HYDROGEOCHEMICAL CHARACTERISATION OF WASTE DEPOSITS FROM A COPPER MINE

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ABSTRACT

Acidic mine seepage from tailings storage facilities (TSFs) is dictated by the presence of sulphides, oxygen, water and bacteria in the TSFs. Sulphides (especially pyrite) oxidise to produce sulphuric acid.A waste characterization was conducted on various facilities containing materials ranging from plagioclase, to carbonates to magnetite. The objectives of the study were to characterise the various waste types and then determine the acid generating potential of each facility and the expected drainage quality. Static, kinetic and physical geochemical tests were conducted on samples collected on each facility, and the results were used to populate hydrogeochemical models.

The results concluded that there was an excess of neutralization potential in the reactive facilities and that acid generation was unlikely. Modeling indicated that co-existing carbonates dominate the quality of the mine water and groundwater in the area. The results further concluded that due to the relatively inert nature of the waste and the neutral conditions maintained in the overwhelming majority of the waste samples, the release of different elements under oxidation is not as significant. Since these facilities are in a low rainfall environment oxidizing conditions are expected, but the sheer volume of waste stored on site over the life of the mine would lead to continued salinity generation.

Key words: Sulphides oxidation, neutralization potential, salt loads.

1. INTRODUCTION

Employment in South African mines has declined over the last two decades, but mining alone still contributed directly to close to 6% of the country's economy by the year 2005 (SAMI, 2006). However, mining is inevitably associated with environmental problems, as tons of waste of all sorts is dumped on land close to the mining areas on a daily basis. This results not only in land surface disturbance, but also in underground and especially groundwater pollution. Moreover, after mining, these dumps are abandoned on site without any treatment or concern. The longterm effects on the environment range from reversible to irreversible; sometimes depending on the pollutants encountered.

Mines face a huge challenge with millions of tons of waste rock and tailings dams stored on its sites. In sulphidescontaining waste material, Acid Mine Drainage (AMD) is produced due to the ingress of oxygen and water mainly from rainfall, and thus subsequent oxidation of sulphide-bearing minerals with the help of bacteria. However, in the presence of sufficient neutralisation potential, alkaline drainage is favoured as carbonated minerals (mainly dolomite and calcite) buffer the acidity. For this study, copper sulphide is recovered from foskorite ore imbedded with carbonatite which helped at the non acidification of the mine site. The study would provide data that could predict the long term geochemical behaviour of each waste material, so as to optimise the management of the waste repositories as part of the Integrated Water and Waste Management Plans (IWWMP), and therefore to predict long term mitigation requirements and environmental impacts.

2. THE STUDY AREA

The underground mine workings are located in the north-eastern part of the Limpopo Province in South Africa and in the Phalaborwa Complex. This complex is unique in that it is the only economically viable carbonatite-hosted copper deposit in the world. The Complex represents the remains of an alkaline volcano that was active 2047 Ma (Wilson and Anhaueusser, 1998). The mine lies in the Region 19 Lowveld, the climate is warm to hot, and the biome is savannah. The greater part of the Lowveld lies at an elevation between 300 and 600 mamsl, and receives between 500 to 600 mm of rain during the summer. The current body of knowledge about groundwater in the region is mostly contained in the set of national groundwater maps (WRC, 1995) and Information and data at the Department of Water Affairs and Forestry (Vegter, 2003).

Groundwater is the sole water source for more than a quarter of a million people in this region; in the Kruger National Park for instance, human consumption and game watering are provided partly from groundwater (Vegter, 2003). Groundwater in the area generally occurs in weathered or fractured granite, gneiss, pegmatite and dolerite (De Villiers, 1967).

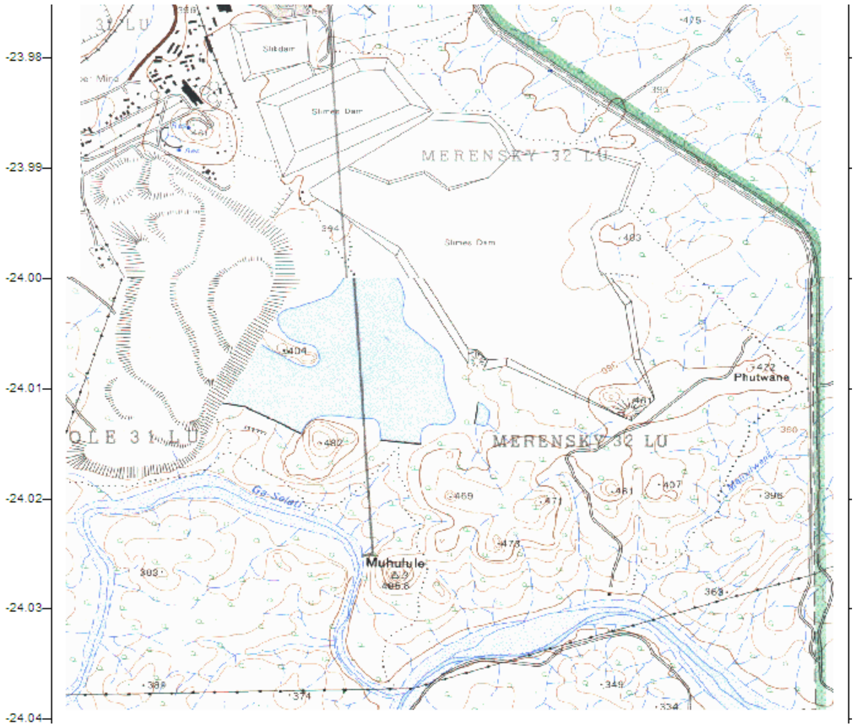

Figure 1. A topographic map of study area showing localities and the locations of tailings dumps.

3. METHODOLOGY

Sampling Procedures

For this dissertation, the main area of interest lies in the possibility of drainage from the waste facilities, and the impacts on receptors, (i.e. human, animal, bio-vegetation). To achieve this, an assessment of the solid waste samples was performed, as well as an in-depth analysis of the groundwater samples. Tailings samples were collected using an Auger driller for samples as deep as four (4) meters, a spade and a hand auger for surface samples were white (presumably salts) deposits where noticed. Waste rock samples were collected using an excavator to depths in excess of 3 m. These samples were then bagged in appropriate plastic bags, and were first tested for radioactivity at the mine’s laboratory before being taken to a laboratory for further analysis. The groundwater data were provided and interpreted based on the monitoring results obtained from the mine, and those data were collated.

Field Measurements

The measurements of pH and electrical conductivity (EC) were taken for each of the tailings and surface samples during sample collection.

Analytical methods

The laboratory methods used in the analysis of the samples include: Acid-Base Accounting (ABA), mineralogy determination and Particle-size distribution. The samples arrived at the laboratory three days after having been collected. For the ABA, the initial pH of the tailings samples were simply obtained by adding distilled water to 5g of each of them and then reading the values from the pH-meter. To obtain an estimate of the final pH of the tailings dams after oxidation, a further 5g were mixed with hydrogen peroxide (H_2O_2).

For the mineralogical analysis, all samples were submitted to a geology department laboratory. Waste rock samples were finely ground, and X-ray fluorescence and X-ray diffraction tests were undertaken with a Siemens D-5000 Xray diffractometer using monochromatic CuKα-radiation and the PC-PDF2 computer programme for mineral identification.

Several samples for the finer grained materials, namely the copper tailing and Hi-Ti and Lo-Ti tailings, were selected for sieve analysis to obtain the average particle size distribution.

4. RESULTS AND DISCUSSION

Tailings Samples

Acid-Base Accounting (ABA)

Results were interpreted using the Acid-Base Accounting Cumulative Screening tool (ABACUS), (Usher, 2000). Figure 2 presents the results of the ABA for the tailings samples and shows that while the initial pH of the samples were between pH 8 and pH 10, the oxidised (final) pH are between pH 6 and pH 8. This indicates that even after oxidation, the samples could not turn acidic; therefore there is excess neutralisation potential in the tailings. This is further observed in Figure 3 where all of the samples are below the acidity line. This is due to the fact that the ore body was interbedded with carbonatite.

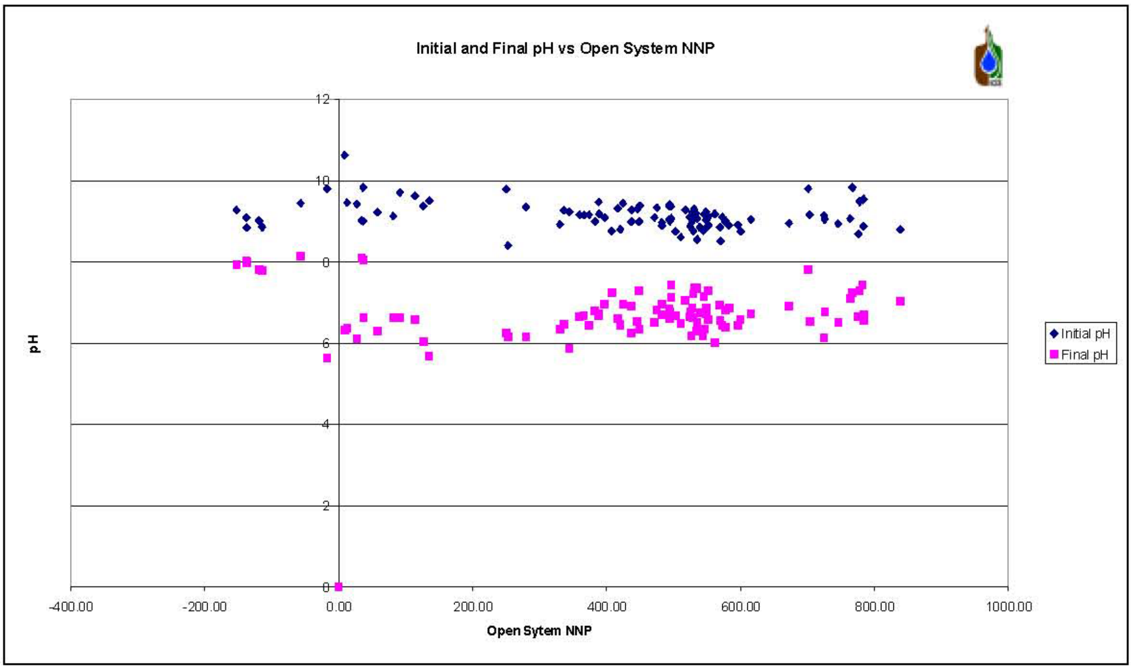

Figure 2. Initial versus final pH of the tailings samples

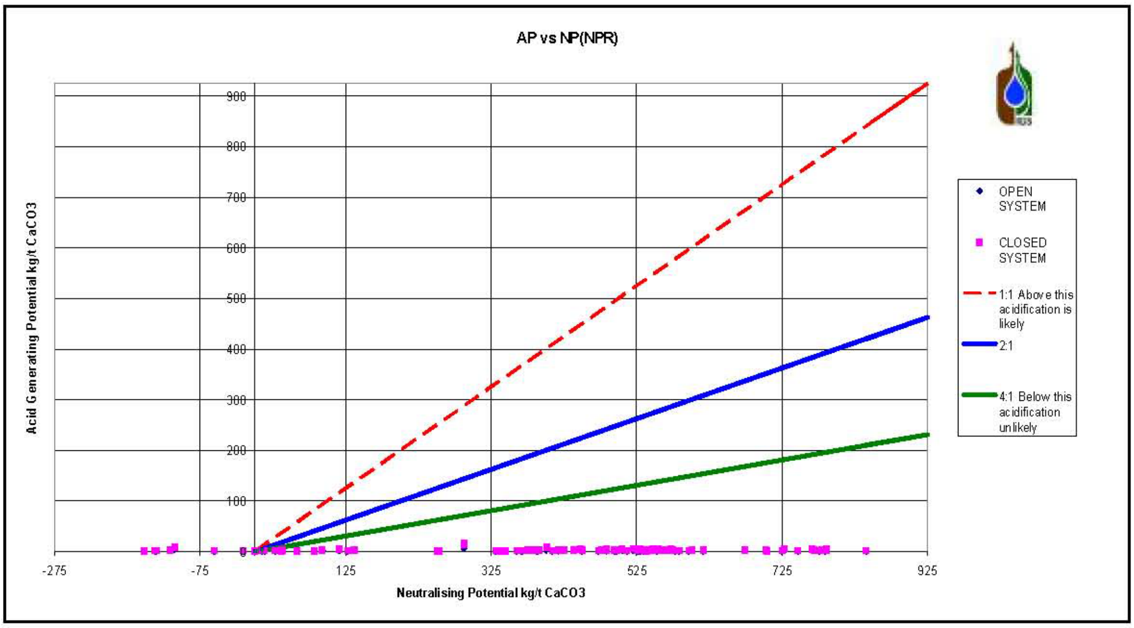

Figure 3. ABA results of the tailings samples.

The following net equations for the neutralisation of chalcocite and covellite have been drawn up to explain the high presence of bicarbonate and gypsum in the groundwater and tailings samples.

$$\text{Net reaction: } CaCO_3 + Cu_2S + O_2 + H_2O \Longleftrightarrow 2Cu^{2+} + Ca^{2+}{}_{(aq)} + SO_4^{2-} + H_2CO_3 + 4e$$

$$\text{Net reaction: } CuS + CaCO_3 + 1.5\ O_2 + H_2O \Longleftrightarrow Cu^{2+} + Ca^{2+}{}_{(aq)} + SO_4^{2-} + H_2CO_3 + 2e$$

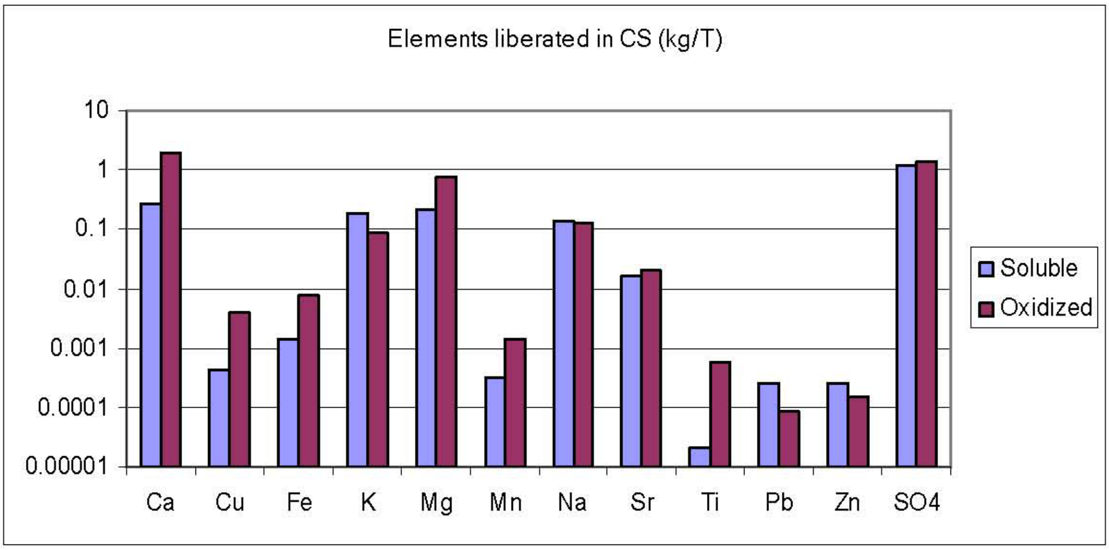

Figure 4:Metals and sulphate released per ton of tailings

One obvious observation (Figure 4) is the increase in the amount of the majority of the elements as they tend to be oxidised in the compounds where they are found. In general, during oxidation, the final pH is expected to fall, and thus more metals are usually liberated. However, Figure 2 indicates that the final pH did not drop considerably (and therefore did not turn acidic) after the samples were oxidised, and thus the difference in the amount metals released is not significant.

Mineralogy

The mineralogical analysis conducted further revealed the presence of abundant neutralising materials.

Table 1. Mineralogy results from the tailings

Quartz	Phlogopite/vermiculite	Magnetite	Apatite	**Dolomite**	**Calcite**
SiO_2	$(MgFe,Al)_3(Al,Si)_4O_{10}(OH)_2.4H_2O$	Fe_3O_4	$Ca_5(PO_4)_3(F,Cl,OH)$	$\mathbf{CaMg(CO_3)_2}$	$\mathbf{CaCO_3}$
Accessory	Major	Minor	Major	**> Major**	**Dominant**

The laboratory results suggest that the vermiculite waste could pose a relatively low salinity risk due to the geochemical compositions. In addition to the carbonates, the silicate minerals also play an interesting role in consuming the acid that could have been generated as they dissolve. The silicates themselves will not play a significant role in the neutralization of acidic drainage over the short term (during the life of the mine) as their slow reaction rates are shadowed by the carbonates' much faster rates, but in the longer run, they help maintain pH values not too high.

Groundwater Samples

Groundwater from the surroundings of the tailings was sampled. Using the geochemical modelling software PHREEQC (Parkhurst and Appelo, 1999), it was possible to determine the saturation indices of the water.

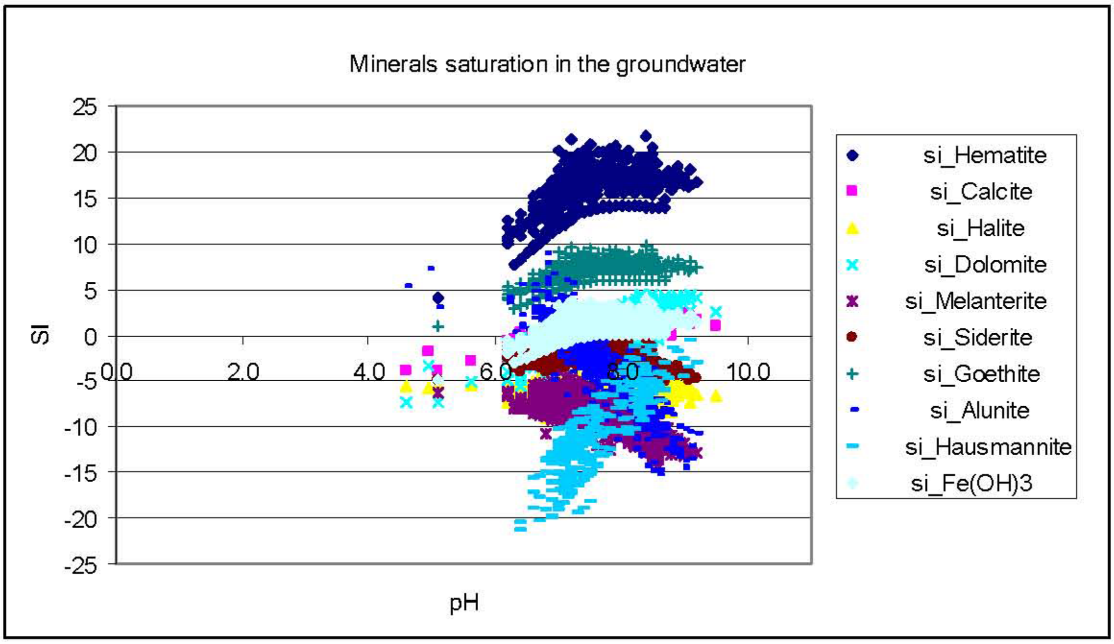

Figure 5. Groundwater saturation indices

While some minerals get to be under-saturated, others super-saturate from a pH to between 6.2 to 9.5, with iron oxides Goethite ($FeO(OH)$) and Hematite (Fe_2O_3) dominating the non-carbonated super-saturated minerals. It is understood as a reminder that if the pH of AMD is increased, as would happen in contact with basic minerals such as calcite ($CaCO_3$) or dolomite ($CaMg(CO_3)_2$) or entry into a water system of higher pH, then metallic ions such as Fe^{3+} and Cu^{2+}, Zn^{2+}, Pb^{2+} and As^{3+} will react to eventually form hydroxides as precipitates by the general reaction:

$$M^{n+} + nOH^{-} \Leftrightarrow M(OH)_n$$

where: OH^- = hydroxyl ion; $M(OH)_n$ = metal hydroxide.

As hematite is the more thermodynamically stable solid form of iron (III), it would not dissolve to a lower concentration that ferrihydrite ($Fe(OH)_3$). However, oxidizing groundwater are generally in equilibrium with ferrihydrite, ($SI \approx 0$), not hematite. In fact, the saturation indices for are often greater than 10, which represents oversaturation by a factor of 10^{10}, (Deutsch, 1997). Moreover, hematite does not precipitate fast enough to control the dissolve iron concentration; thus it is not reactive enough to limit the dissolved concentration. Ferrihydrite may convert to the more stable hematite form of iron given sufficient time, but this process occurs by a mechanism that does not limit dissolved iron concentration to the hematite saturation value. The attenuation of heavy metals concentrations is possible as the result of adsorption and co-precipitation with goethite and other iron oxides, (Herbert, 1994). For instance, investigations have indicated that iron (Fe) solubility can be controlled by siderite ($FeCO_3$) at high pH, $Fe(OH)_3$ at moderate to slightly acid pH values, (Dubrovsky *et al*, 1985), (Levy *et al*, 1996). In general, as metals are transported away from their source, their concentrations in groundwater may be controlled by precipitation-dissolution and co-precipitation reactions, adsorption-desorption reaction and solid-solution substitutions, (Blowes and Jambor, 1990, Anderson *et al*, 1991).

In natural aqueous environments, the redox system may not always be in equilibrium. In a system that has many redox couples, if the redox potential (pe) of all the couples is the same, then the redox system can be considered in equilibrium and the measured pe would be the system pe as was the case in this study, (Chapelle, 2004; Herbert, 1994). Many groundwater systems however are not well balanced, (Lindberg and Runnels, 1984).

5. CONCLUSIONS

The investigation into the acid mine drainage potential and salt loads indicated that the acid potentials determined by hydrogen peroxide oxidation and determination of reactive sulphide, indicate that most of the waste contains very low values of sulphide, and from a reactive perspective most of the waste should be relatively inert. This would suggest that in the majority of cases, the amount of sulphate generated per ton of material would be low. However, as with all these results, the sheer volume of waste material means that despite this inert nature, elevated concentrations of dissolved constituents may still be possible. The neutralization potential of the waste material tested is generally very high, and the waste has a significant potential to neutralize acid. The values obtained, suggest that mildly alkaline waters should persist in the future.

Oxidation of the samples with hydrogen peroxide allows the analysis of the supernatant to provide the quantities of sulphate and metals released by the waste when fully oxidized. In most mining waste high in reactive sulphides, this would release a significant amount of sulphate and an increase of several orders of magnitude for different metals as pH drops. Due to the relatively inert nature of the waste and the neutral conditions maintained in the overwhelming majority of the waste samples, the increase of salt release under oxidation is not as significant. This is a very important finding as most of the waste exists under potentially oxidizing conditions on the site, and suggests that salt loads should not be expected to dramatically increase over time.

An equally significant finding is that due to the prevention of acidic conditions and the consequent near-neutral conditions that will exist, very few metals are significantly soluble.

The mineralogy results generally correspond very well to the acid-base accounting and solubilisation results. The most important findings from this include dolomite as the major neutralising/ alkaline mineral, occurring as part of what is characterized as the carbonatite at the mine. Another interesting characteristic of these tailings is due to the high neutralizing potentials, they can serve as co-disposal sites for acidic tailings.

6. DISCLAIMER

The mine funded the tailings characterization project described here for its IWWMP. This does not reflect the general characterization of copper mines tailings. The ABACUS software has been specifically developed as a tool for ABA methods in South Africa. It has not been verified as yet is only used as an additional tool in interpreting ABA data.

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