Permeable Concrete with Bio-Reactive Layers to Target Heavy Metals and Sulfates in Acid Mine Drainage

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**ABSTRACT**

The aim of this research is to reduce heavy metal and sulfate content of acid mine drainage (AMD) through the methods of passive filtration by combining permeable concrete and organic materials to achieve a low cost, yet effective temporary treatment method for rural/poor communities who are affected by AMD. The acids are filtered through layers of alternating pervious concrete and biological composting layers. The concrete layers target removal of heavy metals such as iron, manganese, potassium, magnesium, etc. through precipitation as well as reduce sulfate content to a small degree along with total dissolved solids. The concrete layers aid in raising the pH of the AMD to more acceptable levels. The biological layers achieve sulfate reduction through the metabolism of sulfate-reducing bacteria (SRB) - this process however will require time and the organic layer thus will be thicker and less permeable than the concrete layers in order to allow seepage to take place at a reduced rate. A wide variation of composting layers were tested including cow manure, chicken manure, sawdust, straw, zoo manure, leaf compost, grass cuttings and river mud to find an optimum mix of materials which allows for the greatest sulfate reduction through SRB’s. Long-term testing and effectiveness of the rigs will be undertaken to establish limitations and lifespan of the filtration system. AMD from the Witwatersrand gold fields and Mpumalanga coal fields with exceptionally high sulfate content were used to test effectiveness of the organic materials over a short period of time with long term testing being conducted with a synthetic AMD due to limited supply of the reagent. The short term testing yielded reductions of sulfates in the region of 56% when using kraal manure as the biological reagent mixed with sawdust for added organic carbon. The filter also successfully raised the pH to 8 while removing a significant portion of heavy metals. The results show promise for using the technology as a low cost, temporary measure to protect locally impacted groundwater, especially for isolated and/or rural communities.

**Keywords**: AMD, SRB, permeable concrete, remediation
INTRODUCTION

Acid Mine Drainage (AMD) is the name given to outflows of water that contain high levels of acidity and heavy metals due to the reaction and oxidation of geological layers which consist of sulfide containing minerals, especially pyrite(FeS\textsubscript{2}). The amount and rate at which AMD is generated is a function of the rock mineralogy and degree of exposure/presence of oxygen and water. The sulfides in the rock oxidise when in contact with these substances to create a highly acidic, sulfate rich mixture with characteristically low pH and often a high content of heavy metals in soluble form.

This acid generating phenomenon is a naturally occurring process resulting from the weathering and erosion of sulfide carrying minerals in exposed rocks weathering on hills and valleys or through ground water seepage. This however creates AMD at a slow rate due to the relatively small exposed surface area; and in the case of ground water seepage the lack of excess oxygen; therefore allowing the surrounding alkaline rocks to neutralise the AMD, and water bodies to dilute it sufficiently before it has a chance to significantly impact the environment (Durand, Meeuvis, & Fourie, 2010).

Mining activities however; such as deep pit excavation, crushing, quarrying, mine waste rock pilling, tailings and tunnelling; result in massive volumes of rock being exposed, which when weathered creates excessive amounts of acid mine drainage. This AMD has greatly adverse effects on the environment, its biodiversity, as well as long-term damage to waterways, aquifers and ultimately our drinking water (Coetzee et. al, 2010). AMD can also cause damage to structures such as culverts and bridge abutments exposed to waterways that have a high concentration of AMD as the high acidity and sulfate levels have an accelerated corrosion effect on steel reinforcing (Gurdeep, 2006). More importantly, AMD carries a health risk to human settlements, especially those of the mining communities often living in low cost, slum/squatter camp type environments adjacent or nearby mine dumps/tailings. Some of the Heavy metals contained in AMD can be extremely harmful if consumed in elevated consecrations and in some cases AMD has been found to be carcinogenic.

Extent of the problem in South Africa

AMD is an extensive problem with coal and gold mining, as marcasite and pyrite (or "fools gold" as it is often known) is highly prevalent in the mine wastes and surrounding mineralogy. South Africa has notably large deposits of these sulfur rich natural resources. The AMD problem faced by the mines in Johannesburg is being further accentuated with the gold mining operations ceasing and mines not being maintained after closure. This is resulting in uncontrolled amounts of AMD welling up inside the mine voids left from deep excavations as the ground water level is no longer being drawn down and controlled to allow for mining along the reef. To put things into perspective, the potential volume of AMD produced by the Witwatersrand Goldfields alone amounts to an approximated 350ML/day which is around 10% of the daily supply of potable water by Rand Water according to Hobbs et al (2009).

There is huge concern regarding the state of the water level at the central basin in Witwatersrand as ground water with high concentrations of AMD has been rising at an average rate of 0.59 metres
per day (m/d) since July 2009 which translates to approximately 15m/month (Akcil and Koldas, 2006).

If this rising water level is not treated and controlled it would threaten to flood the low lying tourist areas of the mine at Gold Reef City and of more consequence, pollute and compromise the shallow ground water resources along with causing damage to the dolomitic strata. This will ultimately affect the dolomites ability to sustain loadings in the southeast part of Johannesburg according to Coetzee et al. (2010). One of the largest concerns of AMD is the accelerated karstification of dolomite (which is soluble in acid) resulting in potentially large sinkholes and soil subsidence coupled with the consequential contamination of aquifers and decanting into waterways. This ultimately pollutes and impacts all types of biodiversity including with time our drinking water. This same threat is faced by the cradle of humankind in Krugersdorp and is of huge concern as the structural stability of the surrounding areas are in question threatening the heritage site and the artefacts contained within its soil as the dolomitic aquifers carry more and more highly acidic AMD into the area (Durand et al. 2010).

According to Case studies done by Hochmann et al. (2010) on coal mining in South Africa, an account of the mining community living at the Maguqa township near an open cast coal mine in the Brugspruit valley was given, where AMD carrying toxic heavy metals is flowing into the Brugspruit stream and from there into the Olifant's river system. The children of the township play soccer on the flat white surfaces of sulfate salt precipitates left by the AMD, oblivious to the potential health risks. Therefore there is a need for a rapid temporary solution which has the potential to reduce the risk to such impacted communities whilst a long term solution is sought.

**Treating AMD**

Treatment of AMD is complex, costly and requires a fairly large amount of capital and infrastructure to be put in place for the treatment methods to be implemented (Hobbs et al., 2009). There are a number of effective treatment techniques, all of which can be broadly characterised as either active or passive. Active treatments are those treatments which involve ongoing and continual input and often involve electrical and mechanical implementations that are highly sophisticated and engineered which make use of chemical dosing or similar techniques to ensure the remediation of the contaminated water [Shabalala (2013), Skousen et al. (2000)]. Passive treatment techniques are those which can operate with little to no input over the long term and often require longer periods of time/processing in order to reach the same level of effectiveness as an active system and don't often involve chemicals or mechanical equipment (Jennings and Blicker 2008). Some of the more commonly used passive methods are discussed further below.

**Anaerobic wetlands**

This system is a modification of an aerobic wetland and incorporates a bed of limestone with a thick layer of organic rich medium above it to promote bacterial growth. This system creates anaerobic conditions when the AMD permeates through the organic material due to microbial activity leading to high oxygen demand. It is thus described as a sub-surface treatment method as it requires sub surface flow of the AMD to be effective unlike the aerobic wetlands where the AMD can flow along the surface. This system can thus treat highly acidic AMD through the dissolution of the fluid due to a limestone layer. This system however requires a large surface area and extended residence time.
within the ponds for effective treatment with low/slow flow rates [Skousen et al. (2000), Zipper et al. (2011)].

Experiments conducted by Sexstone et al. (1993) involving anaerobic wetland setups resulted in good pH reduction resulting in almost neutral levels upon exiting the wetland (pH of 6.5) which was largely attributed to the limestone. The tests were run for a period of four years over which it was observed the systems became less and less effective with metal retention and pH reduction due to the system having a finite capacity and thus highlight the need for larger areas as smaller setups are less effective and have a shorter life span than respectively larger setups. Wieder (1992) documented that the performance of wetlands are different depending on the season and age of the wetland which was attributed to factors such as bacteria activity, current loading of the wetland and ability of the aquatic plants to absorb precipitated heavy metals.

**Permeable reactive barriers (PRBs)**

Permeable reactive barriers are essentially a permeable obstruction placed typically below surface which intersects the AMD plume as it flows along with ground water and treats the influent as it passes through the barrier. The treatment is achieved in the majority of cases through the use of Iron metal and silica sand, with some instances using organic matter to treat nitrate and sulfates depending on the AMD that is to be treated (Powell et. al, 1998). According to work done by Blowes et al. (2000) the use of solid organic matter such as wood chips, sawdust, compost and leaves have positive effects on sulfate reduction in AMD due to the proliferation of sulfate reducing bacteria which reduce sulfate to sulfide which in turn leads to the formation of insoluble metal sulfides. However one of the most important considerations of using a PRB for treatment is the fact that sulfides have low solubility in anaerobic conditions and thus if oxidation occurred metals could be released by the barrier (Blowes et al., 2000). Another drawback is the installation of a PRB is quite costly as often impermeable structures are constructed to channel the AMD to the Barrier and these can be quite large and long such as a slurry piled wall.

One of the limiting factors according to Taylor et al. (2005) is the finite amount of reactive substrate available and the need for the AMD to have low oxygen content upon entering the system to prevent clogging. The organic substrate is consumed in the treatment process which creates void spaces that are then filled with the metal precipitates - compaction and the filling of these void spaces can lead to reduced porosity and effectiveness of the system.

**Bioreactors and (SRB) Sulfate reducing bacteria**

Most passive treatments that target AMD with a high sulfate content will make use of sulfate reducing bacteria (SRB). The bacteria consume organic forms of carbon (CH₂O) under anaerobic conditions to produce bicarbonate; which promotes neutralization of the AMD; and H₂S which creates an environment where low solubility metals will precipitate out as shown in the Equation 1 [Shabalala (2013), Younger et al. (2002)]:

\[
SO_4^{2-} + 2CH_2O \rightarrow H_2S + HCO_3^{-}
\]
This process is highly dependent on the availability of an organic feedstock for the bacteria to proliferate and become increasingly effective. Temperature also plays a role with the bacterial activity where they become increasingly more active at higher temperatures and less so at lower temperatures [Akcil & Koldas (2006), Younger et al. (2002)].

Bioreactors essentially create a concentrated carbon rich environment where these SRBs can thrive and proliferate in order to effectively remove sulfates and heavy metals of fluids that pass through them. Bioreactors are commonly used with most sludge and waste water treatment facilities. The problem with some bioreactors arises where they become inundated with metal precipitations and lose their effectiveness. Replenishment of the carbon source is sometimes needed and removal of the heavy metal rich sludge can be costly and expensive to dispose of.

### Use of Concrete in AMD treatment

The use of concrete in the treatment of AMD has not been extensively tested and its use in conjunction with biological layers is novel. There has been some experimental work done by Ekolu et al. (2013) with concrete in the removal of heavy metals, where it was shown that removal of iron content in the order of 95-99% was achieved through a single pass through a concrete cube. It was also found to have effectiveness in reduction of other such heavy metals and approximately 30% removal of sulfate content. It is also expected that the lime within the Portland cement will react to increase the pH of the AMD solution. Permeable concrete is most effective for the purposes of the research presented here as it will allow AMD fluids to pass through the cube while retaining heavy metals within its macro porous structure. The concrete cube will have a finite life much like the Alkali Limestone Drains solutions due to armouring and preferential flow paths forming through the cube.

### METHODOLOGY

Filters were constructed out of permeable concrete and organic material in an attempt to combine the benefits of anaerobic wetland conditions, permeable reactive barriers, along with the benefits of heavy metal reducing concrete to achieve a low cost yet effective remediation system aimed at the local communities such as those in Johannesburg that are hard hit by rapidly proliferating AMD. Two phases of testing were undertaken. The first phase was aimed at finding a suitable medium for SRB proliferation and tests were conducted over a 2-3 week period to determine effectiveness of the biological layers. Once an effective medium was found, phase one testing was stopped and a long term filtration system was setup for phase 2. These long term setups have a drip system to pass AMD through them continuously and sulfate reduction levels will be monitored over time for a period of 3-6 months in order to gauge/quantify the effectiveness and ability to perform over the short to medium term. These phase 2 experiments are currently underway and are ongoing.

### Permeable concrete

Concrete cubes and cylinders for the filters were batched using Sure build Afrisam 42,5 PPC cement, no fines and 9.5mm dolerite aggregates. Dolerite aggregates were chosen due to their hardness and resistance to acidity which is expected to increase the lifespan of the concrete in AMD remediation. Research conducted by Ekolu et al. (2013) showed that greater sulfate reduction was obtained with dolerites as opposed to granite and limestone. The mix design proportions used for the research are given in the table below:
Table 1 Mix design proportions

<table>
<thead>
<tr>
<th>Material</th>
<th>Quantities Used</th>
</tr>
</thead>
<tbody>
<tr>
<td>Portland Cement</td>
<td>325 kg/m³</td>
</tr>
<tr>
<td>Fine Aggregates</td>
<td>0 kg/m³</td>
</tr>
<tr>
<td>Coarse Aggregate (9.5mm aggregates)</td>
<td>1500 kg/m³</td>
</tr>
<tr>
<td>Water/Cement Ratio</td>
<td>0.3</td>
</tr>
</tbody>
</table>

These values are based on the need for greater permeability to allow movement of the AMD through the concrete while still maintaining workability and ease of placement along with maintaining suitable concrete strength. Once the concrete had been cast it was immediately covered to prevent any moisture loss and allowed to set for 24 hours. Thereafter casts were submerged and allowed to cure for 28 days as per standard cement curing processes.

Filtration systems

Filters for the first phase were constructed out of Perspex sheets and were rectangular with an internal dimension of 105mm in order to accommodate a standard 100x100x100mm concrete cube and have a length of 450mm in order to allow for sufficient space for two concrete cubes and a 200mm thick composting layer in between them. The experimental rigs were placed vertically and AMD was passed through the filter under gravitational force. The base plate as well as the midpoint of the filter has a nozzle to allow samples to be taken during filtration. An example of the phase one setup can be seen in Figure 1.

Figure 1 Short term experimental rigs in operation

An AMD taken from coal mine tailings in Mpumalanga with exceptionally high sulfate content (8200ppm) was used to test the effectiveness of the phase one setups. The composting layers used were varied in order to ascertain an effective medium which maximized SRB population growth and activity while not adding any adverse chemicals or metals to the system. The layers tested consisted of leaf compost, wood chips, kraal manure, chicken manure, zoo manure, elephant dung,
sawdust and straw. Combinations of the above along with additions of lime were also tested once an effective medium had been established.

**Samples and testing**

For the short term experiments samples were taken at 3, 7, 10, 14 and finally at 21 days. These preliminary phase 1 tests were stopped after 21 days as results were showing trend lines of favourable (or otherwise) at this point. Samples were extracted from the bottom, midpoint as well as the top of the filter during phase 1 testing. The samples were tested for sulfate concentration through the use of barium chloride, standard solutions and a spectrograph as per the test methodology stipulated in the sulfate testing methods IS:3025 (Part 24) - Reaffirmed 2003 and ASTM D516 methods.

**RESULTS AND DISCUSSION**

The results presented are an average of the three samples taken from the top, middle and bottom of the filters. The pH of the samples was checked and it was found that the concrete cubes were very effective at raising the pH of the AMD from 3 to an average of 7.68. The test setup with only permeable concrete cubes in them had a pH of 11 after 21 days.

In Figure 2, the data presented indicates that a mixture of kraal manure with sawdust in the proportions 80%:20% had the most significant remedial effect (a kraal is a South African word for an enclosure normally used to house cattle). The manure sourced from the Johannesburg zoo also had a significant effect on sulfate removal but is hard to come by and in short supply. Chicken manure and a mixture of zoo leaf compost with sawdust had the least effect.

![Figure 2 Sulfate removal after 21 days of operation for different organic feedstocks](image)

The effect of residence time on the removal of sulfate for 5 selected scenarios is presented in Figure 3. Similarly to the data shown in Figure 2, kraal and zoo manure were the fastest removers of AMD with chicken manure having almost no effect after 7 days. This could be as a result of the ruminant bacteria which would occur in cattle, elephant, buffalo, and other herbivorous animal dung (which would not be present in the chicken manure). The sharp initial drop in sulfate concentration at the
start of the experiment (shown as the difference between AMD and the series) is attributed to the absorption of sulfates into the permeable concrete and organic materials. This effect, however, is short lived as the filter quickly becomes saturated and sulfate concentrations rise before DSR (Dissimilatory sulphite reductase) begins.

Figure 3  Effect of residence time on sulfate reduction

The permeable concrete cubes were able to reduce sulfates by 25% which is regarded as significant, as well as being effective at raising the pH of the passing AMD. The kraal manure was selected as the best performer and candidate for long term testing due to its ease of sourcing across Southern Africa, especially within the rural mining communities and areas, and is considered the best biological medium for the filters. As can be seen the organic medium typically becomes more effective at sulfate removal with time which correlates to the proliferation of SRBs and the curves typically represent a steady growth rate resulting in accelerated sulfate removal with time. The permeable concrete setups also show the initial drop in sulfates but show steady reduction of approximately 25% throughout the testing cycle which correlates well with the sulphate reductions found by Ekolu et al. (2013) in their experiments.

CONCLUSION

From the results of the research it is concluded that kraal manure is the most effective and readily available on a large scale of the organic feedstocks and when coupled with permeable concrete is able to effectively remove sulfates in a relatively short time frame (favourable results in 2-3 weeks) while raising the pH to almost neutral. The costs of the materials needed to construct these filters is significantly lower than other current passive solutions, and thus the filter system shows great promise as a low cost temporary solution to communities such as those like Maguqa township and others in Johannesburg where AMD is proliferating at high rates.

Due to the promise shown by the research over the short term it will be test further to ascertain the ability of the system to provide favourable remediation over longer periods, while quantifying limitations, capacities and performance of the filter system. The authors have already commenced with this long term testing, and it is ongoing.

Permanent long term solutions in South Africa more often than not require enormous capital outlay and infrastructure from government or mining bodies, and may take a number of years to be implemented. The hope is that the proposed filter system would be able to offer some short term relief to heavily affected receptors, especially in poor and/or rural communities.
REFERENCES


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