0.006	nd	nd – 0.007	nd – 0.006	nd – 0.011
Iron	0.004 – 0.060	0.003 – 0.026	0.004 – 0.065	0.004 – 0.082	0.004 – 0.604
Potassium	4.3 – 173.8	3.9 – 160.3	3.7 – 136.7	4.0 – 119.6	3.2 – 53.9
Magnesium	0.015 – 2.278	0.013 – 0.208	0.012 – 0.061	0.016 – 6.281	0.002 – 0.431
Sodium	11.1 – 588.9	9.0 – 769.3	8.9 – 1349.0	11.3 – 1500.0	10.2 – 938.2
Nickel	0.005 – 0.145	nd – 0.103	nd – 0.093	nd – 0.195	0.001 – 0.039
Lead	nd – 0.016	nd	nd	nd – 0.018	nd – 0.014
Sulphur	7.1 – 1378.0	9.5 – 1533.0	10.8 – 2512.0	9.8 – 3673.0	11.3 – 834.7
Silica	1.49 – 4.17	2.26 – 4.36	1.96 – 4.35	1.14 – 3.36	0.85 – 5.28
Strontium	0.90 – 17.05	1.29 – 25.92	2.12 – 15.57	2.36 – 23.75	3.26 – 30.58
Zinc	0.005 – 0.055	0.003 – 0.164	0.001 – 0.203	0.003 – 0.038	0.003 – 0.033
pH	8.8 – 10.6	9.2 – 10.7	9.4 – 11.2	9.6 – 11.3	10.1 – 11.2

Notes: Concentration in mg/L unless otherwise specified
na - no guideline provided.
nd - readings were below the minimum detection concentration of the icp standard.

Overall the effluent of the CBFA amended mine tailings met the mine effluent guidelines for heavy metals with the exceptions of select samples of nickel that exceeded the 0.1 mg/L USEPA (2003) guideline in the 5%, 10%, and 33% CBFA amended columns. In contrast, the mine tailings control experienced higher concentrations of nickel that exceeded both the USEPA (2003) and the 0.5 mg/L EC-MMER (2003) regulations. Concentrations exceeding regulations occurred in the initial 4 nPV of permeation. Figure 4.3.4a shows the nickel concentrations in the leachate for the mixed columns, mine tailings and CBFA columns with respect to continued permeation with distilled water. Also shown on the figure are the USEPA (2003) and EC-MMER (2003) regulations of 0.1 mg/L and 0.5 mg/L, respectively.

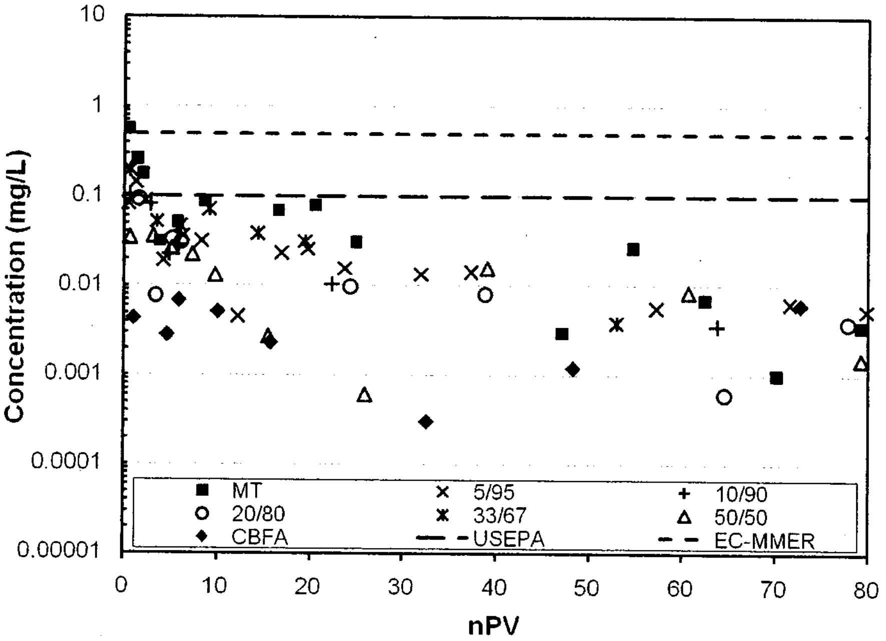

Figure 4.3.4a Effluent leachate nickel concentration versus nPV

Figure 4.3.4b shows the aluminum concentrations in the leachate for the mixed columns, mine tailings and CBFA columns with respect to continued permeation with distilled water. Also shown on the figure is the USEPA (2003) regulation of 1 mg/L. Dissolved aluminum was encountered above the USEPA (2003) mine effluent regulation for all packs amended with CBFA and CBFA by itself. Only the mine tailings control was below the mine effluent regulation. The mine tailings effluent was also found to be predominantly below the CCME

(2007) fresh water aquatic life guideline of 0.1 mg/L. Aluminum concentrations were found to be in the order of 100 times (2 orders of magnitude) greater when mixed with various percentages of CBFA as compared with the mine tailings alone. The increased concentrations are attributed to the dissolution of Al-containing phases in the fly ash and the elevated pH of the CBFA amended columns. Although aluminum is not included in current mine effluent guidelines, its toxicity to fish and other aquatic organisms at levels as low as 5 µg/L (CCME 2007) and in a range of pH values from acidic to alkaline seems well established (WHO 1997).

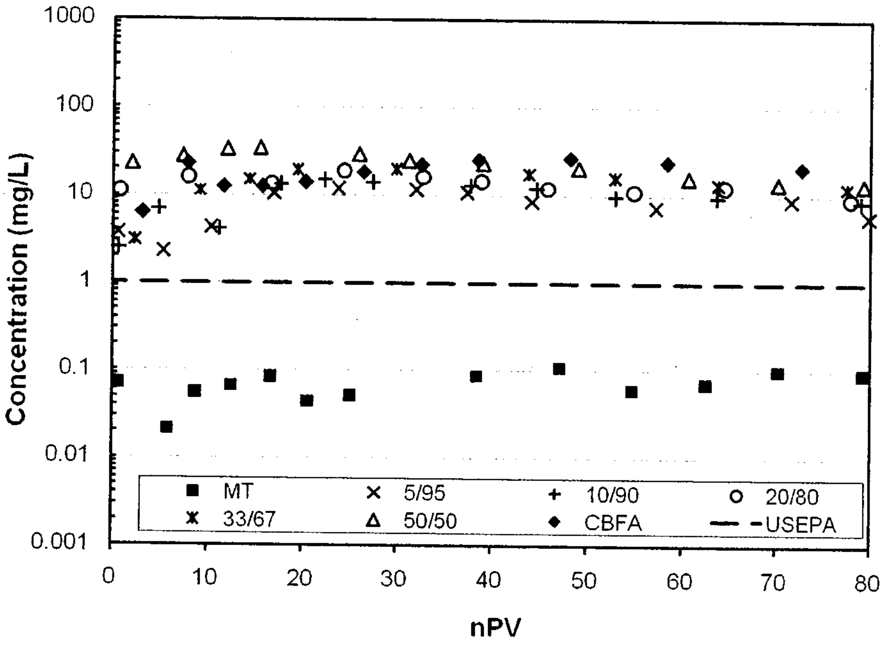

Figure 4.3.4b Effluent leachate aluminium concentration versus nPV

4.3.5 Applications of Findings

Kinetic column tests showed that amending reactive mine tailings with 5% to 50% (by mass) CBFA is effective in buffering pH with minimal leached concentrations of most heavy metals.

In addition minimal changes in hydraulic conductivity were observed. These findings showed that CBFA amended mine tailings have a potential as an alkaline recharge medium to treat/reduce the acidity in existing reactive mine tailings. It can also retard the formation of AMD by increasing the pore water pH. This increase in pH immobilizes heavy metals and decreases the concentration bacteria which assist in the formation of AMD (increase the pH above their effect pH range).

Two applications for the experimental setup are considered. The first simulates co-placement of CBFA and mine tailings in the vadose zone of closed and ongoing mine tailings disposal operations (Figure 4.3.5(A)). The addition of CBFA retards the formation of AMD by increasing the neutralizing potential within the vadose zone while also providing an alkaline recharge to the underlying reactive mine tailings. When used for the closure of disposal operations the required amount of CBFA would have to be sufficient to offset the acid generating potential of the mine tailings (e.g. 60 %wt of CBFA required for the study mine tailings) in areas susceptible to oxidation. For ongoing operations lower concentrations of CBFA may be used if continued disposal is anticipated. As shown during the kinetic column tests, lower concentrations of CBFA were effective in maintaining an alkaline pH throughout the duration of the test. The CBFA's neutralization potential would offset the mine tailings' acid generation potential until depletion of the CBFA's neutralization potential. Under ideal conditions the CBFA amended mine tailings would be submerged by the raising water table prior to depletion of the CBFA's neutralization potential. Upon closure the mine tailings should be submerged under a water layer, covered with a soil layer, or mixed with sufficient CBFA (or other alkaline material) to offset the acid generating potential of the mine tailings. Figure 4.3.5(A) shows this application with sufficient CBFA amended to mine tailings in the vadose zone to offset the acid generating potential of the mine tailings in a closed disposal operation.

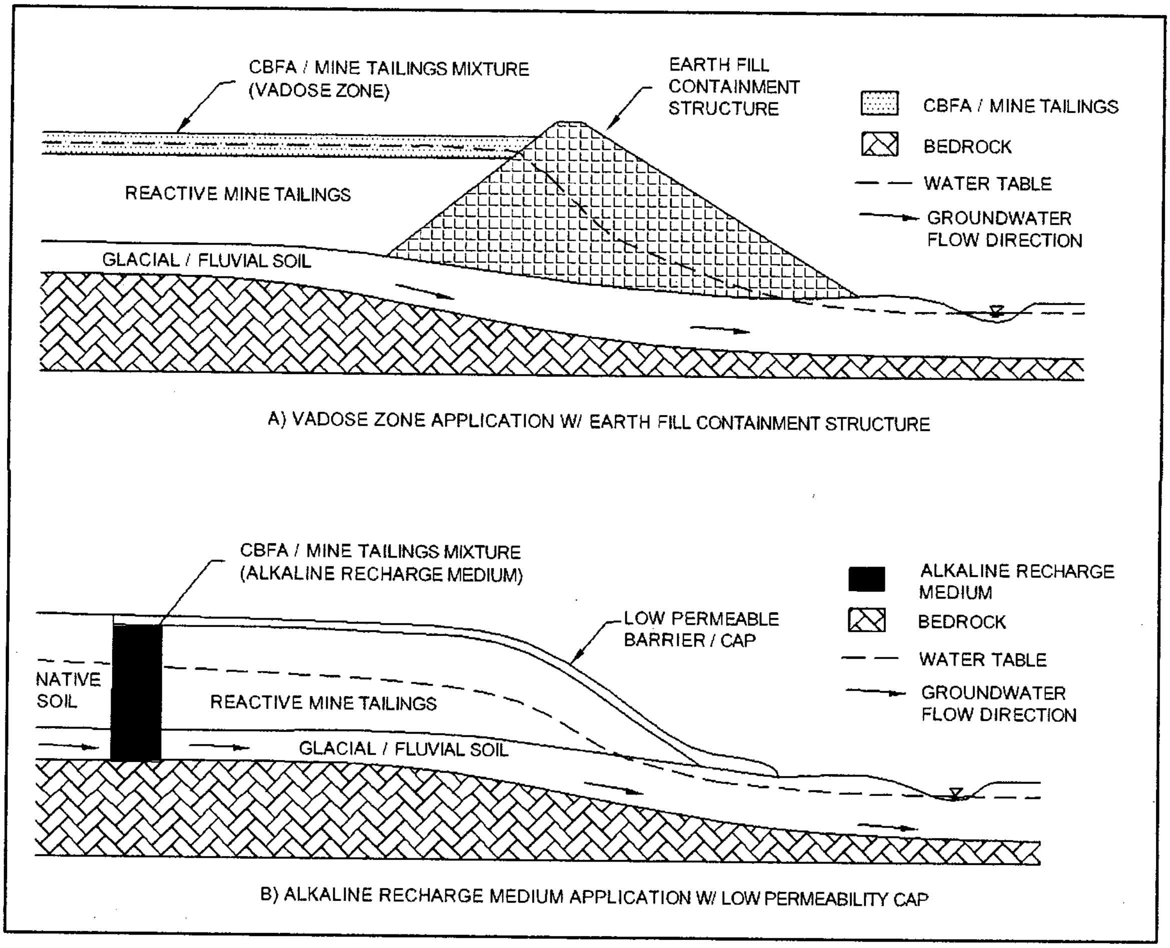

Figure 4.3.5 Co-disposal applications A) Vadose zone application, and B) Alkaline recharge medium application

The second experimental setup simulates the application of an alkaline recharge medium up-gradient of existing reactive mine tailings (Figure 4.3.5(B)). This application is best suited to existing mine tailings spoils where AMD formation is ongoing or anticipated. For this application an alkaline recharge medium is constructed of CBFA amended to the available onsite mine tailings and installed in a trench up-gradient of the mine tailings. As groundwater flows through this medium, the pore water alkalinity increases, which results in an increase in the pH of the pore water flowing through the reactive mine tailings. To further optimize this application the installation of a low permeability cap over the reactive tailings is recommended to further reduce the infiltration of groundwater during precipitation events and reduce the mine tailings exposure to oxygen. The installation of a flow through reactive barrier down-gradient of the mine tailings (as discussed in subsequent chapters) to treat AMD migration offsite is also recommended. Figure 4.3.5(B) shows this application with an alkaline recharge medium up-gradient and the installation of a low permeable cap over the mine tailings.

4.4 CONCLUSIONS

Kinetic column tests showed that amending mine tailings with CBFA was effective in increasing the pH while keeping the concentrations of dissolved (leached) heavy metals low. Aluminum concentrations, although not considered a heavy metal, were significantly increased by the dissolution of Al-containing phases in the CBFA due to the high leachate pH. The hydraulic conductivity of the mine tailings were minimally affected by the addition of CBFA and the continued permeation of distilled water. The CBFA amended mine tailings columns maintained an alkaline pH throughout the duration of the tests, increasing the pH from pH ~7 to a pH between 9 and 11.

The co-disposal of mine tailings and CBFA at ratios to prevent AMD formation (NNP ≥ 0 $CaCO_3$ / 1000 tonnes) for the entire mine tailings disposal is not practical due to the high percentage of CBFA required (60% for this study). Practical applications include the addition (mixing) of CBFA with mine tailings in the vadose zone of ongoing disposal operations and in the upper section of closed mine tailing spoils to prevent oxidization of reactive mine tailings. The increased pH and buffering potential can be further utilized to create an alkaline wetting front to buffer the groundwater flow with respect to pH from the surface during precipitation events. Installation of CBFA amended mine tailings in a trench up-gradient of reactive mine tailings can also be utilized to create an alkaline wetting front to pH buffer the groundwater prior to flowing through the reactive mine tailings. The increase in pore water pH is anticipated to immobilize many of the heavy metal concentrations in solution and retard subsequent oxidation of the mine tailings.

4.5 REFERENCES

American Society for Testing and Materials (ASTM) D422 – 63, 2007. Standard Test Method for Particle-Size Analysis of Soils. ASTM International, West Conshohocken, PA

American Society for Testing and Materials (ASTM) D854 – 06, 2006. Standard Test Methods for Specific Gravity of Soil Solids by Water Pycnometer. ASTM International, West Conshohocken, PA

American Society for Testing and Materials (ASTM) D4318 – 05, 2005. Standard Test Methods for Liquid Limit, Plastic Limit, and Plasticity Index of Soils. ASTM International, West Conshohocken, PA

British Columbia Ministry of Energy Mines and Petroleum Resources (BC-MEMPR) 1989. Draft acid rock drainage technical guide. *British Columbia Acid Mine Drainage Task Force,* Victoria, BC.

Canadian Council of Ministers of the Environment (CCME) 2007. Canadian Water Quality Guidelines for the Protection of Aquatic Life. Winnipeg. http://ceqg-rcqe.ccme.ca/download/ en/134/ (accessed April 2009).

Environment Canada, Metal Mining Effluent Regulations (EC-MMER) 2003. Status report on water pollution prevention and control under the metal mining effluent regulations. Ottawa. http://www. ec.gc.ca/nopp/docs/rpt/waterpollution/mining2003/en/c2.cfm (accessed Feb. 2009)

Health Canada 2008. Guidelines for Canadian drinking water quality. Federal-provincial-territorial committee on drinking water of the federal-provincial-territorial committee on health and the environment, Ottawa, May 2008.

Pandian, N. 2004. Fly ash characterization with reference to geotechnical applications. *Journal Indian Institute Science*, 84: 189-216.

Shang, J., Wang, H., Kovac, V. and Fyfe, J. 2006. Site specific study on stabilization of acid-generating mine tailings using coal fly ash. *Journal of Materials in Civil Engineering*, March/April: 140-151.

United States Environmental Protection Agency (USEPA) 2003. Ore mining and dressing point source category. 40-CRF-440.

World Health Organization, Environmental Health Criteria 194. 1997, Aluminum, Geneva, http://www.inchem.org/documents/ehc/ehc/ehc194.htm#SubSectionNumber:9.2.2 (accessed February 2009).

5.0 UTILIZATION OF COAL/BIOMASS FLY ASH AMENDED WITH REACTIVE MINE TAILINGS IN REACTIVE BARRIERS FOR TREATING AND CONTAINING ACID MINE DRAINAGE[1]

This study investigated the utilization of coal/biomass fly ash (CBFA) amended with mine tailings in reactive barriers for treating and containing acid mine drainage (AMD). Kinetic column tests showed that mine tailings amended with 5 to 50% CBFA (by mass) increased the leachate pH and decrease the dissolved concentrations of many heavy metals in AMD to be in compliance with mine effluent regulations. The large reduction in hydraulic conductivity (by factors up to 2000 times) was attributed to mineral precipitation and/or secondary mineral formation. This reduction was also dependant on the cumulative flow of AMD through the columns and the percent CBFA in the tailings/CBFA mixtures. Applications of CBFA at small concentrations in permeable reactive barriers and at larger concentrations in low-permeability cores of containment dams are discussed.

5.1 INTRODUCTION

The disposal of sulphide-bearing mine tailings in surface facilities is a major environmental concern due to their potential to produce AMD. AMD is formed from the oxidation of sulphide minerals in the presence of oxygen and water. Typically, AMD has a low pH (high acidity) and elevated concentrations of heavy metals.

Control and treatment of AMD, particularly in decommissioned and inactive mine sites, are

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[1] A version of this chapter was presented at the IASTED International Conference on Environmental Management and Engineering (EME 2009), July 2009, Banff, Canada, and published in the conference proceedings, pp 67-73.

major environmental challenges. Often, these mine sites have ongoing AMD formation which impacts the adjacent terrestrial and aquatic ecosystems. With continued infiltration recharge, AMD effluent may easily flow in the groundwater regime as well as adjacent streams and other water bodies down gradient from the disposal site.

Several AMD prevention methods exist, including water covers, soil covers, and base neutralizing additives among others. These methods are often viable options for current and future mine developments but may not be as effective for decommissioned and inactive mine sites, particularly if oxidation is ongoing and AMD has started migrating offsite. Conventional active approaches to treatment involve the collection and treatment of AMD, which often require ongoing operation and maintenance. Passive approaches that can provide a cost effective means to treat the AMD leachate insitu include limestone drains and wetlands (Walton-Day 2003). Reactive barriers are also an effective passive technology for treating groundwater contamination associated with AMD (Blowes et al. 2003a). Installation methods include continuous trenching, excavation and backfill, and slurry trenching.

The use of coal fly ash (CFA) mixed with reactive mine tailings for preventing and/or treating AMD has been investigated in laboratory kinetic column tests (Xenidis et al. 2002, Shang et al. 2006, Wang et al. 2006, Perez-Lopez et al. 2007). These studies showed that CFA mixed with mine tailings substantially reduced the concentrations of heavy metals in the AMD. The pH of the leachate from CFA/tailings mixtures increased from acidic ($pH < 3.8$) to alkaline ($pH > 7$) and the hydraulic conductivity decreased with continued permeation of AMD.

Studies utilizing 100% CFA as a reactive barrier have shown that CFA was effective in reducing heavy metal concentrations and increasing the leachate pH (Shang et al. 2006, Yeheyis et al. 2007). Hydraulic conductivity was found to decrease by three orders of magnitude with continued permeation of AMD. The reduction in hydraulic conductivity was attributed to the clogging of pores in the reactive barrier due to precipitation of heavy metals and the formation of secondary minerals.

This study was conducted to investigate the use of CBFA mixed with reactive mine tailings in reactive barriers to treat AMD. Two applications of reactive barriers were investigated: 1) a flow-through reactive barrier with minimum disruption to the existing flow regime and 2) a low permeability core for construction of containment dams.

5.2 MATERIALS AND METHODS

5.2.1. Coal/Biomass Fly Ash

CBFA was obtained from the Atikokan Thermal Generating Station, in Atikokan, Ontario, Canada, during a 16 % (by mass) wood biomass burn with 84 % lignite coal. Major CBFA constituents reported as oxides are silica (SiO_2), aluminum oxide (Al_2O_3), calcium oxide (CaO), sodium oxide (Na_2O), and iron oxide (Fe_2O_3). The CBFA contained the heavy metals (zinc, lead, copper, nickel, and chromium) at concentrations of a few tens of grams per tonne (see Tables 3.3a and 3.3b). Acid based accounting (ABA) by the Modified Sobek Method (BC-MEMPR 1989) indicated a net neutralizing potential (NNP) of 298 tonnes $CaCO_3$/1000 tonnes.

Grain size analysis conducted in accordance with ASTM standard D422 (ASTM 2007), showed that the CBFA consisted predominantly of particles in the silt size range (~84%) with traces of sand (~10%) and clay (~6%) sized particles. The specific gravity measured by ASTM standard D854 (ASTM 2006) was 2.42. The liquid and plastic limits in accordance with

ASTM standard D4318 (ASTM 2005) could not be measured on particles smaller than 75 µm, indicating that the CBFA was non plastic.

5.2.2. Mine Tailings

Fresh mine tailings were obtained from Vale-Inco, in Sudbury, Ontario, Canada. The tailings were kept in plastic buckets under a layer of water and below 4°C until their use in the column tests. Major constituents reported as oxides are Fe_2O_3, SiO_2, Al_2O_3, CaO, and MgO. A large concentration of sulphur (136,000 g/t) was associated with sulphide and sulphate minerals. The most abundant heavy metals were nickel and copper with concentrations in the thousands of grams per tonne (see Tables 3.3a and 3.3b). ABA indicates a NNP of -416 tonnes $CaCO_3$/1000 tonnes, which corresponds to a strong acid generating capacity.

Grain size analysis on two representative samples showed that the mine tailings predominantly contain particles in the silt size range (~80%) with traces of sand (~10%) and clay (~10%) sized particles. The tailings specific gravity was 3.58. Liquid and plastic limits could not be measured on particles smaller than 75 µm, which indicates that the mine tailings are non plastic.

5.2.3. Synthetic Acid Mine Drainage

A synthetic AMD was prepared in the laboratory by mixing distilled water with metal sulphates, chlorides, and nitrates to a concentration that is typical of field AMD concentrations. These concentrations were similar to values provided by Vale Inco on water samples collected from monitoring wells adjacent to mine tailings spoils (Table 5.2.3). Dissolved concentrations of nickel and copper (the two most abundant heavy metals in the tailings) were 2 and 1.3 mg/L, respectively, in the synthetic AMD.

Table 5.2.3 Composition of synthetic AMD solution

Element/Parameter	Concentration[1]
pH	2.8
Electrical Conductivity (mS/cm)	1.9
Aluminum	10
Arsenic	0.01
Barium	0.04
Calcium	170
Chromium	0.005
Copper	1.3
Iron	40
Potassium	14.5
Sodium	30
Magnesium	23
Nickel	2
Sulphur	300
Silica	0.7
Strontium	0.1
Lead	0.04
Zinc	2.5

Note: [1] in mg/L unless specified

5.3 KINETIC COLUMN TESTS

Laboratory kinetic column tests were carried out to study the effects of AMD flow on the hydraulic conductivity and leachate composition for mixtures of mine tailings and CBFA. The physical properties of the kinetic column packs are summarized in Table 5.3 Percentages (by mass) of CBFA mixed with mine tailings were 0%, 5%, 10%, 20%, 33%, 50%, and 100% CBFA. These mixtures are identified on the figures as MT, 5/95, 10/90, 20/80, 33/67, 50/50, and CBFA, respectively.

Table 5.3 Properties of kinetic column packs (CBFA / mine tailings mixtures permeated with AMD)

Parameter	100% MT[1]	95%MT 5%CBFA	90%MT 10%CBFA	80%MT 20%CBFA	67%MT 33%CBFA	50%MT 50%CBFA	100% CBFA
NNP[2]	-416	-387	-375	-305	-197	-68.6	298
Specific Gravity	3.58	3.52	3.46	3.35	3.19	3.00	2.42
Initial Dry Weight (g)	813.4	251.2	264.0	253.1	249.0	245.5	135.6
Final Dry Weight (g)	811.6	249.5	264.6	253.9	250.6	247.6	136.8
Initial Sample Height (mm)	84	58	62	62	63	63	40
Final Sample Height (mm)	84	58	61	62	63	63	40
Initial Porosity	0.353	0.395	0.396	0.401	0.391	0.361	0.312
Final Porosity	0.343	0.400	0.394	0.397	0.387	0.356	0.306
Initial Pore Volume (cc)	123.9	46.7	50.0	50.6	50.1	46.3	25.4
Final Pore Volume (cc)	120.5	47.2	49.0	50.1	49.6	45.6	24.9

[1] 100% mine tailings control test was conducted in a 75mm diameter column.
[2] Net Neutralizing Potential (t $CaCO_3$/1000 t)

Each column was constructed of 50-mm ID clear acrylic tubing. Inert materials (nylon, vinyl, PVC, and stainless steel) were used as tubing, fasteners, collection containers, etc. Mine tailings and CBFA were thoroughly mixed in a bowl to ensure homogeneity. They were prepared just wet of optimum (~2%) by adding distilled water and placed in the column in three equal layers. This moisture content was used to achieve the minimal hydraulic conductivity while maximizing the density. Each layer was rodded 25 times with a 10 mm diameter plastic rod. After rodding, the sides of the column were tapped to remove air bubbles. Next, the top surface of the pack was trimmed and covered with a porous fabric and stone. Upon final assembly, the pack was confined by tightening a stainless steel bolt which applied a load to the top plate. The columns were then allowed to consolidate for a minimum of 16 hours, after which the bolts were again tightened. The bolts were periodically checked and tightened throughout the test to compensate for consolidation.

A schematic of the column test setup is presented in Figure 5.3. Samples were first permeated with distilled water to determine the reference hydraulic conductivity. Once equilibrium was achieved with distilled water (7.6 to 9.2 nPV), the permeate was switched to synthetic AMD. During the tests, effluent samples were collected, weighed, time recorded, and the hydraulic head measured. The hydraulic gradient, hydraulic conductivity, flow rate, and progressive pore volumes were calculated. All leachate samples were analyzed for pH. Select leachate samples were acidified to pH 3 or less with nitric acid and analyzed for elemental composition by inductively coupled plasma – atomic emission spectrometry (ICP-AES). Upon termination of the tests, the weight, height and moisture contents of the column packs were measured.

Column tests were initially permeated with distilled water for up to 10 progressive pore volumes (nPV) to establish a reference hydraulic conductivity. After which the permeate was switched to AMD and ran for an additional 70 nPV of AMD permeation, or terminated upon reaching a hydraulic conductivity of 10^{-7} cm/s or less (USEPA 1988). Effluent metal concentrations were compared to EC-MMER (2003) and USEPA (2003) mine effluent regulations; CCME (2007) water quality guidelines for the protection of freshwater aquatic life; and Health Canada (2008) fresh water drinking guidelines.

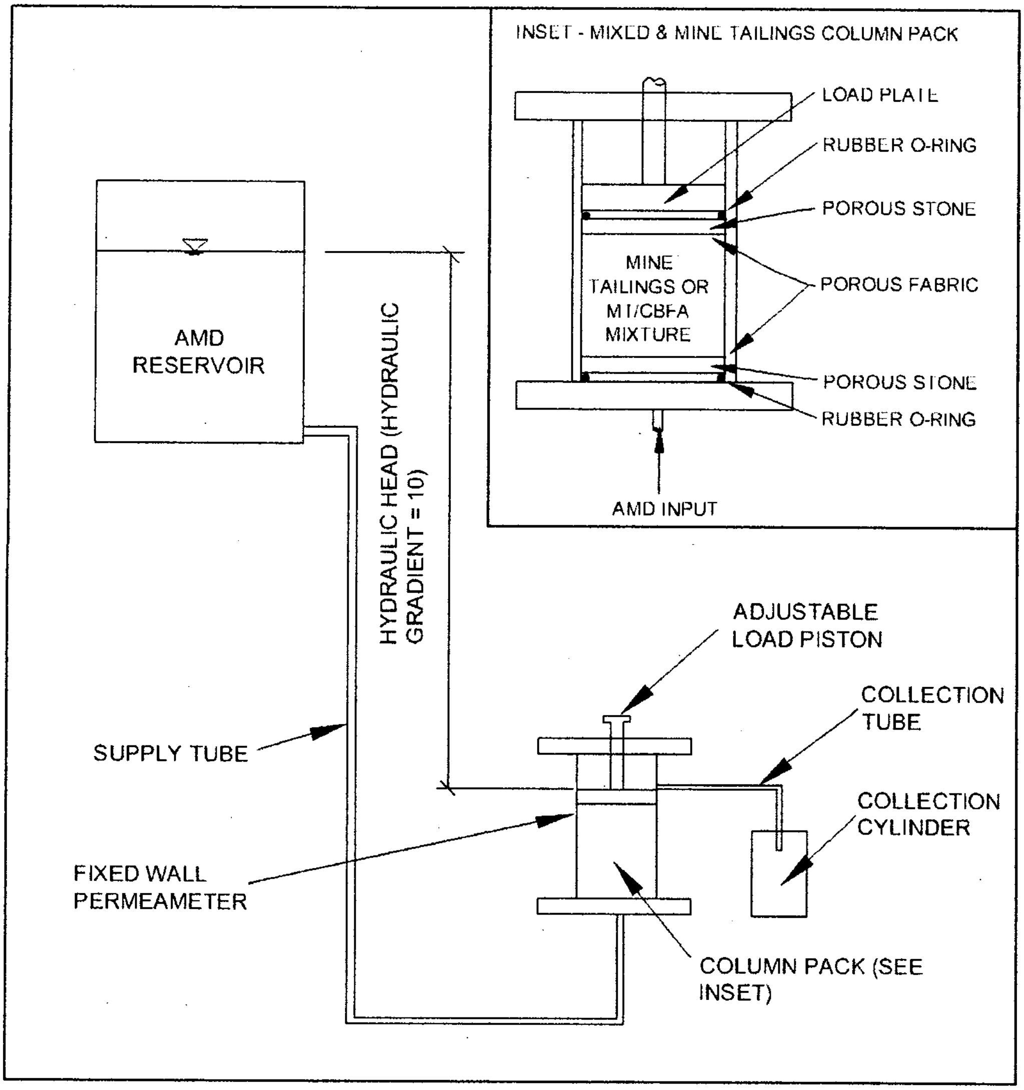


Figure 5.3 Schematic of CBFA / mine tailings permeated with AMD test setup

5.4 RESULTS AND DISCUSSION

5.4.1 Acid Based Accounting

Acid based accounting conducted on all CBFA/tailings mixtures showed a linear relationship between NNP and the percentage of CBFA to mine tailings (see Figure 3.2). Interpolation of these data indicated that approximately 60 percent CBFA was required to reach a NNP of zero tonnes $CaCO_3$/1000 tonnes of mixture and thus to neutralize the acid generating potential of the tailings. All column packs had a net acid generating capacity (negative NNP).

5.4.2 Hydraulic Conductivity

Hydraulic conductivity results for the four CBFA / mine tailings mixtures and the mine tailings and CBFA columns when permeated with AMD are presented in Figure 5.4.2. Hydraulic conductivity ranged from 4.2×10^{-6} cm/s to 1.1×10^{-5} cm/s for columns permeated with distilled water. Upon permeating with AMD, the hydraulic conductivity of all columns decreased.

The number of progressive pore volumes of AMD required for achieving a given reduction in hydraulic conductivity was inversely proportional to the fly ash content of the column pack. The hydraulic conductivity of the mine tailings control column only decreased slightly when permeated with AMD. By contrast, the hydraulic conductivity of the 50/50 CBFA/tailings mixture and 100% CBFA column decreased by nearly 2000 times to 2.6×10^{-9} cm/s and 2.2×10^{-9} cm/s, respectively, in less than 15 nPV of AMD permeation. The reduction in hydraulic conductivity occurred in three phases. During the first phase, the logarithm of hydraulic conductivity decreased linearly as a function of progressive pore volumes of AMD. The second phase coincided with an acceleration in the decrease of hydraulic conductivity. During the third phase, the logarithm of hydraulic conductivity decreased linearly again, but at a much greater rate than during the first phase.

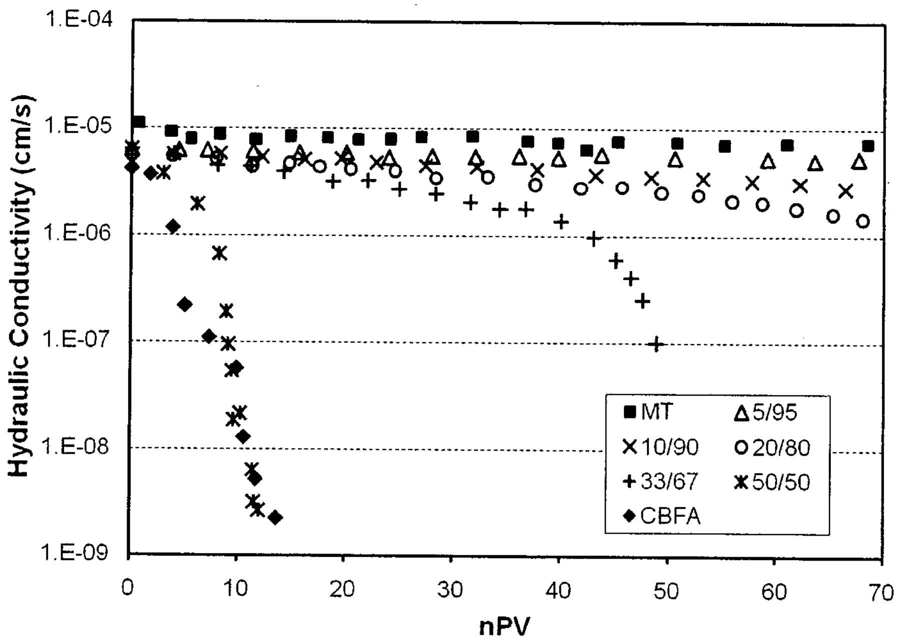


Figure 5.4.2 **Hydraulic conductivity versus nPV (CBFA / mine tailings permeated with AMD)**

5.4.3 Effluent pH

Effluent pH results for all columns when permeated with AMD are shown in Figure 5.4.3. The effluent of the column containing 100% tailings remained slightly alkaline or neutral (7.8 > pH > 6.8) during the first 25 nPV of AMD permeation. Afterwards, the effluent pH dropped and stabilized in a lower range (6.2 > pH > 5.8) until approximately 65 nPV. This pH trend is consistent with the buffering effects of calcite dissolution (7.5 > pH > 6.5) followed by siderite dissolution (6.3 > pH > 4.8) (Bowles et al. 2003b). Further permeation by AMD caused the effluent pH to decrease even more as neutralizing minerals became depleted in the column.

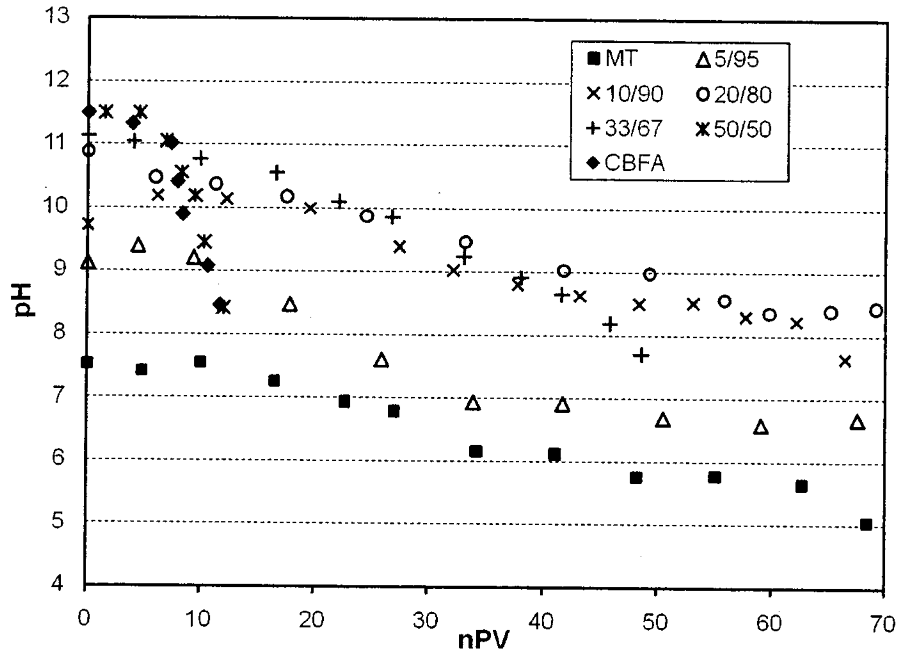


Figure 5.4.3 Effluent pH versus nPV (CBFA / mine tailings permeated with AMD)

The effluent pH of all columns containing fly ash remained alkaline throughout the tests. A slight increase in effluent pH was observed during the initial distilled water permeation and up to 5 nPV of AMD permeation for columns which contained 5%, 10%, and 20% CBFA by mass. This was followed by an approximately linear decrease in effluent pH during the next 25 to 30 nPV. Afterwards, the effluent pH kept decreasing at a reduced and less regular rate.

By contrast, the effluent pH of the columns containing 33% and 50% CBFA and the CBFA control column were highest (pH>11) at the beginning of the test. The trends in effluent pH for both columns followed that of their hydraulic conductivities (compare Figures 5.4.2 and 5.4.3). The effluent pH decreased linearly during the first 40 nPV of AMD permeation for the 33% CBFA column and 5 nPV for the 50% CBFA and the CBFA control columns, and at an accelerated rate thereafter. The low pH values measured near the end of the tests (down to pH ~ 8) are likely an artifact of the sample collection method and do not reflect the true effluent pH. As the hydraulic conductivity decreased, the time interval required to collect a sufficient volume of leachate sample for analysis increased to several days. Since the effluent samples were exposed to the atmosphere, reaction of hydroxide ions with atmospheric CO_2 caused a sharp decrease in pH and the precipitation of calcium carbonate in the collection cylinder, which appeared as a white coating on the cylinder walls.

Metal mining effluent regulations for pH set the pH between 6 to 9 for EC-MMER (2003) and 6 to 9.5 for USEPA (2003). The effluent of all CBFA amended tests were higher than the minimum regulatory pH of 6, however the maximum regulatory pH limits of 9 and 9.5 were exceeded initially by all CBFA amended columns.

5.4.4 Effluent Composition

The ranges of dissolved concentrations of major elements in the column effluents are shown in Table 5.4.4a and Table 5.4.4b. Also shown are the EC-MMER (2003) and USEPA (2003) mine effluent guidelines, the CCME (2007) freshwater aquatic life guidelines, and Health Canada (2008) drinking water guidelines. The percentage changes in concentration between the synthetic AMD and the column effluents are calculated and shown in brackets.

The column containing only mine tailings did not meet the metal mining effluent regulations for pH, nickel, and iron. By contrast, columns amended with fly ash met all the applicable effluent guidelines. The reductions in heavy metal concentrations were not correlated with the percent fly ash in the columns: all columns containing fly ash performed equally well overall. Elevated concentrations of potassium and sodium are likely due to dissolution of K-jarosite and Na-jarosite minerals at a high pH (see saturation curve for K-jarosite in Figure 3.6b)

Table 5.4.4a Effluent analyses of CBFA / mine tailings kinetic column tests permeated with AMD, including regulatory guidelines

Element	EC-MMER Guideline	USEPA Guideline	CCME-FAL Guideline	Health Canada Drinking Water Guideline	100% MT	95% MT 5% CBFA
Aluminum	na	1	0.005 - 0.1	0.1/0.2	0.024 - 0.215 (0.2% - 2.2%)	0.277 - 4.718 (2.8% - 47.2%)
Arsenic	0.5	0.5	0.005	0.01	0.002 - 0.023 (20.0% - 230%)	0.010 - 0.029 (100% - 290%)
Calcium	na	na	na	na	175.8 - 565.5 (103% - 333%)	243.6 - 546.8 (143% - 322%)
Chromium	na	na	0.001	0.05	0.0003 - 0.0019 (6.0% - 38.0%)	0.0001 - 0.0007 (2.0% - 14.0%)
Copper	0.3	0.15	0.002 - 0.004	1	0.0006 - 0.0459 (0.04% - 3.53%)	0.0135 - 0.0844 (1.0 - 6.5%)
Iron	na	1	0.3	0.3	0.1 - 105.2 (0.3% - 263%)	0.007 - 0.033 (0.02% - 0.09%)
Potassium	na	na	na	na	26.2 - 37.0 (181% - 255%)	13.8 - 27.2 (95.2% - 188%)
Magnesium	na	na	na	na	13.16 - 32.38 (57.2% - 141%)	0.13 - 40.16 (0.6% - 175%)
Sodium	na	na	na	200	6.8 - 34.3 (22.7% - 114%)	21.3 - 46.0 (71.0% - 153%)
Nickel	0.5	0.1	0.025 - 0.15	0.02	0.022 - 1.207 (1.1% - 60.3%)	0.004 - 0.015 (0.2% - 0.7%)
Sulphur	na	na	na	500	274.6 - 662.9 (91.5% - 221%)	297.3 - 488.8 (99.1% - 163%)
Silica	na	na	na	na	2.11 - 7.79 (301% - 1112%)	1.67 - 2.32 (239% - 332%)
Lead	0.2	0.3	0.001 - 0.007	0.01	nd	nd
Zinc	0.5	0.5	0.03	5	0.023 - 0.070 (0.9% - 2.8%)	0.010 - 0.095 (0.4% - 3.8%)
pH	6.0 – 9.5	6.0 - 9.0	6.5 - 9.0	6.5 – 8.5	5.1 - 7.7	6.5 - 9.7

Notes: Concentration in mg/L unless otherwise specified.
Percentage of effluent concentration with respect to the AMD are shown in brackets ( ).
Percentages greater than 100% indicate an increase over the AMD concentration.
nd - readings were below the minimum detection concentration of the icp standard.

Table 5.4.4b Effluent analyses of CBFA / mine tailings kinetic column tests permeated with AMD

Element	90% MT 10% CBFA	80% MT 20% CBFA	67% MT 33% CBFA	50% MT 50% CBFA	100% CBFA
Aluminum	1.35 - 10.19 (13.5% - 102%)	1.77 - 11.56 (17.7% - 116%)	1.47 - 24.06 (14.7% - 241%)	11.36 - 34.61 (114% - 346%)	12.62 – 39.66 (126% - 396%)
Arsenic	0.002 - 0.024 (20.0% - 240%)	0.005 - 0.021 (50.0% - 210%)	0.002 - 0.015 (20.0% - 150%)	0.004 - 0.015 (40.0% - 150%)	0.009 - 0.253 (90.0% - 2530%)
Calcium	262.3 - 320.5 (154% - 188%)	81.3 - 301.8 (47.8% - 177%)	96.1 - 240.5 (56.5% - 141%)	7.8 - 159.0 (4.6% - 93.5%)	12.7 – 183.3 (45.5% - 277%)
Chromium	0.0006 - 0.0015 (12.0% - 30.0%)	0.0001 - 0.0010 (2.0% - 20.0%)	0.0001 - 0.0009 (2.0% - 18.0%)	0.0002 - 0.0018 (4.0% - 36.0%)	0.052 - 0.287 (1040% - 5740%)
Copper	0.0003 - 0.0017 (0.02% - 0.13%)	0.0004 - 0.0007 (0.03% - 0.05%)	0.0001 - 0.0008 (0.01% - 0.06%)	0.0006 - 0.0042 (0.05% - 0.32%)	0.0002 - 0.0049 (0.02% - 0.4%)
Iron	0.011 - 0.274 (0.03% - 0.69%)	0.005 - 0.110 (0.01% - 0.28%)	0.009 - 0.043 (0.02% - 0.11%)	0.012 - 0.267 (0.03% - 0.67%)	0.009 - 0.128 (0.02% - 0.32%)
Potassium	20.1 - 22.5 (138% - 155%)	14.6 - 23.2 (101% - 160%)	12.7 - 23.3 (87.6% - 161%)	15.2 - 31.6 (105% - 218%)	0.8 – 24.9 (5.5% - 172%)
Magnesium	0.079 - 1.960 (0.34% - 8.5%)	0.020 - 0.613 0.09% - 2.7%)	0.011 - 0.245 (0.05% - 1.1%)	0.003 - 0.151 (0.01% - 0.7%)	0.01 - 0.16 (0.04% - 0.7%)
Sodium	59.3 - 63.5 (198% - 212%)	72.6 - 84.3 (242% - 281%)	57.7 - 115.9 (192% - 386%)	47.4 - 209.3 (158% - 697%)	21.3 – 139.8 (71.0% - 466%)
Nickel	0.001 - 0.014 (0.05% - 0.7%)	0.003 - 0.009 (0.15% - 0.45%)	0.004 - 0.012 (0.2% - 0.6%)	0.001 - 0.009 (0.05% - 0.45%)	0.0008 - 0.0052 (0.04 - 0.26%)
Sulphur	256.0 - 298.7 (85.3% - 99.6%)	187.9 - 311.5 (62.6% - 104%)	95.9 - 271.1 (32.0% - 90.4%)	26.2 - 121.5 (8.7% - 40.5%)	2.7 – 33.5 (0.9% - 11.1%)
Silica	2.73 - 4.81 (390% - 687%)	2.61 - 16.35 (373% - 2336%)	1.61 - 8.63 (230% - 1233%)	0.88 - 7.23 (125% - 1033%)	0.66 – 2.53 (94.3% - 361%)
Lead	nd	nd	nd	nd	nd
Zinc	0.004 - 0.030 (0.2% - 1.2%)	0.004 - 0.033 (0.2% - 1.3%)	0.007 - 0.029 (0.3% - 1.2%)	0.018 - 0.034 (0.7% - 1.4%)	0.051 - 0.082 (2.0% - 3.3%)
pH	7.6 - 10.9	8.2 - 11.0	7.7 - 11.6	8.4 - 12.0	8.5 - 11.5

Notes: Concentration in mg/L unless otherwise specified.

Percentage of effluent concentration with respect to the AMD are shown in brackets ( ).

Percentages greater than 100% indicate an increase over the AMD concentration.

nd - readings were below the minimum detection concentration of the icp standard.

Figure 5.4.4a shows the evolution of calcium, sulphur, and iron concentrations in the effluent of the mine tailings column. The graph shows the relative concentration as a ratio (C/Co) of effluent concentration (C) to the AMD concentration (Co). A ratio below or above unity indicates an accumulation or depletion, respectively, of the element in the column. Calcium and sulphur concentrations were higher (C/Co > 1) than the synthetic AMD concentrations throughout the test for calcium and for the first 20 nPV for sulphur. This indicates the probable dissolution of gypsum and calcium carbonate in the mine tailings. The iron concentration in the effluent was much lower than in the synthetic AMD (Fe = 40 mg/L) for the first 30 nPV, which indicates that iron was precipitating in the control column (C/Co <1). Afterwards, the iron concentration increased to more than 100 mg/L, coinciding with a drop in effluent pH below 6.2 and the dissolution of iron precipitates.

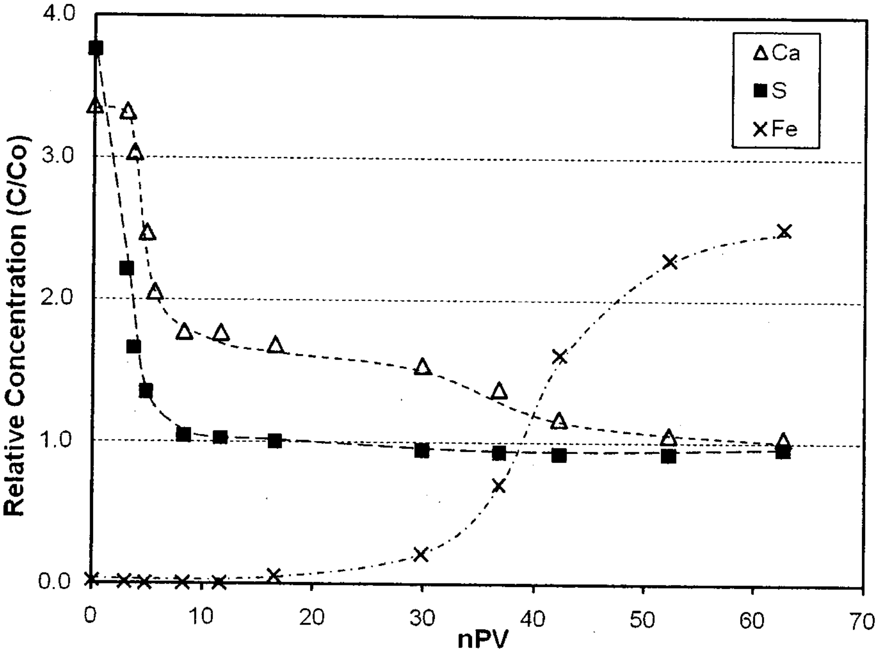


Figure 5.4.4a Relative concentrations of calcium, sulphur and iron in the effluent of the control column versus nPV of AMD permeation

The evolution of calcium, sulphur, and iron concentrations in the effluent of the column containing 33% CBFA (by mass) is shown in Figure 5.4.4b. Columns amended with different percentages of CBFA demonstrated similar trends. By contrast with the mine tailings, the calcium and sulphur concentrations were lower than in the synthetic AMD until 13 nPV of

AMD permeation for calcium and through the test for sulphur. This net accumulation of calcium and sulphur (as sulphate) in the column was likely caused by the precipitation of gypsum, which then contributed to the large drop in hydraulic conductivity. The concentration of iron in the effluent remained well below that in the synthetic AMD throughout the test, which indicated that iron also precipitated in the column.

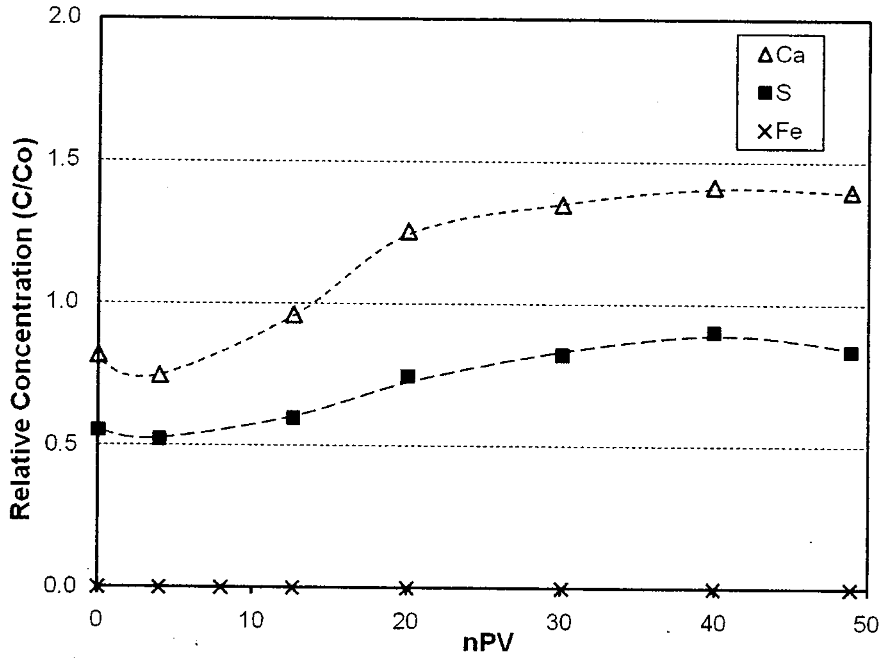


Figure 5.4.4b Relative concentrations of calcium, sulphur and iron in the effluent of the 33% CBFA / 67% MT column versus nPV of AMD permeation

Dissolved aluminum concentrations were lower than 1 mg/L in the mine tailings control column effluent but reached elevated levels (>10 mg/L or C/Co > 1) in the effluent of all columns containing fly ash (Figure 5.4.4c). Although these concentrations decreased as more AMD flowed through the columns, they remained above 1 mg/L even after 70 nPV of AMD permeation. These results are attributed to the dissolution of Al-containing phases in the fly ash and high pH levels in the leachate. Aluminum concentrations in the effluent of a column containing 100% fly ash permeated with distilled water ranged from 10 to 50 mg/L for 70 nPV (see Figure 4.3.4b).

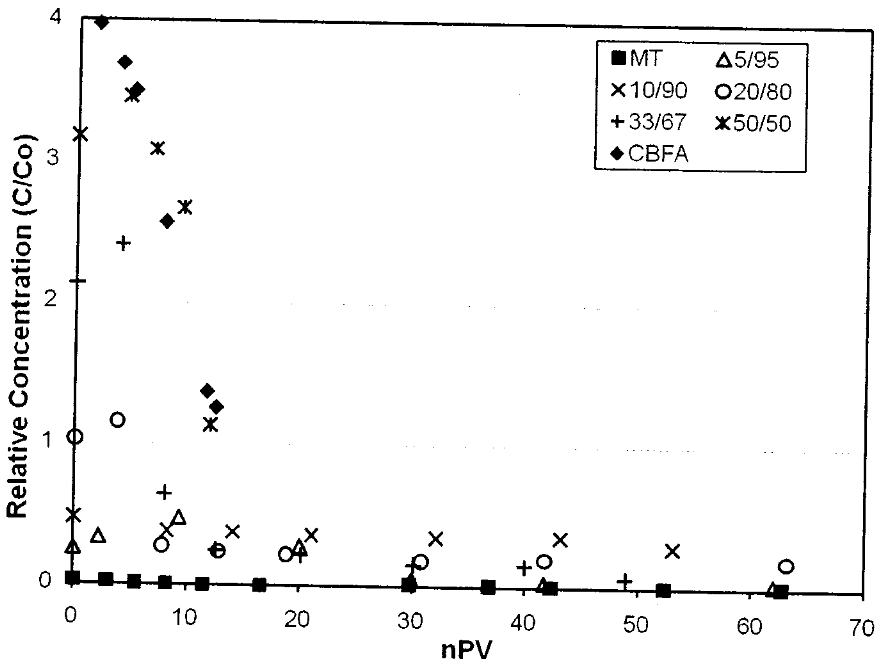


Figure 5.4.4c Relative concentration of aluminum versus nPV of AMD permeation

5.4.5 Post-Testing Solids Analysis

Comparisons of X-Ray diffraction (XRD) patterns obtained from samples of mine tailings, 10% and 50% CBFA mixed with mine tailings before and after column testing were inconclusive in determining the formation of secondary minerals due in part to the complexity of the mine tailings mineralogy (see Figure 5.4.5a for XRD patterns of the mine tailings). Comparisons of XRD patterns obtained from samples of 100% CBFA, however, reveal the formation of gypsum and ettringite during AMD permeation (see Chapter 6).

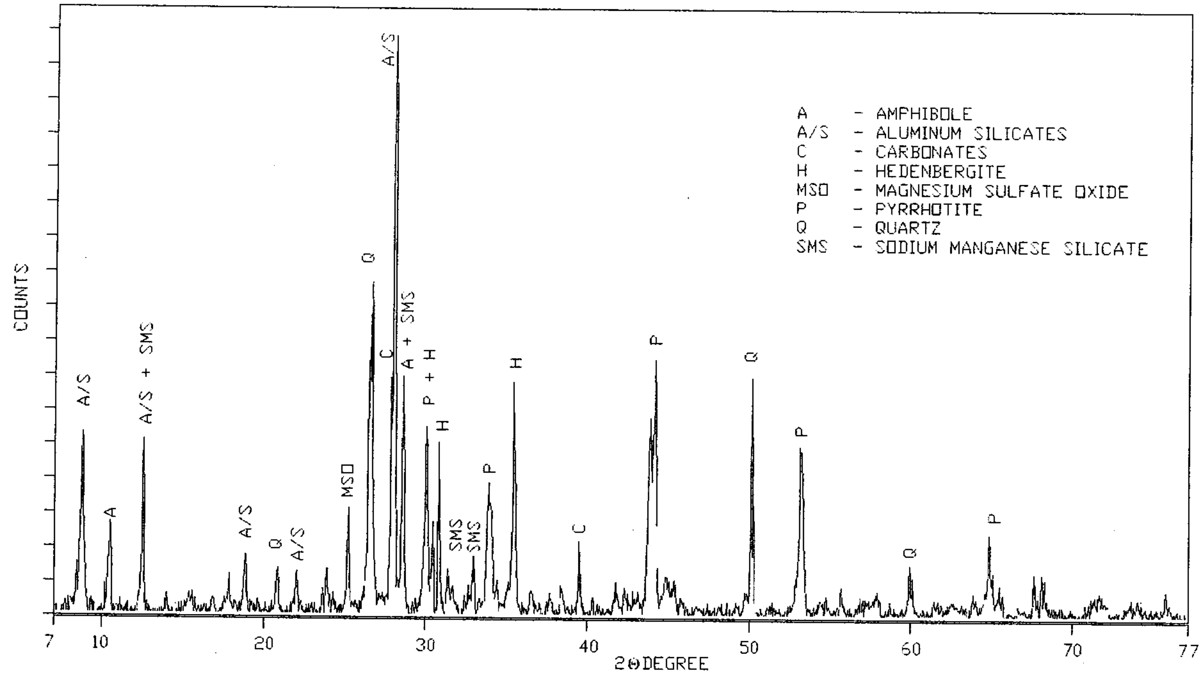


Figure 5.4.5a XRD patterns of mine tailings

Scanning electron microscopy and energy dispersive X-ray analysis (SEM-EDX) were conducted on representative samples of mine tailings and mine tailings amended with 10% and 50% CBFA after permeation with AMD (Figure 5.4.5b). Samples were collected from the bottom of the column pack where the solids were in contact with fresh AMD.

The backscattered electron image of the mine tailings amended with CBFA after AMD permeation (Figures 5.4.5b (B) and (C)) show the conglomeration of fly ash and mine tailings particles after AMD permeation. This conglomeration suggests the formation of a weak cementious aluminum silicate matrix binding the particles together and coating the reactive mine tailing particles. Scheetz et al. (1998) reported that the formation of this cement encapsulates some of the pyrite, rendering it unavailable to oxidize to form AMD. SEM-EDX was inconclusive in determining the presence of new secondary minerals, specifically gypsum and ettringite, due to their low concentration and possible dispersed formation.

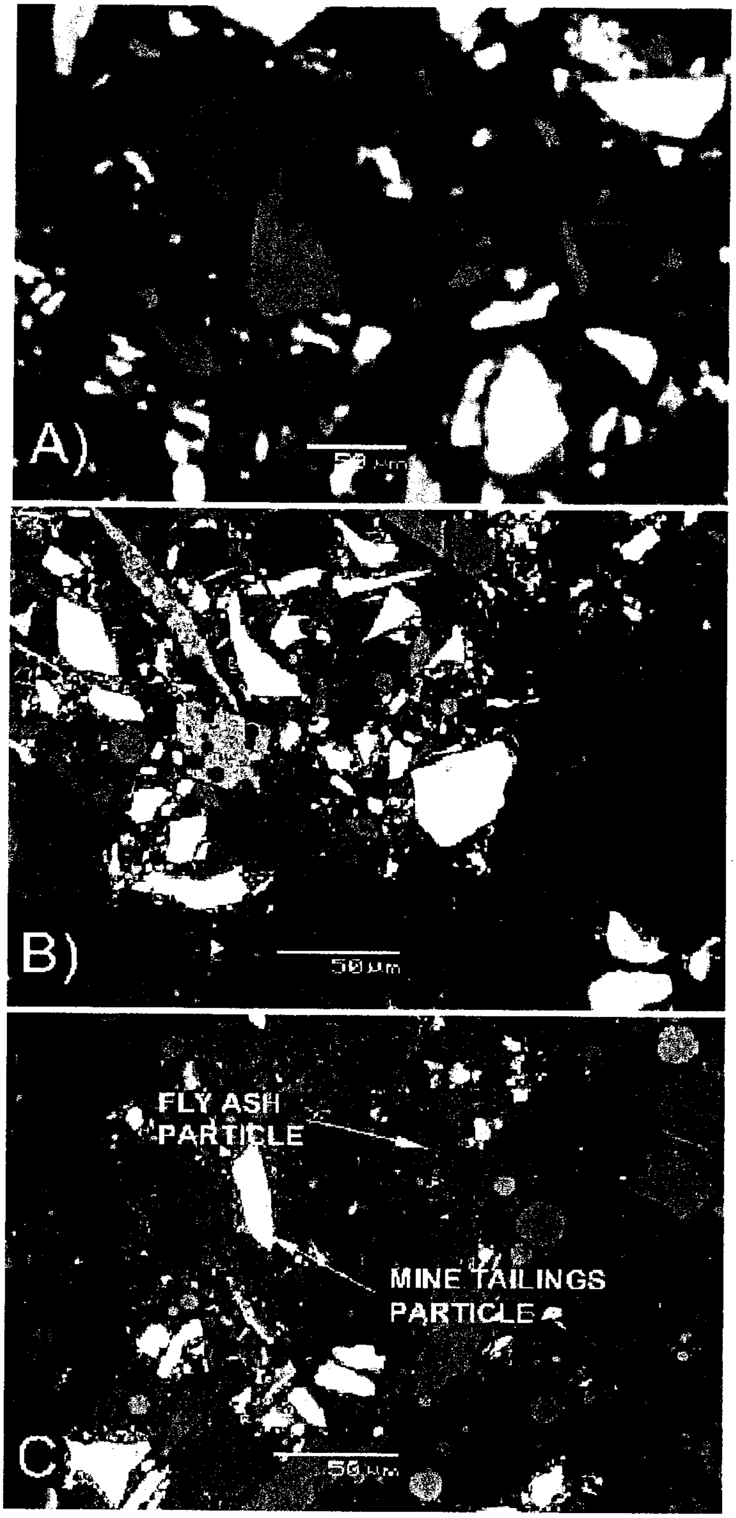


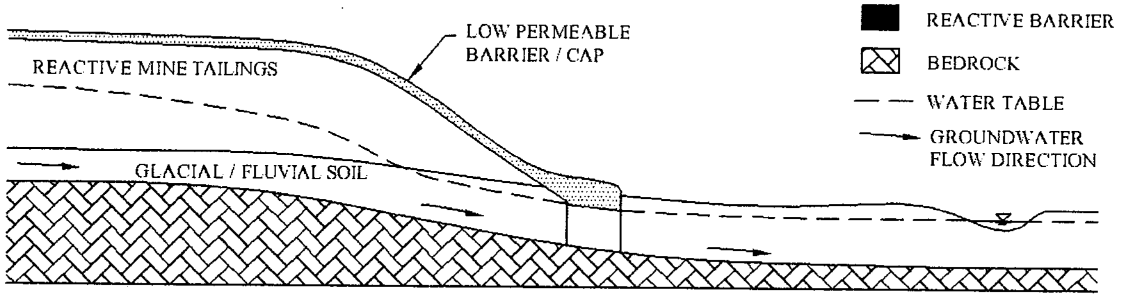
Figure 5.4.5b Backscattered SEM images of a) 100% MT, b) 10% CBFA mixed with 90% MT after AMD permeation, and c) 50% CBFA mixed with 50% MT after AMD permeation.

5.4.6 Applications of Findings

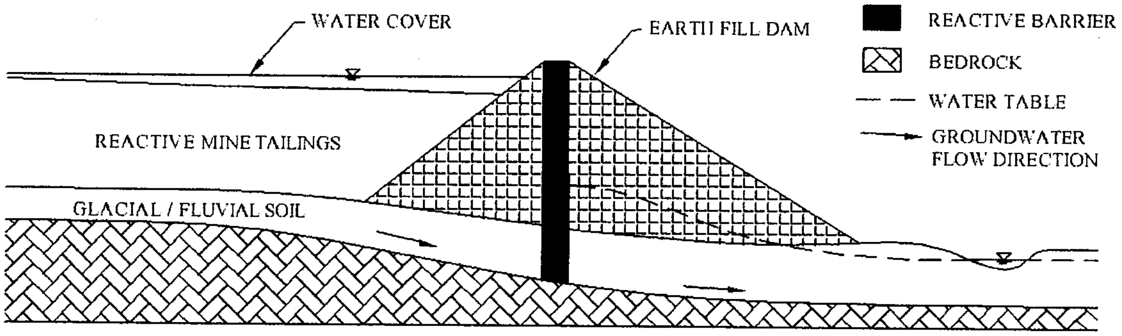
Column test results show that amending acid generating sulphidic tailings with CBFA was effective at reducing the concentrations of many heavy metals found in AMD and at delaying the occurrence of an acidic effluent when compared to un-amended tailings. Aluminum concentrations, however, were significantly increased in the effluent of tailings amended with CBFA. Although aluminum is not included in current mine effluent guidelines, its toxicity to fish and other aquatic organisms at levels as low as 5 µg/L (CCME 2007) and in a range of pH values from acidic to alkaline seems well established (WHO 1997).

Large concentrations of CBFA (33 % or more by mass) caused a substantial reduction in hydraulic conductivity after several pore volumes of AMD were permeated through the columns. Based on these findings, the CBFA could be used in two possible reactive barrier applications.

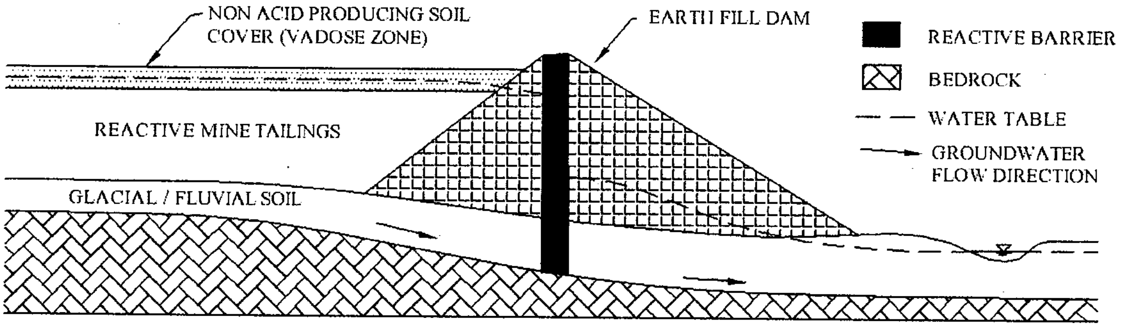
The first application shown in Figure 5.4.6 (A) involves low CBFA concentrations providing a minimal reduction in hydraulic conductivity to create a flow-through reactive barrier. This reactive barrier, installed in a trench or cavity, would intercept and passively treat plumes of contaminated groundwater without affecting the surrounding flow regimes. The barrier must also be located below the water table to prevent oxidation by contact with oxygen.



A) FLOW THROUGH PERMEABLE REACTIVE BARRIER CROSS SECTION



B) LOW PERMEABILITY REACTIVE BARRIER WITH WATER COVER CROSS SECTION



C) LOW PERMEABILITY REACTIVE BARRIER WITH SOIL COVER CROSS SECTION

Figure 5.4.6 Reactive barrier applications. A) Flow-through permeable reactive barrier, B) Low permeability reactive barrier with water cover, and C) Low permeability reactive barrier with soil cover

The second application is shown in Figures 5.4.6 (B and C) and involves the utilization of larger CBFA concentrations to provide dramatic decreases in hydraulic conductivity. This reactive barrier would form the low permeability core of containment dams. During and following construction, the water table elevation would increase due to the reduced hydraulic conductivity, thereby submerging the reactive mine tailings and minimizing their oxidation rate. This application is subject to the surrounding topography, geology and hydrology, but under ideal conditions it could create a containment pond with an adequate water cover (Figure 5.4.6 (B)). Where the formation of a containment pond is not viable, the water table could be raised to an elevation such that the vadose zone would be in a soil cover having a positive NNP (Figure 5.4.6 (C)).

5.5 CONCLUSIONS

Kinetic column tests containing mine tailings amended with CBFA, which simulated a reactive barrier, were effective for increasing the pH and decreasing the dissolved concentrations of heavy metals in the study AMD. All CBFA amended mine tailings effluent met mine effluent regulations for the regulated heavy metals, but did exceed the maximum pH for the initial 40 nPV in the higher percentage CBFA columns. While the high pH is an issue, the flow rates used to conduct the tests were higher than those expected for field applications. Slower flow rates would allow additional time for the precipitation of oxide and hydroxide minerals thereby resulting in a decrease in pH. Further study is required to investigate the effects on the effluent pH at slower flow rates. In addition, study on the reaction of the effluent with the surrounding soil matrix is recommended.

Aluminum concentrations in the effluent are significantly increased by the dissolution of Al-containing phases in CBFA. While the high aluminum concentration is also an issue, the flow rates used to conduct the tests were higher than those expected for field applications. Slower flow rates and the anticipated decrease in pH would also result in the precipitation of aluminum minerals. Further study is required to investigate the aluminum effluent concentrations at slower flow rates. In addition, study on the reaction of the aluminum concentration in the effluent with the surrounding soil matrix is recommended.

The hydraulic conductivity of tailings/CBFA mixtures decreased with the amount of AMD permeated through the column and the percent of CBFA used. This was due to the precipitation of heavy metals in the AMD and the formation of secondary minerals. The formation of a cementious aluminum silicate matrix binding the particles together and coating the surface of reactive mine tailing particles prevented the oxidization of the mine tailings and the formation of AMD.

5.6 REFERENCES

American Society for Testing and Materials (ASTM) D422 – 63, 2007. Standard Test Method for Particle-Size Analysis of Soils. ASTM International, West Conshohocken, PA

American Society for Testing and Materials (ASTM) D854 – 06, 2006. Standard Test Methods for Specific Gravity of Soil Solids by Water Pycnometer. ASTM International, West Conshohocken, PA

American Society for Testing and Materials (ASTM) D4318 – 05, 2005. Standard Test Methods for Liquid Limit, Plastic Limit, and Plasticity Index of Soils. ASTM International, West Conshohocken, PA

British Columbia Ministry of Energy Mines and Petroleum Resources (BC-MEMPR) 1989. Draft acid rock drainage technical guide. *British Columbia Acid Mine Drainage Task Force,* Victoria, BC.

Blowes, D., Bain, J., Smyth, D., and Ptacek, C. 2003a. Treatment of mine drainage using permeable reactive materials. *Environmental Aspects of Mine Wastes, Volume 31 (Chapter 17):* Mineralogical Association of Canada, Vancouver, BC.

Blowes, D., Ptacek, C., and Jurjovec, J., 2003b. Mill tailings: hydrogeology and geochemistry. *Environmental Aspects of Mine Wastes, Volume 31 (Chapter 5)*: Mineralogical Association of Canada, Vancouver, BC.

Canadian Council of Ministers of the Environment (CCME) 2007. Canadian Water Quality Guidelines for the Protection of Aquatic Life. Winnipeg. http://ceqg-rcqe.ccme.ca /download/en/134/ (accessed April 2009).

Environment Canada Metal Mining Effluent Regulations (EC-MMER) 2003. Status report on water pollution prevention and control under the metal mining effluent regulations. Ottawa. http://www.ec.gc.ca/nopp/docs/rpt/waterpollution/mining2003/en/c2.cfm (accessed February 2009).

Health Canada 2008. Guidelines for Canadian drinking water quality. Federal-provincial-territorial committee on drinking water of the federal-provincial-territorial committee on health and the environment, Ottawa, May 2008.

Perez-Lopez, R., Nieto, J. and & Ruiz de Almodovar, G. 2007. Utilization of fly ash to improve the quality of the acid mine drainage generated by oxidation of a sulphide-rich mining waste. *Chemiosphere,* 67: 1637-1646.

Scheetz, B. and Earle, R. 1998. Utilization of fly ash. *Current opinion in solid state & materials science,* 3.5: 510-520.

Shang, J., Wang, H., Kovac, V. and Fyfe, J. 2006. Site specific study on stabilization of acid-generating mine tailings using coal fly ash. *Journal of Materials in Civil Engineering,* March/April: 140-151.

United States Environmental Protection Agency (USEPA) 1988. Design, construction and evaluation of clay liners for waste management facilities. 530/SW-86/007F.

United States Environmental Protection Agency (USEPA) 2003. Ore mining and dressing point source category. 40-CRF-440.

Walton-Day, K. 2003. Passive and active treatment of mine drainage. *Environmental Aspects of Mine Wastes, Volume 31 (Chapter 16)*: Mineralogical Association of Canada, Vancouver, BC.

Wang, H., Shang, Kovac, V, and Ho, K. 2006. Utilization of Atikokan coal fly ash in acid rock drainage control from Musselwhite Mine tailings. *Canadian Geotechnical Journal,* 43: 229-243.

World Health Organization (WHO) 1997. Environmental Health Criteria 194. Aluminum, Geneva, http://www.inchem.org/documents/ehc/ehc/ehc194.htm#SubSectionNumber:9.2.2 (accessed February 2009)

Xenidis, A., Mylona, E. and Paspaliaris, I. 2002. Potential use of lignite fly ash for the control of acid generation from sulphidic wastes. *Waste Management,* 22: 631-641.

Yeheyis, M., Shang, J. and Yanful, E. 2007. Beneficial utilization of coal fly ash as acid mine drainage barrier. *In* Proceedings of the 60th Canadian Geotechnical Conference & 8th Joint CGS/IAH-CNC Groundwater Conference, Ottawa, Canada, October 2007: pp 1494-1499.

6.0 UTILIZATION OF COAL/BIOMASS FLY ASH AND BENTONITE AS A LOW PERMEABILITY BARRIER FOR THE CONTAINMENT OF ACID-GENERATING MINE TAILINGS[2]

This study investigated the feasibility of using coal/biomass fly ash (CBFA) blended with various percentages of bentonite as a low permeable barrier for containing reactive mine tailings and treating acid mine drainage (AMD). CBFA alone could not meet the hydraulic conductivity requirement of less than 1×10^{-7} cm/s (USEPA 1988). Mixing 10% by mass bentonite with CBFA, however, decreased the hydraulic conductivity to 1×10^{-7} cm/s or less throughout the entire permeation by water and AMD. The installation of a layer of pure CBFA upstream of the bentonite/CBFA mixture caused a further decrease in hydraulic conductivity over time by decreasing the collapse of the bentonite double layer and favoring precipitation of gypsum and ettringite in the CBFA layer. The effluent from all tested bentonite/CBFA barriers met the metal mining regulatory requirements for chemical parameters, except for aluminum which was leached from the CBFA at a high pH.

6.1 INTRODUCTION

The disposal of sulfide-bearing mine tailings in surface facilities is a major environmental concern due to their potential to produce AMD, which is formed from the oxidation of sulfide minerals in the presence of oxygen and water. Typically, AMD has a low pH, high acidity, and elevated concentrations of heavy metals.

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[2] A version of this chapter was presented in the 62nd Canadian Geotechnical Conference and 10th Joint CGS/IAH-CNC Groundwater Conference, Halifax, September 2009, and published in the conference proceedings, pp. 867 to 874.

Control and treatment of AMD, particularly in decommissioned and inactive mine sites, are major environmental challenges. Often, these mine sites have ongoing AMD formation which impacts the adjacent terrestrial and aquatic ecosystems. With continued infiltration recharge, the AMD effluent may easily flow in the groundwater regime as well as adjacent streams and other water bodies down gradient from the disposal site.

Several AMD prevention methods exist, including water and soil covers. Construction of new mine tailings containment ponds often required engineered structures to improve their geotechnical and hydrological properties. These structures frequently include a low permeable liner and containment dams and dykes. In areas where a water cover is not practical, a low permeable cover may be used as a cap to prevent oxidation of reactive mine tailings and to reduce the flow of AMD into the groundwater and subsequent surface water flow regimes.

Current low permeability technologies include geosynthetic membranes, geosynthetic clay membranes, and compacted clay liners. Due to the large size of many projects and their remoteness, the costs associated with these technologies can affect the project feasibility. The combined utilization of fly ash and bentonite may provide a cost effective, low-permeability material for containing reactive mine tailings and treating AMD seepage.

A number of recent studies (Xenidis et al. 2002, Shang et al. 2006, Wang et al. 2006, Yeheyis et al. 2007, Perez-Lopez et al. 2007) have investigated the effects of AMD on coal fly ash (CFA) using laboratory kinetic column tests. Continued permeation of AMD through CFA decreased its hydraulic conductivity by several orders of magnitude to less than 1×10^{-7} cm/s. This decrease was attributed to precipitation of heavy metals and the formation of secondary minerals which clogged the pores in the packs. CFA was also effective in reducing heavy metal concentrations and increasing the pH of AMD.

Yeheyis et al. (2007) studied the effects of AMD on CFA amended with 5% and 10% bentonite (by mass) in laboratory kinetic column tests and found that the addition of bentonite can reduce the initial high hydraulic conductivity of CFA. The hydraulic conductivity of CFA blended with 5 wt% bentonite further decreased with continued AMD permeation. By contrast, the hydraulic conductivity of CFA blended with 10 wt% bentonite increased upon switching the permeate from water to AMD, and remained unchanged thereafter. The CFA/bentonite mixtures were also effective in reducing the studied heavy metal concentrations and increasing the pH of AMD.

The effect of AMD on pure bentonite has been investigated in laboratory kinetic column tests (Kashir et al. 2001). While bentonite initially increased the pH and reduced the concentrations of heavy metals in AMD, this effect decreased rapidly with continued AMD permeation. Pure bentonite was ineffective in treating AMD after 5 progressive pore volumes (nPV) and the hydraulic conductivity increased by up to 10 times (one order of magnitude) after switching the permeate from distilled water to AMD. Similar results were obtained when blending bentonite with mineral soil (Kashir et al. 2000).

This study was conducted to investigate the use of CBFA and CBFA/bentonite mixtures as a low permeability barrier to contain acid-generating mine tailings and treat AMD. Three cases were investigated: 1) CBFA only; 2) CBFA amended with low percentages of bentonite; and 3) layering of CBFA and CBFA amended with bentonite. Practical geoenvironmental applications for low permeability CBFA or bentonite/CBFA mixtures include a cap overlying reactive mine tailings, a containment pond liner, and a core in containment dams and dykes.

6.2 MATERIALS AND METHODS

6.2.1 Coal/Biomass Fly Ash

CBFA was obtained from the Atikokan Thermal Generating Station, in Atikokan, Ontario, during a 16 % (by mass) wood biomass burn with 84 % lignite coal. Major CBFA constituents reported as oxides were silica (SiO_2), aluminum oxide (Al_2O_3), calcium oxide (CaO), sodium oxide (Na_2O), and iron oxide (Fe_2O_3). The CBFA contained heavy metals (zinc, lead, copper, nickel, and chromium) at concentrations of a few tens of grams per tonne (see Tables 3.3a and 3.3b). Acid based accounting (ABA) by the Modified Sobek Method (BC-MEMPR 1989) indicated a net neutralizing potential (NNP) of 298 kg $CaCO_3$/1000 kg.

Grain size analysis conducted in accordance with ASTM standard D422 (ASTM 2007) on three representative CBFA samples showed that it consists predominantly of particles in the silt size range (~84%) with trace to some sand (~10%), and trace of clay (~6%) sized particles. The specific gravity measured by ASTM standard D854 (ASTM 2006) was 2.42. The liquid and plastic limits in accordance with ASTM standard D4318 (ASTM 2005) could not be measured on particles smaller than 75 µm, indicating that the CBFA was non plastic.

6.2.2 Bentonite/CBFA Mixtures

Bentonite used in this study was laboratory grade sodium montmorillonite from Wyoming, USA. Major constituents reported as oxides were SiO_2, Al_2O_3, Fe_2O_3, Na_2O, and CaO. The bentonite was typically inert with only the heavy metals, zinc and copper, at concentrations of a few tens of grams per tonne (see Tables 3.3 a and 3.3b).

CBFA mixed with 2.5%, 5%, 7.5%, 10%, and 20% bentonite (by mass) were prepared and analyzed for their geotechnical properties. Grain size analysis showed that the bentonite/CBFA mixtures predominantly contain particles in the silt size range (73.8% to 82.6%) with a trace of sand (7.1% to 9.8%) and trace to some clay (7.6% to 19.1%) sized particles. Their specific gravity ranged from 2.42 to 2.62. Liquid and plastic limits were measured on all mixtures and ranged from 27 to 130 for the liquid limit and from 20 to 37 for the plastic limit (see Table 6.2.4a).

6.2.3 Synthetic Acid Mine Drainage

Two synthetic AMD solutions, AMD-L and AMD-H were prepared in the laboratory. The solution AMD-L was only used in conjunction with the 100% CBFA column. The solution AMD-H was used to permeate the other columns and had higher concentrations of heavy metals. The AMD compositions and pH are shown in Table 6.2.3.

Table 6.2.3 Composition of synthetic AMD-L and AMD-H solutions

Element/Parameter	AMD-L Concentration[1]	AMD-H Concentration[1]
pH	2.8	2.7
Electrical Conductivity (mS/cm)	1.9	1.9
Aluminum	10	5.6
Arsenic	0.01	0.001
Calcium	170	83.8
Chromium	0.005	0.005
Copper	1.3	12.9
Iron	40	55
Potassium	14.5	5.5
Sodium	30	26.5
Magnesium	23	17.8
Nickel	2	20.1
Sulphur	300	178
Silica	0.7	0.5
Strontium	0.1	0.07
Lead	0.04	4.3
Zinc	2.5	21

Note: [1] in mg/L unless specified

6.2.4 Kinetic Column Tests

Laboratory kinetic column tests were carried out to study the effects of AMD flow on the hydraulic conductivity and leachate composition of CBFA and CBFA amended with bentonite. The physical and geotechnical properties of the 100% CBFA and amended kinetic column packs are summarized in Table 6.2.4a.

Table 6.2.4a Properties of CBFA and bentonite amended CBFA kinetic column packs

Parameter	100% CBFA	2.5% Bent. 97.5% CBFA (mixed)	5% Bent. 95% CBFA (mixed)	7.5% Bent. 92.5% CBFA (mixed)	10% Bent. 90% CBFA (mixed)
Specific Gravity	2.42	2.42	2.47	2.52	2.59
% Sand	10	9.8	8.7	8.4	8.1
% Silt	84	82.6	82	79.2	75.7
% Clay	6	7.6	8.7	9.3	12.4
Initial Dry Weight (g)	133.8	109.3	101.9	85.7	73.6
Final Dry Weight (g)	138.7	111.4	104.2	89.8	75.0
Initial Height (mm)	39	37	40	39	40
Final Height (mm)	39	36	37	32	31
Initial Dry Density (g/cc)	1.75	1.50	1.30	1.12	0.94
Final Dry Density (g/cc)	1.81	1.58	1.43	1.43	1.23
Initial Porosity	0.278	0.362	0.475	0.556	0.638
Final Porosity	0.251	0.348	0.419	0.433	0.524
Initial Pore Volume (cc)	21.3	26.3	37.3	42.6	50.1
Final Pore Volume (cc)	19.2	24.6	30.5	27.2	31.9
Liquid Limit	-	27	46	57	105
Plastic Limit	-	20	22	30	37

Two layered kinetic column tests were also conducted. Layered packs consisted of a 20-mm layer of CBFA/bentonite mixture overlying a 20-mm layer of CBFA. The AMD entered first the CBFA layer at the bottom of the column and the leachate exited at the top of the mixed layer.

The physical properties of the layered kinetic column packs are summarized in Table 6.2.4b.

Table 6.2.4b Properties of layered CBFA and bentonite amended CBFA kinetic column packs

Parameter	Top layer: 10% Bentonite / 90% CBFA Bottom layer: 100% CBFA	Top layer: 20% Bentonite / 80% CBFA Bottom layer: 100% CBFA
Initial Height (mm)	40	39
Final Height (mm)	40	39
Initial Dry Weight (g)	118.6	96.4
Final Dry Weight (g)	119.7	96.8
Initial Dry Density (g/cc)	1.51	1.26
Final Dry Density (g/cc)	1.52	1.26
Initial Porosity	0.383	0.427
Final Porosity	0.377	0.423
Initial Pore Volume (cc)	30.9	37.7
Final Pore Volume (cc)	30.5	37.5

Columns were constructed of 50-mm ID clear acrylic tubing. Inert materials (nylon, vinyl, PVC, and stainless steel) were used as tubing, fasteners, collection containers, etc. A schematic of the column test setup is presented in Figure 6.2.4. CBFA/bentonite samples were prepared by thoroughly mixing the dry mass percentages of CBFA and bentonite in a bowl. Next, distilled water was added and mixed until the samples had a soft clay like texture. The mixed samples were placed in plastic re-sealable bags and allowed to moisture condition overnight. The samples were placed in the columns in two successive 20-mm layers. Each layer was rodded 25 times with a 10 mm diameter plastic rod. After rodding, the sides of the column were tapped to remove air bubbles. The top surface of the pack was trimmed and covered with a porous fabric and stone. Upon final assembly, the pack was confined by tightening a stainless steel bolt which applied a confining load to the top plate.

The columns were then allowed to consolidate for a minimum of 16 hours, after which time the bolts were again tightened and the initial sample length recorded. These bolts were periodically checked and tightened throughout the test to compensate for consolidation and collapse of the bentonite double layer.

Samples were first permeated with distilled water to establish the reference hydraulic conductivity. Once equilibrium was achieved, after 8.4 to 12.7 nPV, the permeate was switched to AMD. The hydraulic gradient was adjusted throughout the test to allow for the collection of an acceptable volume of effluent (30 ml or more) in a reasonable time period (1 to 5 days). During the tests, effluent samples were collected, weighed, time recorded, and the hydraulic head measured. The hydraulic gradient, hydraulic conductivity, flow rate, and progressive pore volumes were calculated. All leachate samples were analyzed for pH. Select leachate samples were acidified to a pH of 3 or less with nitric acid and analyzed for elemental composition by inductively coupled plasma – atomic emission spectrometry (ICP-AES). Upon termination of the tests, the weight, height and moisture contents of the column packs were measured.

Column tests were run for a minimum of 80 nPV, or terminated upon reaching a hydraulic conductivity of 10^{-7} cm/s or less (USEPA 1988). Effluent metal concentrations were compared to EC-MMER (2003) and USEPA (2003) mine effluent regulations. CCME (2007) water quality guidelines for the protection of freshwater aquatic life and Health Canada (2008) fresh water drinking guidelines were also compared.

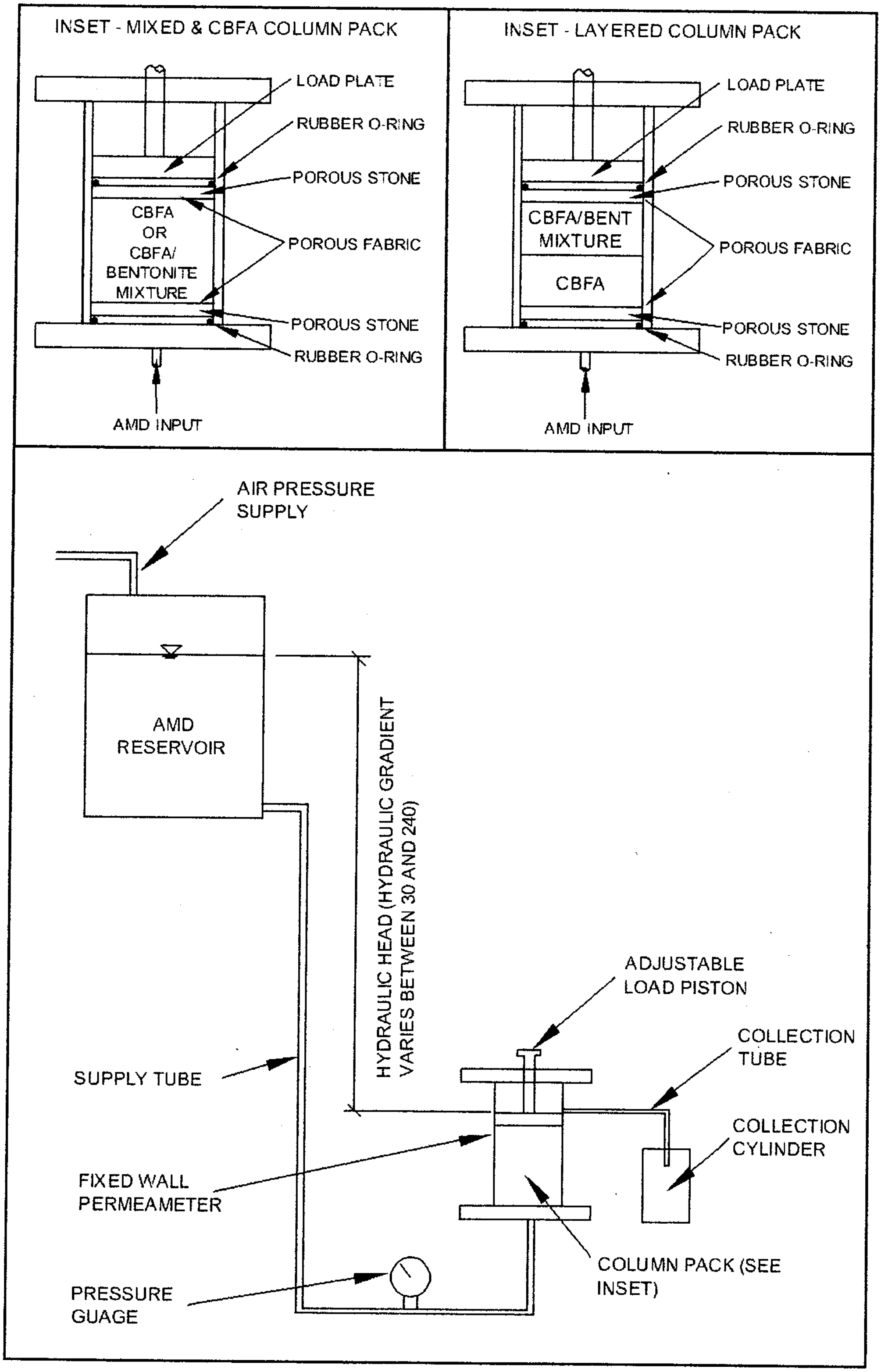

Figure 6.2.4 Schematic of CBFA / bentonite kinetic column test setup

6.3 RESULTS AND DISCUSSION

6.3.1 Hydraulic Conductivity

Hydraulic conductivity results for the four mixed bentonite/CBFA and the 100% CBFA columns are presented in Figure 6.3.1a. The dashed vertical line represents the switch from distilled water to AMD permeate. The hydraulic conductivity when permeated with distilled water is shown to emphasis the increase in hydraulic conductivity for the bentonite amended CBFA packs upon switching the permeate to AMD.

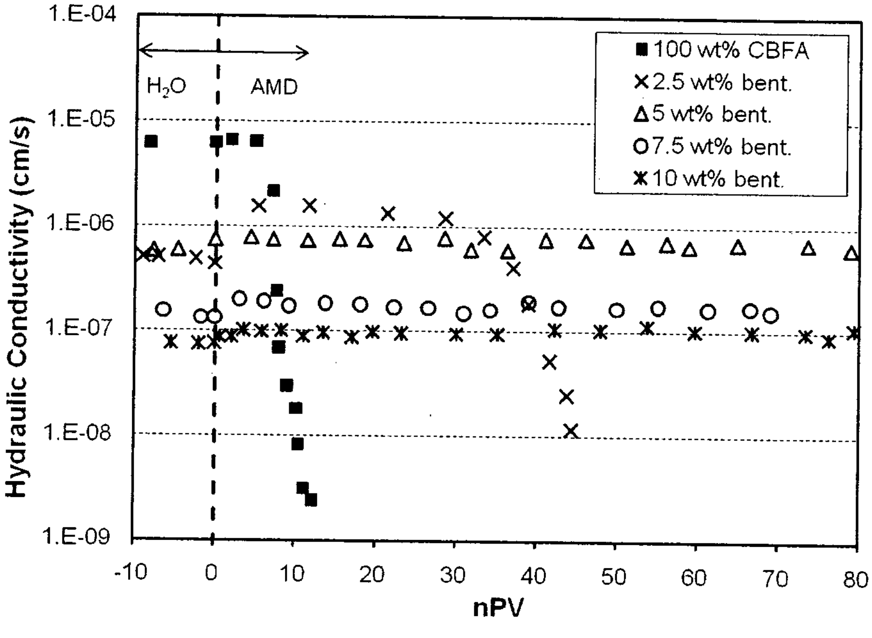

Figure 6.3.1a Hydraulic conductivity versus nPV of permeate (CBFA and bentonite/CBFA mixtures)

The hydraulic conductivity of 100% CBFA permeated with distilled water was 6.3x10^{-6} cm/s. Mixing bentonite with CBFA decreased the hydraulic conductivity by one to two orders of magnitude depending on the amount of added bentonite. The hydraulic conductivity during distilled water permeation was 4.5×10^{-7} cm/s, 7.4×10^{-7} cm/s, 1.4×10^{-7} cm/s, and 7.5×10^{-8} cm/s for the 2.5%, 5%, 7.5%, and 10% mixed bentonite/CBFA columns, respectively. An increase in the hydraulic conductivity by as much as 2.5 times was observed in the mixed CBFA/bentonite columns upon switching the permeate from distilled water to AMD. This increase, however, did not occur in the 100% CBFA column. The hydraulic conductivity of the 100% CBFA column decreased dramatically after 5 nPV and became less than 10^{-8} cm/s after 10 nPV.

Continued permeation of AMD did not affect the hydraulic conductivity of bentonite/CBFA mixtures, with the exception of the 2.5% bentonite mixture. The hydraulic conductivity of the 2.5% bentonite mixture decreased rapidly after 30 nPV and reached 1.2×10^{-8} cm/s in 45 nPV of AMD. Only the column containing 10% bentonite maintained a hydraulic conductivity $\leq 1.0 \times 10^{-7}$ cm/s during permeation with distilled water and AMD. The reduced effect of AMD on the hydraulic conductivity of columns containing bentonite may be attributed to the physical coating of the CBFA with bentonite and the increased void ratio for the bentonite/CBFA columns compared with 100% CBFA. The coating of the CBFA with bentonite reduced the reactivity of the AMD with the CBFA. The increased void ratio required additional AMD permeation for secondary minerals and metal precipitates to clog the voids, as indicated by the 30 nPV of AMD required to observe a decrease in hydraulic conductivity in the 2.5% mixture. All other percentages of bentonite were terminated before a drop in hydraulic conductivity was observed.

The increase in hydraulic conductivity after switching the permeate from distilled water to AMD in the bentonite amended columns was also observed by Yeheyis et al. (2007) and Kashir et al. (2000 and 2001), who attributed this increase to the collapse of the bentonite's double layer structure. This explanation is consistent with our observation that the pack heights decreased by 2.7%, 7.5%, 17.9%, and 22.5% when the columns containing 2.5%, 5%, 7.5%, and 10% bentonite, respectively, were switched from distilled water to AMD.

Hydraulic conductivity results for the two layered bentonite/CBFA columns are presented in Figure 6.3.1b and compared with the 100% CBFA column. The layering decreased the hydraulic conductivity to distilled water by one to two orders of magnitude. Adjusting the percentage of bentonite in the mixed layer and/or its thickness can decrease the overall hydraulic conductivity to less than 1.0x10^{-7} cm/s throughout the test. Increasing the bentonite percent to 20% in the mixed layer decreased the hydraulic conductivity to distilled water to approximately 1.0x10^{-7} cm/s.

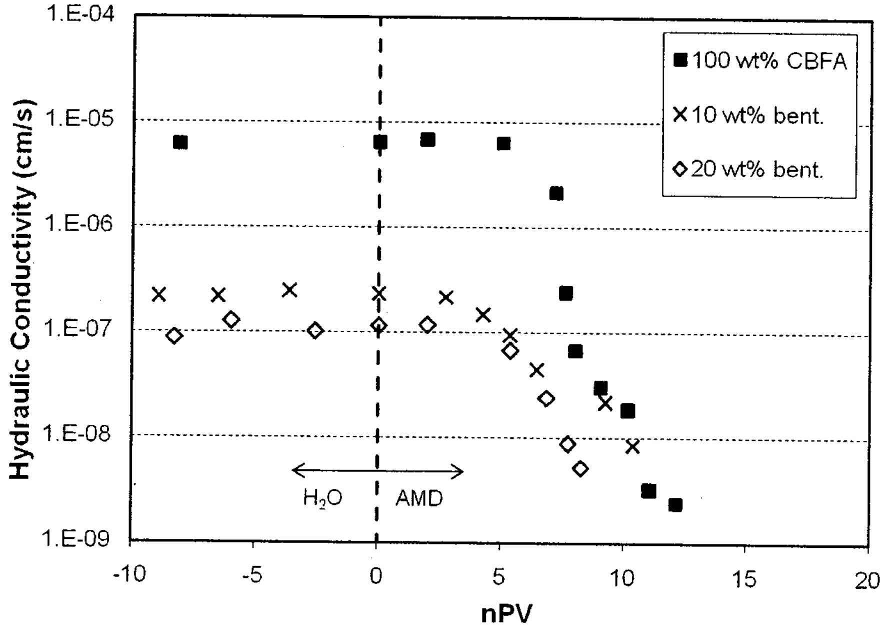

Figure 6.3.1b Hydraulic conductivity versus nPV of permeate (CBFA and layered bentonite/CBFA mixture)

After switching the permeate to AMD, the hydraulic conductivity of the layered columns decreased to values similar to those measured with the 100% CBFA column (<10^{-8} cm/s) in less than 10 nPV. Layering was also effective in eliminating the consolidation of the packs, as pack heights remained unchanged during the tests (Table 6.2.4b). This is likely explained by the AMD first flowing through the lower layer of 100% CBFA, which increases pH and reduces the concentrations of heavy metals before flowing through the upper mixed layer. The alkaline pH and low concentrations of heavy metals prevent or significantly minimize the collapse of the bentonite double layer, thereby avoiding the consolidation and the increase in the hydraulic conductivity which occurred in the mixed columns.

6.3.2 Effluent pH

Effluent pH results are shown in Figure 6.3.2a and 6.3.2b for the mixed and layered columns, respectively. The effluent of all the columns remained alkaline ($7.6 < pH < 12.1$) throughout the tests.

The trends in effluent pH for the 100% CBFA, 2.5% bentonite mixture, and both layered columns were similar to the trends of their hydraulic conductivities (compare Figure 6.3.1a with Figure 6.3.2a, and Figure 6.3.1b with Figure 6.3.2b). The effluent pH of these columns decreased semi-linearly to pH 10.5 – 11 when permeated with distilled water. After switching to AMD, the effluent pH remained approximately unchanged ($pH > 10$) until the hydraulic conductivity began decreasing. Following this, the effluent pH decreased at an accelerated rate. The low pH values measured near the end of the tests (down to a pH of approximately 8) are likely an artifact of the sample collection method and do not reflect the true effluent pH. As the hydraulic conductivity decreased, the time interval required to collect a sufficient volume of leachate sample for analysis increased to several days. Since the effluent samples were exposed to the atmosphere, reaction of hydroxide ions with atmospheric CO_2 caused a sharp decrease in pH and the precipitation of calcium carbonate in the collection cylinder, which appeared as a white coating on the cylinder walls.

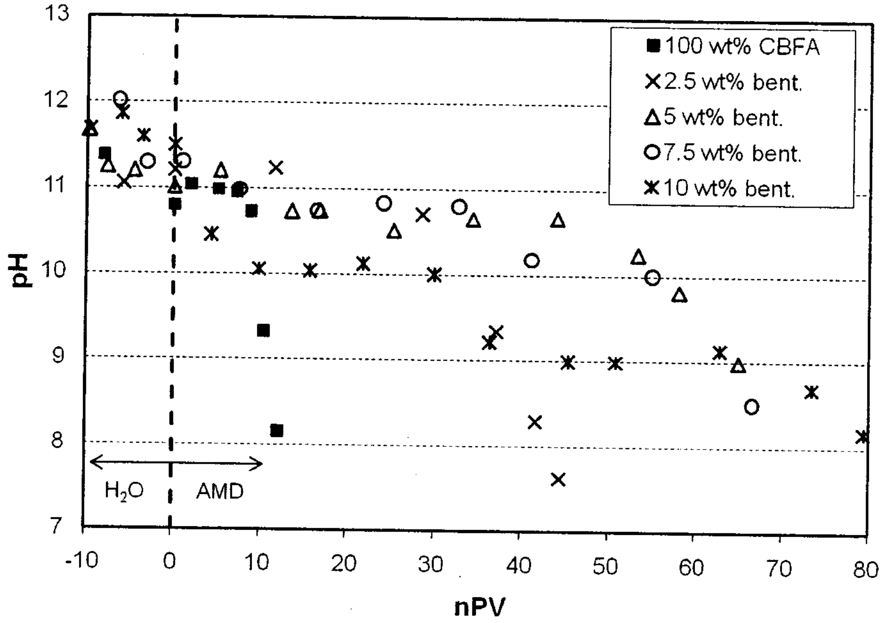

Figure 6.3.2a Effluent pH versus nPV of permeate (CBFA and bentonite/CBFA mixtures)

The effluent pH for the 5%, 7.5%, and 10% bentonite/CBFA mixtures plateaued at pH 10 – 11 for several nPVs after the permeate was switched to AMD and then decreased to pH 8.2 - 8.7 at the termination of the test. This decrease in pH is attributed to depletion of the buffering capacity of fly ash particles not physically coated with bentonite and to the subsequent coating of these fly ash particles with precipitates such as metal hydroxides.

Metal mining effluent regulations for pH set the pH range between 6.0 to 9.0 for EC-MMER (2003) and 6.0 to 9.5 for USEPA (2003). All bentonite amended CBFA tests were higher than the minimum pH of 6.0 but the maximum pH limits of 9.0 and 9.5 were exceeded initially (up to 60 nPV) by all columns.

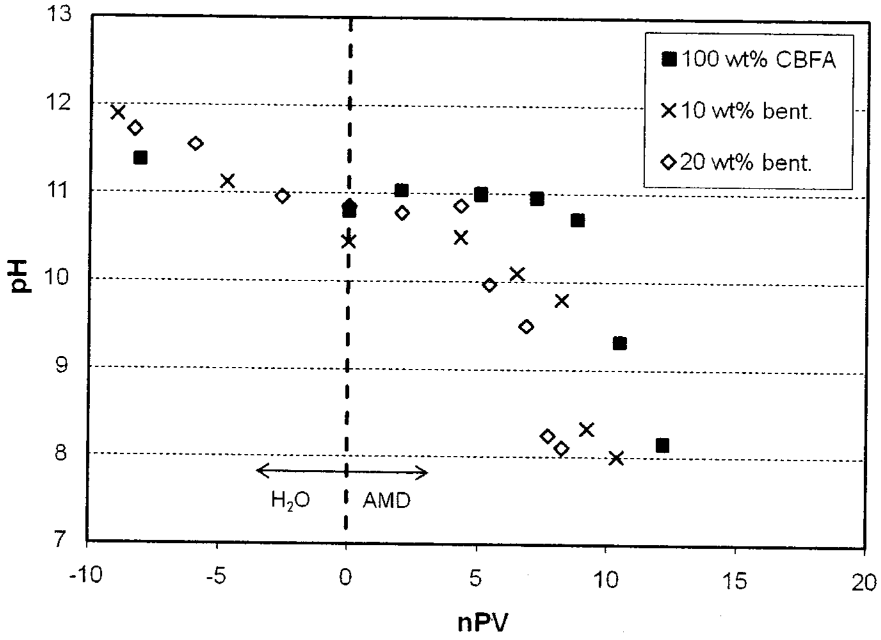

Figure 6.3.2b Effluent pH versus nPV (CBFA and layered bentonite/CBFA mixture)

6.3.3 Effluent Composition

Tables 6.3.3a and 6.3.3b show the range of dissolved concentrations of major elements in the column effluents and compare them with concentrations in AMD, EC-MMER (2003) and USEPA (2003) mine effluent regulations, the CCME (2007) freshwater aquatic life guidelines, and the Health Canada (2008) drinking water guidelines. The percentage changes in concentration between the synthetic AMD and the column effluents are also shown.

All column effluents met the metal mining effluent regulations, except that for aluminum. Although aluminum is not included in current mine effluent guidelines, its toxicity to fish and other aquatic organisms at levels as low as 5 µg/L (CCME 2007) and in a range of pH values from acidic to alkaline seems well established (WHO 1997).

Table 6.3.3a Effluent analyses of CBFA / bentonite layered tests kinetic column tests permeated with AMD, including effluent guidelines

Element	EC-MMER Guideline	USEPA Guideline	CCME-FAL Guideline	Health Canada Guideline	10% Bentonite (Layered)[1]	20% Bentonite (Layered)[1]
Aluminum	na	1	0.005 - 0.1	0.1/0.2	1.10 - 19.41 (19.6% - 347%)	8.18 - 16.35 (146% - 292%)
Arsenic	0.5	0.5	0.005	0.01	0.003 - 0.029 (300% - 2900%)	0.001 - 0.010 (100% - 1000%)
Calcium	na	na	na	na	78.9 - 100.3 (94.2% - 120%)	93.9 - 142.7 (112% - 170%)
Chromium	na	na	0.001	0.05	0.094 - 0.140 (1880% - 2800%)	0.088 - 0.143 (1760% - 2860%)
Copper	0.3	0.15	0.002 - 0.004	1	0.0062 - 0.0183 (0.05% - 0.14%)	0.0116 - 0.0142 (0.09% - 0.11%)
Iron	na	1	0.3	0.3	0.004 - 0.008 (0.01% - 0.02%)	0.004 - 0.054 (0.01% - 0.10%)
Potassium	na	na	na	na	0.63 - 3.82 (11.5% - 69.5%)	0.61 - 2.68 (11.1% - 48.7%)
Magnesium	na	na	na	na	0.06 - 0.18 (0.34% - 1.01%)	0.05 - 0.12 (0.28% - 0.67%)
Sodium	na	na	na	200	16.2 - 65.3 (61.1% - 246%)	20.4 - 67.0 (77.0% - 253%)
Nickel	0.5	0.1	0.025 - 0.15	na	0.0002 - 0.0026 (0.001% - 0.013%)	0.0020 - 0.0048 (0.010% - 0.024%)
Sulphur	na	na	na	500	12.0 - 48.3 (6.7% - 27.1%)	8.1 - 78.5 (4.6% - 44.1%)
Silica	na	na	na	na	1.43 - 2.09 (286% - 418%)	1.83 - 3.26 (366% - 652%)
Lead	0.2	0.3	0.001 - 0.007	0.01	nd	nd
Zinc	0.5	0.5	0.03	5	0.015 - 0.077 (0.07% - 0.37%)	0.013 - 0.083 (0.06% - 0.40%)
pH	6.0 - 9.5	6.0 - 9.0	6.5 - 9.0	6.5 - 8.5	7.9 - 10.5	8.1 - 10.8

Notes: Concentration in mg/L unless otherwise specified.
Percentage of effluent concentration with respect to the AMD are shown in brackets ( ).
nd - readings were below the detection limit.
[1] Synthetic AMD-L for bentonite/CBFA packs.
[2] Synthetic AMD-H for 100% CBFA pack.

Table 6.3.3b Effluent analyses of CBFA / bentonite mixed kinetic column tests permeated with AMD

Element	100% CBFA^2	2.5% Bentonite (Mixed)^1	5% Bentonite (Mixed)^1	7.5% Bentonite (Mixed)^1	10% Bentonite (Mixed)^1
Aluminum	12.62 – 39.66 (126% - 396%)	0.53 - 26.03 (9.5% - 465%)	1.21 - 11.52 (21.6% - 206%)	0.57 - 18.53 (10.2% - 331%)	0.62 - 33.20 (11.1% - 593%)
Arsenic	0.009 – 0.253 (90.0% - 2530%)	0.007 - 0.012 (700% - 1200%)	0.004 - 0.027 (400% - 2700%)	0.004 - 0.021 (400% - 2100%)	0.004 - 0.033 (400% - 3300%)
Calcium	12.7 – 183.3 (7.5% - 108%)	189.1 - 293.2 (226% - 350%)	201.0 - 323.0 (240% - 385%)	122.9 - 368.0 (147% - 439%)	20.4 - 276.8 (24.3% - 330%)
Chromium	0.052 – 0.287 (1040% - 5740%)	0.065 - 0.140 (1300% - 2800%)	0.045 - 0.096 (900% - 1920%)	0.042 - 0.113 (840% - 2260%)	0.017 - 0.128 (340% - 2560%)
Copper	0.0002 - 0.0049 (0.015 - 0.378%)	0.0030 - 0.0141 (0.02% - 0.11%)	0.0013 - 0.0051 (0.01% - 0.04%)	0.0016 - 0.0902 (0.01% - 0.70%)	0.0026 - 0.0159 (0.02% - 0.12%)
Iron	0.009 - 0.128 (0.023% - 0.32%)	0.019 - 0.168 (0.03% - 0.31%)	0.027 - 0.070 (0.05% - 0.13%)	0.008 - 0.028 (0.01% - 0.05%)	0.019 - 0.062 (0.03% - 0.11%)
Potassium	0.8 – 24.9 (5.5% - 172%)	0.88 - 28.00 (16.0% - 509%)	1.54 - 8.99 (28.0% - 163%)	1.91 - 10.42 (34.7% - 189%)	2.25 - 7.59 (40.9% - 138%)
Magnesium	0.01 - 0.16 (0.04% - 0.7%)	0.28 - 1.59 (0.17% - 8.93%)	0.05 - 0.11 (0.28% - 0.62%)	0.004 - 0.14 (0.02% - 0.78%)	0.001 - 0.11 (0.01% - 0.62%)
Sodium	21.3 – 139.8 (71.0% - 466%)	42.2 - 143.3 (159% - 541%)	37.4 - 62.2 (141% - 235%)	50.6 - 81.3 (191% - 307%)	52.1 - 286.4 (197% - 1081%)
Nickel	0.0008 - 0.0052 (0.04% - 0.26%)	0.0006 - 0.0048 (0.003 - 0.024%)	0.0008 - 0.0059 (0.004 - 0.029%)	0.0001 - 0.0048 (0.001% - 0.024%)	0.0005 - 0.0048 (0.003% - 0.024%)
Sulphur	2.7 – 33.5 (0.9% - 11.1%)	95.3 - 170.5 (53.5% - 95.8%)	75.7 - 216.4 (42.5% - 122%)	22.5 - 268.5 (12.6% - 151%)	23.0 - 205.3 (12.9% - 115%)
Silica	0.66 – 2.53 (94.3% - 361%)	4.65 - 8.38 (930% - 1676%)	3.30 - 8.27 (660% - 1654%)	3.13 - 8.25 (626% - 1650%)	5.13 - 8.72 (1026% - 1744%)
Lead	nd	nd	nd	nd	nd
Zinc	0.051 - 0.082 (2.0% - 3.3%)	0.018 - 0.076 (0.09% - 0.36%)	0.019 - 0.067 (0.09% - 0.32%)	0.017 - 0.046 (0.08% - 0.22%)	0.018 - 0.369 (0.09% - 1.76%)
pH	8.0 - 11.0	7.6 - 11.2	8.7 - 11.2	8.3 - 11.0	8.2 - 11.3

Notes:
Concentration in mg/L unless otherwise specified.
Percentage of effluent concentration with respect to the AMD are shown in brackets ( ).
nd - readings were below the detection limit.
[1] Synthetic AMD-L for bentonite/CBFA packs.
[2] Synthetic AMD-H for 100% CBFA pack.

Figure 6.3.3a shows the evolution of calcium and sulphur concentrations in the effluent of the 100% CBFA column in terms of the ratio (C/Co) of effluent concentration (C) to AMD concentration (Co). A ratio below or above unity indicates an accumulation or depletion, respectively, of the element in the column. Sulphur accumulated in the column throughout the entire time that the column was permeated with AMD. Calcium underwent depletion during the first 5 nPV of AMD permeation, but later accumulated in the column. The concurrent accumulations of calcium and sulfur (as sulfate) in the column after 5 nPV was likely caused by the precipitation of gypsum and/or ettringite, and coincided with the beginning of the large drop in hydraulic conductivity (see Figures 6.3.1a and 6.3.1b).

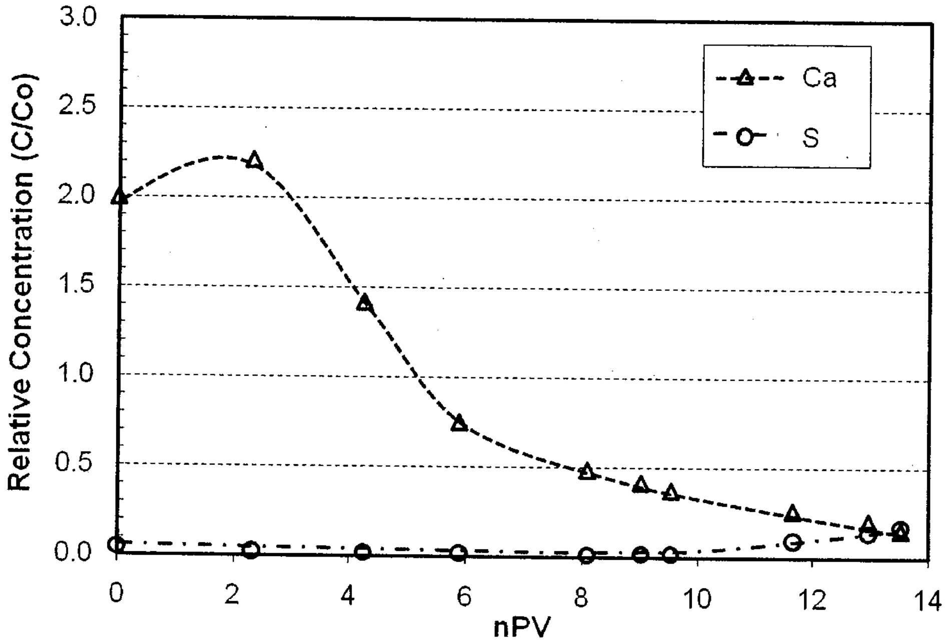

Figure 6.3.3a Evolution of the relative concentrations of calcium and sulphur in the effluent of the 100% CBFA column versus nPV of AMD permeation

Figure 6.3.3b shows the evolution of calcium and sulphur concentrations in the effluent of the 2.5% bentonite/CBFA mixture. Calcium was depleted from the column during the entire permeation with AMD ($C/C_0 > 1$), while the sulphur (as sulphate) accumulated much less than in the 100% CBFA column. These results suggest that gypsum and/or ettringite formation was minimal compared to the 100% CBFA column. Similar trends in the calcium and sulphur concentrations were observed with the other (5%, 7.5%, and 10%) bentonite/CBFA mixtures.

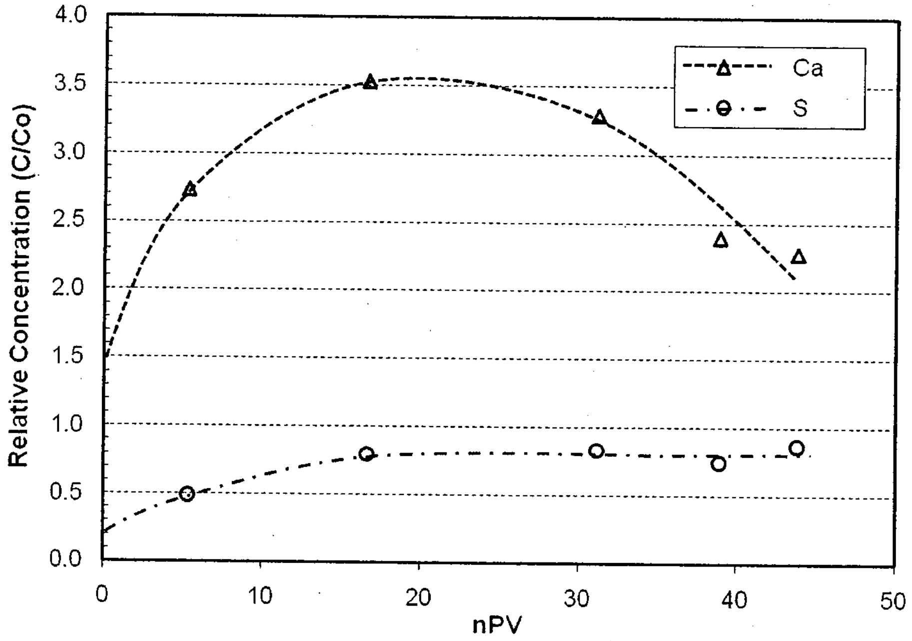

Figure 6.3.3b **Evolution of the relative concentrations of calcium and sulphur in the effluent of the 2.5% bentonite / 97.5% CBFA mixed column versus nPV of AMD permeation**

Dissolved aluminum (Figure 6.3.3c) was the only element that exceeded USEPA effluent guidelines (1 mg/L). The aluminum concentration in the effluent of the 100% CBFA column constantly exceeded the aluminum concentration in the AMD permeate ($C/C_0 > 1$), indicating that aluminum was released by the dissolution of Al-containing phases in the fly ash. By contrast, the 2.5% bentonite/AMD mixture released lower aluminum concentrations in its effluent ($C/C_0 < 1$ after 5 nPV). This reduction in aluminum dissolution was likely explained by coating of the fly ash particles with bentonite thereby preventing the Al-containing phases of the fly ash from disolving. Similar results were obtained with the other bentonite/CBFA mixtures. Aluminum concentrations in the effluent 20% bentonite layered column were also reduced compared to the 100% CBFA column.

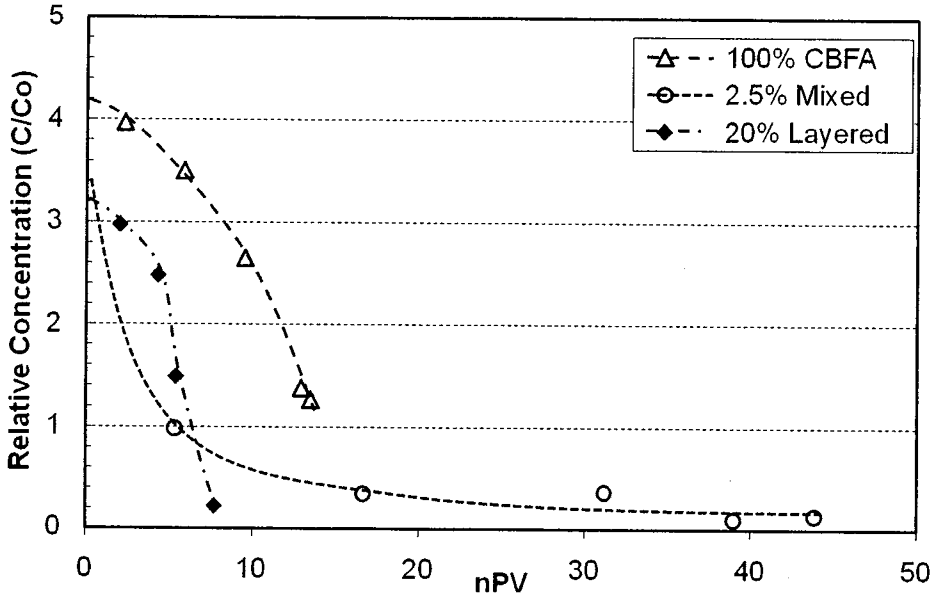

Figure 6.3.3c **Evolution of the relative concentration of aluminum in the effluent of the 100% CBFA, 2.5% bentonite / 97.5% CBFA mixed, and 20% bentonite / 80% CBFA layered columns versus nPV of AMD permeation**

6.3.4 Post-Testing Solids Analysis

Comparisons of X-Ray diffraction (XRD) patterns obtained from samples of CBFA before and after column testing (Figure 6.3.4a) reveal the formation of gypsum and ettringite during AMD permeation. Although not immediately apparent in Figure 6.3.4a (B), two distinct peaks for gypsum and quartz were present at 2Θ ~ 21° after AMD permeation. The quartz peak was almost unchanged in intensity after AMD permeation but the gypsum peak was much larger. Ettringite and gypsum were also identified by Yaheyis et al. (2007) on XRD patterns of coal fly ash permeated with AMD. The formation of ettringite from the reaction of calcium aluminates with calcium sulphate in the early stages of hydration was also reported by Shang et al. (2007) and Lu et al. (2008).

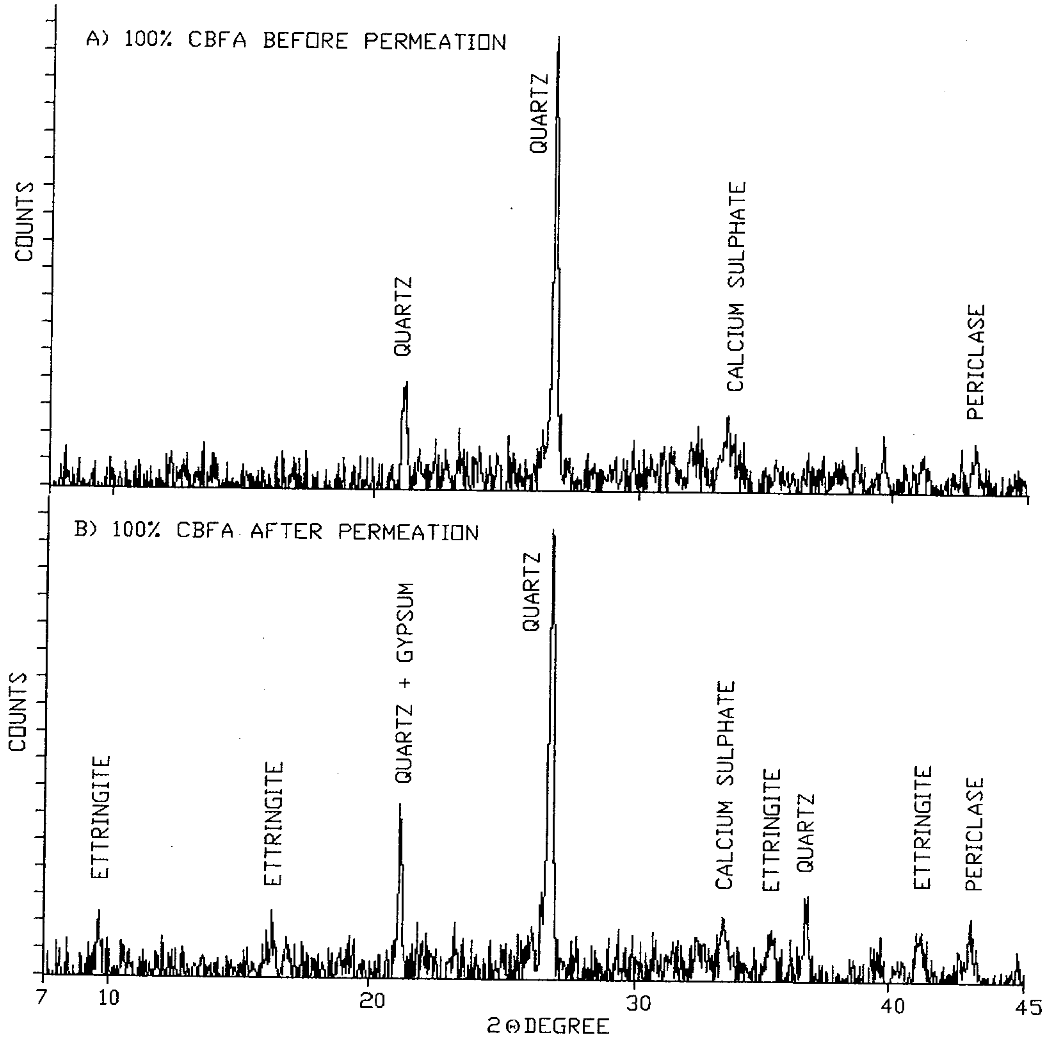

Figure 6.3.4a **Comparison of XRD patterns for 100% CBFA: A) before AMD permeation; B) after AMD permeation**

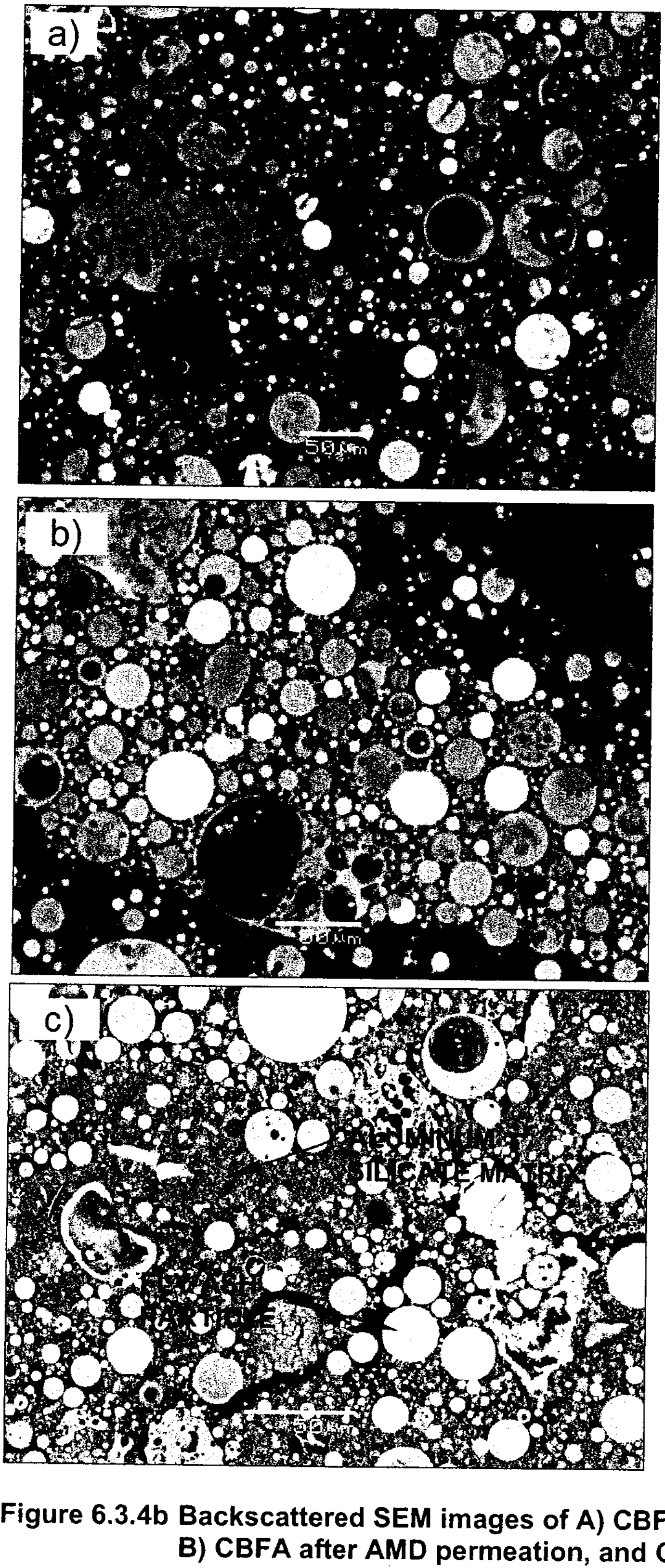

Figure 6.3.4b Backscattered SEM images of A) CBFA prior to AMD permeation, B) CBFA after AMD permeation, and C) 10% bentonite/CBFA mixture after AMD permeation

Scanning electron microscopy and energy dispersive X-ray analysis (SEM-EDX) were conducted on representative samples of CBFA and CBFA amended with 10% bentonite after permeation with AMD (Figure 6.3.4b). Samples were collected from the bottom of the column pack where the solids were in contact with fresh AMD. The backscattered electron image of CBFA before (Figure 6.3.4b (A)) and after (Figure 6.3.4b (B)) AMD permeation showed the conglomeration of fly ash particles after AMD permeation. This conglomeration suggests the formation of a cementious aluminum silicate matrix binding the particles together. The SEM-EDX analysis was inconclusive in determining the presence of gypsum and ettringite, due to their low concentration and possible dispersed formation. The backscattered electron image of the 10% bentonite/CBFA sample (Figure 6.3.4c (C)) showed an aluminum silicate matrix that physically encapsulated many of the fly ash particles.

6.4 CONCLUSIONS

Although pure CBFA was effective as a reactive barrier to treat most toxic metals in AMD, its initial hydraulic conductivity exceeded the maximum regulatory requirement of 1.0×10^{-7} cm/s. Amending CBFA with 10% bentonite maintained the hydraulic conductivity at or below 1.0×10^{-7} cm/s. Hydraulic conductivity is a function of grain size distribution and compactive effort, therefore the required percentage of bentonite is affected by the CBFA properties and the methods of construction.

Kinetic column tests containing pure CBFA and CBFA amended with bentonite, which simulated a low permeability barrier, were effective for increasing the pH and decreasing the dissolved concentrations of heavy metals in the study AMD. All effluent met mine effluent regulations for the regulated heavy metals, but did exceed the maximum regulatory pH for up to 60 nPV initially. While the high pH is an issue, the flow rates used to conduct the tests were higher than those expected for field applications. Slower flow rates would allow additional time for the precipitation of oxide and hydroxide minerals, thereby resulting in a decrease in pH. Further study is required to investigate the effects on the effluent pH at slower flow rates. In addition, study on the reaction of the effluent with the surrounding soil matrix is recommended.

Aluminum concentrations were elevated due to the dissolution of Al-containing phases in the CBFA. The addition of bentonite was effective in decreasing the mobilization of aluminum compared to pure CBFA. While the high aluminum concentration is also an issue, the flow rates used to conduct the tests were higher than those expected for field applications. Slower flow rates and the anticipated decrease in pH would also result in the precipitation of aluminum minerals. Further study is required to investigate the aluminum effluent concentrations at slower flow rates. In addition, study on the reaction of the aluminum concentration in the effluent with the surrounding soil matrix is recommended.

The collapse of the bentonite double layer in the bentonite / CBFA mixtures at the start of AMD permeation caused an increase in hydraulic conductivity and a consolidation of the mixtures. The installation of a layer of pure CBFA upstream of the bentonite/CBFA mixture maintained the bentonite double layer and thus largely prevented any increase in hydraulic conductivity and consolidation. Furthermore, precipitation of ettringite and gypsum by reaction of AMD with CBFA led to a progressive decrease in hydraulic conductivity with continued AMD permeation.

6.5 REFERENCES

American Society for Testing and Materials (ASTM) D422 – 63, 2007. Standard Test Method for Particle-Size Analysis of Soils. ASTM International, West Conshohocken, PA

American Society for Testing and Materials (ASTM) D854 – 06, 2006. Standard Test Methods for Specific Gravity of Soil Solids by Water Pycnometer. ASTM International, West Conshohocken, PA

American Society for Testing and Materials (ASTM) D4318 – 05, 2005. Standard Test Methods for Liquid Limit, Plastic Limit, and Plasticity Index of Soils. ASTM International, West Conshohocken, PA

British Columbia Ministry of Energy Mines and Petroleum Resources (BC-MEMPR) 1989. Draft acid rock drainage technical guide. *British Columbia Acid Mine Drainage Task Force,* Victoria, BC.

Canadian Council of Ministers of the Environment (CCME) 2007. Canadian Water Quality Guidelines for the Protection of Aquatic Life. Winnipeg. http://ceqg-rcqe.ccme.ca/download/ en/134/ (accessed April 2009)

Environment Canada Metal Mining Effluent Regulations (EC-MMER) 2003. Environment Canada Status report on water pollution prevention and control under the metal mining effluent regulations. Ottawa. http://www.ec.gc.ca/nopp/docs/rpt/waterpollution/mining2003/en/c2.cfm (accessed February 2009).

Health Canada 2008. Guidelines for Canadian drinking water quality. Federal-provincial-territorial committee on drinking water of the federal-provincial-territorial committee on health and the environment, Ottawa, May 2008.

Kashir, M. and Yanful, E. 2001. Hydraulic conductivity of bentonite permeated with acid mine drainage. *Canadian Geotechnical Journal,* 38: 1034-1048.

Kashir, M. and Yanful, E. 2000. Compatibility of slurry wall backfill soils with acid mine drainage. *Advances in Environmental Research,* 4: 251-268.

Lu, P., Li, Q., and Zhai, J. 2008. Mineralogical characterization and reaction path modeling of the pozzolanic reaction of fly ash-lime systems. *Journal of the American Ceramic Society,* 91: 955-964.

Perez-Lopez, R., Nieto, J. and & Ruiz de Almodovar, G. 2007. Utilization of fly ash to improve the quality of the acid mine drainage generated by oxidation of a sulphide-rich mining waste. *Chemiosphere,* 67: 1637-1646.

Shang, J., Wang, H., Kovac, V. and Fyfe, J. 2006. Site specific study on stabilization of acid-generating mine tailings using coal fly ash. *Journal of Materials in Civil Engineering,* March/April: 140-151.

Sheng, G., Li, Q., Zhai, J. and Li, F. 2007. Self-cementitious properties of fly ashes from CFBC boilers co-firing coal and high-sulphur petroleum coke. *Cement and Concrete Research,* 37: 871-876.

United States Environmental Protection Agency (USEPA), 1988. Design, construction and evaluation of clay liners for waste management facilities. 530/SW-86/007F.

United States Environmental Protection Agency (USEPA), 2003. Ore mining and dressing point source category. 40-CRF-440.

Wang, H., Shang, Kovac, V, and Ho, K. 2006. Utilization of Atikokan coal fly ash in acid rock drainage control from Musselwhite Mine tailings. *Canadian Geotechnical Journal,* 43: 229-243.

World Health Organization, Environmental Health Criteria 194. 1997, Aluminum, Geneva, http://www.inchem.org/documents/ehc/ehc/ehc194.htm#SubSectionNumber:9.2.2 (accessed February 2009)

Xenidis, A., Mylona, E. and Paspaliaris, I. 2002. Potential use of lignite fly ash for the control of acid generation from sulphidic wastes. *Waste Management,* 22: 631-641.

Yeheyis, M., Shang, J. and Yanful, E. 2007. Beneficial utilization of coal fly ash as acid mine drainage barrier. *In* Proceedings of the 60th Canadian Geotechnical Conference & 8th Joint CGS/IAH-CNC Groundwater Conference, Ottawa, Canada, October 2007: pp 1494-1499.

7.0 UTILIZATION OF COAL/BIOMASS FLY ASH AND GLACIAL TILL AS A FLOW-THROUGH REACTIVE BARRIER FOR THE TREATMENT OF ACID MINE DRAINAGE[3]

This study investigated the feasibility of using coal/biomass fly ash (CBFA) amended with glacial till soil as a reactive barrier to treat acid mine drainage (AMD) while minimizing any change in the groundwater flow regime. Various percentages (5%, 10%, 20%, and 33%) by mass of CBFA amended with glacial till soil were found to be effective in buffering the AMD pH from acidic (pH 2.8) to alkaline (pH > 7), with a minimal change in hydraulic conductivity. Leachate analysis conducted on 10% and 33% CBFA amended with glacial till soil showed that the addition of CBFA to soil was effective in treating AMD. Continued permeation of AMD through the columns showed reductions in the AMD heavy metal concentrations by up to three orders of magnitude.

7.1 INTRODUCTION

The disposal of sulfide-bearing mine tailings in surface facilities is a major environmental concern due to the mine tailings potential to produce acid mine drainage (AMD). AMD is formed from the oxidation of sulfide minerals in the presence of oxygen and water. Typically, AMD has a low pH, high acidity and elevated concentrations of heavy metals.

Control and treatment of AMD, particularly in decommissioned and inactive mine sites, are major environmental challenges. Often, these mine sites have ongoing AMD formation which impacts the adjacent terrestrial and aquatic ecosystems. With continued infiltration recharge,

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[3] A version of this chapter has been submitted to the 25th International Conference on Solid Waste Technology and Management, Philadelphia, PA, U.S.A. March, 2010.

AMD effluent may easily flow in the groundwater regime as well as adjacent streams and other water bodies down gradient from the disposal site.

Conventional active approaches to treatment involve the collection and treatment of AMD, which often require ongoing operation and maintenance. Passive approaches can provide cost effective insitu means to treat the AMD. These approaches include limestone drains and wetlands to treat surface runoff (Walton-Day 2003). Reactive barriers are also an effective passive technology for treating groundwater contamination associated with AMD (Blowes et al. 2003a). Installation methods include continuous trenching, excavation and backfill, and slurry trenching.

The use of coal fly ash (CFA), either by itself or amended with other materials (e.g. mine tailings and bentonite) for treating and/or containing AMD has been investigated in laboratory kinetic column tests (Xenidis et al. 2002, Shang et al. 2006, Wang et al. 2006, Yeheyis et al. 2007, Perez-Lopez et al. 2007). These studies showed that AMD permeated through various percentages of CFA can substantially increase its pH from acidic (pH < 3.8) to alkaline (pH > 7), and reduce its concentrations of heavy metals. A decrease in hydraulic conductivity was observed when higher percentages of CFA were used.

This study was conducted to investigate the potential of using CBFA amended with a glacial till soil in a flow-through reactive barrier to treat AMD. The reactive barrier application involves the construction of a continuous trench, down gradient of an AMD plume, to treat the AMD as it flows through the barrier. This application requires minimum disruption to the existing groundwater flow regime.

7.2 MATERIALS AND METHODS

7.2.1 Coal/Biomass Fly Ash

CBFA was obtained from the Atikokan Thermal Generating Station, in Atikokan, Ontario, during a 16 % (by mass) softwood biomass burn with 84% western Canadian lignite coal. Major CBFA constituents reported as oxides were silica (SiO_2), aluminum oxide (Al_2O_3), calcium oxide (CaO), sodium oxide (Na_2O), and iron oxide (Fe_2O_3). The CBFA contained heavy metals (zinc, lead, copper, nickel, and chromium) at concentrations of a few tens of grams per tonne (see Tables 3.3a and 3.3b). Acid based accounting (ABA) by the Modified Sobek Method (BC-MEMPR 1989) indicated a net neutralizing potential (NNP) of 298 tonnes $CaCO_3$/1000 tonnes.

Grain size analysis conducted in accordance with ASTM standard D422 (ASTM 2007), on three representative CBFA samples, showed that CBFA consists predominantly of particles in the silt size range (~84%) with trace to some sand (~10%) and trace of clay (~6%) size particles. The specific gravity measured by ASTM standard D854 (ASTM 2006) was 2.42. The liquid and plastic limits in accordance with ASTM standard D4318 (ASTM 2005) could not be measured on particles smaller than 75 μm, indicating that the CBFA is non plastic.

7.2.2 Glacial Till and CBFA/Glacial Till Mixtures

The soil used in this study was a glacial till obtained from a pit near a decommissioned base metals (zinc, lead, and copper) mine near the community of Buchans, Newfoundland and Labrador. Major soil constituents reported as oxides were silica (SiO_2), aluminum oxide (Al_2O_3), sodium oxide (Na_2O), iron oxide (Fe_2O_3), and potassium oxide (K_2O). The soil contained trace amounts of heavy metals (e.g. copper and zinc) at concentrations of a few tens of grams per tonne (see Tables 3.3a and 3.3b). Acid based accounting on this soil indicated a NNP of -1.2 with low calcium (0.8% as CO) and sulphur (0.006% as S) concentrations, resulting in low acid and neutralizing potentials (AP<0.2; NP=-1.2).

Four samples were prepared by mixing, 5%, 10%, 20%, and 33% CBFA (by mass) with glacial till soil. A control column was prepared using 100% glacial till soil. While the insitu gradation of this soil ranged from cobble to clay sizes, only particles passing 425 μm in diameter were used in the study. Soil particles retained on the 425 μm sieve composed approximately 50% of the insitu soil and were removed to allow for controlled testing due the small size of the test apparatus. Grain size analysis of the till passing 425 μm soil, shows the soil as predominantly sand (54.7%) and silt (37.4%) size particles with a trace of clay (7.9%). The specific gravity was 2.41. The liquid and plastic limits could not be measured on particles smaller than 75 μm, indicating that the soil is non plastic.

7.2.3 Synthetic Acid Mine Drainage

A synthetic AMD solution was prepared in the laboratory. Major constituents of this solution are presented in Table 5.2.3.

7.2.4 Kinetic Column Tests

Laboratory kinetic column tests were carried out to study the effects of AMD flow on the hydraulic conductivity and leachate composition for the glacial till soil and the soil amended with CBFA. These tests were conducted to simulate a flow-through reactive barrier for the treatment of AMD migration offsite. Percentages of amended CBFA investigated include 5%, 10%, 20%, and 33% by mass and a 100% glacial till soil control. These mixtures are identified on the figures as 5/95, 10/90, 20/80, 33/67, and GT, respectively. The physical and geotechnical properties of the kinetic column packs are summarized in Table 7.2.4.

Table 7.2.4 Properties of soil and CBFA amended soil kinetic column packs

Parameter	100% Soil	5% CBFA 95% Soil	10% CBFA 90% Soil	20% CBFA 80% Soil	33% CBFA 67% Soil
Initial Height (mm)	56	56	56	57	55
Final Height (mm)	56	56	56	57	55
Initial Dry Mass (g)	216.9	211.7	215.8	224.5	216.2
Final Dry Mass (g)	215.2	209.3	214.1	224.3	217
Initial Dry Density (g/cc)	1.90	1.86	1.89	1.94	1.93
Final Dry Density (g/cc)	1.89	1.84	1.88	1.93	1.94
Initial Porosity	0.210	0.229	0.215	0.197	0.200
Final Porosity	0.217	0.238	0.221	0.198	0.197
Initial Pore Volume (cc)	32.11	33.75	31.83	29.85	27.93
Final Pore Volume (cc)	32.77	34.66	32.47	29.92	27.60

The column was constructed of 50-mm ID clear acrylic tubing. Inert materials (nylon, vinyl, PVC, and stainless steel) were used as tubing, fasteners, collection containers, etc. Packs were thoroughly mixed in a bowl to ensure homogeneity. They were prepared just wet of optimum (~2%) by adding distilled water and placed in the column in three equal layers. This moisture content was used to achieve the minimal hydraulic conductivity while maximizing the density. Each layer was rodded 25 times with a 10 mm diameter plastic rod. After rodding, the sides of the column were tapped to remove air bubbles. Next, the top surface of the pack was trimmed and covered with a porous fabric and stone. Upon final assembly, the pack was confined by tightening a stainless steel bolt which applied a confining load to the top plate. The columns were then allowed to consolidate for a minimum of 16 hours, after which the bolts were again tightened. The bolts were periodically checked and tightened throughout the test to compensate for consolidation. A schematic of the column test setup is presented in Figure 7.2.4.

Samples were first permeated with distilled water to establish the reference hydraulic conductivity. Once equilibrium was achieved (10.6 to 20.5 progressive pore volumes), the permeate solution was switched to synthetic AMD. Column tests were then ran for a minimum of 120 nPV of AMD permeation.

During the tests, effluent samples were collected, weighed, time recorded, and the hydraulic head measured. The hydraulic gradient, hydraulic conductivity, flow rate, and progressive pore volumes were calculated. All leachate samples were analyzed for pH. Select leachate samples were acidified to a pH of 3 or lower with nitric acid and analyzed for elemental composition by inductively coupled plasma – atomic emission spectrometry (ICP-AES). Effluent metal concentrations were compared to EC-MMER (2003) and USEPA (2003) mine effluent regulations. Upon termination of the tests, the weight, height and moisture contents of the column packs were measured.

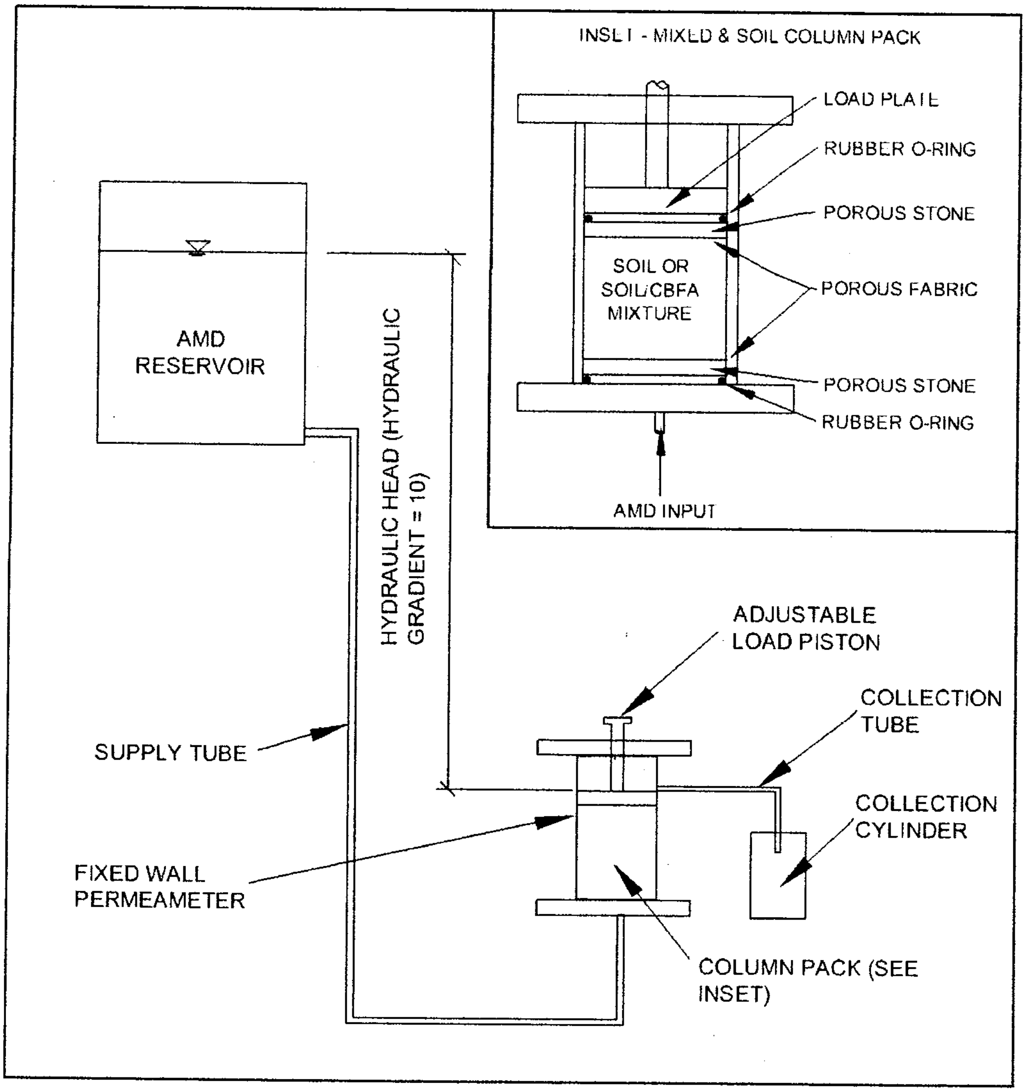

Figure 7.2.4 Schematic of CBFA / soil kinetic column test setup

7.3 RESULTS AND DISCUSSION

7.3.1 Hydraulic Conductivity

Hydraulic conductivity results for the four CBFA / glacial till mixture columns and the 100% glacial till control column are presented in Figure 7.3.1. The dashed vertical line represents the switch from distilled water to AMD permeate (distilled water on the left and AMD permeate on the right). The hydraulic conductivity when permeated with distilled water was 1.2×10^{-5} cm/s for the glacial till soil (GT); 6.8×10^{-6} cm/s for 5% CBFA / 95% GT (5/95); 6.6×10^{-6} cm/s for 10% CBFA / 90% GT (10/90); 9.4×10^{-6} cm/s for 20% CBFA / 80% GT (20/80); and, 4.8×10^{-6} cm/s) for 33% CBFA / 67% GT (33/67) mixtures.

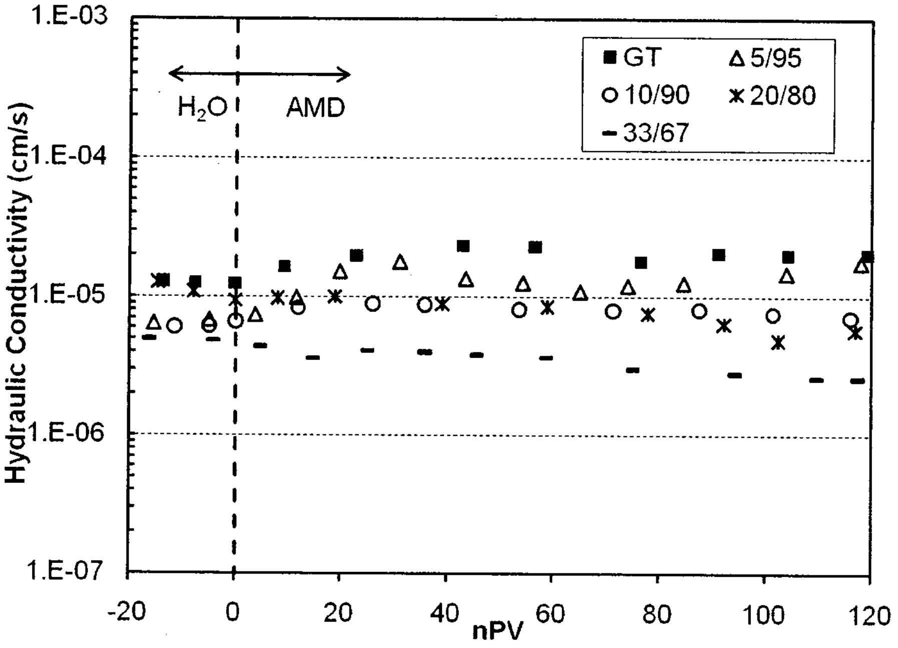

Figure 7.3.1 Hydraulic conductivity versus nPV (CBFA / soil)

As shown in Figure 7.3.1, slight increases in the hydraulic conductivity were observed in the glacial till control test and in the 5 and 10% CBFA amended columns upon switching the permeate from distilled water to AMD. The higher CBFA amended columns, 20% and 33% CBFA, observed a slight decrease in hydraulic conductivity with continued AMD permeation (9.4×10^{-6} cm/s to 4.9×10^{-6} cm/s and 4.8×10^{-6} cm/s to 2.6×10^{-6} cm/s, respectively). Similar trends in hydraulic conductivity when switching the permeate from distilled water to AMD was also observed by Wang et al. (2006), who investigated amending mine tailings with coal fly ash. The increase in hydraulic conductivity of the glacial till control and the lower CBFA percentages (5% and 10%) may be attributed to the dissolution of soluble minerals in both the GT and fly ash. The decrease in hydraulic conductivity at higher CBFA percentages (20% and 33%) may be attributed to the formation of secondary minerals and precipitation of heavy metals from the AMD. Minor observed fluctuations in the hydraulic conductivity may be due to the establishment of new flow paths through the column packs. It should be noted that screening of particles larger than 425 μm from the glacial till soil for this test would likely result in a hydraulic conductivity that is less than the unscreened glacial till soil.

7.3.2 Effluent pH

Effluent pH results are shown in Figure 7.3.2 for the mixed and control columns. The effluent pH of all packs were alkaline (pH > 7) when permeated with distilled water (start of test). The pH of the glacial till soil (control) leachate decreased to pH < 4.5 in less than 20 nPV of AMD permeation and was below the mine effluent regulatory guidelines pH of 6.0 within 15 nPV. After 20 nPV the pH remained constant with minor fluctuation between pH 4.5 and pH 4.0 for the remainder of the test.

A slight increase in pH (<0.3) was observed in the CBFA amended packs upon switching to AMD. This increased pH continued for approximately 20 nPV of AMD permeation, at which point the pH decreased in a linear fashion with continued AMD permeation. The rate of pH decrease, increased with a decreased CBFA content. Columns amended with CBFA were effective in meeting the mine effluent regulatory pH guidelines for more than 90 nPV of AMD permeate. The leachate pH from the 5% CBFA amended column decreased below pH 6 in 90 nPV to a minimum of pH 4.3 at termination of the test (120 nPV). The leachate pH from the 10% CBFA amended soil column decreased to pH 6 at the termination of the test in 120 nPV of AMD permeation.

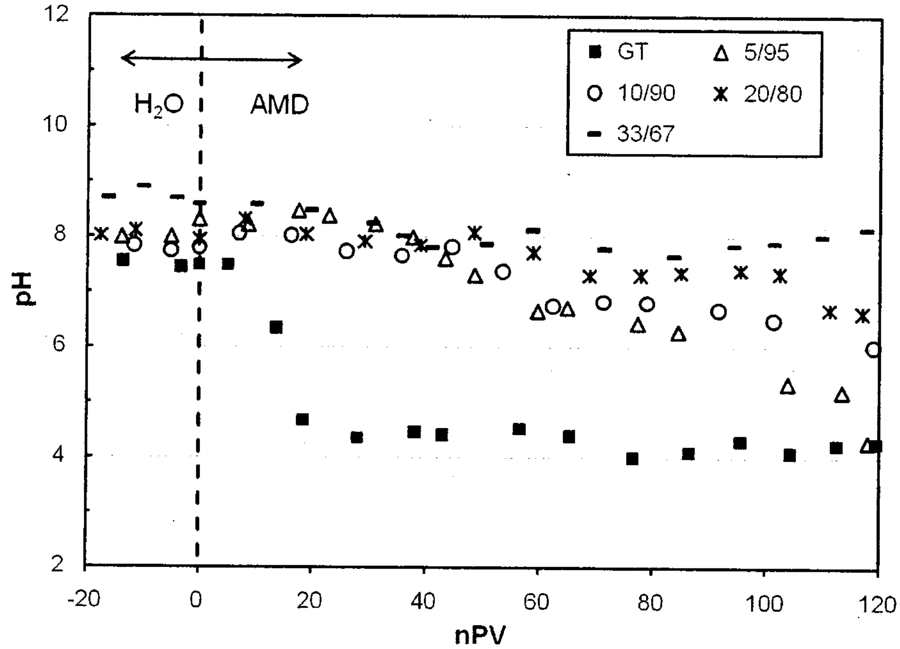

Figure 7.3.2 Effluent pH versus nPV (CBFA / soil)

7.3.3 Effluent Composition

The range of dissolved concentrations of major elements in the effluents of the glacial till control (100% soil), and the 10% and 33% CBFA amended packs are shown in Table 7.3.3. Also shown are the EC-MMER (2003) and USEPA (2003) mine effluent guidelines. Leachate from the 5% and 20% CBFA amended packs was not analyzed.

As seen in Table 7.3.3 the glacial till control column was ineffective in treating the AMD to the regulatory values for all elements with the exception of arsenic and lead. The elevated aluminum, copper, nickel, lead, and zinc (above the AMD concentration) may be due to the decrease in pH and dissolution of minerals containing these elements within the soil pack (see Tables 3.3a and 3.3b). On the other hand, the 10% and 33% CBFA amended columns were effective in reducing most of the heavy metal concentrations to the regulatory guidelines when the effluent pH was within the regulatory guidelines (i.e pH > 6).

Table 7.3.3 Effluent analyses of CBFA / soil kinetic column tests permeated with AMD

Element	EC-MMER Guideline	USEPA Guideline	100% Glacial Till (Control)	10% CBFA 90% Glacial Till	33% CBFA 67% Glacial Till
Aluminum	na	1	0.20 - 48.02 (5.8% - 480%)	0.18 - 1.48 (1.8% - 14.8%	3.07 - 36.47 (30.7% - 365%)
Arsenic	0.5	0.5	nd - 0.009 (nd - 94%)	nd - 0.023 (nd - 231%)	nd - 0.014 (nd - 138%)
Calcium	na	na	7.4 - 193.6 (4.3% - 113%)	86.2 - 250.6 (50.7% - 147%)	76.6 - 324.6 (45.0% - 191%)
Chromium	na	na	0.0009 - 0.0032 (18.0% - 64.0%)	nd - 0.0044 (nd - 88.0%)	0.0021 - 0.046 (42.0% - 920%)
Copper	0.3	0.15	0.029 - 1.744 (2.2% - 134%)	0.007 - 0.104 (0.52% - 8.0%)	0.002 - 0.097 (0.12% - 7.5%)
Iron	na	1	0.094 - 9.306 (0.23% - 23.3%)	0.009 - 0.586 (0.03% - 1.5%)	0.011 - 0.235 (0.03% - 0.59%)
Potassium	na	na	1.74 - 21.32 (12.0% - 147%)	0.54 - 17.35 (3.7% - 120%)	0.34 - 17.38 (2.3% - 120%)
Magnesium	na	na	1.0 - 23.6 (4.3% - 103%)	21.98 - 46.36 (95.6% - 202%)	0.62 - 24.04 (2.7% - 104%)
Sodium	na	na	2.2 - 33.3 (7.3% - 111%)	11.8 - 42.4 (39.3% - 141%)	6.7 - 45.5 (22.4% - 152%)
Nickel	0.5	0.1	0.011 - 2.80 (0.55% - 140%)	0.001 - 1.015 (0.05% - 50.8%)	0.001 - 0.005 (0.06% - 0.27%)
Sulphur	na	na	2.4 - 286.9 (0.80% - 95.6%)	99.8 - 292.7 (33.3% - 97.6%)	25.4 - 277.1 (8.5% - 92.4%)
Silica	na	na	6.24 - 12.97 (891% - 1853%)	0.93 - 9.93 (132% - 1418%)	0.08 - 0.35 (11.6% - 49.9%)
Lead	0.2	0.3	nd - 0.051 (nd - 127%)	nd (nd)	nd (nd)
Zinc	0.5	0.5	0.083 - 3.89 (3.3% - 156%)	0.017 - 0.713 (0.69% - 28.5%)	0.009 - 0.107 (0.35% - 4.3%)
pH	6.0 - 9.5	6.0 - 9.0	4.0 - 8.0	6.0 - 8.0	7.6 - 8.6

Notes: Concentration in mg/L unless otherwise specified.
Percentage of effluent concentration with respect to the AMD concentration are shown in brackets ( ).
Percentages greater than 100% indicate an increase over the AMD concentration.
nd - readings were below the minimum detection concentration of the icp standard.

Nickel was found to exceed the regulatory guidelines of 0.1 mg/L (USEPA 2003) and 0.5 mg/L (EC-MMER 2003) after approximately 50 and 80 nPV of AMD, respectively for the 10%

CBFA amended soil. Zinc was found to exceed the regulatory guideline of 0.5 mg/L (USEPA 2003, EC-MMER 2003) after approximately 90 nPV of AMD (pH ≤ 6.5) for the 10% CBFA amended soil. Aluminum, although not considered a heavy metal was found to exceed the USEPA (2003) mine effluent regulatory guideline for all three analyzed columns.

The evolution of dissolved aluminum in the effluent is shown in Figure 7.3.3a for the glacial till control and the 10% and 33% CBFA amended columns. The graph shows the relative concentration as a ratio (C/Co) of effluent concentration (C) to the AMD concentration (Co), where a value less than 1 indicates a reduction in concentration (precipitation) and above 1 indicates an increase in concentration (dissolution). Aluminum concentrations in the CBFA amended columns were observed to be dependent on CBFA concentration, with higher effluent concentrations encountered for higher CBFA percentages. Aluminum concentrations were also dependant to a lesser degree on pH, with higher concentrations at higher pH (compare Figure 7.3.3a and Figure 7.3.2). The permeation of AMD in the glacial till control column caused a decrease in the leachate pH (pH 4.0 to 4.5), resulting in dissolution of aluminum in the soil pack, which exceeded the effluent guideline (1 mg/L set by the USEPA 2003 – corresponding with C/Co = 0.1) after 10 nPV of AMD permeation.

The reduction in aluminum concentration in the leachate in comparison to the AMD (i.e. C/Co < 1), indicated that aluminum precipitated within the 10% CBFA pack throughout the test and after 20 nPV for the 33% CBFA pack. Aluminum concentrations further decreased with continued AMD permeation. Aluminum concentrations for the 10% CBFA decreased below the USEPA (2003) 1 mg/L regulation (C/Co > 0.1) in 20 nPV of AMD, while the 33% CBFA exceeded the regulation throughout the test (C/Co ≥ 0.1). The increased concentration when permeated through increased concentrations of CBFA is attributed to the dissolution of aluminum containing minerals in the fly ash.

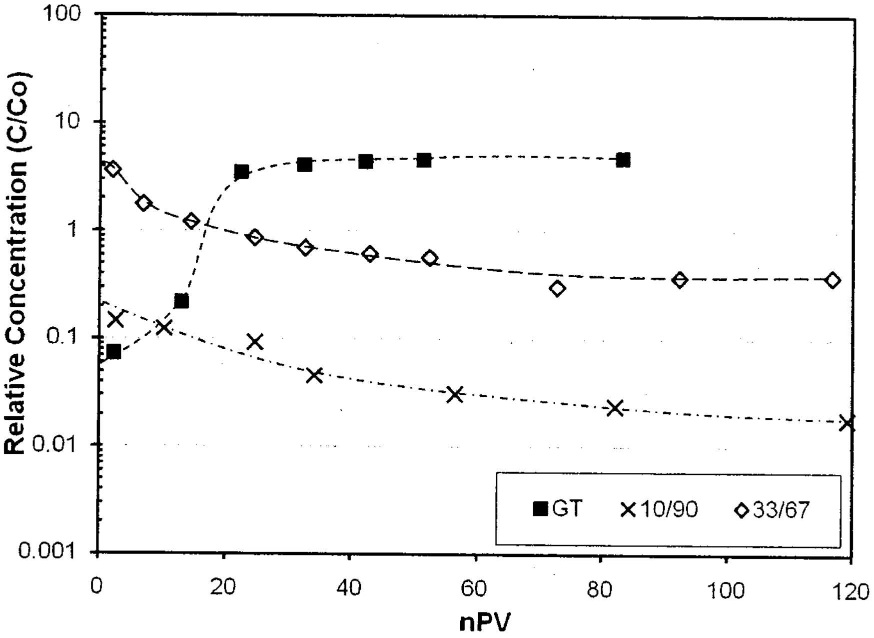

Figure 7.3.3a **Relative concentration of aluminum in the effluent of the 100% soil, 10% CBFA and 33% CBFA mixed columns versus nPV of AMD permeation**

Aluminum concentrations in the effluent of a column containing 100% fly ash permeated with distilled water (see Figure 4.3.4b) ranged from 10 to 50 mg/L (corresponding with C/Co = 1 to 5) for > 80 nPV. Although aluminum is not included in current mine effluent guidelines, its toxicity to fish and other aquatic organisms at levels as low as 5 µg/L (CCME 2007) and in a range of pH values from acidic to alkaline seems well established (WHO 1997).

Two heavy metals, nickel and zinc, were of interest because they had exceeded the regulatory guidelines for the glacial till control and 10% CBFA amended packs. Figure 7.3.3b and Figure 7.3.3c show the evolution of nickel and zinc respectively within the glacial till control, 10% CBFA and 33% CBFA amended packs.

Dissolved nickel was observed to be dependent on pH and CBFA concentrations (compare Figure 7.3.3b and Figure 7.3.2). A decrease in pH (pH < 4.5) in the glacial till soil control column caused 100% flow through of the AMD nickel concentration within 15 nPV of AMD permeation. Effluent concentrations for the soil control exceeded the regulatory guidelines (0.1 mg/L (C/Co = 0.05) set by the USEPA (2003) and 0.5 mg/L (C/Co = 0.25) set by EC-MMER (2003) after 5 nPV and 10 nPV of AMD permeation, respectively.

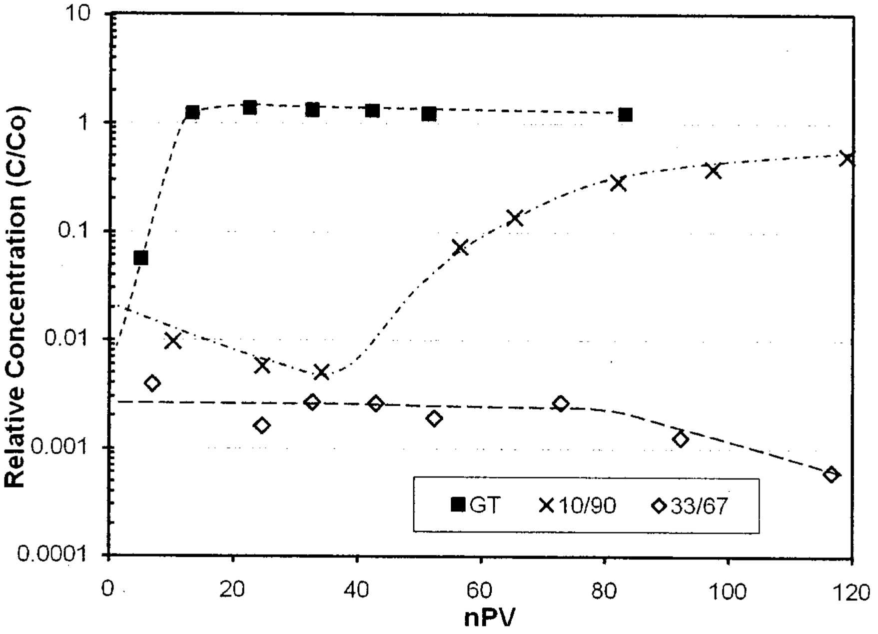

Figure 7.3.3b Relative concentration of nickel in the effluent of the 100% soil (GT), 10% CBFA / 90% soil mixed (10/90), and 33% CBFA / 67% soil mixed columns (33/67)

The reduction in nickel concentration in the leachate in comparison to the AMD (C/Co < 1) indicated that nickel precipitated within the CBFA amended packs throughout the test for both the 10% and 33% CBFA amended packs. Effluent concentrations for the 10% CBFA amended pack did exceed the regulations set by USEPA (2003) and EC-MMER (2003) in approximately 50 nPV and 80 nPV, respectively. The 33% CBFA amended pack was below the regulations throughout the test. The increase in concentration for the 10% CBFA amended pack is attributed to the decrease in leachate pH below pH 7.0 (compare Figure 7.3.3b and Figure 7.3.2).

Dissolved zinc was also observed to be dependent on pH and CBFA concentrations (compare Figure 7.3.3c and Figure 7.3.2). A decrease in pH (pH < 4.5) in the control glacial till soil column caused 100% flow through of the zinc in the AMD, within 15 nPV of AMD permeation. Afterwards the leachate zinc concentration exceeded the AMD concentration (i.e. Co/C > 1) by approximately 50% (Co/C = 1.5). This increase is attributed to dissolution of zinc minerals in the soil pack (see Tables 3.3a and 3.3b). Effluent concentrations for the soil control exceeded the regulatory guidelines of 0.5 mg/L (corresponding to C/Co = 0.2) set by both the USEPA (2003) and Environment Canada (2003) after 5 nPV.

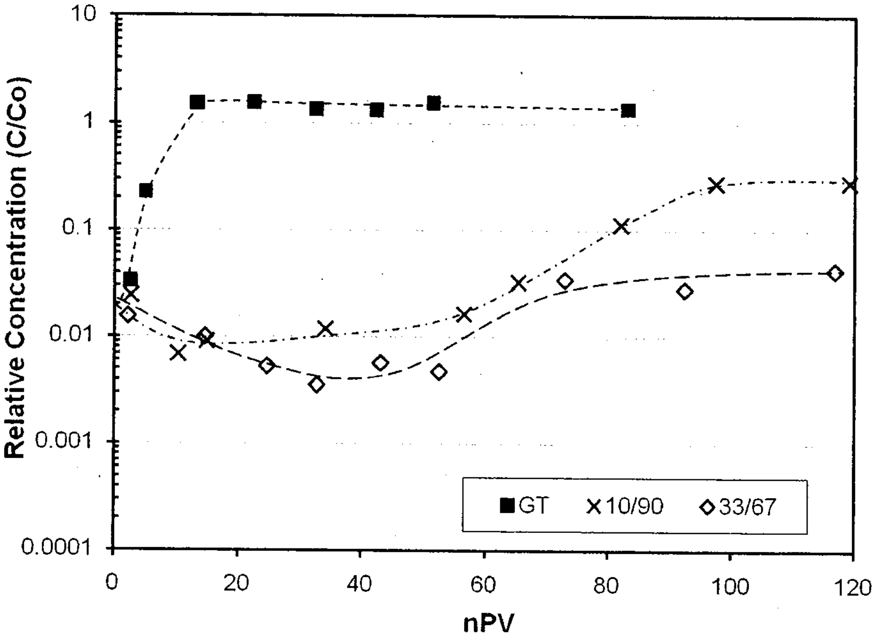

Figure 7.3.3c Relative concentration of zinc in the effluent of the 100% soil (GT), 10% CBFA / 90% soil mixed (10/90), and 33% CBFA / 67% soil mixed columns (33/67)

As seen in Figure 7.3.3c, a reduction in zinc concentration in the leachate in comparison to the AMD (i.e C/Co < 1) occurred. This indicates that zinc precipitated throughout the test for both the 10% and 33% CBFA amended packs. Zinc concentrations for the 10% CBFA amended pack exceeded the limits set by both USEPA (2003) and EC-MMER (2003) regulations after 90 nPV of AMD permeation. The concentration in the 33% CBFA was below the limits set by the regulators throughout the test. The increase in concentration for the 10% and 33% CBFA packs after 50 nPV are attributed to the dissolution of zinc minerals within the packs from the continued permeation of AMD.

7.3.4 Applications of Findings

Kinetic column test show that amending glacial till soil with 10% and 33% (by mass) CBFA is effective in buffering pH and reducing the concentrations of most of the heavy metals found in AMD while causing little change in hydraulic conductivity. These findings show CBFA amended soil to have a potential as a flow-through reactive barrier to treat AMD migration offsite.

The experimental setup simulated a flow-through reactive barrier installed in a trench or cavity down gradient of a reactive mine tailings spoil (see Figure 7.3.4). This reactive barrier would intercept and passively treat plumes of AMD contaminated groundwater, prior to its discharge into the environment. This application requires that the barrier not affect the surrounding groundwater flow regimes. A similar hydraulic conductivity to the surrounding soil and reactive mine tailings is required, along with a minimal change in hydraulic conductivity with continued AMD permeation. This application can be used in combination with the other AMD control and treatment applications, such as an alkaline recharge and capping of the mine tailings spoil, to further treat and control AMD.

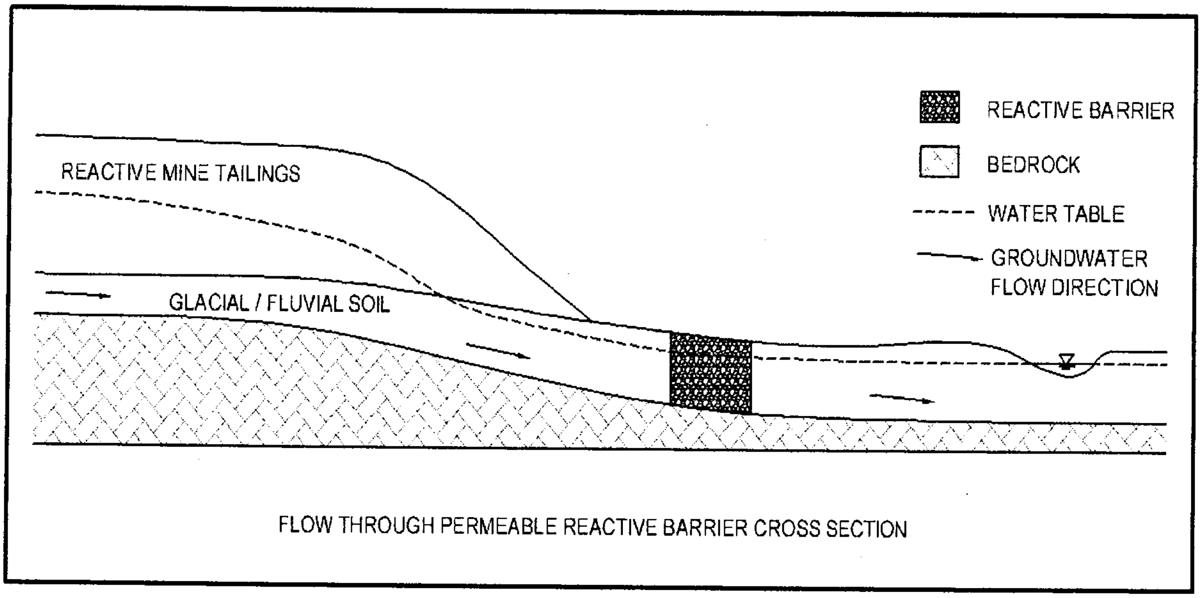

Figure 7.3.4 Flow-through reactive barrier application

7.4 CONCLUSIONS

Kinetic column test showed that amending glacial till soil with 10% and 33% CBFA was effective in increasing the pH and decreasing the dissolved concentrations of most heavy metals in AMD effluent to meet mine effluent regulations. While leachate samples from the 5% and 20% CBFA amended glacial till packs were not analyzed, similar findings are expected. The 5% CBFA amended glacial till leachate pH decreased below the mine effluent regulations pH of 6 in 90 nPV. The nickel and zinc concentrations in the leachate effluent of the 10% CBFA amended glacial till soil exceeded the regulatory guidelines after 50 nPV and 90 nPV respectively. Therefore the lower concentration of CBFA (10%) had limited treatment potential (only effective up to 50 nPV of AMD), while the higher concentration (33%) was effective for the duration of the test (120 nPV of AMD).

Aluminum concentrations, although not considered a heavy metal, did exceed the USEPA

(2003) regulatory value when higher concentrations of CBFA were used. While aluminum exceeded the regulations and zinc and nickel exceeded upon depletion of the pH buffering potential in the lower CBFA content packs. Both the 10% CBFA and 33% CBFA amended glacial till soil tests did show an overall reduction in heavy metal concentrations in the effluent versus the AMD concentration (i.e C/Co < 1).

While other studies have shown substantial reductions in hydraulic conductivity, due to the reaction between AMD and coal fly ash; no substantial changes where observed in this study. This feature is advantageous as a flow-through reactive barrier, due to the groundwater flow regime remaining unaltered during the life of the barrier. In addition, unlike the amending of CBFA with mine tailings, the leachate did not exceed the regulatory USEPA (2003) and EC-MMER (2003) upper pH values (9 and 9.5 respectively).

7.5 REFERENCES

American Society for Testing and Materials (ASTM) D422 – 63, 2007. Standard Test Method for Particle-Size Analysis of Soils. ASTM International, West Conshohocken, PA

American Society for Testing and Materials (ASTM) D854 – 06, 2006. Standard Test Methods for Specific Gravity of Soil Solids by Water Pycnometer. ASTM International, West Conshohocken, PA

American Society for Testing and Materials (ASTM) D4318 – 05, 2005. Standard Test Methods for Liquid Limit, Plastic Limit, and Plasticity Index of Soils. ASTM International, West Conshohocken, PA

British Columbia Ministry of Energy Mines and Petroleum Resources (BC-MEMPR) 1989. Draft acid rock drainage technical guide. *British Columbia Acid Mine Drainage Task Force,* Victoria, BC.

Blowes, D., Bain, J., Smyth, D., and Ptacek, C. 2003a. Treatment of mine drainage using permeable reactive materials. *Environmental Aspects of Mine Wastes, Volume 31 (Chapter 17):* Mineralogical Association of Canada, Vancouver, BC.

Blowes, D., Ptacek, C., and Jurjovec, J., 2003b. Mill tailings: hydrogeology and geochemistry. *Environmental Aspects of Mine Wastes, Volume 31 (Chapter 5)*: Mineralogical Association of Canada, Vancouver, BC.

Canadian Council of Ministers of the Environment (CCME) 2007. Canadian Water Quality Guidelines for the Protection of Aquatic Life. Winnipeg. http://ceqg-rcqe.ccme.ca /download/en/134/ (accessed April 2009)

Environment Canada Metal Mining Effluent Regulations (EC-MMER) 2003. Environment Canada Status report on water pollution prevention and control under the metal mining effluent regulations. Ottawa. http://www.ec.gc.ca/nopp/docs/rpt/waterpollution/mining2003 /en/c2.cfm (accessed February 2009).

Lu, P., Li, Q., and Zhai, J. 2008. Mineralogical characterization and reaction path modeling of the pozzolanic reaction of fly ash-lime systems. *Journal of the American Ceramic Society,* 91: 955-964.

Perez-Lopez, R., Nieto, J. and & Ruiz de Almodovar, G. 2007. Utilization of fly ash to improve the quality of the acid mine drainage generated by oxidation of a sulphide-rich mining waste. *Chemiosphere,* 67: 1637-1646.

Shang, J., Wang, H., Kovac, V. and Fyfe, J. 2006. Site specific study on stabilization of acid-generating mine tailings using coal fly ash. *Journal of Materials in Civil Engineering,* March/April: 140-151.

Sheng, G., Li, Q., Zhai, J. and Li, F. 2007. Self-cementitious properties of fly ahes from CFBC boilers co-firing coal and high-sulphur petroleum coke. *Cement and Concrete Research,* 37: 871-876.

United States Environmental Protection Agency (USEPA) 1988. Design, construction and evaluation of clay liners for waste management facilities. 530/SW-86/007F.

United States Environmental Protection Agency (USEPA) 2003. Ore mining and dressing point source category. 40-CRF-440.

Walton-Day, K. 2003. Passive and active treatment of mine drainage. *Environmental Aspects of Mine Wastes, Volume 31 (Chapter 16)*: Mineralogical Association of Canada, Vancouver, BC.

Wang, H., Shang, Kovac, V, and Ho, K. 2006, Utilization of Atikokan coal fly ash in acid rock drainage control from Musselwhite Mine tailings. *Canadian Geotechnical Journal,* 43: 229-243.

World Health Organization (WHO) 1997. Environmental Health Criteria 194. Aluminum, Geneva, http://www.inchem.org/documents/ehc/ehc/ehc194.htm#SubSectionNumber:9.2.2 (accessed February 2009)

Xenidis, A., Mylona, E. and Paspaliaris, I. 2002. Potential use of lignite fly ash for the control of acid generation from sulphidic wastes. *Waste Management,* 22: 631-641.

Yeheyis, M., Shang, J. and Yanful, E. 2007. Beneficial utilization of coal fly ash as acid mine drainage barrier. *In* Proceedings of the 60th Canadian Geotechnical Conference & 8th Joint CGS/IAH-CNC Groundwater Conference, Ottawa, Canada, October 2007: pp 1494-1499.

8.0 SUMMARY, CONCLUSIONS AND RECOMENDATIONS

This thesis presented an experimental study on the utilization of coal/biomass fly ash (CBFA) to control and treat acid mine drainage (AMD) for applications in existing and abandoned mine sites and tailing disposal sites. Based on material characterization, kinetic column tests, and leachate analysis, the addition of CBFA blended with reactive mine tailings, bentonite and glacial till soil, were found to be effective in treating AMD. In some applications the addition of CBFA was found to be effective in controlling the seepage of AMD and to reduce its subsequent formation.

The preliminary conclusions of the four case studies and their associated permeation tests include:

- When permeated with distilled water, reactive mine tailings amended with CBFA and CBFA alone had a minimal change in hydraulic conductivity while being effective in producing an alkaline leachate.

- When permeated with AMD, reactive mine tailings amended with CBFA and CBFA alone had varying degrees of reduction in hydraulic conductivity (from negligible to 3 orders of decrease), while being effective in producing an alkaline leachate with substantial reductions in the AMD heavy metal concentrations.

- When permeated with AMD, CBFA amended with bentonite was effective in reducing the hydraulic conductivity to governing regulations, while being effective in producing an alkaline leachate with substantial reductions in the AMD heavy metal concentrations.

- When permeated with AMD, glacial till soil amended with CBFA had a minimal change in hydraulic conductivity, while being effective in producing an alkaline leachate with substantial reductions in the AMD heavy metal concentrations.

Other conclusions from the study include:

- The addition of 60% CBFA to mine tailings was required to offset the acid generating potential of the mine tailings, in accordance with acid based accounting tests.
- The hydraulic conductivity of the CBFA/mine tailings mixtures permeated with AMD decreased with an increased ratio of CBFA.
- Increased pH buffering was observed with an increase in the CBFA content, which resulted in a reduction in heavy metal concentrations.
- An increase in the aluminium concentration was observed with an increase in the CBFA content and with increased pH.
- A minimal change in hydraulic conductivity is advantageous for the application as a flow through reactive barrier to treat AMD, while substantial reductions in hydraulic conductivity is advantageous for the application as a low permeability barrier to contain AMD.

- Permeation of AMD through bentonite and bentonite amended CBFA resulted in the collapse of the bentonite double layer, which resulted in an increase in the hydraulic conductivity and consolidation of the bentonite/CBFA matrix.

- Layering of bentonite amended CBFA with a lower (first contact) layer of CBFA reduced the effect of collapse of bentonite double layer and showed no increase in hydraulic conductivity or consolidation when subjected to AMD permeation.

Further research is recommended to:

- Study the effects on the hydraulic conductivity, leachate pH and chemistry by reducing the AMD flow rate through the various CBFA mixtures with mine tailings, bentonite, and soil.

- Study the effects of dissolved aluminum concentrations and high pH within the underlying mine tailings when used as a cap and within the surrounding soil when used in other applications.

- Study effective methods of reducing the concentration of aluminium in the effluent and/or prevent the leaching of aluminium from the CBFA.

- Investigate the application of utilizing CBFA and bentonite in conjunction with other materials, particularly low sulphur mine tailings and native soil, for applications as a low permeability barrier to contain AMD.

- Perform field pilot tests on the various applications to determine their applicability when subjected to field conditions.