# Utilization of coal/biomass fly ash and bentonite as a low permeability barrier for the containment of acid-generating mine tailings



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# ABSTRACT

This study investigates 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  $1 \times 10^{-7}$  cm/s. Mixing 10% by mass bentonite with CBFA, however, decreased the hydraulic conductivity to  $1 \times 10^{-7}$  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 preventing the collapse of the bentonite/CBFA barriers met the regulatory requirements for chemical parameters, except for aluminum which was leached from the CBFA.

# RÉSUMÉ

Cette étude examine la faisabilité de l'utilisation des cendres volantes provenant de la combustion de charbon et de biomasse (CVCB) mélangées avec divers pourcentages de bentonite comme barrière de faible perméabilité pour contenir des résidus miniers réactifs et traiter le drainage minier acide (DMA). Les CVCB utilisées seules n'ont pas permis de satisfaire au critère de conductivité hydraulique de moins de 1 x 10<sup>-7</sup> cm/s. Par contre, le mélange de 10% de bentonite en masse avec les CVCB a réduit la conductivité hydraulique à 1 x 10<sup>-7</sup> cm/s ou moins durant toute la durée d'infiltration par l'eau et le DMA. L'installation d'une couche de pures CVCB en amont du mélange bentonite/CVCB a produit une réduction supplémentaire et progressive de la conductivité hydraulique en empêchant l'effondrement de la double couche de la bentonite et en favorisant la précipitation de gypse et d'ettringite dans la couche de CVCB. Les effluents de toutes les barrières de bentonite/CVCB testées ont satisfait aux règlements des paramètres chimiques, à l'exception de l'aluminium qui est lixivié dans les CVCB.

# 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.

Control and treatment of AMD, particularly in decommissioned and inactive minesites, are major environmental challenges. Often, these minesites 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 affect the project feasibility. The combined utilization of fly ash and bentonite may provide a cost effective, low-permeability material for contain 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 1x10<sup>-7</sup> 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 blended with bentonite 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 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 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 coal/biomass fly ash (CBFA) and CBFA/bentonite mixtures as a low permeability barrier to contain acidgenerating 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.

## 2 MATERIALS AND METHODS

#### 2.1 Coal/Biomass Fly Ash

CBFA was obtained from the Atikokan Thermal Generating Station, in Atikokan, Ontario, during a 16 percent, by mass, wood biomass burn with lignite coal. Major CBFA constituents reported as oxides are silica  $(SiO_2 - 45.2\%)$ , aluminum oxide  $(Al_2O_3 - 21.5\%)$ , calcium oxide (CaO - 13.6%), sodium oxide  $(Na_2O - 7.3\%)$ , and iron oxide  $(Fe_2O_3 - 4.0\%)$ . Acid based accounting (ABA) by the Modified Sobek Method (BC Ministry of Energy, Mines and Petroleum Resources, 1989) indicates a net neutralizing potential (NNP) of 298 kg CaCO<sub>3</sub>/1000 kg.

Grain size analysis in accordance with American Society of Testing Materials (ASTM) D422 on three representative CBFA samples show that it consists predominately 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 D854 is 2.42. The liquid and plastic limits (ASTM D4318) could not be measured on particles smaller than 75  $\mu$ m, indicating that the CBFA is non plastic.

## 2.2 Bentonite/CBFA Mixtures

Bentonite used in this study was laboratory grade sodium montmorillonite from Wyoming, USA. Major constituents reported as oxides are SiO<sub>2</sub> (~60%) Al<sub>2</sub>O<sub>3</sub> (~16%), Fe<sub>2</sub>O<sub>3</sub> (~3%), Na<sub>2</sub>O (~2.5%), and CaO (~2%).

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 shows that the bentonite/CBFA mixtures predominately 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 1).

#### 2.3 Synthetic Acid Mine Drainage

Two synthetic AMD solutions, AMD-L and AMD-H were prepared in the laboratory with chemical compositions typical of AMD encountered at mine sites. 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 3.

#### 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 mixed kinetic column packs are summarized in Table 1.

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 2.

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 1. 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 resealable 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 leveled 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.

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 Height (mm)	39	37	40	39	40
Final Height (mm)	39	36	37	32	31
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
Liquid Limit	-	27	46	57	105
Plastic Limit	-	20	22	30	37

Table 1. Properties of control and mixed kinetic column packs

Table 2. Properties of layered kinetic column packs

Parameter	Top layer: 10% Bentonite/ 90% CBFA	Top layer: 20% Bentonite/ 80% CBFA	
	Bottom layer: 100% CBFA	Bottom layer: 100% CBFA	
Initial Height (mm)	40	39	
Final Height (mm)	40	39	
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	

Samples were first permeated with distilled water to determine the reference hydraulic conductivity. Once equilibrium was achieved after 8.4 to 12.7 nPV, the permeate was switched to AMD. The concept of progressive pore volumes (nPV), which is the total of quantity of leachate flowing through the sample divided by the initial pore volume of the sample, allows comparing results from test columns having different initial pore volumes. 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 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 run for a minimum of 80 nPV, or terminated upon reaching a hydraulic conductivity of 10<sup>-7</sup> cm/s or less (USEPA, 1988). Effluent metal concentrations were compared to the Environment Canada metal mining effluent regulations (EC-MMER, 2003) and the United States Environmental Protection Agency (USEPA, 2003) mine effluent regulations.



Figure 1. Schematic of test setup

### 3 Results and Discussion

### 3.1 Hydraulic Conductivity

Hydraulic conductivity results for the four mixed bentonite/CBFA and the 100% CBFA columns are presented in Figure 2. The dashed vertical line represents the switch from distilled water to AMD permeate. Hydraulic conductivities to distilled water were  $6.3 \times 10^{-6}$  cm/s for the 100% CBFA column. Mixing bentonite with CBFA decreased the hydraulic conductivity by one to two orders of magnitude depending on the amount of added bentonite. The hydraulic conductivities to distilled water

were  $4.5 \times 10^{-7}$  cm/s,  $7.4 \times 10^{-7}$  cm/s,  $1.4 \times 10^{-7}$  cm/s, and  $7.5 \times 10^{-8}$  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<sup>-8</sup> cm/s after 10 nPV.



Figure 2. Hydraulic conductivity versus nPV of permeate (CBFA and bentonite/CBFA mixtures)

Continued permeation of AMD did not affect the hydraulic conductivity of bentonite/CBFA mixtures, with the exception of the 2.5% mixture whose hydraulic conductivity decreased rapidly after 30 nPV and reached 1.2x10<sup>-8</sup> cm/s at termination of the test (~45 nPV). Only the column containing 10% bentonite provided a hydraulic conductivity consistently  $\leq 1.0 \times 10^{-7}$ cm/s during permeation with distilled water or AMD. The lack of effect of AMD on the hydraulic conductivity of columns containing more than 2.5% bentonite may be attributed to coating of the fly ash particles with bentonite, which reduces their ability to react with AMD to produce secondary minerals. In addition, the increased void ratio of bentonite/CBFA columns (compared with 100% CBFA) reduces the potential of secondary minerals and metal precipitates to clog the voids.

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 3 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  $1.0 \times 10^{-7}$  cm/s throughout the test. Increasing the bentonite percent to 20% in the mixed layer decreased the hydraulic conductivity to distilled water to approximately  $1.0 \times 10^{-7}$  cm/s.



Figure 3. Hydraulic conductivity versus nPV of permeate (CBFA and layered bentonite/CBFA)

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 2). 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.

### 3.2 Effluent pH

Effluent pH results are shown in Figure 4 and 5 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 2 with Figure 4, and Figure 3 with Figure 5). 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 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.



Figure 4. Effluent pH versus nPV of permeate (CBFA and bentonite/CBFA mixtures)



Figure 5. Effluent pH versus nPV (CBFA and layered bentonite/CBFA)

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 tests. This decrease in pH is attributed to depletion of the buffering capacity of fly ash particles not coated with bentonite and to the subsequent coating of these fly ash particles with precipitates such as metal hydroxides.

#### 3.3 Effluent Composition

Table 3 shows the ranges of dissolved concentrations of major elements in the column effluents and compares them with concentrations in AMD, Environment Canada metal mining effluent regulations (EC-MMER, 2003) and the United States Environmental Protection Agency (USEPA, 2003) mine effluent regulations. All column effluents met the regulations, except that for aluminum, Although aluminum is not included in current Canadian mine effluent guidelines, its toxicity to fish and other

aquatic organisms at levels as low as  $25 \mu g/L$  and in a range of pH values from acidic to alkaline seems well established (World Health Organization, 1997).

Figure 6 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 (CaSO<sub>4</sub>·2H<sub>2</sub>O) and/or ettringite ((CaO)<sub>6</sub>(Al<sub>2</sub>O<sub>3</sub>)  $(SO_3)_3 \cdot 32 H_2O)$ , and coincided with the beginning of the large drop in hydraulic conductivity (see Figures 2 and 3).



Figure 6. Evolution of the relative concentrations of calcium and sulphur in the effluent of the 100% CBFA column



Figure 7. Evolution of the relative concentrations of calcium and sulphur in the effluent of the 2.5% bentonite / 97.5% CBFA mixed column

Figure 7 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 precipitation of gypsum and/or ettringite was hindered by the presence of bentonite. Similar trends in the calcium and sulphur concentrations were observed with the other (5%, 7.5%, and 10%) bentonite/CBFA mixtures.

Dissolved aluminum (Figure 8) 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<sub>0</sub> < 1 after 5 nPV). This reduction in aluminum dissolution was likely explained by coating of the fly ash particles with bentonite. 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, likely because fly ash particles were coated with bentonite in the top layer of the column.

Table 3. Summary of effluent analyses during the kinetic column tests while permeated with AMD

Element	AMD-H <sup>1</sup>	EC-MMER Guideline	USEPA Guideline	2.5% Bentonite (Mixed)	5% Bentonite (Mixed)	7.5% Bentonite (Mixed)	10% Bentonite (Mixed)
Aluminum	5.6	na	1	0.53 - 26.03	1.21 - 11.52	0.57 - 18.53	0.62 - 33.20
Arsenic	0.001	0.5	0.5	0.007 - 0.012	0.004 - 0.027	0.004 - 0.021	0.004 - 0.033
Calcium	83.8	na	na	189.1 - 293.2	201.0 - 323.0	122.9 - 368.0	20.4 - 276.8
Chromium	0.005	na	na	0.065 - 0.140	0.045 - 0.096	0.042 - 0.113	0.017 - 0.128
Copper	12.9	0.3	0.15	0.0030 - 0.0141	0.0013 - 0.0051	0.0016 - 0.0902	0.0026 - 0.0159
Iron	55	na	1	0.019 - 0.168	0.027 - 0.070	0.008 - 0.028	0.019 - 0.062
Potassium	5.5	na	na	0.88 - 28.00	1.54 - 8.99	1.91 - 10.42	2.25 - 7.59
Magnesium	17.8	na	na	0.28 - 1.59	0.05 - 0.11	0.004 - 0.14	0.001 - 0.11
Sodium	26.5	na	na	42.2 - 143.3	37.4 - 62.2	50.6 - 81.3	52.1 - 286.4
Nickel	20.1	0.5	0.1	0.0006 - 0.0048	0.0008 - 0.0059	0.0001 - 0.0048	0.0005 - 0.0048
Sulphur	178	na	na	95.3 - 170.5	75.7 - 216.4	22.5 - 268.5	23.0 - 205.3
Silica	0.5	na	na	4.65 - 8.38	3.30 - 8.27	3.13 - 8.25	5.13 - 8.72
Lead	4.3	0.2	0.3	nd	nd	nd	nd
Zinc pH	21 2.7	0.5 6.0 - 9.5	0.5 6.0 - 9.0	0.018 - 0.076 7.6 - 11.2	0.019 - 0.067 8.7 - 11.2	0.017 - 0.046 8.3 - 11.0	0.018 - 0.369 8.2 - 11.3

Element	AMD-H <sup>1</sup>	EC-MMER Guideline	USEPA Guideline	10% Bentonite (Layered)	20% Bentonite (Layered)	AMD-L <sup>2</sup>	100% CBFA
Aluminum	5.6	na	1	1.10 - 19.41	8.18 - 16.35	10	12.62 - 42.84
Arsenic	0.001	0.5	0.5	0.003 - 0.029	0.001 - 0.010	0.01	0.009 - 0.253
Calcium	83.8	na	na	78.9 - 100.3	93.9 - 142.7	170	10.1 – 183.3
Chromium	0.005	na	na	0.094 - 0.140	0.088 - 0.143	0.005	0.052 - 0.287
Copper	12.9	0.3	0.15	0.0062 - 0.0183	0.0116 - 0.0142	1.3	0.0002 - 0.0284
Iron	55	na	1	0.004 - 0.008	0.004 - 0.054	40	0.009 - 0.128
Potassium	5.5	na	na	0.63 - 3.82	0.61 - 2.68	14.5	0.8 - 36.3
Magnesium	17.8	na	na	0.06 - 0.18	0.05 - 0.12	23	0.01 - 0.16
Sodium	26.5	na	na	16.2 - 65.3	20.4 - 67.0	30	21.3 – 139.8
Nickel	20.1	0.5	0.1	0.0002 - 0.0026	0.0020 - 0.0048	2	0.0008 - 0.0052
Sulphur	178	na	na	12.0 - 48.3	8.1 - 78.5	300	2.7 – 33.5
Silica	0.5	na	na	1.43 - 2.09	1.83 - 3.26	0.7	0.66 - 2.53
Lead	4.3	0.2	0.3	nd	nd	0.04	nd
Zinc	21	0.5	0.5	0.015 - 0.077	0.013 - 0.083	2.5	0.051 - 0.082
рН	2.7	6.0 - 9.5	6.0 - 9.0	7.9 - 10.5	8.1 - 10.8	2.8	8.0 - 11.0
Notes:	Concentration in mg/L unless otherwise specified. nd - readings were below the detection limit. <sup>1</sup> Synthetic AMD for bentonite/CBFA packs.						

<sup>2</sup> Synthetic AMD for 100% CBFA pack.



Figure 8. 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

# 3.4 Post-Testing Solids Analysis

Comparisons of X-Ray diffraction (XRD) patterns obtained from samples of CBFA before and after column testing (Figure 9) reveal the formation of gypsum and ettringite during AMD permeation. Although not immediately apparent in Figure 9b, two distinct peaks for gypsum and quartz were present at  $2\Theta \sim 21^{\circ}$  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 sulfate in the early stages of hydration was also reported by Shang et al. (2007) and Lu et al. (2008).



Figure 9. Comparison of XRD patterns for 100% CBFA: a) before AMD permeation; b) 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 10). Samples were collected from the bottom of the column pack where the solids were in contact with fresh AMD.



Figure 10. Backscattered SEM images of a) CBFA prior to AMD permeation, b) CBFA after AMD permeation, and c) 10% bentonite/CBFA mixture after AMD permeation

The backscattered electron image of CBFA before (Figure 10a) and after (Figure 10b) AMD permeation shows the conglomeration of fly ash particles after AMD permeation, which suggest the formation of a weak cementious aluminum silicate matrix binding the particles together. SEM-EDX 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 10c) clearly shows an aluminum silicate matrix that effectively encapsulates the fly ash particles.

## 4 Conclusions

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

Pure CBFA and CBFA amended with bentonite are similarly effective in buffering pH and decreasing heavy metal concentrations in the AMD effluent. Aluminum concentrations were elevated due to the dissolution of Alcontaining phases in the CBFA .The addition of bentonite was effective in decreasing the mobilization of aluminum compared to pure CBFA.

The collapse of the bentonite double layer in 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.

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