Application of a jet loop reactor to enhance removal of sulphates from mine water using coal fly ash, lime and aluminium hydroxide

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Abstract
Recent studies have shown that a combination of coal fly ash (FA) and aluminium hydroxide (Al(OH)₃) can be used to treat neutral mine drainage (NMD) and reduce sulphate concentration to within South African drinking water quality standards. The shortcoming of this method is the large amounts of coal FA required to raise the pH to greater than 11 (3:1 liquid to solid ratio) so that Al(OH)₃ can be added to facilitate further removal of sulphate to less than 400 mg/L through ettringite precipitation. This means that very large silos will be required to store FA. Too much FA in the water makes the mixture difficult to mix and pump using normal methods, making scaling up of this treatment technology impracticable. In the current study, the amount of fly ash needed to increase the pH to greater than 11 was reduced, by adding 0.25 % of lime (w/v ratio) with a combination of 6:1 mine water to coal FA ratio using a jet loop reactor. Addition of 83.2 g of amorphous Al(OH)₃ to 80 L of NMD resulted in a decrease in the sulphate concentration to less than 500 mg/L, which is within the allowable limit of South African drinking water Class II standard (400-600 mg/L). Bench scale studies using 0.25 % (w/v) of lime and 6:1 coal mine water to coal FA ratio could not reduce the sulphates to below 500 mg/L. Therefore the impingement and cavitation mixing techniques in a jet loop reactor played an important role in enhancing sulphate removal.

Keywords: sulphates, neutral mine drainage, jet loop reactor, ettringite, impingement and cavitation

Introduction
Mining activities have left underground voids that are filled with water. The mine water can be acidic or alkaline depending on the type of geology that was disturbed during mining. Mine water results from the oxidation of pyrite (FeS₂) in the presence of water to produce acidity (Lottermoser 2007).

\[ FeS_2 + \frac{7}{2}O_2 + H_2O \xrightarrow{\text{bacteria}} Fe^{3+} + 2H^+ + 2SO_4^{2-} \]  

(1)

The acidity generated results in chemical weathering of the surrounding rock thereby leaching potential toxic elements such as Al, Mn, As and Cr into the water. If the surrounding rock contains alkaline minerals such as limestone, sodium
hydroxide or dolomite, the resultant water will be circumneutral due to in situ neutralisation of the acidity from FeS₂ oxidation as shown in Equations 2 to 4 (Bankset al. 1997, Younger et al. 1997; Lottermoser 2007).

$$FeS_2 + CaMg(CO_3)_2 + \frac{3}{2} H_2O + \frac{15}{4} O_2 \rightarrow Fe(OH)_3 + Ca^{2+} + Mg^{2+} + 2CO_2 + 2SO_{4}^{2-}$$ (2)

$$FeS_2 + CaCO_3 + \frac{3}{2} H_2O + \frac{17}{4} O_2 \rightarrow Fe(OH)_3 + Ca^{2+} + CO_2 + 2SO_{4}^{2-}$$ (3)

$$FeS_2 + NaOH + 2H_2O + 5O_2 \rightarrow Fe(OH)_3 + Na^+ + 2SO_{4}^{2-} + 2OH^-$$ (4)

Chemical treatment of mine water is a costly process (Potgieter-Vermaak et al. 2006). Previous studies on the treatment of mine water with coal FA have shown that Fe, Al, Mn and sulphate concentration in acid mine drainage (AMD) were significantly decreased (Gitari, et al. 2006, Petrik, et al. 2003, Vadapalli, et al. 2008). Coal FA provides a cheaper technology for the treatment of mine water because is readily available close to the coal mines that produce AMD. Removal of sulphates from NMD with coal FA was found to be pH dependent and significant removal of sulphates was noticed after precipitating out Mg²⁺ ions from the system at pH greater than 11 (Madzivire, et al. 2011). It was also discovered that addition of Al(OH)₃ at pH greater than 11 resulted in sulphates concentration decreasing to below the World Health Organisation (WHO) guidelines for drinking water through ettringite precipitation (Madzivire, et al. 2010).

$$6Ca^{2+} + 3SO_{4}^{2-} + 2Al(OH)_3 + 32H_2O \leftrightarrow 3CaO.3CaSO_4.Al_2O_3.32H_2O + 6H^+$$ (6)

The challenge experienced with this treatment was the high amount of fly ash needed, which means large silos would be needed to store the fly ash at the treatment plant. Also liquid to solid ratios of 3:1 and 2:1 were needed using an overhead stirrer mixing technique. These liquid to solid ratios produce thick slurry that cannot be easily handled by normal pumps, making scaling up of this process impracticable.

Superior mixing with a jet loop reactor that uses cavitation and impingement mixing techniques can reduce the amount of FA utilized in the treatment of mine water. The jet loop reactor has been used in the selective hydrogenation of palm olein. It promotes a faster reaction rate by exerting higher mass transfer rate and mixing intensity compared to continuous stirred tank reactor (Sin 2005). A jet loop reactor works by pumping a solution through the section marked “water in”. The solution is then distributed into a section containing two jets each on opposite sides as shown in Figure 1(a). At each section the water is then forced through a small diameter called a jet (jets A and B) which is water under extreme high pressure as shown in Figure 1(b). The water jets under high pressure meet and collide at the impingement plane (IP), causing the solution to mix efficiently (Gavi et al. 2007).
In this study it is envisaged that the use of the jet loop reactor with its increased mass transfer rate and mixing intensity will reduce the amount of coal fly ash utilized in the treatment process.

**Methods**

The mine water used was collected from a coal mine in Mpumalanga province, South Africa and the FA was collected from a nearby coal power station. The mine water was analysed using inductively coupled plasma optical emission spectroscopy (ICP-OES) and ion chromatography (IC). The FA was analysed using x-ray florescence spectroscopy (XRF) for the elemental composition and x-ray diffraction spectroscopy (XRD) for mineralogy.

*Optimization of the amount of fly ash and lime required*

The following experiments were conducted in order to find the optimum conditions (the jet sizes, the amount of fly ash and the minimum amount of lime).
required to increase the pH of the mine water to pH greater than 11 in order to precipitate sulphate in the form of ettringite.

A. Mine water (80 L) was mixed with FA (13 kg) (liquid to solid ratio 6:1) using a jet loop reactor with jet nozzle sizes set at 8 mm. The mixture was mixed by a combination of impingement and cavitation in the reactor. The pH and EC were measured after every 15 min and samples were collected after every 30 min. The samples were filtered using a 0.45 µm pore size and analysed using ICP-OES and IC.

B. Mine water (80 L) was mixed with FA (16 kg) (liquid solid was reduced to 5:1) using a jet loop reactor with jet nozzle sizes set at 8 mm. The mixture was mixed by a combination of impingement and cavitation in the reactor. The pH and EC were measured after every 15 min. Aliquot samples were collected, filtered using a 0.45 µm pore size and analysed using ICP-OES and IC after every 30 min.

C. The jet nozzle sizes were then changed from 8 mm to 6 mm. Then mine water (80 L) and coal FA (16 kg) (liquid to solid ratio of 6:1) were mixed, the pH and EC were measured after every 15 min and samples collected for analysis using ICP-OES and IC after every 30 min.

D. Mine water (500 ml) was mixed with coal FA (83 g) in a liquid to solid ratio of 6:1 using an overhead stirrer. Different amounts of lime were added to the mixture. The various w/v % of lime added were 0.25, 0.5, 0.75, and 1 %. For each mixture, the pH and EC were measured after 15 min at which 0.52 g of Al(OH)₃ was added. The reaction continued after adding Al(OH)₃, with the pH and EC measured and samples collected after every 30 min. The samples were analysed with ICP-OES and IC.

Optimization of the jet loop reactions

Jet loop experiments were further carried out using a combination coal FA and 0.25 % of lime (w/v) at liquid to solid ratio of 6:1 in a jet loop reactor. The first set of three experiments was done to investigate the effect of jet size on sulphate removal. The jet nozzle sizes were varied from 6, 8, 10 and 12 mm. Mine water (80 L) was reacted with FA (13 kg) and 0.25 % lime (w/v %). After 15 min 83.2 g of Al(OH)₃ was added. The reaction was allowed to proceed for 150 min with the pH and EC measured after every 15 min. Samples were collected after every 30 min, filtered through a 0.45 µm pore size and analysed using ICP-OES and IC.

The last set of experiments was conducted in order to compare the effect of cavitation only to that of cavitation and impingement. The jet nozzle sizes were maintained at 12 mm and mine water (80 L) was mixed with FA (13 Kg) and one pair of jets on one side was closed. After 15 min 83.2 g of Al(OH)₃ was added and samples were collected after every 30 min for 150 min. The pH and EC were measured after every 15 min.

Results and Discussion

The mine water used in this study was neutral mine drainage (NMD) with a pH of 8.0 (Lottermoser 2007). The water contained high concentration of Na and
sulphate, with very low concentration of Fe, Al, Mn, Ca and Mg, as shown in Table 1. This was because of the in situ neutralization of FeS$_2$ oxidation by NaOH according to Equation 4.

Coal FA and NMD were reacted together using a liquid to solid ratio 6:1 and 5:1 in a jet loop reactor with jet sizes set at 8mm. The 5:1 and 6:1 liquid to solid ratios could not overcome the pH barrier to achieve a pH greater than 11 unless the mixture was left overnight, as shown in Figure 2. The pH in NMD and FA mixture increased due to the dissolution of lime in FA into the mine water.

Table 2: The composition of the mine water used in this study

<table>
<thead>
<tr>
<th>Parameter</th>
<th>mg/L ± stdev</th>
<th>Parameter</th>
<th>mg/L ± stdev</th>
<th>Parameter</th>
<th>mg/L ± stdev</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>8.0</td>
<td>Sr</td>
<td>2.05 ± 0.09</td>
<td>Ni</td>
<td>0.02 ± 0.15</td>
</tr>
<tr>
<td>Alkalinity</td>
<td>554</td>
<td>Si</td>
<td>1.28 ± 0.78</td>
<td>Ti</td>
<td>0.017 ± 0.021</td>
</tr>
<tr>
<td>Sulphate</td>
<td>1475.25 ± 15.23</td>
<td>Se</td>
<td>1.12 ± 1.65</td>
<td>Be</td>
<td>0.017 ± 0.012</td>
</tr>
<tr>
<td>Cl-</td>
<td>24 ± 0</td>
<td>P</td>
<td>1.03 ± 1.55</td>
<td>Mn</td>
<td>0.0094 ± 0.025</td>
</tr>
<tr>
<td>Na</td>
<td>886.58 ± 36.77</td>
<td>Al</td>
<td>0.55 ± 0.42</td>
<td>As</td>
<td>0.0014 ± 0.002</td>
</tr>
<tr>
<td>Ca</td>
<td>70.35 ± 7.93</td>
<td>Zn</td>
<td>0.41 ± 0.72</td>
<td>Cd</td>
<td>0.005 ± 1.07</td>
</tr>
<tr>
<td>Mg</td>
<td>39.54 ± 1.87</td>
<td>Ba</td>
<td>0.20 ± 0.04</td>
<td>Cr</td>
<td>BDL</td>
</tr>
<tr>
<td>K</td>
<td>9.94 ± 2.37</td>
<td>Cu</td>
<td>0.19 ± 0.05</td>
<td>V</td>
<td>BDL</td>
</tr>
<tr>
<td>B</td>
<td>2.61 ± 1.34</td>
<td>Li</td>
<td>0.18 ± 0.02</td>
<td>Co</td>
<td>BDL</td>
</tr>
<tr>
<td>Hg</td>
<td>2.43 ± 1.92</td>
<td>Fe</td>
<td>0.06 ± 0.14</td>
<td>Pb</td>
<td>BDL</td>
</tr>
<tr>
<td>Mo</td>
<td>BDL</td>
<td></td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

NOTE: BDL means below detection limit; Stdev means standard deviation

Optimization of the amount of fly ash and lime required

The pH above 11 was required so that Al(OH)$_3$ could be added to precipitate out sulphate as ettringite. Ettringite is only stable at pH 11.5 to 12.5, therefore no Al(OH)$_3$ was added at this stage (Myneni et al. 1998).

The jet nozzle sizes were changed from 8 mm to 6 mm in an attempt to increase the mixing of coal fly ash and mine water through the increase in cavitation. This did not achieve a pH of greater than 11.5 as shown in Figure 3.

The treatment of the mine water with coal FA in a jet loop reactor, with jet sizes set at 8 mm using a liquid to solid ratio 6:1 (Fig 4(a)) and 5:1 (Fig 4(b)) results showed that the Na concentration remained constant, Ca and sulphate concentration increased due to leaching from coal FA into the mine water while the concentration of Mg decreased to almost zero after 60 min when the pH of the mixture increased to above 10. Magnesium is known to precipitate out as Mg(OH)$_2$ at pH greater than 10 (Madzivire, et al. 2011). The increase in the concentration of Ca and sulphate resulted in the increase in EC (Fig 2 and 3).
Changing the jet nozzle size from 8 mm to 6 mm and maintaining the liquid to solid ratio at 5:1 did not result in a significant difference from the results obtained using a jet size of 8 mm (Fig 5). The Na concentration remained the same, while Ca and sulphate leached from FA into the water. The magnesium concentration decreased by almost 100% after the pH increased above than 10 after 60 min.
**Figure 3** pH, electrical conductivity (EC) and temperature profile during treatment of NMD with coal FA in a jet reactor with jet sizes set at 6 mm (liquid to solid ratio of 5:1).

**Figure 4** Na, Ca, Mg and sulphate concentration during treatment of NMD with coal FA in a jet loop reactor with jet sizes set of 8 mm [liquid to solid ratio 6:1 (a) and 5:1 (b)]
The concentration of sulphate (Figures 6 and 5) could not be decreased since \( \text{Al(OH)}_3 \) had not been added to precipitate sulphate as ettringite (Equation 5). Ettringite is stable at pH 11.5 to 12.5 (Myneni, et al. 1998) but the pH of the mixture could not be taken up to greater than 11. This prompted a series of bench scale experiments to evaluate the minimum amount of lime together with coal FA that could be added in order to increase the pH to greater than 11. The mine water to coal FA was maintained at 6:1 and the amount of lime added was varied. Mine water (500 ml) was reacted with a combination of FA (83 g) and various amounts of lime. The amount of lime was varied between 0.25-1 % lime (w/v) and the results obtained are shown in Figure 6. From the results shown in Figure 6, it can be seen that the pH was greater than 11 for all the mixtures evaluated after 15 min at which, 0.52 g of \( \text{Al(OH)}_3 \) was then added to the mixture. After the addition of \( \text{Al(OH)}_3 \) the pH and EC showed a gradual increase. The samples were collected at 30, 60, 90 and 150 min intervals, filtered and the supernatant analysed for anionic and cationic species composition. The results are shown in Figure 7. From the ICP-OES and IC results of the bench scale experiments, the most sulphate removal was noted in 1 % lime only. This is because there was no sulphate ions initially leached into the water. In experiments where a combination of lime and FA was used, sulphate ions initially leached into the water from FA and then started precipitating after addition \( \text{Al(OH)}_3 \). Magnesium concentration dropped to almost zero after 30 min. This is due to the precipitation of \( \text{Mg(OH)}_2 \) at pH greater than 12 which was achieved after only 15 min (Figure 6). On the other hand, Na remained in solution, while Ca leached from coal FA into the mine water.
**Figure 6** pH and EC profile during treatment of NMD with different proportions of lime and FA using an overhead stirrer (0.25 % lime (a), 0.5 % lime (b), 0.75 % lime (c), 1 % lime (d) and 1% of lime only (e))
Optimization of the Jet Loop Reactions

From the bench scale experiments it was found out that the combination of 0.25 % of lime and coal FA (mine water to FA ratio of 6:1) can achieve a pH of greater than 11. The results obtained using a jet loop reactor with jet sizes 6, 8, 10 or 12 mm showed that pH increased after mixing mine water with coal FA and 0.25 % lime such that after 15 min the pH was greater than 11. The temperature of the mixture increased gradually in the jet loop reactor. The EC increased after addition of coal FA and lime and started to decrease after addition of Al(OH)₃ as shown in Figure 8.
Figure 7 Na, Ca and sulphate concentrations during NMD treatment with different proportions of lime and FA using an overhead stirrer (0.25 % lime (a), 0.5 % lime (b), 0.75 % lime (c), 1 % lime (d) and 1% of lime only (e))
d) Figure 8 pH, EC and temperature during treatment of NMD with FA (solid to liquid ratio 6:1), lime 0.25 % (w/v) and Al(OH)$_3$ in a jet loop reactor with jet sizes set at 6 mm (a), 8 mm (b), 10 mm (c) and 12 mm (d).

Treatment of NMD with FA and 0.25 % lime for 15 min followed by addition of 83.2 g of Al(OH)$_3$ has showed that sulphate ions can be reduced from 1465 mg/L to 400-500 mg/L after 120 min (Fig 9), which is within the for the Class II drinking water guidelines (Department of Water Affairs and Forestry 1996). The Na concentration remained constant implying that there was no mineral phase that could take out the Na from the solution. Mg concentration of dropped by almost 100 % after 15 min.

As depicted in Figure 9 above the Ca and the sulphate concentration initially increased during the initial 30 min. This was due to leaching Ca and sulphate into water from the FA. After addition of Al(OH)$_3$ the Ca and sulphate concentration started dropping due the formation of ettringite (Equation 6).

Comparison of the XRD spectra of the FA, Al(OH)$_3$ and lime to that of the solid residues that form after treating NMD is shown in Figure 10 below. From Figure 10, lime (CaO) and calcite (CaCO$_3$) peaks from lime and fly ash spectra and the boehmite (AlOOH) and bayerite (AlOH)$_3$ peaks in the Al(OH)$_3$ spectra disappeared and new peaks of ettringite appeared in the solid residue spectrum. The appearance of ettringite peaks in the XRD spectrum of the solid residue after treating NMD proved that indeed sulphate and Ca concentration dropped due the formation of ettringite crystals (Equation 1).
Figure 9 Na, Ca and sulphate concentrations during treatment of NMD with FA (solid to liquid ratio 6:1), lime 0.25 % (w/v) and Al(OH)₃ in a jet loop reactor with jet sizes set at 6 mm (a), 8 mm (b), 10 mm (c) and 12 mm (d)

Figure 10 The XRD spectrum of fly ash, Al(OH)₃, lime and the solid residues after treating NMD in a jet loop reactor for 120 min (L-lime; C-calcite; Bo-boehmite; E-ettringite; M-mullite; Q-quartz; H-hematite)

Analysis of coal FA after treatment of mine water has showed an increase in the concentration of sulphates, Ca and Mg. This correlates well with the drop in the concentration of these elements in the mine water during treatment with coal and lime.
### Table 3: Comparison of the composition of FA before and after treating NMD for 120 min in a jet loop reactor

<table>
<thead>
<tr>
<th></th>
<th>Major elements</th>
<th>Minor elements</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>% oxide</td>
<td>Fly ash before</td>
<td>Fly ash (120 min)</td>
<td>Fly ash</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>48.27 ± 0.044</td>
<td>43.99 ± 0.039</td>
<td>2079 ± 12.80</td>
<td>1991 ± 13</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>30.89 ± 0.22</td>
<td>28.99 ± 0.18</td>
<td>226.02 ± 26</td>
<td>223.66 ± 14.04</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>2.81 ± 0.027</td>
<td>2.90 ± 0.014</td>
<td>16.08 ± 6.89</td>
<td>18.35 ± 5.70</td>
</tr>
<tr>
<td>MnO</td>
<td>0.020 ± 0.0004</td>
<td>0.024 ± 0.00052</td>
<td>89.34 ± 2.29</td>
<td>80.56 ± 8.30</td>
</tr>
<tr>
<td>MgO</td>
<td>2.12 ± 0.041</td>
<td>2.57 ± 0.050</td>
<td>117.26 ± 3.38</td>
<td>114.20 ± 3.84</td>
</tr>
<tr>
<td>CaO</td>
<td>6.71 ± 0.083</td>
<td>9.29 ± 0.062</td>
<td>51.50 ± 1.80</td>
<td>48.94 ± 1.99</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>0.55 ± 0.0094</td>
<td>0.65 ± 0.013</td>
<td>88.97 ± 6.41</td>
<td>83.80 ± 3.82</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>0.84 ± 0.0086</td>
<td>0.81 ± 0.011</td>
<td>100.25 ± 4.02</td>
<td>107.86 ± 4.42</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>1.26 ± 0.016</td>
<td>1.25 ± 0.010</td>
<td>72.48 ± 0.89</td>
<td>67.58 ± 0.30</td>
</tr>
<tr>
<td>P$_2$O$_5$</td>
<td>0.89 ± 0.013</td>
<td>1.020 ± 0.0096</td>
<td>3495.55 ± 5.63</td>
<td>3445.37 ± 2.88</td>
</tr>
<tr>
<td>SO$_3$</td>
<td>0.19 ± 0.0024</td>
<td>0.35 ± 0.0030</td>
<td>46.60 ± 3.33</td>
<td>52.18 ± 5.10</td>
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<tr>
<td>LOI</td>
<td>5.24 ± 0.03</td>
<td>7.38 ± 0.01</td>
<td>U</td>
<td>63.28 ± 2.43</td>
</tr>
<tr>
<td>Sum</td>
<td>99.81 ± 0.07</td>
<td>99.23 ± 0.06</td>
<td>66.58 ± 1.73</td>
<td>63.17 ± 6.03</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>V</td>
<td>64.91 ± 6.24</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Zn</td>
<td>64.61 ± 4.41</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Zr</td>
<td>787.7 ± 3.35</td>
</tr>
</tbody>
</table>
Conclusions
From the results obtained, sulphates and Ca initially leached into the mine water from fly ash. This is because the mine water is under saturated with respect to gypsum. After addition of Al(OH)$_3$ to the mixture the concentration of sulphates and Ca started to decrease due to the precipitation of ettringite. Na remained almost constant during treatment of mine water with fly ash, while the concentration of Mg dropped to approximately to zero when pH was increased to greater than 12. Experiments conducted using an overhead stirrer have shown low sulphate removal as compared to jet loop experiments. The treatment technology promises to be a cheaper active technology for mine water treatment since fly ash and mine water are waste materials, which are found close to each other. This is due to the increased rate of formation of ettringite caused by the superior mixing in a jet loop reactor as compared to an overhead stirrer. Jet sizes did not have any effect on sulphate removal. Changing of the mixing technique from a combination of impingement and cavitation to cavitation only did not result any noticeable difference on sulphate removal. Finally, cavitation and impingement mixing of NMD and fly ash resulted in a gradual increase in temperature of the mixture.

References


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