Hydro-Geochemical Properties of Class F Fly Ash When Leached with Acid Mine Drainage

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Abstract

The aim of this study is to assess the hydraulic and geochemical properties of fly ash with reference to acid mine drainage (AMD). In the laboratory, ash was leached with natural AMD to assess the changes in hydraulic conductivity and chemical leachate over time. Influent and effluent was monitored for pH, EC and metal concentrations, while monitoring discharge volumes as well. Hydraulic conductivity exhibited overall decreasing trends over time, reducing from 10^{-1} m/d to 10^{-3} m/d. Calcium was the dominant cation that leached out, with sulphate being the dominant anion. Ash backfill will improve current discharging AMD water quality.

Keywords: Hydraulic conductivity, opencast coalmine, Backfill

Introduction

There are various historic coalmine sites in the Mpumalanga Province of South Africa. According to McCarthy (2011), some of these mines have collapsed over time and many of them are discharging acid mine drainage (AMD) into the environment, thus having negative effects on the water quality of downstream rivers, streams and dams. Additionally, vast amounts of fly ash are produced at coal-fired power stations and are disposed onto landfills, with limited space. Therefore, a need arises to mitigate or prevent AMD generation from pre-existing mines and to find alternative ash disposal methods.

Ash backfill as a monolith into pre-existing and future coalmines might potentially mitigate the generation and effects of AMD. However, there is limited knowledge on how South African fly ash would behave under opencast backfilled conditions and its effect on the immediate environment of the proposed opencast mine sites. Thus, the aim of this study is to assess the hydraulic and geochemical properties of fly ash with reference to AMD that leaches from the mines and comprehend how ash backfill would affect the natural water environment (groundwater and surface water).

Materials

Ash: Ash from two coal-fired power stations were used in this study and were collected directly off the conveyor belts. Ash 1 that was collected from the first power station is named K-ash, whereas, ash 2 from another power station are named T-ash. Ash from both power stations show characteristics of Class F ash, making it a natural pozzolanic material. Both K-Ash and T-Ash have a SiO_2 + Al_2O_3 + Fe_2O_3 weight above 70%, with a low CaO (CaO < 10 wt. %) content which is common for South African fly ash. Additionally, K-ash has a slightly higher CaO (6.9 %) and MgO (1.28 %) weight percentage compared to the CaO (5.3 %) and MgO (1.14 %) weight percentage in the T-ash.

AMD: Natural AMD water with a pH = 2.5, was collected from Driefontein, a pit lake at an old opencast coalmine site in the Witbank area in Mpumalanga. According to Bell et al. (2001) the pit lake is a product of a historical shallow underground coal mine that collapsed due to multiple pillar failures. As a result, the mine voids filled up with water and discharged to form the pit lake. The water in the pit lake is of an acidic nature resulting from the reaction with oxygen and pyrite minerals in unmined coal and host rocks.

AMD had Iron (Fe) content > 130 mg/L and Sulphate (SO_4) content > 2000 mg/L.

Methods

The hydro-geochemical properties of ash were determined in the laboratory by leaching ash with AMD through the use of a constant head permeameter test (Darcy constant head column test) in accordance with a modified version of method 1314 from the LEAF methodology and ASTM D 4874 leaching standard (Ecology 2003; USEPA 2014). Testing lasted approximately 6 months where fly ash was leached continuously with natural AMD. Method 1314 from the LEAF methodology was modified with the aim of achieving the closest field conditions. Thus, instead of distilled water, natural AMD water was used as the leaching liquid (influent) due to the high probability of fly ash being backfilled into AMD generating environments. Furthermore, ash was not packed into the columns as according to the ASTM D 4874 leaching standard but, rather mixed to a slurry at 40%, 50% and 60% moisture respectively before it was poured into the columns. All the columns were cured for 28 days before hydraulic conductivity testing. Columns named K40, K50, K60, T40, T50 and T60 were 0.2 m in length, whereas, columns named K60b and T60b were 0.5m in length, indicating that the 0.5 m columns consisted of substantially larger volumes of fly ash.

A total of 8 columns filled with ash were connected to a headwater reservoir through a piping system (Figure 1). The hydraulic test was performed by introducing AMD water to the ash columns under constant hydraulic gradient (ΔH) conditions. AMD moved from head 1 (H_1) down the piping and upwards through the ash sample in the column until it eventually discharges at head 2 (H_2). The upward flow of AMD through the ash sample ensured fully saturated conditions as the distribution of AMD spreads evenly through the cross-sectional area (A) of the column. At outflow, the discharge (Q) was measured as length cubed per unit time. Initially, discharge (effluent) was measured 4 - 8 times a day during the first two weeks of testing. Thereafter, discharge was measured twice a day as the flow rates decreased until week 5 of testing. Final flow measurements were measured once every 3 days. The hydraulic conductivity (K) is then calculated through applying the measured parameters into Darcy's equation:

$$Q = KIA$$

Where:

Q = Discharge in units of length cubed per unit time (m^3/d)

K = Hydraulic conductivity in units of length per unit time (m/d)

I = Hydraulic gradient (Δ H) measured as the difference in head $(H_1 - H_2)$ in meters over the length (L) of the sample in meters (m/m).

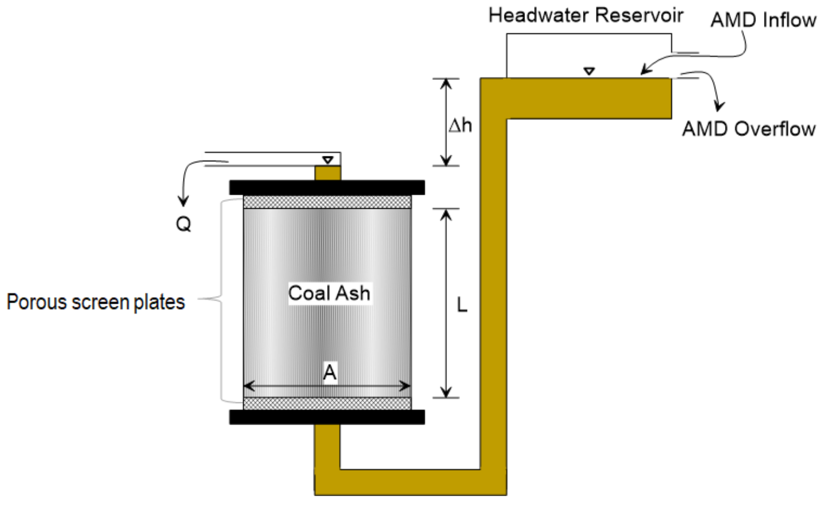

Figure 1. A schematic depiction of a constant-head permeameter (after Fetter, 2001).

A = Cross sectional area in units of length squared (m^2)

Influent and the effluent from 4 columns (K50, T50, K60b and T60b) were routinely collected throughout the testing period. Samples were sent to the laboratory for chemical metal analysis, to evaluate the influence of ash on AMD water quality. The target elements in the evaluation were the concentrations of Fe, Ca and S as SO_4. Additionally, pH and EC was monitored throughout the testing period.

Results and Discussion

Hydraulic conductivity results are depicted in Figure 2, whereas the pH is presented in Figure 3. Moisture in the ash during mixing and curing, allows for pozzolanic reactions to occur, solidifying the ash and resulting in the initial low K of 10^{-1} m/d. During leaching, calcium oxide in the ash dissolves at the bottom of the columns and causes gypsum precipitation towards the middle and top of the columns. Gypsum precipitation towards the middle and top of the columns causes void spaces to decrease, thereby lowering the hydraulic conductivity to 10^{-2} m/d. Variations in hydraulic conductivity of ash are also highly influenced by the high mineral content in the AMD, such as high iron and sulphate concentrations. Also, $Fe(OH)_3$ in the ash dissolves at low pH at the reaction front between ash and AMD, jarosite minerals form which is stable Fe-sulphate in acidic conditions and clogs up pore spaces. This results in the lowering of the K at the reaction front by an order of magnitude compared to deeper in the ash, reducing the K to 10^{-3} m/d. One of the columns (K40) completely clogged up and flow through stopped (Figure 2).

The alkaline nature of the ash initially neutralizes the acidic levels of AMD from inflow pH = 2.5 to an outflow pH = 11. Acidification of the outflow from pH = 11 towards a pH = 4 is observed during testing (Figure 3). According to Nhan et al. (1996), the initial pH of the effluent is controlled by the dissolution of $Ca(OH)_2$ and $Mg(OH)_2$ in the ash. Moreover, K-Ash columns exhibited a stronger buffering behaviour compared to the buffering behaviour of the T-Ash columns. K-Ash also consists of slightly higher concentrations of CaO and MgO compared to the T-Ash, hence the stronger buffering behaviour. Overall, the K decreased by 2 orders of magnitude from an initial K of 10^{-1} m/d to 10^{-3} m/d, with the AMD iron concentration of above 130 mg/L playing the dominating role in reducing the hydraulic conductivity under the lower pH conditions at the reaction face between AMD and ash.

The temporal trend in electrical conductivity (EC) of influent compared to effluent are shown in Figure 4 and Figure 5. It was observed that the EC concentrations of the effluent remained lower than the EC of the influent AMD. The overall EC peak of the effluent measured during the testing period, was 490 mS/m for most of the columns. General EC concentrations in the effluent ranged between 350 mS/m and 490 mS/m. In contrast, effluent of T40 exhibited higher EC values, with a peak of 525 mS/m. T40 also exhibited the highest initial hydraulic conductivity peaking at 0.6 m/d, suggesting that the ash had partial effect on the AMD quality due to the higher flow rates during the initial stages of testing. Overall, the effluent

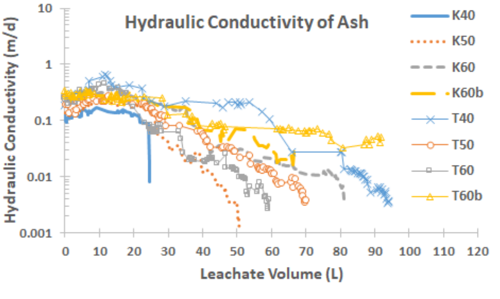

Figure 2. Hydraulic conductivity of Tutuka and Kendal ash columns.

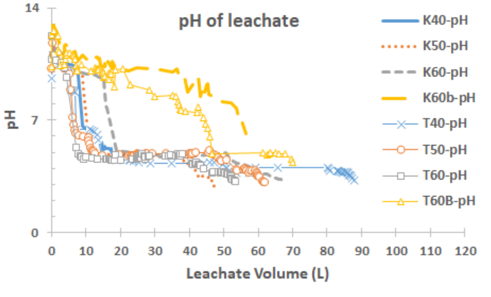

Figure 3. pH of effluent from Kendal and Tutuka ash columns.

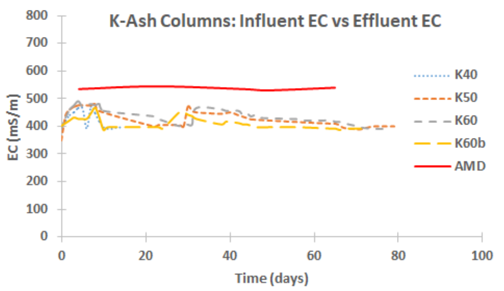

Figure 4. *Influent EC compared with the effluent EC for the Kendal columns.*

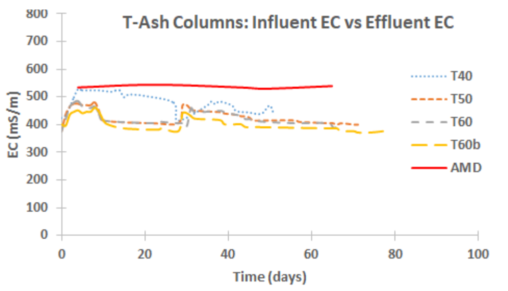

Figure 5. *Influent EC compared with the effluent EC of the Tutuka columns.*

EC concentrations from all the columns were lower than the EC of influent AMD.

Iron concentrations in the AMD ranged between 138 mg/L and 190 mg/L throughout the leaching period. The early time Fe concentrations in the effluent of all the columns were measured at 10^{-2} mg/L. Effluent Fe concentrations from the K60b and T60b columns persisted at 10^{-2} mg/L (mostly below detection limit of 0.06 mg/L) throughout the entire testing period. However, due to lesser volumes of fly ash in the shorter K50 and T50 columns, the Fe concentrations in the effluent increased after 22 days of leaching, with the K50 effluent concentrations increasing to 10^{+1} mg/L and the T50 effluent concentration to 10^{0} mg/L until the testing was concluded. Overall, the Fe concentrations in the effluent from all the columns remained lower than the Fe concentrations in the influent AMD water, suggesting that ash retains Fe concentrations (Figure 6).

Calcium was the dominant cation that leached out, with sulphate being the dominant anion. Sulphate concentrations was high in the leachate due to the high sulphate content in the AMD (Figure 7). Ca originates from both the lime in the ash (that neutralise the acid) and the influent AMD (Figure 8). S concentrations in the AMD and the effluent of the K50 and T50 columns, showed very similar results throughout the duration of the leaching period. Effluent concentrations from the K60b and T60b columns showed S concentrations of about 1000 mg/L lower than the AMD S concentrations. The S concentrations in the K60b and T60b increased at day 22 of leaching, however, it remained below the AMD S concentration for the remainder of the leaching period (Figure 7).

It is expected that an ash monolith deposited at the discharging position of the backfill pit as shown in Figure 9, would hydraulically and geochemically behave similar to the laboratory column testing. As a result, the water table in the backfill will be substantially influenced by the monolith. Initially, the water table is expected to be at the lowest discharge elevation in the backfill area, however, with the decreasing hydraulic properties of fly ash over time, it is expected that flow through will be limited resulting in the rise of the water table. If the water table rises over time, it limits the pyrite minerals in the backfill spoils to oxygen exposure. Ultimately, resulting in reduced discharge volumes from the backfill as well as limiting AMD generation due to reduced oxygen exposure to spoils (Figure 9).

Conclusions

The hydraulic conductivity testing of ash showed decreasing trends of K over time. Overall, the hydraulic conductivity decreased from initial K values of 10^{-1} m/d to 10^{-3} m/d. These changes in hydraulic conductivity over time, are initially subjected to the pozzolanic bindings that formed during the curing phase of the experiment. During the experiment, secondary mineralization occurs induced by calcium rich minerals which are deposited in the flow paths, causing a decrease in K to 10^{-2} m/d. Lastly, the Fe (>130 mg/L) and SO_4 (>2000 mg/L) concentrations in the AMD together with the low pH =

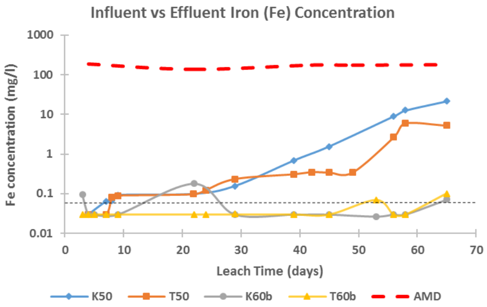

Figure 6. Influent Fe concentrations vs effluent Fe concentrations.

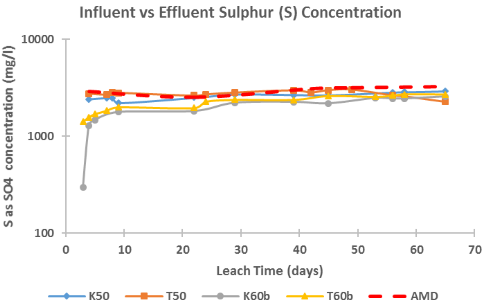

Figure 7. Influent S concentrations vs effluent S concentrations.

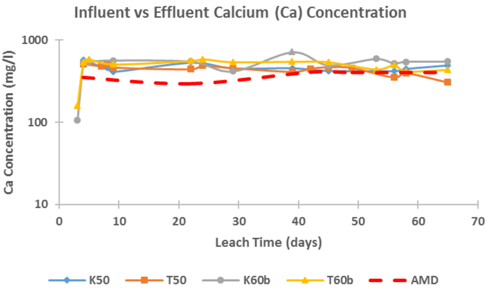

Figure 8. Influent Ca concentrations vs effluent Ca concentrations.

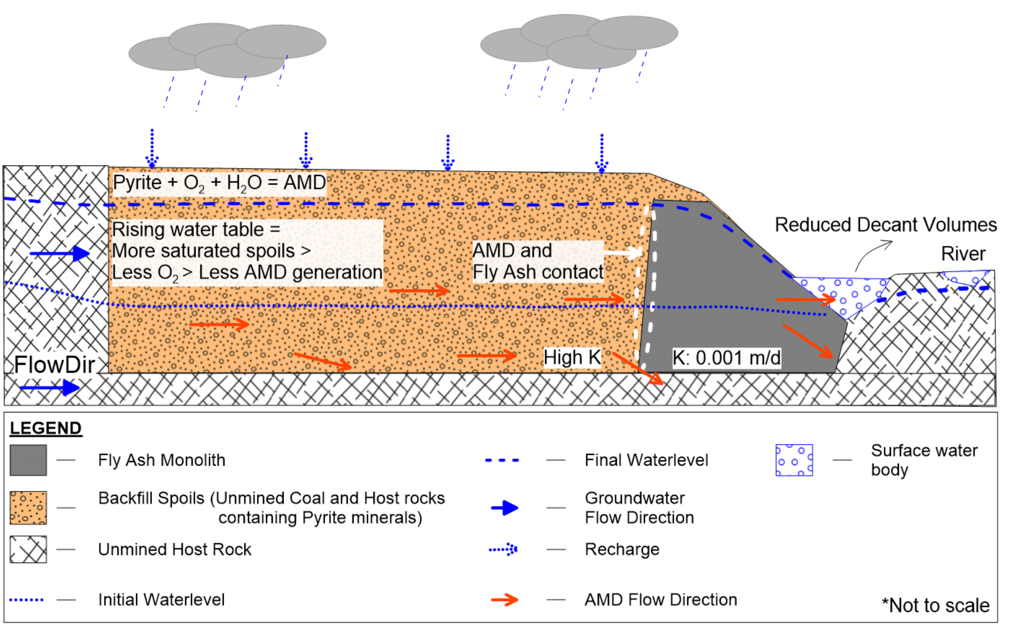

Figure 9. A conceptual depiction of ash backfilled in an opencast mine.

2.5 causes a clogging effect at the front face of the fly ash, which ultimately causes the hydraulic conductivity to decrease towards 10^{-3} m/d. Within 8 columns being tested, one column experienced a complete clog up which indicates that fly ash may become impermeable over time if exposed to AMD with low pH and high concentrations of iron and sulphate.

From the geochemical leach test results, it was observed that most of the leachate water was of a better quality than the influent AMD water quality. The effluent pH (from pH = 11 towards pH = 4) was higher than the pH of the influent AMD (pH = 2.5). Overall EC reduced in discharge compared to inflow AMD (EC_{inflow}: 535 – 545 mS/m versus $EC_{outflow}$: 350 – 490 mS/m). Although sulphate was the dominant anion that leached out, Fe (10^{-2} – 10^{+1} mg/L) and SO_4 (10^{+2} – 10^{+3} mg/L) in the effluent showed lower concentrations when compared to the inflow Fe (10^{+2} mg/L) and SO_4 (10^{+3} mg/L) concentrations.

Based on this research, an ash monolith backfilled into an opencast coal mine would improve the discharging AMD water quality. An ash monolith deposited at the discharging position within the backfill, may have positive influences, including:

1. Increases pH of the water that do flow through the ash monolith, and the associated reduction in concentrations of Fe and SO_4 of the AMD water, thus retaining some contaminants.
2. Due to decreasing hydraulic conductivity of the ash, the water table in the backfill is expected to rise to the top of the monolith over time, thereby reducing oxygen exposure of the waste rocks in the backfill, ultimately reducing AMD generation.

The topography, hydraulic conductivity and the water table within the backfill may be altered to manage the discharge position, elevation and improve water quality from the ash monolith backfilled coal mines.

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