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A CASE STUDY OF IRON DUKE MINE

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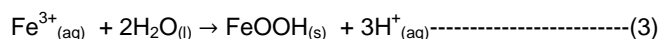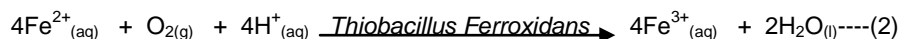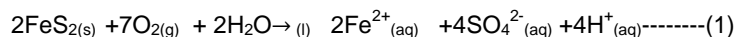[1]kmpofu1985@gmail.com, [2]smushiri@sirdc.ac.zw, [3]elijahnyoni@yahoo.com

ABSTRACT

IDM acid mine drainage (AMD) was found to have high concentrations of SO_4^{2-} (>3500mgl^{-1}), electrical conductivity (E.C >20 000µScm^{-1}) and acidic pH (<2.0) levels before neutralization by Trojan mine coal ash. Three treatments (CaO, Ca (OH)$_2$ and Coal ash) were used to neutralize affected soil from the Environ-Green site which was polluting the river system. The resultant effluent from the treated pots was pure representation of the groundwater and was chemically characterized to establish the suitable liming application level. The high application level of 560kg/tonne of soil was recommended since at this level, the SO_4^{2-} neutralization was optimal in 92% region and precipitation of Fe was high in the 99.4% region. Analysis of the heavy metals was done using Atomic Absorption Spectrometer (AAS), NO_3^{-} and SO_4^{2-} was analyzed by a spectrophotometer and E.C and pH were determined by an electrode potential. Statistical analysis of results was done using Kruskal-Wallis statistic test. At 95% significance level, SO_4^{2-} reduction rate was the same in all liming materials. A field application rate of 2 184.1 tonnes of coal ash /Ha of affected site or 560kg/tonne of affected soil was recommended.

Keywords: acid mine drainage; environmental pollutant; coal ash
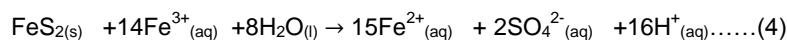
1. INTRODUCTION

1.1. Mining and acid mine drainage

Iron Duke Mine is the only active pyrite mine in Zimbabwe since 1914 and is located in the green belt iron mask range at a 53km peg along Harare-Bindura highway. It has to be born in mind that the mining company offers employment to the population of the rest of Zimbabwe in a wide span of professions. The company's business is centred on the mining of iron pyrite (FeS_2). Acid Mine Drainage (AMD) is an environmental pollutant of major concern at Iron Duke and throughout the world in mining regions. AMD occurs as a result of the oxidation of sulphide minerals when exposed to oxygen and water during the mining process (Jage *et al.,* 2001). Formation of AMD is primarily a function of the geology, hydrology and mining technology employed at the mine site (Kepler & McCleary, 1994). The resulting water is usually high in acidity and dissolved heavy metals. The metals stay dissolved in solution until the pH raises to a level where precipitation occurs. The process for AMD formation is commonly represented by the following chemical reactions (Zipper, 2001):

$$2FeS_{2(s)} + 7O_{2(g)} + 2H_2O \rightarrow_{(l)} 2Fe^{2+}_{(aq)} + 4SO_4^{2-}_{(aq)} + 4H^+_{(aq)} \text{--------(1)}$$

$$4Fe^{2+}_{(aq)} + O_{2(g)} + 4H^+_{(aq)} \underline{\textit{Thiobacillus Ferroxidans}} \longrightarrow 4Fe^{3+}_{(aq)} + 2H_2O_{(l)} \text{----(2)}$$

$$Fe^{3+}_{(aq)} + 2H_2O_{(l)} \rightarrow FeOOH_{(s)} + 3H^+_{(aq)} \text{------------------------(3)}$$

The process is initiated with the oxidation of pyrite and the release of ferrous Iron (Fe^{2+}), sulphate and acidity reaction (1). The sulphide-oxidation process is accelerated by the presence of *Thiobacillus* bacteria reaction (2). Ferrous Iron (Fe^{2+}) then undergoes oxidation forming ferric Iron (Fe^{3+}). Finally Fe^{3+} is hydrolyzed, forming insoluble hydroxide (FeOOH), an orange-colored precipitate, and releasing additional acidity reaction (3).

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Lastly, pyrite can also be oxidized by Fe^{3+} as shown below:

$$FeS_{2(s)} + 14Fe^{3+}_{(aq)} + 8H_2O_{(l)} \rightarrow 15Fe^{2+}_{(aq)} + 2SO_4^{2-}_{(aq)} + 16H^{+}_{(aq)}......(4)$$

The Fe^{3+} is generated from reaction (2). This is the cyclic and self-propagating part of the overall reaction and takes place very rapidly and continues until either ferric Iron or pyrite is depleted. In the reaction, Iron is the oxidizing agent (Hadley and Snow 1974).

According to a South African Water Research Commission, sources of water related pollution originate from mining activities (Du Plessis, 1997). For instance, upon infiltration by rainwater, spoil heaps leach highly acidic AMD to ground waters as a result of pyrite oxidation that forms sulphuric acid, which in turn mobilizes toxic metal species by dissolution. AMD is characterized by a pH of 2 or less, total dissolved solids (TDS) in the order of 4000-5000mg/l, high Fe content, high Al and Mn concentrations and a high sulphate content (Bullock and Bell, 1997). Treatment of AMD is currently done by natural means or by active treatment and passive treatment. The most commonly used chemicals for treating AMD are; CaO, $Ca(OH)_2$,$CaCO_3$,$NaOH$,NH_3 and Na_2CO_3 (Hedin, *et al.,*1994).These systems require the installation of a plant with agitated reactors, precipitators, clarifiers and thickeners (Gazea *et al.,* 1996).

1.2. Coal Ash

Chemical compositions reveal that all natural elements can be found in the coal ash. The major elements in coal ash are Fe, Al and Si together with significant amounts of Ca, K, Na and Ti. The most common minerals that constitute coal ash include: quartz (SiO_2), mullite ($Al_6Si_2O_{13}$), hematite (Fe_2O_3), magnetite (Fe_3O_4) and small portion of unburnt carbon. In addition to these minerals anhydrite ($CaSO_4$), lime (CaO) and periclase (MgO) are also included. The free alkalinity imparted by CaO (approx.7wt %) and the fact that coal ash has a very high surface area due to small particle size makes it a good neutralization agent (O'Brien. 2000). An analysis of coal ash material has shown that many toxic elements are present (Adriano *et al.,* 1980). Minerals such as; sulphates, carbonates, phosphates, silicates and clay minerals enrich the inorganic component of coal with elements such as Si, Fe, S and P. These toxic elements remaining in coal ash arise from rock weathering into coal basins or from trace element enrichment of humus formed from the original vegetable matter. Coal ash can leach out toxic metals, anions and cations from the ash heap during rainfall. This caustic (pH>12) leachate contains high concentrations of hydroxides, carbonates and sulphates and precipitates minerals such as Iron oxides and sulphate (Adriano *et al.,* 1980).

Pilot studies indicated that co-disposal of AMD with aqueous extracts of Eskimo fly ash neutralizes the corrosive waste. Precipitation of alumino-silicates and iron compounds occurred at a pH of 10. Direct mixing of various ratios of simulated AMD and Eskimo fly ash to a predetermined pH in the co-disposal process enhanced the formation of gypsum and soil components. These secondary aluminosilicate and/or aluminocalcium sulphate (ettringitic) or ferrihydrite ($Fe_2(SO_4)_3$) precipitates have the capacity for mutual beneficiation of water quality in co-disposed AMD and fly ash (Burgers. 2002).

1.3. Characteristics of Pyrite (Fes₂)

Pyrite is also known as "*Fool's gold".* There are other shiny, brassy yellow minerals, but pyrite is by far the most common and the most often mistaken for gold. It is so common in the earth's crust that is found in almost every possible environment. Pyrite is a polymorph of marcasite i.e. it has the same chemistry as marcasite but different structure and therefore different symmetry and different crystal shape. Pyrite (FeS_2) frequently occurs in the shales and coaly material present in spoil heaps. On weathering, it gives rise to sulphuric acid, (Fe^{2+}) and (Fe^{3+}) and ferric hydroxides (Fe $(OH)_3$), which lead to acidic conditions in the weathered material. Oxidation of pyrite within spoil heap waste is governed by the access of air which in turn, depends upon the particle size distribution, degree of water saturation and degree of compaction. If highly acidic oxidation products develop, they may be neutralized by alkaline materials in the waste. Surface water run-off can leach out soluble salts, especially chlorides. This may result in the

loss of up to 1tonne of Cl⁻ (aq) per hectare of exposed spoil heap per annum under average (British) rainfall conditions (Bell, 1998).

1.4. Problem Statement

AMD has contaminated the soil-water chemistry through seepage from contaminated site; the pollution levels in the river system have attracted astronomical amounts in environmental charges. The high acidity of acid mine drainage and the high amounts of dissolved heavy metals (such as copper and zinc) generally make acid mine drainage extremely toxic to most organisms (Du Plessis, 1997). The Yellow Jacket stream is largely devoid of life for a long way downstream. Drainage water from Environ-green site is initially clear but turns into a vivid orange colour as it becomes neutralized because of the precipitation of iron oxides and hydroxides. This precipitate often called ochre, is very fine and smothers the riverbed with very fine silt. Thus, aquatic life that used to feed on the bottom of the stream can no longer feed and so are depleted. Because these animals are at the bottom of the aquatic food chain, this has impacts higher up the food chain into fish. So, even if the acidity and heavy metals are neutralized, acid mine drainage still affects wildlife a long way down stream because of these indirect effects. In addition to killing bottom dwelling organisms, this smothering ochre or orange precipitate reduces the amount of gravel for fish to lay their eggs on, and hence affecting fish breeding (Bullock and Bell, 1997).

The acidification of the water has immediate deleterious effects on aquatic ecosystems. A direct effect is the conversion below pH 4.2 of all carbonate and bicarbonate into carbonic acid, which dissociates into carbon dioxide and water. This destroys the bicarbonate buffer system in the water, which acts as a control on acidity (Ashton et al., 2001). Since many photosynthetic organisms use bicarbonate as their inorganic carbon source, their ability to photosynthesise is limited or destroyed altogether as bicarbonate decomposes and becomes less available. The iron hydroxide flocs block light penetration, thus further limiting photosynthesis (Kelly, 1988).

Contamination of the water poses risks to health and integrity of structures, as well as economical loss. In high quantities, heavy metals can affect plant life. Not only is the A.M.D. detrimental to the health of the plant, plants that uptake heavy metals will pass them onto animals within the food chain. Growth and reproduction can be adversely affected in both aquatic animals and in terrestrial animals where drinking water is contaminated. Aquatic species are most at risk, as many are not tolerant to pH fluctuations, with most species having a defined pH tolerance range. Physical structures can be compromised as acid corrodes infrastructures such as bridges (Jage *et al.,* 2001).

1.5. Justification of the Study

Coal ash has been used as a liming material for AMD reclamation in other countries but in Zimbabwe, no such practice has been conducted therefore this was a virgin and fertile opportunity for the showcase of environmental expertise. Research findings will be used to bridge the theory-practical gap through provision of long time monitoring data for testing and optimization of acidification models which would be effected through sound documentation of AMD's effects on soil and soil-water chemistry. Active treatment methods that are used are expensive whereas passive treatment (where AMD is passed through constructed wetlands) is not efficient enough to immobilize the toxic metals and hence this would offer a more cost-effective/convenient AMD treatment method.

The objectives of the study were:
- To reduce toxicity levels for selected metals (Fe, Al, and Mn) and SO_4^{2-} to acceptable levels.
- To neutralize acidity discharged to surface and ground water.

The hypothesis of the study is that Coal ash has the same neutralizing effect as lime on acid mine drained material.

2. METHODOLOGY

2.1. Site Description

The research was carried out at Iron duke mine (**Figure 1**). Specifically, it was conducted at the Waste dump site (**Figure 2**) where rock waste was being deposited since 1935 until 1998. The former dump site has been

rehabilitated to avoid acidity from entering the water course .The site is engineered in such a way that it is in three steep slopes which avoid rain water to seep into dump but only allows runoff. The third lower site was selected, as this is visibly most affected area. This gave unbiased results since the ratio that was effective at this level would also be effective at the above slopes. The excess lime sank to the bottom and through seepage neutralized acidity at lower levels.
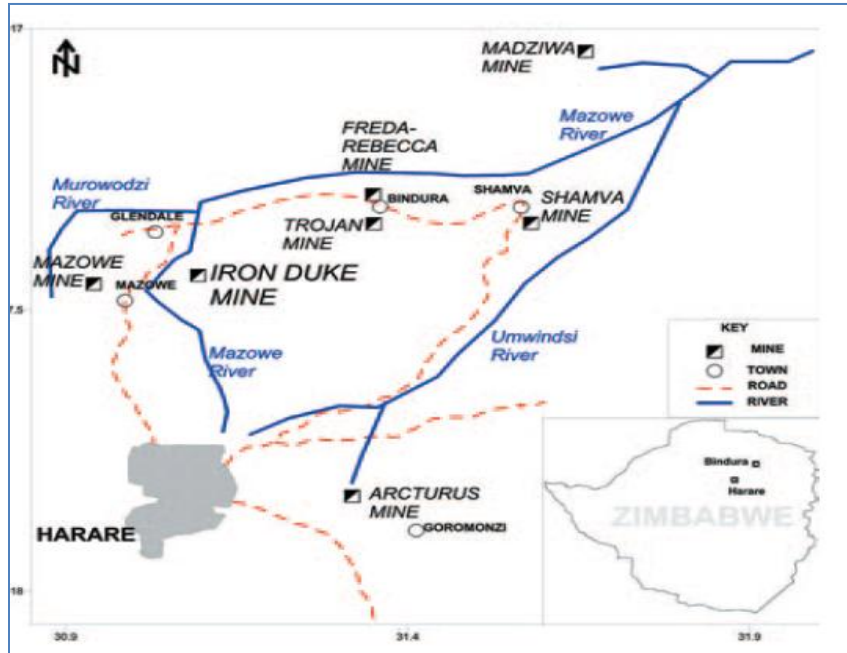

Figure 1: Location of Iron Duke Mine (Source: Ravengai et al, 2005)
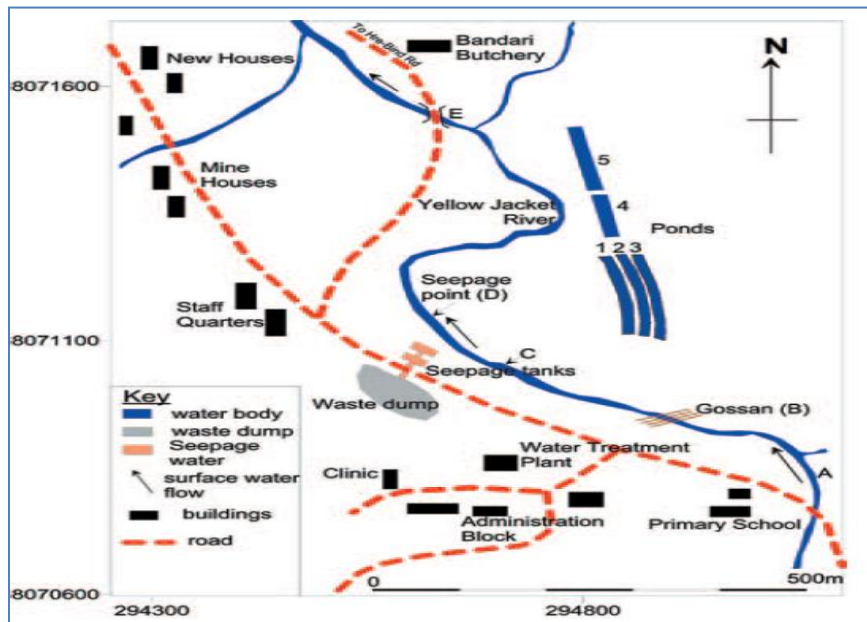

Figure 2: Surface plan of Iron Duke Mine infrastructure in relation to the

Yellow Jacket River (Source: Ravengai et al, 2005)
From the dump site the seepage enters into the Yellow Jacket river stream as shown in Figure 2. Seepage into the river is rich in dissolved heavy metals, high E.C and high acidity.

2.2. Sampling Technique

The area where soil samples were collected was divided into portions and a sampling procedure was adopted. These portions were based on the spacing that was once used during the re-vegetation process that failed some years ago. Systematic sampling was used to collect samples from the site as this would spread the sample more evenly over the site. It is also easier to conduct than a simple random sample. The site had 125 holes that had once been planted with the gum seedlings. Sixty (60) holes were sampled and the collected soil mixed to give a composite sample. This was done to evenly distribute the acidity, since at some points at the same site; some gum plants were able to survive whilst others failed. Therefore a suspicion was raised that such unevenness could be as a result of uneven distribution of the acidity at the site.

2.3. Determination of Lime Application Levels

The acidity was first quantified that is suspected to be a result of oxidation of pyrite from the Environ-Green site. Data used were based on the calculations in Bard (2006), who quantified the pyrite oxidized on a yearly basis and found it to be 35 tonnes. The calculations to quantify the acidity at the dump site were based on the following chemical reaction by Zipper (2001):

$FeS_{2(s)} + 15/4 O_{2(g)} + 7/2 H_2O_{(l)} \rightarrow Fe(OH)_{3(aq)} + 2SO_4^{2-}{}_{(aq)} + 4H^+{}_{(aq)}$………(13)
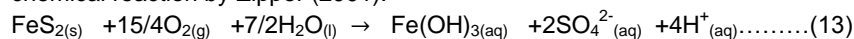
From the calculations made, the medium application level of a liming material was found to be 800g for CaO and 1000g for Ca (OH)$_2$.

Table 1: Liming application levels and liming equivalence.

Application rate (kg/tonne)	Liming Equivalence
680	1.5:1
560	2:1
400	2.5:1
320	3:1
240	4:1
160	6:1
40	25:1
Control	AMD

The effluent/leachate, which represented the seepage water into the river, was filtered and analyzed for the chemical parameters using an Atomic Absorption Spectrometer (AAS) for the heavy metals and Spectrophotometer for the nitrates and sulphates. Results were analyzed statistically by Kruskal-Wallis test for sulphates.

2.4. Experimental Design

1. Coal ash was mixed with a fixed mass of AMD affected soil in different ratios. Samples were collected from the dumping site.
2. Three treatments were used (CaO, Ca (OH)$_2$ and Coal Ash). They had three replicates for every application rate.
3. The effluents from the experiment were drained for chemical characterization every month.

2.5. Instrumentation

Post process water was drained from the sample bags and it is a pure representation of the underground water that would come from the site. The samples were collected in a container that was placed below the wire mesh where the polythene bag was placed. The samples were taken to the laboratory for analysis of the heavy metals (Mn and Fe), Al, sulphates and nitrates. The heavy metals were analyzed using Atomic Absorption Spectrometer (AAS), sulphates and nitrates were measured by a spectrophotometer. Electro conductivity (E.C) and pH were measured by electrode potential method at the site.
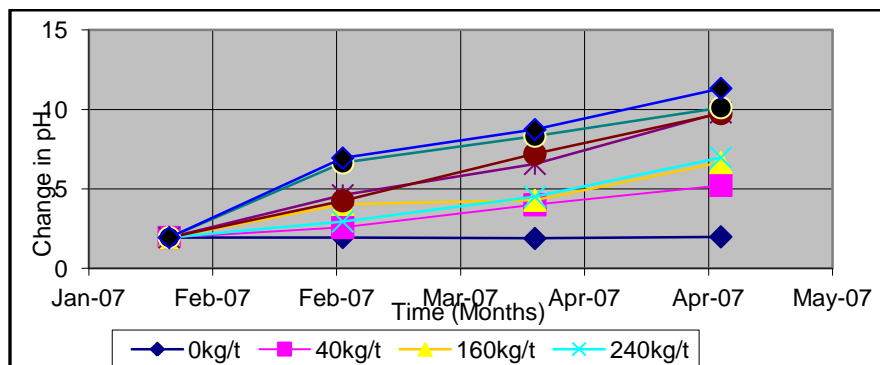
3. RESULTS

Figure 3: pH change in Coal Ash over three months.

For the different application levels of coal ash, three application levels could be able to neutralize the acidity during the contact time of the research. Application levels of 560kg/t and 680kg/t attained neutral condition after a month and further raised the pH conditions up to 11.33 and 10.12 for 680 kg/t and 560 kg/t respectively. Application levels of 240kg/t and below could not achieve the neutral conditions of pH 7.
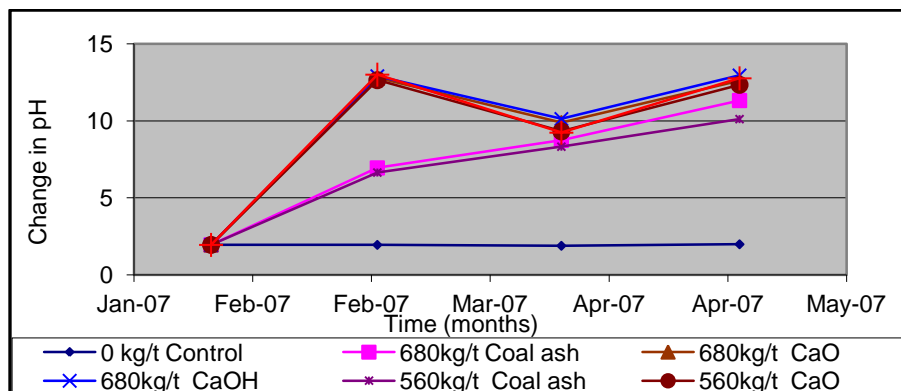

Figure 4: pH change in high application levels over three months

High application levels (680 kg/t) from all the three liming materials reveal that neutralization process is constant in application levels of coal ash that constantly increases with time for the three-month period.
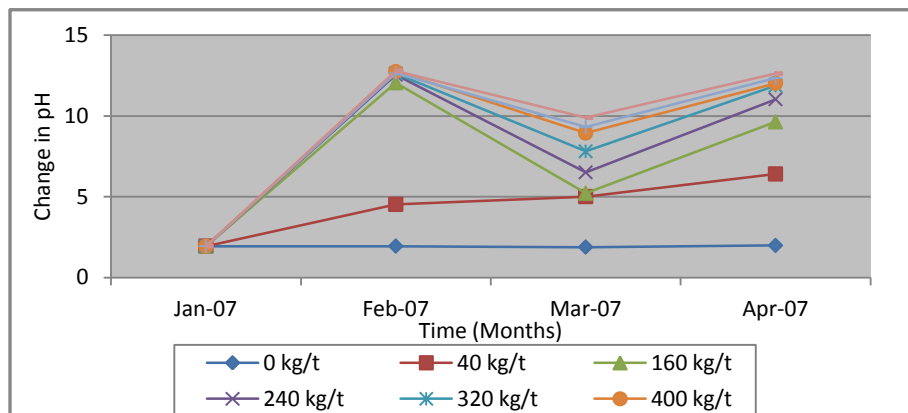
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Figure 5: pH changes in CaO over three months

The highest attained pH value was 12.79 for application level of 680 kg/t. Application level of 40kg/t could not attain to the neutral condition of pH 7.
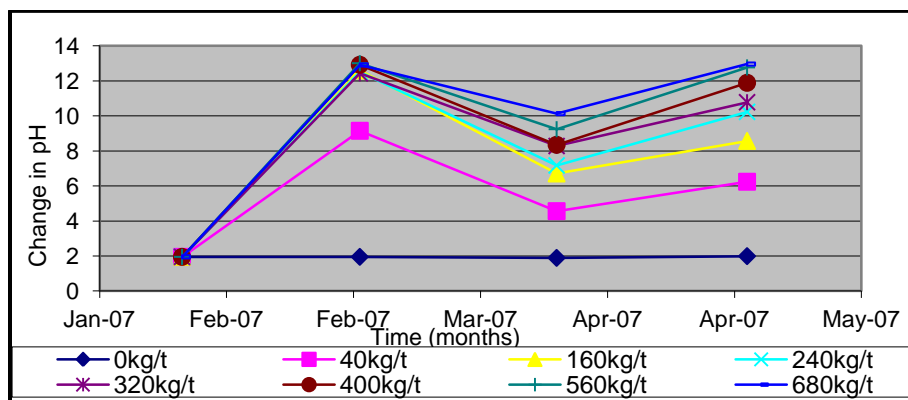

Figure 6: pH changes in Ca (OH)$_2$ over three months.

Generally the pH trends in Ca (OH)$_2$ was similar to that in CaO except for the fact that the 40 kg/t application level went beyond pH 7 in February before finally dropping to pH 6.24 in April. The highest attained pH value was 12.91 for application level of 680 kg/t.
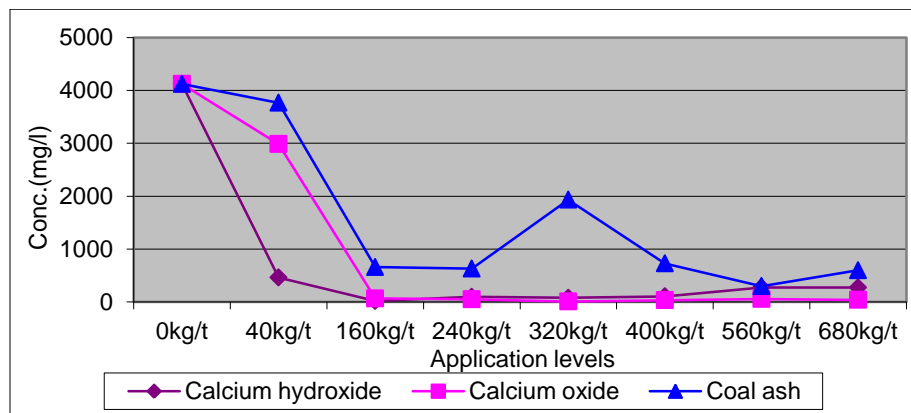
Figure 7: SO_4^{2-} reductions in all liming materials

Kruskal- Wallis statistic test was used to test the formulated hypotheses.

H_O: SO_4^{2-} reduction rate was the same in all three liming materials.
H_1: SO_4^{2-} reduction is not the same in the three liming materials.
H_C= 10.72; $H_{0.05}$ (7, 7, 7) = 14, 1

Since H_C < H0.05 (7, 7, 7) we accept H_O and conclude that SO_4^{2-} reduction rate was the same in all three liming materials. However, the Calcium hydroxide liming material proved more superior that the rest in reducing SO_4^{2-} concentrations in the 0 kg/t-160 kg/t application levels.
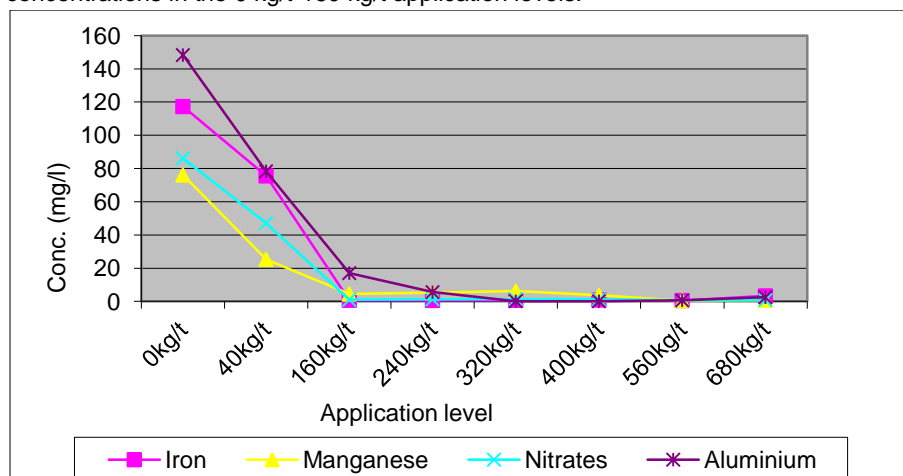

Figure 8: Contaminants reduction in Coal Ash

For chemical components of this research had similar reduction trend starting with the highest value being reduced to the smallest possible concentration. For Iron (Fe), the concentration increased slightly in the high application levels. This however could be explained by the fact that burnt coal ash, has a lot of Fe oxides which sequester transition anions and immobilize the mobility of the heavy metals. Hence at high levels they might be in the liquid phase which can be detected by the AAS. High levels of NO_3^- can be attributed to the rock formation chemistry which might have high nitrogen content.

Figure 9: Change in E.C in Coal Ash

E.C reduction was generally successful such that by the 2nd month it had reduced to less than 10000µS/cm in all but two applications (0 kg/t and 40 kg/t).
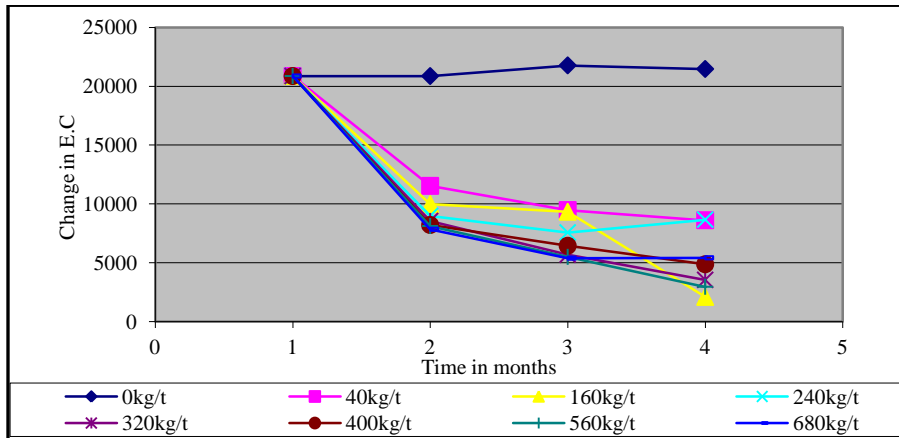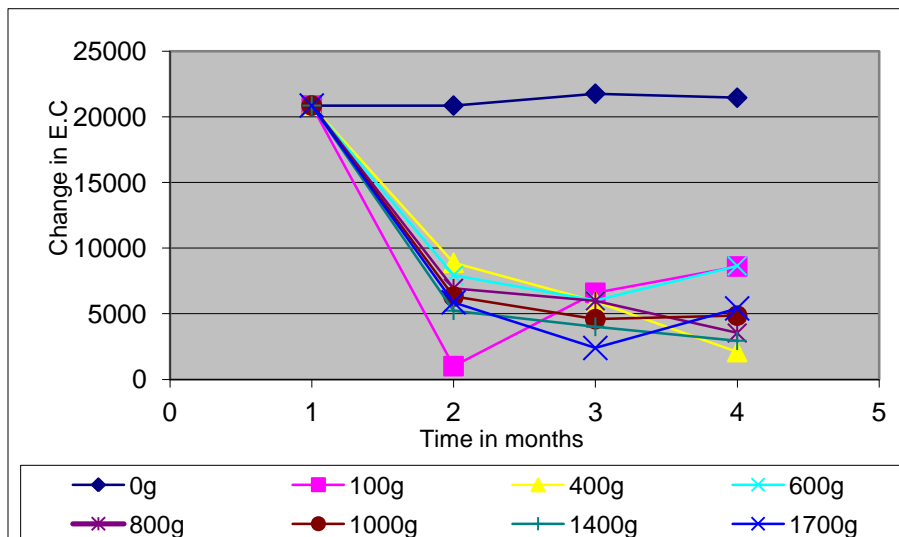

Figure 10: Changes in E.C in CaO

E.C reduction was generally successful such that by the 2nd month it had reduced to less than 10000µS/cm in all but one application.
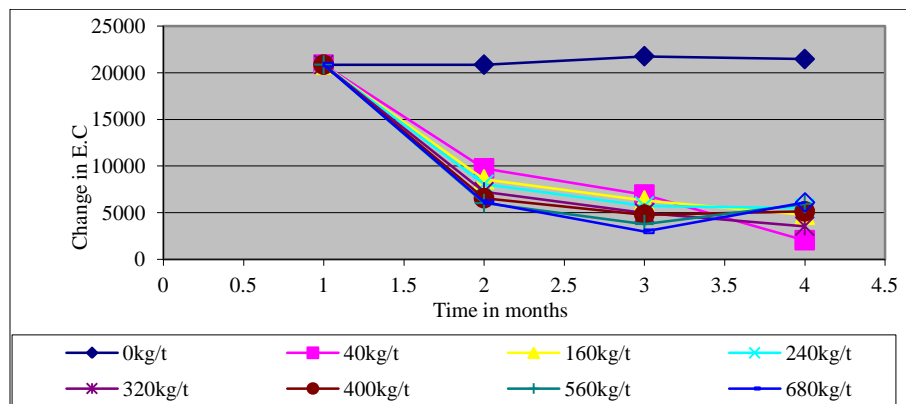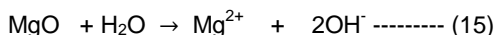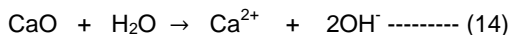
Figure 11: Changes in E.C in Ca (OH)$_2$

E.C reduction was also generally successful such that by the 2nd month it had reduced to less than 10000μS/cm in all but one application. By the last month, E.C had fallen to below 7000μS/cm.

4.   DISCUSSION OF RESULTS

4.1. pH Changes

The evolution of pH values with time for AMD; coal ash were characterized by two buffer regions at pH 4.5-5.0 and at pH 9.0 as shown in **Figure 1**. The buffering region at pH 9.0 could be attributed to the formation of soluble hydrous complexes by cations such as Al(OH)$_4^-$ at high pH. There are two opposing processes, which establish the pH value for the solution in this neutralization process. The dissolution and hydrolysis of oxide components such as CaO and MgO from coal ash contributes to an increase in solution pH.

$$CaO \ + \ H_2O \ \rightarrow \ Ca^{2+} \ + \ 2OH^- \ \text{---------} (14)$$

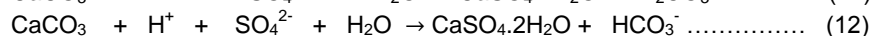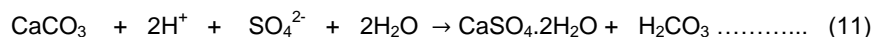$$MgO \ + H_2O \ \rightarrow \ Mg^{2+} \ + \ 2OH^- \ \text{---------} (15)$$

Hence the increasing trends shown by Figures 3, 4, 5, 6 and 7 are as a result of the dissolution of the oxides to become available in the liquid phase. Reardon et al. (1995) conducted leaching studies of coal ash at two different water/solid ratios and they were able to detect the existence of mineral solubility control for some elements. In the AMD: Coal ash neutralization reactions the elements occurring as soluble salts on the surfaces of the coal ash particles undergo initial rapid dissolution and mineral precipitation will occur depending on the species concentration. After several weeks a stable solution composition was achieved especially for elements whose hydroxides are highly soluble or exist as anions in solution (Mo, Se, and B).

After several weeks of dissolution and precipitation reactions, the kinetics slowed down substantially and a relatively stable solution composition was attained. This was shown by **figures 5** and **6**. CaO and Ca (OH)$_2$ neutralization trends for these liming materials were similar, characterized by a depression after about two months period. At high pH, Fe3$^+$ reacts with $O_{2(g)}$ and H_2O and forms ferric hydroxide, which precipitates.

$$Fe^{3+} \ + 3H2O \ \ \rightarrow Fe \ (OH)_{3(S)} \ + \ \ 3H^+ \ \text{……………..}(3)$$
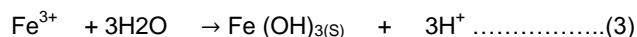
High pH values can be maintained by neutralizing minerals in waste rock as shown below:

$$CaCO_3 \ + \ 2H^+ \ + \ SO_4^{2-} \ + \ 2H_2O \rightarrow CaSO_4.2H_2O + \ H_2CO_3 \ \text{………....} \ (11)$$
$$CaCO_3 \ + \ H^+ \ + \ SO_4^{2-} \ + \ H_2O \rightarrow CaSO_4.2H_2O + \ HCO_3^- \ \text{……………} \ (12)$$

Relative rates of the above depend on pH and are responsible for the efficiency of the neutralization process. Fe^{2+} oxidation rate increases with increasing pH,

$$4Fe^{2+} + O_{2(g)} + 4H^+ \rightarrow 4Fe^{3+} + 2H_2O \ldots\ldots\ldots\ldots(2)$$
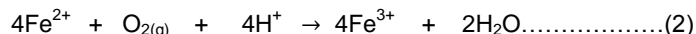
and the neutralization potential of the reactions (11) and (12) decreases when pH increases. This leads to a stoichiometric incompatibility between acid-generating and acid-neutralizing reactions.

4.2. Mn, Fe, Al, NO_3^- and SO_4^{2-} trends

Acid mine drainage was reacted with coal ash in a two and a half months equilibration time to produce neutral and alkaline process waters and remove major and minor elements from solution. The elemental concentration trends with time in the solution were used to discern which elements have solubility control in the neutralization process. According to Bell (1998), SO_4^{2-} concentrations generally are not affected by neutralization unless mineral saturation with respect to gypsum is attained. Hence, SO_4^{2-} and E.C sometimes maybe used as an overall indicator of the extent of acid generation after neutralization by acid-consuming minerals. By that basis it can be safely concluded that the results showed that there were no differences at the rate at which SO_4^{2-} was neutralized and removed from the soil-water (**Figure 7**).Therefore sulphate concentrations were found to be controlled by the precipitation of gypsum ($CaSO_4.2 H_2O$) at low pH, ettringite ($Ca_6Al_2O_6 (SO_4)_3.32 H_2O$) at high pH (Maree et al, 1996). Hydrolysis of AMD constituents such as Fe^{3+}, Al^{3+}, Fe^{2+} and Mn^{2+}; offsets the pH increase that is contributed by the dissolution of the oxide components. According to Gitari et al, (2004), the relative quantities of soluble bases (oxides) in coal ash and hydrolysable constituents in AMD dictate whether the final solution at a given contact time will have a dominant acid or basic character.

Coal ash consists mainly of aluminosilicate glass matrix in addition to crystalline mullite and quartz (Hullet and Weinbeger, 1980). The glass phase in coal ash has been attributed to the formation of soluble salts of; As, Na, Mg, K, Sr, B, on the surface of coal ash spheres which aids in the reduction in concentration of these elements Early, et al, (1990). The highly soluble CaO occurring as sub-micron fragments on the coal ash particles is highly reactive and was utilized in the neutralization of acid mine drainage. The highly soluble CaO in coal ash increased the pH of the AMD on contact. As pH increases, Fe^{3+}, Al^{3+} and Mn concentration decreased primarily due to precipitation of hydrous oxides such as amorphous iron (iii) hydroxide, ferrihydrite, schwertmannite, or goethite and amorphous Al (iii) hydroxide or poorly crystalline gibbsite. Iron oxides with their high surface area sequester cations such as transition metals and radionuclides, in proportions that are a function of solution composition and pH. Fe-oxides are also strong adsorbers of anionic complexes such as AsO_4^{3-}, CrO_4^{2-}, and PO_4^{3-} (Randall, 2001). Therefore Iron compounds are useful for retarding transport and immobilizing contaminants. They play a great role in the coal ash/AMD treatment process.

Co-disposal of Iron Duke Mine AMD by utilizing Trojan coal ash is a suitable method for the low-cost treatment of acid mine drainage. Hence neutralization of AMD waste streams with coal ash allows water purification by co-disposal of two hazardous wastes, without additional use of liming agents or standard water purification chemicals such as strong acids or bases and simultaneously allows the precipitation of high capacity adsorbents such as zeolites.

4.3. E.C changes

The formation and accumulation of these hydrous oxides promotes sorption and co-precipitation of dissolved Mn, Cu, Co, Ni and Zn (Cravotta &Traham, 1999), hence stabilizing them in the co-disposal solids. In the AMD: coal ash neutralization reactions, Fe^{3+} is expected to be rapidly precipitated and Fe^{2+} quickly oxidized and hydrolyzed once the mixture attains optimum pH (>5.0). With the high SO_4^{2-} content (> 10 000 ppm) of the AMD, it is likely that some of the SO_4^{2-} could be incorporated into the structure or adsorbed on the surface of the Iron oxides/oxyhydroxides. Hence the E.C values generally would be expected to be high as this indicates the total dissolved solids present in the effluent as shown by **Figure 9, 10** and **11**.

The application of coal ash to control AMD generation from sulphidic wastes such as mine tailings and coal spoils has been studied (Xenidis , et al 2002). Most of the studies on treatment of AMD with coal ash have used synthetic AMD consisting mainly of the major parameters (SO_4^{2-}, Fe^{3+}, Fe^{2+}, Al^{3+}, and Mn). A preliminary co-disposal study, using a synthetic AMD with leachate derived from an Eskom fly ash was undertaken O'Brien, 2000). This study showed that the pH and EC of the leachate could successfully be reduced by the addition of synthetic acid mine drainage (SAMD). Several authors pointed out that the dominant chemical characteristics of a coal ash leachate (pH and E.C) are usually established within minutes of addition of water. This results from the flush of ions to the solution from readily soluble minerals present in the solution (Reardon et al, 1995). As a case study at IDM, the E.C had a reduction trend which was similar and consistent in all liming treatments.

5. CONCLUSIONS

The objective of this research was to evaluate the chemistry of the resulting process water as the sulphate and metal rich AMD interact with coal ash, to relate the solution chemistry to that of process water from the standard liming reagents. Pollution control of Iron Duke Mine AMD has been shown to be possible by application of a process for removal of toxic ionic impurities. Kruskal-Wallis test showed that at 95% significance, SO_4^2 level was the same in all liming materials. Since the concentration of SO_4^2 is the indicator of the heavy metals mobility, it is hereby concluded that objective 1 was achieved. Most significantly, two waste products (AMD and coal ash) were neutralized and when reacted together, produced much cleaner water broadly comparable to post process water derived from lime or limestone treated AMD. Post process waters were significantly purified, with only relatively low concentration of some species of toxic elements remaining in solution at high pH, normal for these elements.

There are two factors that finally dictate the final pH of the process waters:

a)   AMD: coal ash ratio
b)   Contact time

Increased removal of elements such as Mg, Mn, Al, Si and Fe was observed at the lower AMD: coal ash ratios indicating the importance of the application levels in this process. The alkalinity of coal ash (primarily present as CaO) was used to neutralize AMD. The dissolution and hydrolysis of oxide components such as CaO and MgO from coal ash on contact with AMD contributes to an increase in solution pH. This newly developed co-disposal procedure worked best for treating high TDS AMD. Sulphate removal rates were in the region of 92% at 560kg/t application level; Fe at 99.3% and Mn at 98% at the same application level. Al and heavy metal removal was often total depending on the final pH.

6. RECOMMENDATIONS

The research results showed that an application rate of 560kg of coal ash/tonne of affected soil would bring best results. At the same level, Sulphate removal rate was 92% efficient, Fe was 99.3% and Mn was 98% at the same application level. Since the kinetic tests that have been conducted so far, showed that AMD generation is a continuous and self-generating process, lime application frequency should always be determined. This can be done through the continuous monitoring of the acidification models and constant checking compliance with the regulations. Trojan mine is located near Iron Duke Mine less than 50kilometres away whereas BIMCO (where lime is collected) is hundreds of kilometers away from the mine. Close proximity of Trojan mine provides a good opportunity to co-dispose the two pollutants (coal ash and AMD).

Lime is very costly since transport cost and purchasing costs are included but coal ash has no marketable value and it is a waste which is posing a disposal problem. According to the cost analysis results by the learner, as at 07 July 2007, a tonne of lime was ZIM\$5 434 787.80 against \$0.00 of coal ash. Hence the use of coal ash to neutralize AMD would be the most cost-effective method the mine can adopt. Coal ash was found to neutralize AMD with no stoichiometric incompatibilities**.** In CaO and Ca (OH)$_2$ graphs, pH would temporarily decrease then it would rise. In the field, this would delay the attainment of neutral conditions.

The alkalinity of coal ash may not be as high as that of lime or limestone, but availability in large quantities offers a cost effective method of neutralizing acid mine drainage. Moreover, the formation of stable mineral phases with trace metal co-precipitation and adsorption in this process could result in residues suitable for disposal than the unreacted coal ash. Hence a method of using coal ash for pyrite mines backfilling with no risk of ground water contamination was sought.

Comparison of coal ash with different 'liming agents' ($Ca(OH)_2$ and CaO) indicated that co-disposal of AMD is feasible with coal ash. Coal ash simultaneously neutralized two highly corrosive waste streams (ground water and soils). Direct mixing of various ratios of simulated AMD and Trojan coal ash to a predetermined pH in the co-disposal process enhanced the formation of gypsum and soil components. The soil components/secondary aluminosilicate and/or aluminocalcium sulphate (ettringitic) or ferrihydrite precipitates have the capacity for mutual beneficiation of water quality in co-disposal AMD and coal ash (Burgers (2002). If such materials are to be precipitated at Iron Duke mine, they may also be of value in low-cost attenuation of toxic metallic waste streams. The neutralized process water would then contain only residual sulphate and low concentrations of ionic species that may be recovered by zeolitic adsorbents or electro dialysis reversal (EDR) systems using a variety of high capacity ion exchange materials.

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