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1. INTRODUCTION

Acid mine drainage (AMD) is the water discharged from an active, inactive, or abandoned mine and from areas affected by surface mining, which often has pH of less than 6.0. AMD has been long recognized to be the largest environmental liability facing the mining industry. The oxidation of sulphide minerals and consequent release of acid in tailings impoundments lead to movement of heavy metals and damage to the ecosystem. The collective liability from the sulphide containing mine wastes was estimated to be between $2 and $5 billion in Canada (Feasby et al., 2000). In Ontario, it is estimated that there are 1000 million tonnes of AMD generating tailings, the largest quantity among all provinces (Feasby et al., 2000). At present, 4000 tonnes of tailings are produced daily from the Musselwhite Mine of Placer Dome Canada Ltd. It is projected that 19 million tonnes tailings will be generated by the time of mine closure in 2012. The quantity of tailings that will be deposited in the basin under water covers is 13 million tonnes, which means alternative methods for tailings disposal must be implemented for the remaining 6 million tonnes. It is proposed to stock pile the remaining tailings above the water table in the basins and cover with a non-acid generating solid material. The tailings are subject to oxidation after several years of disposal due to precipitation-induced infiltration into the dry cover.

Fly ash is the finely divided mineral residue resulting from combustion of ground or powdered coal at electric generating plants. At Ontario Power Generation (OPG) Atikokan Generating Station in Northern Ontario, between 40,000 and 60,000 tonnes of lignite fly ash are generated every year. Currently about 80% of the fly ash is utilized in concrete and cement manufacturing industries, with the rest 20% being disposed in landfill.

The scientific principles of co-placement of coal fly ash and acid generating mine tailings are based on the fact that coal fly ash containing substantial CaO generates alkaline leachate upon in contact with water (Stouraiti et al., 2002). It is, therefore, anticipated that with proper engineering design, coal fly ash can be utilized in mine tailings management to stabilize tailings, to prevent AMD generation and to immobilize heavy metals. Studies have been conducted by researchers on using coal fly ash for water quality control in coal opencast mine rehabilitation (van den Berg et al., 2001). One of the main conclusions of the study by van den Berg et al. (2001) is that coal fly ash can be used in-pit, above the water table as a cover to minimize rain-water and oxygen ingress into the tailings.

In this study the engineering properties of Atikokan coal fly ash (AFA hereafter) and Musselwhite mine tailings (MT hereafter) are investigated, with the focus on the co-placement of two materials to prevent, control and mitigate acid mine drainage.

2. MATERIAL CHARACTERIZATION

2.1 Atikokan Coal Fly Ash (AFA)

Due to its thermal history and electrostatic precipitation collection method, AFA is a well-graded fine powdery material with the comparable particle size distribution of a
The clay-size fractions (% finer than 2 μm by weight) in the ash are less than 11%. The specific gravity of AFA is 2.69. From Harvard compaction test, the optimum water content of AFA is 11% and the max dry density is 1.93 Mg/m³. The tan colour of AFA is considered as an index of high lime content.

The major oxides of AFA are SiO₂, Al₂O₃, Fe₂O₃, and CaO; the combination of these oxides is about 80%. According to the classification system developed by Mehta and Monteiro (1993), the ash is specified as high-calcium fly ashes (CaO 15.7%). Hence high neutralization potential to acidic solutions is expected. When these oxides contact with water, the hydration products of coal fly ash, e.g. calcium silicate gel and calcium aluminate gel, encourage the precipitation of dissolved heavy metals and bind inert particles together.

Mineralogical analysis of AFA indicated that because of its thermal history and chemical composition, AFA shows very poorly crystalline. It is estimated that AFA has a small quantity of magnesioferrite (Fe₂MgO₄) with trace very poorly crystalline. It is estimated that AFA has a small quantity of magnesioferrite (Fe₂MgO₄) with trace amorphous materials. According to Berry et al. (1989), the prominent amount of amorphous materials implies that AFA is a calcium-rich fly ash. Mineralogical analysis also found the total amount of 1.29% calcite and dolomite.

2.2 Musselwhite Mine Tailings (MT)

MT has the similar grain size distribution of the well-graded silty soil. The specific gravity of MT reaches to 3.28. From the Harvard compaction test on air-dried MT sample, the optimal water content is 15%, which is comparable with the counterpart of Atikokan fly ash. This feature facilitates the compaction of AFA and MT mixtures.

Current sulphide separation technology adopted in Musselwhite mine reduces the sulphur content of MT to 1.21%. Part of the sulphur content is in the form of pyrrhotite (Fe₁₋₄S (x=0 to x=0.2)). This kind of sulphide mineral is one of the most reactive ferrous sulphide species. When these ferrous sulphides and other sulphides are exposed to atmosphere and water, a cyclic and self-propagating series of reactions to generate AMD is triggered. On the other hand, mineralogical analysis demonstrated that MT contains 1.21% of calcite and dolomite. These carbonates provide the pH buffer capacity before they are consumed by AMD.

3 EXPERIMENTAL PROGRAM

Two series of column permeation tests, i.e. S2_1 and S2_2, were conducted to study the leaching properties of AFA sample and AFA-MT mixtures. Table 1 summarized the initial setting and final parameters of the tests. Series S2_1 tests include two permeation cells, S2C1 and S2C2. To monitor the hydraulic conductivity and pH buffering capacity of AFA, the AFA samples were permeated with water and AMD respectively. Based on the results of series S2_1 tests, series S2_2 focused on the long-term behavior of AFA and MT mixtures. There are four permeation cells included in S2_2, from S2C4 to S2C7. The mixtures with different mass ratios were tested to determine the optimal mass ratio of AFA and MT. The mass ratios assigned to S2C4 ~ S2C7 were 1:1, 1:2, 1:3 and 1:4 respectively. The permeant in this series tests is weak acid extraction solution of MT (WAE-MT hereafter, pH 3.8). The reason of utilization of WAE-MT is no natural AMD derived from MT is available. Thus, WAE-MT was applied as a substitution of AMD. The four permeation cells were operated under the same conditions to ensure the results comparable.

The instrument involved in the experiment is a constant flow permeation testing system. In this system, column permeation tests were executed with an accelerated constant feed rate flow. All solid samples in the permeation cells were compacted to their maximum density under the optimal water contents.

The main purposes of series S2 tests include:
- Quantify the effluents and calculate the hydraulic conductivities;
- Monitor effluent pH versus progressive pore volume;
- Measure the concentrations of elements, and compare regulated trace elements with the leachate quality criteria of MOE (MOE, 2000);
- Determine the optimal setting of AFA-MT co-placement.

4 RESULTS

The results of the column permeation tests are presented in terms of the progressive pore volume (nPV), which is defined as the total quantity of flow normalized by the initial pore volume of the solid materials compacted in the testing cell.

4.1 Leaching Properties of Series S2_1 Tests

Figure 1 presents the hydraulic conductivity (kh) data for AFA permeated by water and AMD-S respectively.

- The total progressive pore volumes of S2C1 and S2C2 are nPV = 62 and 78.
- When AFA was permeated by water, the hydraulic conductivity of test S2C1 fluctuated between the range of 1.0X10⁻⁷ cm/s and 1.0X10⁻⁶ cm/s at the first 30 nPV. The fluctuation in this period is mainly attributed to the saturation process. Part of dissolvable particles was flushed out from the system. As a result, the void ratio of the sample was increased. From 30 nPV, the hydraulic conductivity increased one order of magnitude to 1.0X10⁻⁵ cm/s, and fluctuated at this level.
- Since AMD was employed as permeant in the test S2C2, the complex chemical reactions promoted the instability of the saturation process. Significant fluctuation was observed in the test S2C2 during the first 20 nPV. After a short period of equilibrium status from 20 to 30 nPV, the hydraulic conductivity
decreased about three orders in magnitude to $4.0 \times 10^{-9}$ cm/s at the end of the test. Along with the consolidation of AFA, the secondary minerals formed from the reactions of the cementitious materials, which is derived from coal fly ash, clogged the voids among solid particles.

The high calcium content in AFA leads to an advanced reactivity of the fly ash. Apart from promoting the formation of amorphous phases, the calcium content encourages the presence of hydrated calcium phases. Thus, the interaction of the fly ash with water favours the hydration of lime and gypsum to promote pozzolanic reactions.

It is notable that the measurement of $k_h$ for S2C2 was not complete. To avoid the damage of pressure transducer, which was used to detect the pressure in the permeation cell, the vent valve of the system had to be opened to release the overly high pressure. As a function of the pressure, the actual hydraulic conductivity is anticipated lower than the value presented in the figure.

Fig. 1. Hydraulic conductivity of Atikokan coal fly ash in tests S2C1 & S2C2

The pH profile of tests S2C1 and S2C2 are presented in Fig. 2.

- The pH of S2C1 decreased slowly from the initial value of 12.5 with the progressive pore volumes, and reached to an equilibrium status with pH 10. The decrease of pH may be mainly attributed to the impact of water dilution of initial alkaline pore fluid.
- The pH values of test S2C2 were synchronized with those of S2C1 for over 40 nPV. When the pH buffer capacity of carbonates mentioned above in the material characterization section was exhausted by the acidic AMD, the pH curve of S2C2 displayed a rapid decrease from 40 nPV.

Fig. 2. Effluent pH of Atikokan coal fly ash in tests S2C1 & S2C2

4.2 Comparison of Hydraulic Conductivities of Various Mass Ratio AFA-MT Mixtures in S2_2 Tests

In series S2_2 tests, four AFA and MT mixtures were prepared at various ash-tailings mass ratios (1:1 to 1:4) and compacted into the column permeation cells with densities, water contents and void ratios recorded in Table 1. The mixtures were permeated with WAE-MT. The hydraulic conductivities of the four tests during the first 100 nPV permeation are presented in Fig. 3 for comparison.

- During the first 10 nPV, because of the saturation process, no clear trends were observed for the hydraulic conductivities. With the increase of progressive pore volumes, the $k_h$ curves showed significant difference for four tests. Generally, with the percentage of AFA in MT increased, more secondary minerals were composed. Thus, the hydraulic conductivity was reduced.
- When the mass ratio of AFA:MT is less than 1:3, e.g. tests S2C6 and S2C7, no significant change of $k_h$ was observed. The impact of solid particles dissolution offset that of the secondary minerals formed from acid-base reactions. In the tests S2C4 and S2C5, more ash particles were presented in the mixture. The precipitation of dissolved metals and other ions overcame the dissolution; secondary minerals, e.g. ettringite, blocked the flow path and led to the $k_h$ decrease.
- The result of hydraulic conductivity is reasonable, because the equilibrium $k_h$ of MT ($1.6 \times 10^{-5}$ cm/s) is more than one order of magnitude higher than that of AFA ($1.5 \times 10^{-6}$ cm/s).
Figure 3. Hydraulic conductivities of the mixtures of Atikokan coal fly ash and Musselwhite mine tailings in tests S2C4 - S2C7

Figure 4 presents the hydraulic conductivity versus the percentage of AFA in MT.
- The data for 0% ash is from the previous test conducted by authors and the data for 100% ash is from the test S2C1 (Fig. 1, ~ 60 nPV). The rest data derived from the series S2_2 tests at the same progressive pore volumes (Fig. 3, ~ 90 nPV).
- The results demonstrated that the introduction of less than 30% AFA to MT had reduced the hydraulic conductivity of tailings to an order of magnitude. With more AFA was added into MT, the hydraulic conductivity of the AFA-MT mixture was reduced.
- It was realized that with proper mass ratio, the kh of mixture could even be lower than the hydraulic conductivities of two reference materials, AFA and MT. The clogging in the void space, which is led by the chemical reactions between alkaline wet AFA and acidic wet MT, caused this hydraulic conductivity reducing.
- Based on the cost efficient concern and engineering feasibility, the optimal mass ratio of AFA:MT is between 30% to 40%. In the four tests of series S2_2, S2C5 is a qualified candidate with suitable mass ratio. Further analysis is based on this test.

Table 1 summarized the initial setting and final status of series S2_2 tests.
- Compared with the other tests in series S2_2, S2C5 has the maximum decreased in total volume, which reached to 9.7%. This feature is valuable for the disposal. In another words, with the optimal mass ratio, the containing capacity of a landfill site is able to improve almost 10%.
- Following the same compaction procedure and similar water contents, the maximum dry density (2.4 Mg/m³) and the minimum initial pore volume (0.29) were achieved in test S2C5. Furthermore, the final pore volume in this test is far below the other tests. It is expected that with the optimal mass ratio, the mixture of AFA:MT has potential benefits in engineering practice.

Table 1. Summary of Constant Flow Column Permeation Tests

<table>
<thead>
<tr>
<th>Cell No.</th>
<th>S2C1</th>
<th>S2C2</th>
<th>S2C4</th>
<th>S2C5</th>
<th>S2C6</th>
<th>S2C7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Material</td>
<td>AFA</td>
<td>AFA</td>
<td>AFA:MT</td>
<td>AFA</td>
<td>AFA</td>
<td>AFA</td>
</tr>
<tr>
<td>Mass Ratio</td>
<td>1:1</td>
<td>1:2</td>
<td>1:3</td>
<td>1:4</td>
<td>1:3</td>
<td>1:4</td>
</tr>
<tr>
<td>Influent Water</td>
<td>AMD</td>
<td>WAE-MT</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample Height (cm)</td>
<td>2.00</td>
<td>2.00</td>
<td>2.00</td>
<td>2.00</td>
<td>2.00</td>
<td>2.00</td>
</tr>
<tr>
<td>Water Content</td>
<td>10.4%</td>
<td>10.4%</td>
<td>12.2%</td>
<td>12.8%</td>
<td>12.6%</td>
<td>13.8%</td>
</tr>
<tr>
<td>Dry Density (Mg/m³)</td>
<td>1.8</td>
<td>1.9</td>
<td>2.3</td>
<td>2.4</td>
<td>2.0</td>
<td>2.0</td>
</tr>
<tr>
<td>Initial Total Volume (cm³)</td>
<td>45.80</td>
<td>45.80</td>
<td>45.80</td>
<td>45.80</td>
<td>45.80</td>
<td>45.80</td>
</tr>
<tr>
<td>Final Total Volume (cm³)</td>
<td>44.64</td>
<td>41.34</td>
<td>45.78</td>
<td>45.09</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Δ_Total Volume</td>
<td>-2.5%</td>
<td>-9.7%</td>
<td>0.0%</td>
<td>-1.6%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pore Volume (cm³)</td>
<td>15.03</td>
<td>14.06</td>
<td>10.22</td>
<td>10.18</td>
<td>16.75</td>
<td>16.86</td>
</tr>
<tr>
<td>Initial Void Ratio</td>
<td>0.29</td>
<td>0.29</td>
<td>0.58</td>
<td>0.58</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Final Void Ratio</td>
<td>0.52</td>
<td>0.38</td>
<td>0.59</td>
<td>0.57</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Δ_Void Ratio</td>
<td>79.3%</td>
<td>31.0%</td>
<td>1.7%</td>
<td>-1.7%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mass Loss (%)</td>
<td>17.2</td>
<td>15.9</td>
<td>0.9</td>
<td>0.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NPV</td>
<td>62</td>
<td>78</td>
<td>154</td>
<td>154</td>
<td>91</td>
<td>93</td>
</tr>
</tbody>
</table>

Note:
- AFA - Atikokan coal fly ash
- MT - Musselwhite mine tailings
- AFA:MT - mass ratio of AFA and MT
- AMD - Acid mine drainage from Sudbury mine
- WAE-MT - Weak acid extraction of air-dried MT
- NPV - Progressive pore volume
4.3 pH and Heavy Metal Elements of the Optimal Mass Ratio Mixture

The effluent pH profile of the optimal mass ratio AFA-MT mixture is presented in the Fig. 5.
- For pH, it is noted that the permeant in the test was a synthetic AMD (pH 3.8) prepared by weak acid extraction on air-dried MT. The pH curve showed considerable scattering, ranging from pH 8 to pH 11.5. Experimental errors may contribute to some of the scattering. However, the results indicate that after 150 pore volumes of WAS-MT passing through the coal fly ash and tailings mixture, the effluent maintained alkaline at pH above 8.
- AFA showed considerable neutralization capacity in test S2C5. The carbonates in both AFA and MT, along with high content of CaO in AFA, ensure the environmental security of long term leaching.

![Fig. 5. Effluent pH of the optimum mass ratio mixture of Atikokan coal fly ash and Musselwhite mine tailings](image)

There are two types of leaching patterns of trace elements in the effluent, early leaching pattern and delayed leaching pattern. Early leaching pattern is defined as the concentration of the element decreases after one pore volume of flow. Delayed leaching pattern is characterized by low initial element concentrations increasing with additional pore volumes of flow. Figure 6 presents two typical leaching patterns of heavy metals in test S2C5. The relative element concentrations in test S2C2 were plotted as a reference.
- In Fig. 6a, one of the potential toxic trace elements, Cr, was monitored with time during series S2_2 operating. When the AFA-MT mixture permeated with WAS-MT, the concentration of chromium displayed an obvious delayed leaching pattern. The concentration peak of Cr in S2C5 appeared after 50 nPV permeation, while the counterpart in S2C2 showed up at the beginning. The leaching pattern is dependent upon the element distribution in solid particles. The element Cr is mainly dispersed between matrix and nonmatrix material of fly ash (Hansen and Fisher, 1980). When AFA was permeated with AMD, element Cr was dissolved into pore fluid and flushed out from the ash sample; while AFA-MT mixture permeated with WAE-MT, the secondary minerals generated from chemical reactions between AFA and MT encapsulated the solid particles. Therefore, the dissolution of Cr was postponed.
- The intensities of Cr concentration peaks in tests S2C2 and S2C5 are fairly close. Either in S2C2 or in S2C5, none of the chromium concentrations exceeded the Leachate Quality Criteria set by the local regulatory authority (MOE, 2000).
- Since the element Mo is concentrated on the surface of the ash particles (Hansen and Fisher, 1980), its concentration curves were shown as early leaching pattern, see Fig. 6b. Even in S2C5, the formation of secondary minerals can hardly hinder the dissolution of Mo. On the other hand, the secondary minerals elongated the release of molybdenum from the solid particles.

![Fig. 6. Concentrations of trace elements (a) Cr in tests S2C2 & S2C5, (b) Mo in tests S2C2 & S2C5](image)

5 CONCLUSION

Two series of column permeation tests were performed to study the possibility of co-placement of AFA and MT. The hydraulic conductivity, pH, and concentrations of trace elements were monitored to assess the impact of co-placement and determine the optimal mass ratio. The following summary can be made based on the preliminary findings from this research:
When permeated with AMD, AFA demonstrated approximately three orders of magnitude decrease in the hydraulic conductivity (from $2.0 \times 10^{-6}$ cm/s to $4.0 \times 10^{-9}$ cm/s) due to secondary minerals precipitation. Thus, AFA can be a possible part of cover or liner in MT disposal in the future.

AFA has high neutralization potential. When permeated with continuous AMD (pH 3.8), AFA are capable of maintaining an alkaline environment in the permeation cell for a considerable time (up to 60 nPV).

The experiments on mixtures of AFA and MT indicated that, with proper design, the hydraulic conductivity of the tailings decreased with the increased additive of coal fly ash. The optimal mass ratio is between 30% and 40%. Furthermore, the addition of coal fly ash at optimal mass ratio can benefit the engineering operation in compaction and decrease the quantity of leachate.

When the AFA-MT mixture was permeated with WAE-MT, the secondary minerals encapsulated the mine tailings particles. Therefore, co-placement of AFA and MT prevents or mitigates the oxidization of mine tailings.

The addition of AFA into MT helps to immobilize the dissolved heavy metals by the precipitation process. The dissolution of most elements were postponed or elongated in the tests, which provided more time for treatment. Results of trace elements released from the mixtures indicated that the trace element concentrations are well below the Leachate Quality Criteria in Ontario Regulation 558/00.

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REFERENCES

Feasby, Tremblay, G.A., and Weatherell, C.J. 2000. A Decade of Technology Improvement to the Challenge of Acid Drainage A Canadian Perspective. DMEND Secretariat, CANMET, Natural Resources Canada


MOE 2000. Ministry of the Environment Regulation 558/00, Schedule 4. Publication of the Ministry of the Environment, Ontario, Canada
