

Prediction of Acid Neutralizing Potential of Wetlands Affected By Gold Mining in a Semi-Arid Area

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ABSTRACT

South Africa's mining activities play an important role in ensuring the country's position in the global market. Unfortunately, the country's mining history also has resulted in dramatic environmental consequences especially, in the case of acid rock drainage (ARD) production from gold mines of the Witwatersrand. The legacy of mining continues to affect water resources even long after mining operations have ceased.

The issue of ARD at both historic and active mines has led to the worldwide need to implement prediction methods and for the assessment of the acid generation potential during the exploratory phase of mine development.

In this study, static acid base accounting (ABA) tests were conducted on and around an active gold mine tailings dam to predict the risk of acid generation at the site. Sediment samples were collected from wetlands (natural and constructed) and tailings materials were obtained from a Tailings storage facility that has been built about a century ago. The Sobek method was used for the ABA test. Total metals and speciation (BCR extraction) analyses were also carried out on the collected samples.

Results of ABA tests showed variable Net Neutralization Potentials (NNPs) for surface samples (generally negative for tailings and positive for sediments), although the obtained NNPs fell within the range of uncertainty (i.e. $-20 < \text{NNP} < 20$), which demonstrated the need for kinetic tests. Natural wetland samples appeared to have a greater acid forming potential compared to the constructed ones. Moreover, the experiment also showed that acidic conditions would dominate after complete oxidation of the samples. Metals studies revealed not only high total metals values in the samples but also, for several metals, a strong correlation between fraction of "reducible" species (metals bound to sulfides or organic matters) and sulfur. Once exposed to oxygen, these non-soluble metals-sulfides can generate ARD and become available in acidic waters.

Keywords: Acid-Base Accounting, Net Neutralization Potential, Acid Mine Drainage

INTRODUCTION

Acid rock drainage (ARD) is produced by the oxidation of sulfide minerals, frequently pyrite (FeS_2). This is a natural chemical reaction that proceeds when minerals are exposed to air and water. ARD is found around the world as a result of both naturally occurring processes and activities associated with land disturbances, such as mining where acid-forming minerals are exposed at the surface of the earth. Mine tailings and waste rock have much greater surface area than in-place geologic material due to their smaller grain size and are, therefore, more prone to generating ARD. Metals that were once part of the host rock are solubilized and exacerbate the deleterious effects of low pH on terrestrial and aquatic receptors (Jennings *et al.*, 2008). Water contaminated by ARD often contains elevated concentrations of metals, which are toxic to aquatic organisms, leaving receiving streams devoid of most living creatures (Kimmel, 1983).

As elsewhere in the world, the activities of the mining sector in South Africa have resulted in serious environmental consequences, notably with respect to poor environmental and water management and, in the case of the gold mines of the Witwatersrand, production of ARD. Reappraisal of the risks attributable to ARD formation has become increasingly necessary in view of the looming crisis in the mining basins of the Witwatersrand region (Inter-ministerial committee, 2010). ARD and the mitigation thereof are critically important to South Africa. Mine waste particularly tailings, are a large contributing factor to ARD generation. Characterization of the acid generating properties of mine waste is fraught with uncertainty and deficiencies that create difficulties in evaluating and selecting suitable interventions for mitigating associated ARD risks in line with cleaner production and sustainable development principles (Kotelo, 2013).

Accurate prediction of acidic drainage from proposed mines is recognized as a critical requirement of mine permitting and long-term operation (Skousen and Ziemkiewicz, 1996). Mine drainage chemistry can be quantitatively predicted by investigating the geochemistry of rocks to be disturbed by mining (Pope *et al.*, 2010).

Prediction of acid generating potential from geologic formation, referred to as acid-base accounting (ABA), is essentially the ability to identify and quantify both acid-forming and neutralizing minerals in the geologic materials to be unearthed during mining operations (Skousen *et al.*, 2002; Smart *et al.*, 2002). A standardized EPA protocol known as the Sobek method (Sobek *et al.*, 1978) was developed to characterize mine soil and overburden. Although, this method is still used mainly due to its simplicity and low cost analytical procedures (USEPA, 1994), various modifications of the original procedure have been developed that “correct” some of the observed drawbacks from the original method (Chotpantarat, 2011).

In this study, the modified Sobek method (Skousen *et al.*, 1997) was adopted to predict the acid neutralizing potential of wetlands sediments and tailings materials collected from an active gold mine site in South Africa. This method involves the addition of hydrogen peroxide (H_2O_2), which oxidizes the ferrous iron in the dissolved siderite, yielding lower alkalinity predictions.

METHODOLOGY

Sampling

Forty-five sediments profile samples were collected at a gold mine site near Carletonville (North-West Province, South Africa). The samples were obtained from both natural (31 samples) and constructed wetlands (5 samples) near a tailings storage facility (TSF) which was built more than seven decades ago, and tailings materials (9 samples). The constructed wetlands (CWs) in the area are reed beds that are part of a succession from young trees colonizing water ponds and are less than five years old. Sediments in the CWs were “tailings like”, especially at the surface, and were characterized by a low percentage carbon (between 0.2 and 1.3 %). Due to the wet conditions of the ponds on the day of sampling, only one CW profile (down to 50 cm depth) was collected from a relatively dryer pond. Natural wetlands (NWs) were characterized by a natural plants colonization and the sediment had a percentage carbon that varied between 0.3 to 2.1% with the highest values mostly measured at top layers. NW profiles were collected down to 100 cm depth whereas tailings materials were obtained from the TSF in horizontal profiles of 40 and 50 cm length. All profiles were later on divided, where possible, into layers of 10 cm each.

Analytical methods

Once in the laboratory, samples were homogenized and a representative aliquot of each sample was dried then pulverized with a pestle and mortar to approximately < 2 mm.

The samples were digested in a microwave assisted extraction system at 800 W for 30 min using a mixture of HCl, HNO₃, HF and H₃BO₃. The samples were then diluted with deionized water and stored in a fridge until analysis. A sequential extraction was performed according to the procedure recommended by the Standards, Measurements and Testing Programme of the European Union (SM& T, formerly BCR), for the determination of some elements of interest in the collected samples. The chosen extraction scheme is an operationally defined and standardized procedure (Tokalioglu *et al.*, 2003; Davidson *et al.*, 1999) in which the reagent used at each stage is intended to release metals associated with particular soil phases such as acid soluble, reducible, oxidizable, and residual. Reported results were related to the extraction step numbers as shown in Table 1. Thus, Fe1, Fe2, and Fe3 refer to the concentration of iron (Fe) in fraction 1, 2, and 3, respectively. Metal determination in the extracts was carried out by ICP-OES.

Table 1 The BCR three-stage sequential extraction scheme.

Extraction step	Reagents/ concentration/ pH	Solid phase
1	CH ₃ COOH (0.11 M) pH 2.85	Exchangeable, water & acid soluble (e.g. carbonates)
2	NH ₂ OH.HCl (0.1 M) pH 2	Reducible (e.g. Fe/Mn oxides)
3	H ₂ O ₂ (8.8 M) following by CH ₃ COONH ₄ (1.0 M) pH 2	Oxidizable (e.g. organic substance and sulfides)

Total sulfur (S) used for ABA was determined using a LECO S632 analyzer, and Statistica software (Statistica® 7, USA) was used to check for correlation between the different studied parameters.

Static tests

Static ABA was performed on each pulverized sample. The following are the procedures used for the static ABA studies:

Initial pH

A sample mass of 5 g was weighed and added 50 ml of deionized water and was left for 24 hrs., after which the initial pH was measured (Usher *et al*, 2003).

Final pH

A volume of 80 ml of H₂O₂ (30% w/v) was added to a mass of 2 g of pulverized sample. The reaction was left to oxidize for 24 hrs, after which the final pH was measured (Usher *et al*, 2003).

The acid production potential

The acid production potential (AP) was determined from the total S content as follows:

$$\text{AP (kg CaCO}_3\text{/t equivalent)} = 31.25 \times \%S$$

Neutralization Potential (NP)

The peroxide siderite correction for Sobek method, as developed by Skousen *et al.* (1997), was used for determination of neutralization potential (NP). An initial fizz test was performed to select the volume and normality of HCl that was added to the sample prior titration. After the HCl addition, the sample was boiled until the reaction was complete. The resulting solution was back titrated to pH 7 with NaOH to determine the amount of acid consumed in the reaction between HCl and the sample. Blank titrations were also carried out to determine the blank constant critical for the calculation of the amount of acid consumed. NP was then calculated as follows:

$$\text{NP (kg CaCO}_3\text{ equivalent / ton of material)} = (\text{ml of acid consumed}) \times (25.0) \times (\text{Normality of added HCl}).$$

The net neutralizing potential (NNP) was determined by subtracting the AP from the NP and is a measure of the difference between the neutralizing and acid forming potentials.

RESULTS AND DISCUSSION

Elemental analysis

The results of selected elements concentrations in surface sediments and tailings materials are shown in Table 2. High metal concentrations relative to background levels were measured in the study samples with values sometimes reaching the percentage level, as was the case for aluminum (Al), Fe, and manganese (Mn), to mention a few. The measured concentrations are a clear indication of a pollution occurring at the site, probably from surrounding TSFs. Analysis of wetlands surface waters (Table 3) also revealed elevated concentrations in both CWs and NWs for elements such as Ca, Fe, Mg, Mn and S.

Table 2 Selected element concentrations (mg kg⁻¹) in surface sediments and tailings

Sample	Al	As	Co	Cu	Fe	Hg	Mn	Pb	S	Zn
NW1	15913	34	23	32	33301	0.3	5486	65	1070	67
NW2	12898	18	18	18	22877	0.5	5096	154	9102	35
NW3	14832	89	109	6309	28473	0.8	14191	112	1755	334
CW	13926	29	23	41	28571	0.1	284	22	1176	29
Tailings	53373	100	70	98	40103	0.9	662	84	3289	180
Background	7000	7	10	8	25246	0.1	234	80	220	24

Table 3 Mean values for field parameter and selected elements concentrations (mg kg⁻¹) in wetlands waters

Sample	pH	Eh (mV)	EC (mS cm ⁻¹)	Al	Ca	Co	Cu	Fe	Mg	Mn	Ni	S	Zn
CW	5.8	460	5.1	2.14	390	0.68	0.02	0.70	346	25.4	0.06	354	0.32
NW	6.4	246	4.1	0.09	125	0.24	0.02	12.5	207	27.9	0.05	490	0.48

Acidity in ARD is comprised of mineral acidity (Fe, Al, Mn, and other metals depending on the specific metal-sulfide minerals present) and hydrogen ion acidity (Skousen *et al.*, 2000). The extremely high concentrations of Fe (and S) could be due to the abundance of pyrite (FeS₂) in the overburden material. It was observed that Fe had a positive linear correlation with S (Figure 1). BCR sequential extraction procedure (SEP) also showed, in some cases, positive correlations between Fe₃ (i.e. oxidizable) and S (Figure 1).

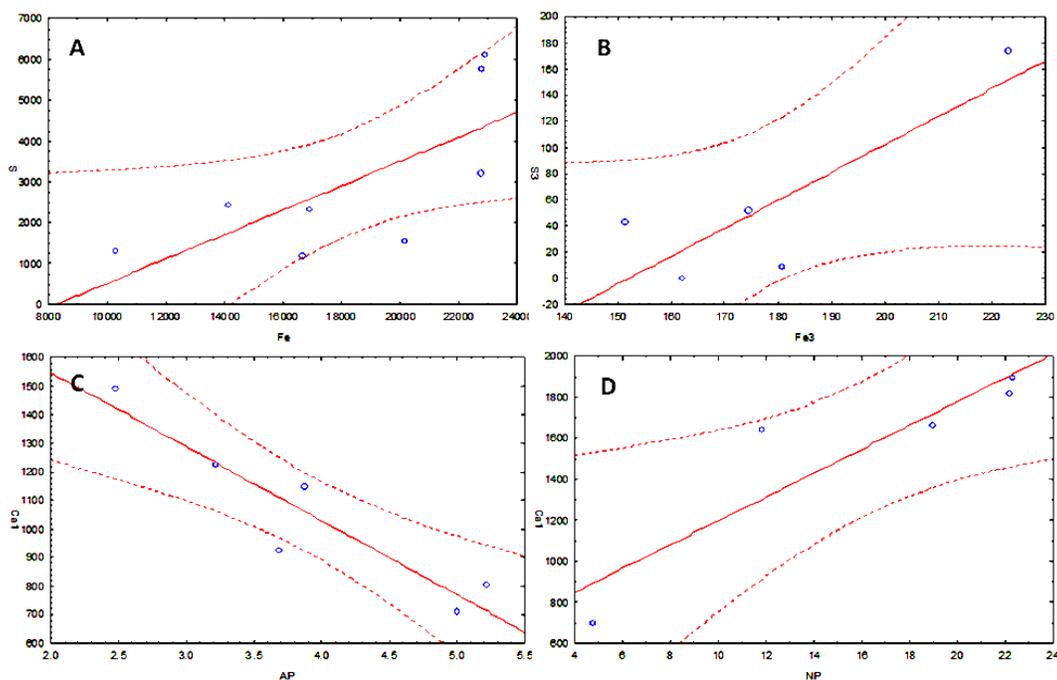


Figure 1 Correlation plots between total Fe and S (A), oxidizable Fe and S (B); Exchangeable Ca and AP (C), and Exchangeable Ca and NP (D), in natural wetlands sediments. Concentrations are in mg kg⁻¹.

The observed correlations could indicate the presence of pyrite in the overburden material, although other forms of Fe-S (e.g. pyrrhotite or FeSO₄) could also be present in the samples, as a good correlation was also found between total Fe and S. Good correlations were also observed between S and oxidisable cobalt (Co), copper (Cu), Mn and zinc (Zn) (Figure 2). It is known that these metals can complex with sulfides to form chalcopyrite (CuFeS₂), covellite (CuS), and sphalerite (ZnS). Pyrite commonly occurs with these other metal sulfides, and therefore ARD is likely to occur where Cu, Pb, and Zn are mined. The determination of the samples' mineralogy is, therefore, critical to reaching better conclusions about specific deposits.

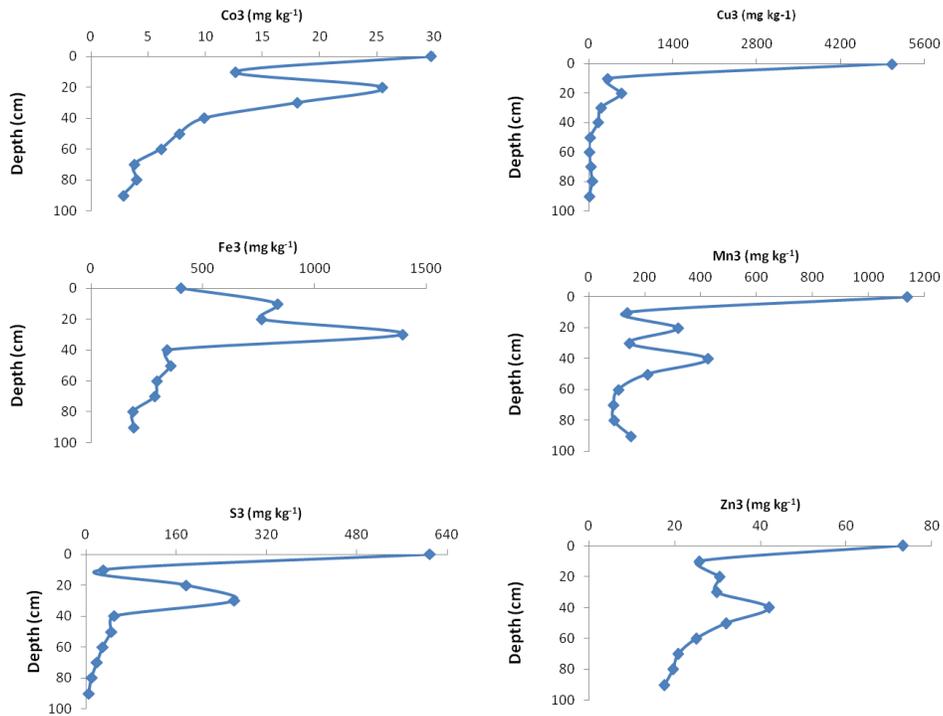


Figure 2 Trends of oxidizable forms of selected elements in a natural wetland sediment profile

Static tests

A plot of average pHs of the samples (Figure 3) shows that the initial average pH values ranged of 5.1 to 6.9.

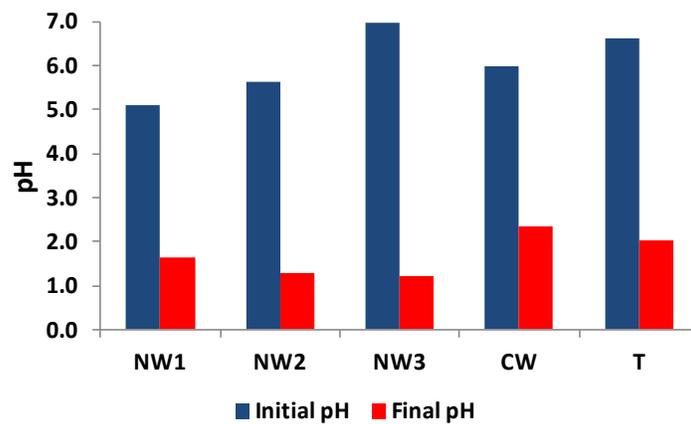


Figure 3 Average pH values of the samples before and after oxidization

The initial pH indicates the immediate acidic or basic characteristic of the sample and it could also indicate if acid generation has already been generated (Usher *et al.*, 2003). Note that, with the exception of NW3 which showed initial pH values close to neutrality, the majority of NW and CW samples had acidic pH, especially in bulk sediments where pH values as low as 3.8 were measured. This could be an indication that acid generation is already occurring at the site as a result of the oxidation of the above mentioned pyrite in the area. Acidic pH values were also measured in wetlands waters (Table 3). The final pH values suggest that after complete oxidation, the pH of each of the study samples would be less than 2.5

ABA tests revealed (Table 4) that the NNP (and NPR) values for the majority of the samples fell within the range of uncertainty (i.e. $-1.3 \geq \text{NNP} \leq 9.1$, or $0.9 \geq \text{NPR} \leq 2.8$), except for the sample profile collected from one of the natural wetlands (i.e. NW1), which had an average NNP of 85.2 and falls within the non-acid forming range. This location exhibited higher NP values (up to about 190 Kg CaCO₃/t) at deeper layers (30 to 70 cm depth).

Table 4 ABA results of study samples

Sample	n	AP (Kg CaCO ₃ /t)			NP (Kg CaCO ₃ /t)			NNP (Kg CaCO ₃ /t)		
		Min	Mean	Max	Min	Mean	Max	Min	Mean	Max
NW1	11	3.3	6.2	9.5	4.7	91.5	187.6	-0.5	85.2	181.6
NW2	10	3.7	8.7	19.1	2.1	7.44	14.3	-13.9	-1.3	5.6
NW3	10	4.6	26.2	63.8	8.54	25.3	50.7	-51.8	-0.9	22.7
CW	5	1.3	5.0	7.7	-4.7	14.1	22.3	-6.0	9.1	16.9
Tailings	9	5.6	7.2	8.8	5.4	8.7	11.6	-0.2	1.5	2.8

These results may suggest an important source of acid-consuming constituents at this location. Since carbonates are known to be one of the main sources of alkalinity production (Sobek *et al.*, 2000), correlations have been plotted between the BCR SEP exchangeable fractions of selected elements and NP or AP, as that BCR fraction is known to contain carbonate-bound metals. Among all the study elements, a positive correlation was found between Ca1 (i.e. exchangeable Ca) and NP whereas a strongly negative correlation was observed for the same Ca fraction and AP (Figure 1), indicating that CaCO₃ could be the main acid-neutralizing agent in the study samples. Additionally, it has to be noted that the sample profile NW1 had the highest concentrations of exchangeable Ca.

With the exception of the above-mentioned sediment profile NW1, all the sediments also showed a strongly positive correlation (r^2 up to 0.899) between the pH after oxidization (final pH) and NNP. This implies that samples with the lower final pH (NW2 and NW3) might have been depleted of the total available carbonates leaving a lesser source of alkalinity to buffer the acid. Another reason may be that there were more acid-producing constituents than acid-consuming constituents in the sample as these two sample profiles had negative average NNP (i.e. Average AP > Average NP). Sample profile NW3 showed the lowest mean final pH, the lowest NNP, as well as the highest AP (Figure 2). The high AP values obtained in this profile may suggest an important presence of acid-producing constituents, such as metal sulfides. Furthermore, at the point where the lowest NNP was recorded, the concentration of total S was as high as 2% and NP was at one of its lowest recorded values in this profile (i.e. 12 kg CaCO₃/t). The more negative NNP could also imply,

therefore, that the sediment did not have enough CaCO₃ to neutralize the acidity in the soil hence there was a potential of ARD in the area.

It is important to recall that the method used in this study is based, in part, on calculation of potential acidity from total S measurements. However, potential acidity is known to be overestimated where organic S, sulfate S, and some sulfide compounds make up a substantial portion of the total S content (Schumann *et al.*, 2012). Thus, a method speciating S, such as the chromium reducible S (CRS) method, would be useful to refine the obtained results.

In general, NNP values were lower at depth in the sediments profiles (Figure 4). This could be attributed to anoxic conditions encountered at deeper layers in wetland sediments, which favor the reduction of sulfate, as well as \ formation of non-soluble metal-sulfides. Thus, in case of land disturbance (or water infiltration), there is a possibility for these sulfide-rich layers to become exposed to oxygen and undergo different reactions that lead to ARD generation and subsequent solubilization of toxic metals.

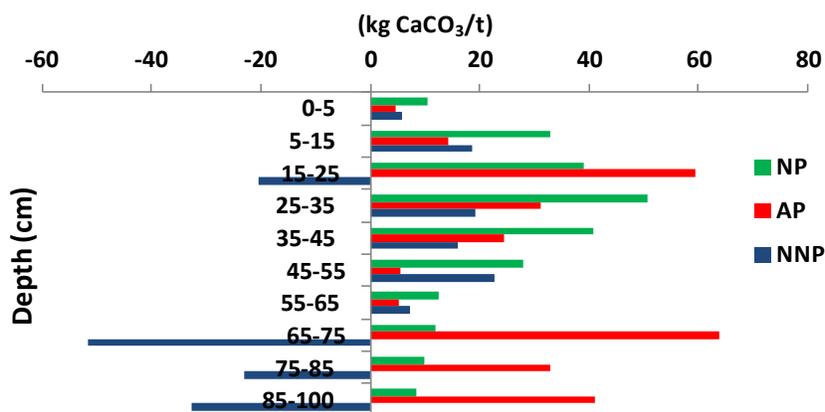


Figure 4 ABA results of the sediment profile NW3

CONCLUSION

Static ABA tests were performed in different samples collected from a gold mine site. Results showed that NNP (and NPR) values were mostly in the range of uncertain acid production, which suggests the need for kinetic tests, although pH tests revealed a risk of acid production if samples were exposed to more oxidizing conditions. Elemental analysis showed contamination already occurring at the site, and the pollution source is believed to be the presence of massive TSFs at the site. Generally, sample from the natural wetlands (and tailings) exhibited higher acid-forming potential than the constructed wetlands. BCR extraction helped to identify FeS₂ and CaCO₃ as the likely sources of acid- and alkalinity-production, respectively, in the samples. Mineralogical data would be necessary to verify the specific minerals contributing to ABA analysis and reported results.

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