



# The use of factor analysis and acid base accounting to probe the speciation of toxic metals in gold mine waste

O. A. Abegunde<sup>1</sup> · C. Okujeni<sup>1</sup> · L. Petrik<sup>2</sup> · A. M. Siad<sup>1</sup> · G. Madzivire<sup>2,3</sup> · C. Wu<sup>1</sup>

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## Abstract

The generation of acidic drainage has become pervasive over the years and toxic elements are released due to exposure to oxidising agents, unforeseen circumstances, and human interactions. Uncontrolled acidic mine drainage release can result in substantial ecological disruption in sensitive and productive receiving waters. This study probes the element mobility of gold tailings with regard to various zones identified, based on possible phenomena such as the natural water medium, or acidic and alkaline media using sequential extraction and multivariate analyses. Factor analysis results, coupled with mineralogy, were corroborated with acid generation potential to identify various relationships that exist and establish the efficacy of the research towards predicting acid mine drainage generation potential. The statistical analysis was able to establish that pH or acidity, Fe ions, Ca<sup>2+</sup> and Mg<sup>2+</sup> played a major role in the released metals. Out of the four factors (80.8% accounted for) identified in factor analysis results for water fraction (WF), Fe contributed to three factors which showed the presence of Fe ions (assuming Fe<sup>2+</sup> and Fe<sup>3+</sup>) responsible for the increased acidity of the tailings. The net acid producing potential and cumulative net acid producing potential showed that overall; the tailings would generate acidity due to the high presence of leachable sulphides. The trends observed in the carbonate phase indicated that despite the posit of acidity, the tailings contain a considerable amount of neutralising agent to serve as a buffer.

**Keywords** Tailings · Acid generation potential · Assessment · Statistics · Contamination · Prediction · Sequential extraction · Drainage

## Introduction

New mines or active old mines are obliged to provide proof that waste materials produced in the course of processing are stockpiled in a way that will inhibit or alleviate the release of acidic drainage, minimise the transport of elements that contaminate runoff, and prevent drainage and seepage, including downstream channels during mining and in future when mines are closed down (Lawrence and Scheske 1997). Despite this, the generation of acidic drainage has become pervasive over the years, and many studies have been done to confirm this.

However, the process that determines the possibility of toxic elements being sequestered or released in mine wastes is based on mineral–water interactions, to comprehend the chemical reaction complexities, fresh and weathered material needed to be characterised, in depth, for the existing reactive minerals (Jamieson et al. 2015). Uncontrolled acidic mine drainage released could result in substantial ecological disruption in sensitive and productive receiving waters.

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O. A. Abegunde: Iphakade No 223.

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✉ O. A. Abegunde  
3207599@myuwc.ac.za

- <sup>1</sup> Department of Earth Sciences, University of the Western Cape, Bellville, Cape Town, South Africa
- <sup>2</sup> Department of Chemical Science, University of the Western Cape, Bellville, Cape Town, South Africa
- <sup>3</sup> Council for Geoscience, Mine Water and Solid Residues Management, Sustainable Resources and Environment Competency, 280 Pretoria Street, Silverton, Pretoria 0084, South Africa

When sulphide minerals in the waste rock and tailings environment are borne to the atmosphere (water and oxygen), they tend to swiftly oxidise. This process is frequently catalysed by bacteria. Pyrite and pyrrhotite, commonly found as gangue minerals in several ore deposits, are mostly responsible for the generation of low-pH (acidic) waters. As soon as this acidic environment is established, other sulphides, silicates, oxides, and carbonate minerals are dissolved and discharged. Also, depending on the nature of the ore deposit, metals such as Zn, Cu, Ni, Pb, Al, Cd, Hg, Co, Mn, and U, as well as metalloids, including Sb and As are leached (Jamieson et al. 2015).

Several methods have been used to understand such complexities, including acid base accounting (Skousen et al. 2002; Price et al. 1997; Paktunc 1999; Parbhakar-Fox and Lottermoser 2015; Bouzahzah et al. 2014), sequential and/or selective extraction procedures (Favas et al. 2011; Martin et al. 1987; Yong et al. 1993; Gleyzes et al. 2002; Eze et al. 2013), column leaching techniques (Tutu et al. 2008), and chemometric evaluation (Abollino et al. 2011)

Several studies predicted elemental mobility in gold tailings coupled with factor analysis to measure species leachability and behaviour of tailings dump material over long periods of time (Cukrowska et al. 2004; Tutu et al. 2008). However, mineral forms of elements of interest and their predominant geochemical conditions play a major role in environmental mobility (e.g. solubility and sorption-desorption) and the risk it poses to human and environmental health. Factor analysis has not been as extensively used as principal component analysis in probing single and sequential extraction results (Abollino et al. 2011).

Hence, the use of multivariate statistics to probe environmental analytical data sets has been successfully applied. Most studies focused on certain parts of tailings dams. However, the whole (not only its bottom, sides, or surface) profiling of the tailings dam during sampling collection preferably would have been of great significance for constant monitoring and elemental mobility valuation (Tutu et al. 2008).

This study probes the element mobility of gold tailings with regard to various zones identified (Abegunde et al. 2016), based on possible phenomena such as the natural water medium or acidic and alkaline media using sequential extraction and multivariate analysis. In addition, the study evaluates the state of tailings, environmental conditions for the release of element, the control of mineralogy within tailings, and the pattern of elements released under different environmental condition. Factor analysis and mineralogical evaluation were used to extract more information from a three-step modified sequential extraction procedure (SEP) method. This approach aids better understanding of the elemental speciation or mobility from Mogale tailing dam in Randfontein area, Witwatersrand Basin, South Africa. The

use of acidic potential determination of the tailings and its bulk chemistry in predicting the acid mine drainage (AMD) loads discharged into the environment over time was done. Furthermore, factor analysis results were corroborated with acid generation potential to identify various relationships that exist and establish the efficacy of the research towards predicting AMD generation potential.

## Materials and methods

### Study area

The study area is located along the Randfontein and Krugersdorp (R28) road in the Gauteng province (see Fig. 1).

The tailing dam was constructed around 1952 and it is about 70 m deep from the top to the ground surface. This tailing dam is partially vegetated (some parts are vegetated and others non-vegetated) and in some exposed parts, some parts of the tailings dam have been exposed

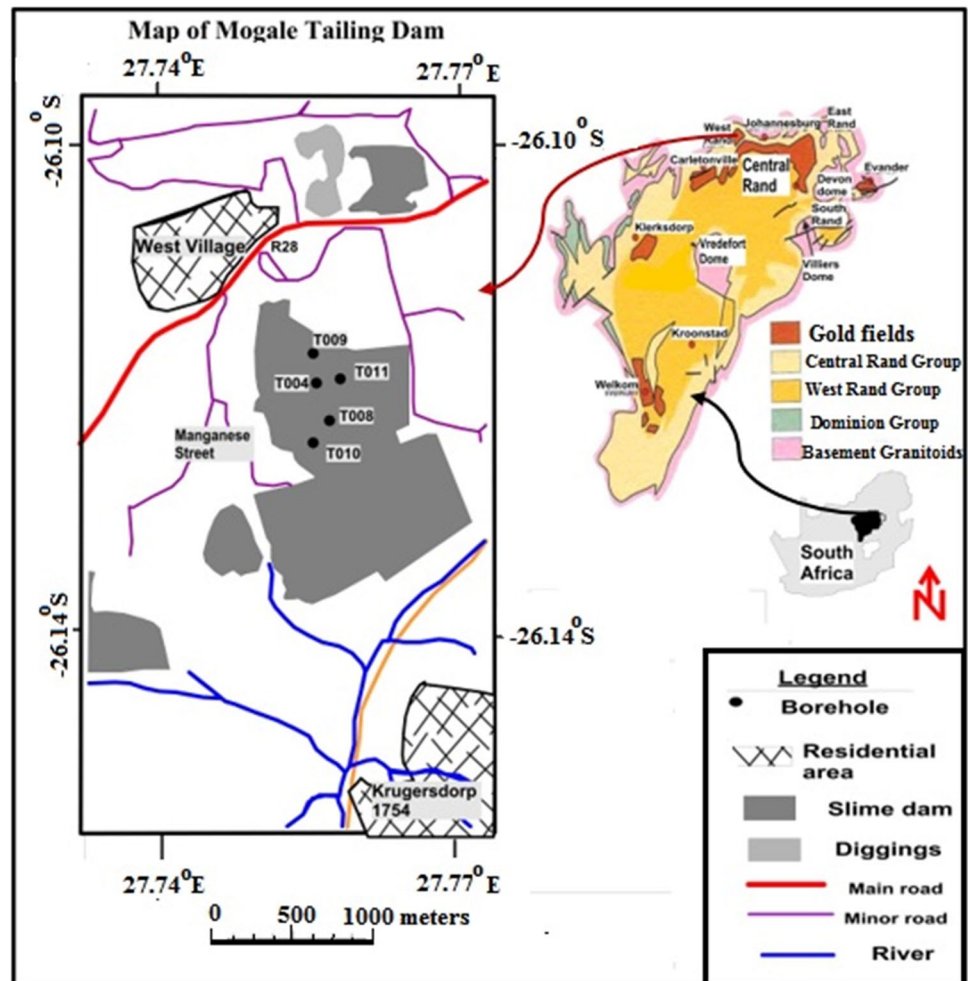
The climatic condition of this area is well known. It has a similar condition to Johannesburg, since it is situated in its northwest. The annual rainfall is about 750 mm and is strongly seasonal, while potential evaporation is about 1600 mm/annum. Most rain falls during the summer, between the October and February period. Thunderstorms of short duration account for most of the rainfall. Temperature averages about 20 °C during the summer months and about 15 °C in winter (Naicker et al. 2003).

The study area is located within the lower unit of the Witwatersrand Supergroup called the West Rand Group. The West Rand Group is divided into hospital hill series, the government reef series, and the Jeppesstown series, and all in ascending order and each division corresponding to shales and quartzite groups (Mccarthy and Rubisge 2005; Viljoen and Reimold 2002). According to Schneiderhan (2008), 1600 m-thick lavas of the Ventersdorp supergroup, which were deposited between 2.714 and 2.665 Ga, overlie the Witwatersrand supergroup. Below the Ventersdorp supergroup (consisting mostly a sequence of igneous rock) lie a layer of sedimentary rock known as the (gold-bearing layer) Ventersdorp contact reef. This gold-bearing layer consists of the sediments deposited as a result of partial erosion of the Witwatersrand supergroup discordantly.

### Field sampling and sample preparation

Five holes were drilled by an auger, locally termed as 'sand-drill', through the tailing dam to a depth of 10 m, and samples were taken at every 1 m. The drill cores were logged for changes in colour, texture, mineralogy, and additional samples collected where necessary (Abegunde et al. 2016). Each hole was drilled through the oxidised zone into the primary

**Fig. 1** Map of the study area showing various goldfields in Witwatersrand basin



grey tailings before termination. Although the Mogale tailing dump is up to 75 m high, the sampling was restricted to the first 10 m. According to Nengovhela et al. (2007) and Bezuidenhout and Rousseau (2006), AMD discharge is most distinct within the upper 5 m (unsaturated zone) in the West Rand. Fifty-six tailing samples were collected, wrapped separately in plastic tubing, and then packed in boxes. All samples were dried at 40 °C for 16 h (since temperature does not exceed the boiling points of the most volatile targeted elements) (EPA 2015), then homogenised and a portion pulverised by Dickie and Stockler milling machine.

### Analytical procedures

The mineral phase and composition of the sample were analysed using Zeiss Gemini Auriga high-resolution scanning electron micro-analyser (HR-SEM), furnished with a CDU-lead detector at 25 kV and a tungsten filament. The current and illumination were fixed at 5 kV and 0.1 mrad, whereas the magnification, working distance, and resolution were captured on each sample micrograph. The qualitative

elemental composition for each analysed sample focus spot was analysed by energy-dispersive spectroscopy (EDS).

Fifty-one samples were sent to ACME Analytical Laboratories Ltd (Vancouver) for multi-elemental analysis. All major oxides were analysed by X-ray fluorescence (XRF), and trace elements by inductively coupled plasma–mass spectrometry (ICP-MS) techniques following a lithium metaborate fusion and nitric acid digestion. Standards used were STD GS311-1, STD GS910-4, STD OREAS45EA, STD OREAS72A, STD SO-18, STD SY-4(D), STD DS9, and STD OREAS45EA.

The total sulphur and carbon were also determined by Leco analysis, while the estimated sample acid production was determined by paste pH method along with electrical conductivity (EC).

About 34 samples, as identified by Abegunde et al. (2016), were selected according to various zones and subjected to a three-step modified sequential extraction (Eze et al. 2013). Multi-elemental analysis of each sequential leach phase was analysed by inductively coupled plasma–optical emission spectrometry (ICP-OES) techniques.

Following the three-step sequential extraction, the results generated in each phase were analysed using multivariate statistics (such as cluster analysis, discriminant function analysis, and factor analysis). The factor analysis was used to probe the relationship and source pattern within each phase to help understand the mobility of elements.

**Water leach (step 1)** The water-leach phase targeted the most labile species present in the wastes. Hence, the most labile and bio-available elements leached represent the effect of rainwater on the waste in the environment. 3 g of selected gold tailings sample was measured into a 50 mL centrifuge tube and 45 mL of ultrapure water (H<sub>2</sub>O) was added at 25 °C. The samples were then placed in a mechanical shaker for 2 h. The process was repeated to produce duplicate samples, and the solution was made to stand for 1 h. Afterwards, each sample was placed in a centrifuge at 5000 rpm for 20 min and the supernatant filtered through a 42 µm filter paper. The remaining solid portion was carefully decanted into a 100 mL plastic clear bottle to reduce weight loss. The filtered supernatant solution obtained was prepared for analysis of major and trace species with ICP-MS by using a dilution factor of 10. The solid residue remaining after the extraction of each sample was quantitatively recovered and kept in a refrigerated condition for the next extraction method.

**Ammonium acetate leach (Extraction at pH 5)** Ammonium acetate leach depicted the exchangeable metals and/or those soluble in slightly acidic conditions. 45 mL of 1 M ammonium acetate buffer solution at pH 5 was poured into the solid remains recovered from step 1 at 25 °C. The centrifuging and recovery procedure given in Step 1 was followed again.

**Hydroxylamine hydrochloride leach** Hydroxylamine hydrochloride leach identified metals associated with Fe and Mn oxides that can be leached out if conditions alter from oxic to anoxic state (Favas et al. 2011; Eze et al. 2013). 45 mL of hydroxylamine hydrochloride (0.25 M) in nitric acid (0.025 M) solution was added to each sample of the solid residue recovered from step 3. The solution was shaken for 1 h at room temperature. The same process given in Step 1 was followed.

Prior to the sequential extraction, a pre-analysis was performed to determine the most suitable sample matrix and leaching agent used, in terms of weight of samples, run time for leaching, the concentration of leaching agents, as well as the weight of tailings sample required (Fig. 2). Triplicate samples generated were analysed to ascertain which was the best method of combination. Lower concentration of hydroxylamine and pH 5 buffer solution of ammonium acetate released more of our targeted elements. Based on concentration, lower conc of hydroxylamine tends to release more Cu, Ni, Zn while ammonium acetate at pH 5 buffer release more elements.

Precision and accuracy of all data were determined using pulp duplicates, triplicates (SEP) and reference materials

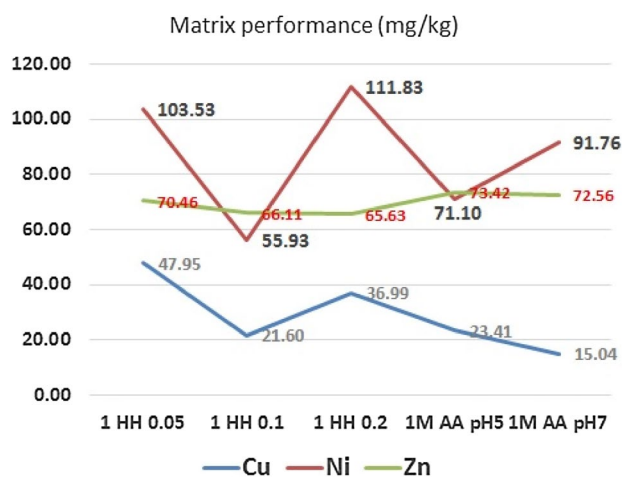


Fig. 2 Matrix performance for some selected trace elements

(Abzalov 2008; Piercey 2014). The precision error for all major elements and LOI (excluding MgO, K<sub>2</sub>O, and TiO<sub>2</sub>) is less than 5%. The precision error for trace elements is less than 10%. The accuracy for all major elements falls within 0.34–4.26% and for trace elements between 0.18 and 6.25%. Percentage relative difference is given by  $(\%RD) = 100 \times (M_e - STD_e) / STD_e$ , where  $M_e$  is the mean value of element  $e$  in the standard over a number of replicate analyses results of the reference or standard material.  $STD_e$  is the certified or known value of element  $e$  for the standard or reference materials used. The % RD values fall below  $\pm 7\%$  which shows that the data quality is very good.

## Statistical analyses

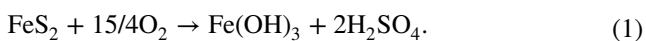
Factor analysis was carried out to probe, identify, and predict the speciation based on relationships. Complete statistical analysis of sequential extraction procedure results (each phase analysed differently) was performed by using IBM SPSS 20<sup>®</sup> software. As part of the analytical processes, factor analysis emphasised the main factors that defined the compositional variation patterns of major element and heavy metals present within each sequential extraction phase. The principal component method was used to establish the eigenvalue > 1 (Loska and Wiechuła 2003; Slavkovic et al. 2004; Alkarkhi et al. 2009; Mil-Homens et al. 2013). A varimax rotation method that suppresses small coefficient greater than 0.3 was used.

## Acid base accounting (ABA)

Acid base accounting (ABA) was used to infer the acid potential of the tailings sample, based on the assumption that the values of the total %S in samples can be used to

calculate the acid base accounting parameters for the tailings (Price 2009; Parbhakar-Fox and Lottermoser 2015; Skousen 2017). To avoid significant overestimation, the sulphide-sulphur test was done. For the measurement of the sulphide-sulphur, 1 g of tailing samples was dissolved in 45 ml of 0.2 M ammonium oxalate, at pH 3.0, at a temperature of 80 °C and leached for 2 h.

More so, static test (form of ABA) was done to assess and quantify the acid-generating potential (Gautama and Kusuma 2008; Oh et al. 2017) of mine wastes. The total %S is assumed to be a conventional estimate of the sulphide content of the sample synonymous to the total amount of sulphur present in the tailings that can be oxidised, while total sulphide-sulphur is the potential sulphides that can generate acidic leachates (Parbhakar-Fox and Lottermoser 2015). The maximum potential acidity was calculated, assuming that 100% of the sulphur present is available to produce acid. The reaction given below will be considered. It is important that the role sulphur plays in the speciation of the tailings is probed, including its relationships to various phases and their elemental mobility.



From the balanced stoichiometric reaction above, the mass of 1% pyrite translates to 30.6 kg of  $\text{H}_2\text{SO}_4$  per tonne of materials (kg  $\text{H}_2\text{SO}_4/\text{t}$ ). From this, the maximum potential acidity is calculated as the product of the weight of the total sulphur (in %) multiplied by 30.6.

In addition, since calcium carbonate ( $\text{CaCO}_3$ ) reacts to neutralise  $\text{H}_2\text{SO}_4$  generated on a 2:1 stoichiometric ratio, the comparative acid-neutralising capacity is a function of the amount of CaO content present, which is expressed in the weight of  $\text{H}_2\text{SO}_4$ .



From Eq. 2, to express % CaO with respect to % S, a conversion factor is required. This is because the molecular weight of CaO is 56, which is greater than S (32). In this study, 0.57 is used as the conversion factor. From the % CaO, the neutralisation potential (NP) of the tailings can be calculated by assuming that, % CaO is responsible for the neutralisation process in the tailings. Then, this is calculated as % CaO multiplied by 30.6 kg of  $\text{H}_2\text{SO}_4$  per tonne of materials and the conversion factor.

Another method used in this study is the calculation of the MgO NP. This approach is made possible by considering the substantiality of the MgO. This demonstrates its involvement in the neutralisation process by having similar characteristics to undergo the same reaction as CaO. Therefore, the summation of all the materials that are responsible for neutralisation is calculated as follows:

$$\begin{aligned} & (\% \text{CaO} \times 30.6 \times \text{conversion factor for CaO (0.57)} \\ & + \% \text{MgO} \times 30.6 \times \text{conversion factor for MgO (0.8)}) \\ & = \text{cumulative neutralisation potential (CNP)}. \quad (3) \end{aligned}$$

## Results and discussion

### Data summary

Table 1 lists the selected major and trace elements for the whole composite dataset and SEP phase analysis of samples from the Mogale tailings dam. An appraisal of Table 1 shows that  $\text{SiO}_2$  (84.24%),  $\text{Al}_2\text{O}_3$  (6.25%),  $\text{Fe}_2\text{O}_3$  (2.64%) and LOI (3.28%) defined about 97.05% of the whole composition of the samples, while concentrations of U, Au, Ni, As, Cu, and Zn have maximum values of 655.5 mg/kg, 1.4177 mg/kg, 274.1 mg/kg, 471.4 mg/kg, 308.8 mg/kg, and 817 mg/kg, respectively (Abegunde et al. 2016). The average arsenic contents are also well above 100 mg/kg.

Based on the selected elements, Table 1 compares the whole sample data with their corresponding leached values for each SEP leached phase. For the major elements, their equivalent values in % oxide for the whole sample were converted to mg/kg to allow proper comparison. Except for Ca, Mn, Cu, Zn, Co and Ni, all other elements' maximum concentration is lower than the minimum concentration of their corresponding whole composite value. The percentage leached for each selected element was calculated based on their average values.

However, subject to the mean, Ca, Mg, Fe, K, and Na are generally the prevalent concentration (see Table 1) of the bulk composition of the samples in each sequential extraction phase. Except for Zn and Ni in the water phase and Na in the hydroxylamine phase, the percentage of each element leached from the whole sample was less than 10% (majority are also less than 5%) of the composite concentration. For water phase, the mean leaching of the major elements such as Ca (13.01–1105.91 mg/kg), Mg (0.49–259.13 mg/kg), K (21.15–108.5 mg/kg), Na (0.006–27.44 mg/kg), Mn (0.003–133.77 mg/kg), and Fe (0.017–1238.84 mg/kg) were 370.39, 77.02, 5.76, 53.28, 15.40, and 255.09 mg/kg, respectively. Trace elements Pb (0.25 mg/kg), Cu (2.15 mg/kg), As (0.59 mg/kg), Zn (13.52 mg/kg), Co (3.22 mg/kg), and Ni (10.87 mg/kg) were leached out to a considerable amount in the water phase (WF). The percentages leached for Ca, Mg, K, Na, Mn, Fe, Pb, Cu, As, Zn, Co, and Ni were 9.78%, 3.19%, 1.89%, 0.86%, 3.31%, 1.20%, 0.5%, 4.19%, 10.46%, 8.46% and 10.89%, respectively. For the ammonium acetate leach (AMF), the average sample concentration for Ca (34.61–1280.83 mg/kg), Mg (9.21–96.67 mg/kg),

**Table 1** Selected major and trace element contents for all composite data and each SEP fraction (percentage leach of element) in the Mogate tailings dam

	Composite mg/kg value						Water fraction (mg/kg)						Ammonium acetate fraction (mg/kg)						Hydroxylamine fraction (mg/kg)					
	Composite oxide %		Composite mg/kg value		Water fraction (mg/kg)		Ammonium acetate fraction (mg/kg)		Hydroxylamine fraction (mg/kg)		Composite oxide %		Composite mg/kg value		Water fraction (mg/kg)		Ammonium acetate fraction (mg/kg)		Hydroxylamine fraction (mg/kg)					
	Min	Max	Ave	Min	Max	Ave	Min	Max	Ave	%Leach	Min	Max	Ave	Min	Max	Ave	%Leach	Min	Max	Ave	%Leach			
<b>Major elements</b>																								
Ca	0.06	2.75	0.53	429.00	19,654.00	3788.00	13.01	1105.91	370.39	9.78	34.61	1280.83	370.90	9.79	1.95	235.67	82.93	2.19						
Mg	0.09	0.86	0.40	543.00	5188.00	2413.00	0.49	259.13	77.02	3.19	9.21	96.67	29.53	1.22	3.15	74.14	23.54	0.98						
Na	0.02	0.28	0.09	148.00	2077.00	668.00	0.01	27.44	5.76	0.86	0.43	10.84	3.94	0.59	5.72	377.58	117.86	17.64						
K	0.17	0.65	0.34	1411.00	5396.00	2823.00	21.15	108.50	53.28	1.89	10.09	546.98	157.11	5.57	1.54	81.14	29.39	1.04						
Mn	0.01	0.65	0.06	77.00	5034.00	465.00	0.00	133.77	15.40	3.31	0.00	174.93	12.95	2.78	0.12	148.13	4.94	1.06						
Fe	0.86	9.31	3.03	6015.00	65,114.00	21,192.00	0.02	1238.84	255.09	1.20	2.19	268.74	36.91	0.17	4.62	531.42	213.86	1.01						
<b>Trace elements</b>																								
Pb	Nil	Nil	Nil	15.40	150.20	49.66	0.00	1.40	0.25	0.50	0.01	2.33	0.61	1.23	0.12	6.20	0.83	1.67						
Cu	Nil	Nil	Nil	3.80	308.80	51.29	0.01	11.34	2.15	4.19	0.00	2.15	0.28	0.55	0.13	4.37	0.76	1.48						
As	Nil	Nil	Nil	15.30	471.40	123.12	0.00	6.16	0.59	0.48	0.51	2.67	1.41	1.15	0.11	6.66	1.08	0.88						
Zn	Nil	Nil	Nil	4.00	817.00	129.31	0.01	86.43	13.52	10.46	0.01	3.58	0.72	0.56	0.13	19.75	2.15	1.66						
Co	Nil	Nil	Nil	0.90	125.90	38.06	0.00	13.35	3.22	8.46	0.01	1.55	0.46	1.21	0.11	3.14	0.61	1.60						
Ni	Nil	Nil	Nil	3.80	274.10	99.79	0.00	54.93	10.87	10.89	0.06	7.32	1.56	1.56	0.11	12.93	1.27	1.27						
<b>Leco</b>																								
TOT/C	0.01	0.22	0.07	100.00	2200.00	700.00	Paste pH	2.61	8.69	4.50														
TOT/S	0.26	2.19	1.14	2600.00	21,900.00	11,400.00	EC (mS/cm)	0.43	3.99	1.27														
Sulphide_S	0.15	2.11	0.84	1508.53	21,100.00	8394.03																		

Na (0.43–10.84 mg/kg), K (10.09–546.98 mg/kg), Mn (0.004–174.93 mg/kg), and Fe (2.19–268.74 mg/kg) were 370.9 mg/kg, 29.53 mg/kg, 3.94 mg/kg, 157.11 mg/kg, 12.95 mg/kg, and 36.91 mg/kg. For the hydroxylamine leach (HF), Ca (1.95–235.67 mg/kg), Mg (3.15–74.14 mg/kg), Na (5.72–377.58 mg/kg), K (1.54–81.14 mg/kg), Mn (0.12–148.13 mg/kg), and Fe (4.62–531.42 mg/kg) average concentrations were 82.93, 23.54, 117.86, 29.39, 4.94, and 213.86 mg/kg, respectively. The water leach (WF) showed the highest leaching values for most elements compared to other leachants. Trace elements such as Pb (0.61 mg/kg), Cu (0.28 mg/kg), As (1.41 mg/kg), Zn (0.72 mg/kg), Co (0.46 mg/kg), and Ni (1.56 mg/kg) were leached out in the AMF, while in the HF Pb (0.83 mg/kg), Cu (0.76 mg/kg), As (1.08 mg/kg), Zn (2.15 mg/kg), Co (0.61 mg/kg), and Ni (1.27 mg/kg) were also leached out. The average total sulphur of the composite samples (11,400 mg/kg) was greater than the sulphide-sulphur (8394.03 mg/kg) present, indicating that the tailings had a considerable amount of oxidizable sulphide. The average total carbon was 700 mg/kg. The average pH of 4.5 showed that the mine tailings were generally acidic. An average EC value of 1.27 mS/cm showed a considerable presence of leachable elements (Abegunde et al. 2016).

### Mineralogical and textural description of the tailings

As described in a study performed by Abegunde et al. (2016), the morphology of a few randomly selected tailing samples were studied using SEM–EDS based on the specific horizons in the cores as displayed in Fig. 3. The SEM image measured at 25 µm shows non-spherical shapes of varying particle sizes. Sample MT020 (1 m depth) showed inhomogeneity that did not distinguish the grains properly. The high presence of Si, Al, and low S in EDS indicated possible oxidised zones. The EDS result for Sample MT005 (5 m depth) showed a flake-like shape with sharp edges with high values of Si, S, and Fe, yet demonstrated low Al levels compared to MT001 that indicated a more enrich zone, which was altered and contained some sulphides. Sample MT007 (about 7.8 m in depth) showed smaller round shapes, flake-like shapes, and bigger particles. A low Si, but high Fe and S content in this sample compared to others indicated the presence of Fe mineral, associated with sulphides. For sample MT025 (6 m depth), the image is characterised by varying particle shapes that show high Fe and other elements. Additionally, more elements were identified in the EDS analysis. In general, the EDS analysis showed inhomogeneous distribution of particles and metals for all samples.

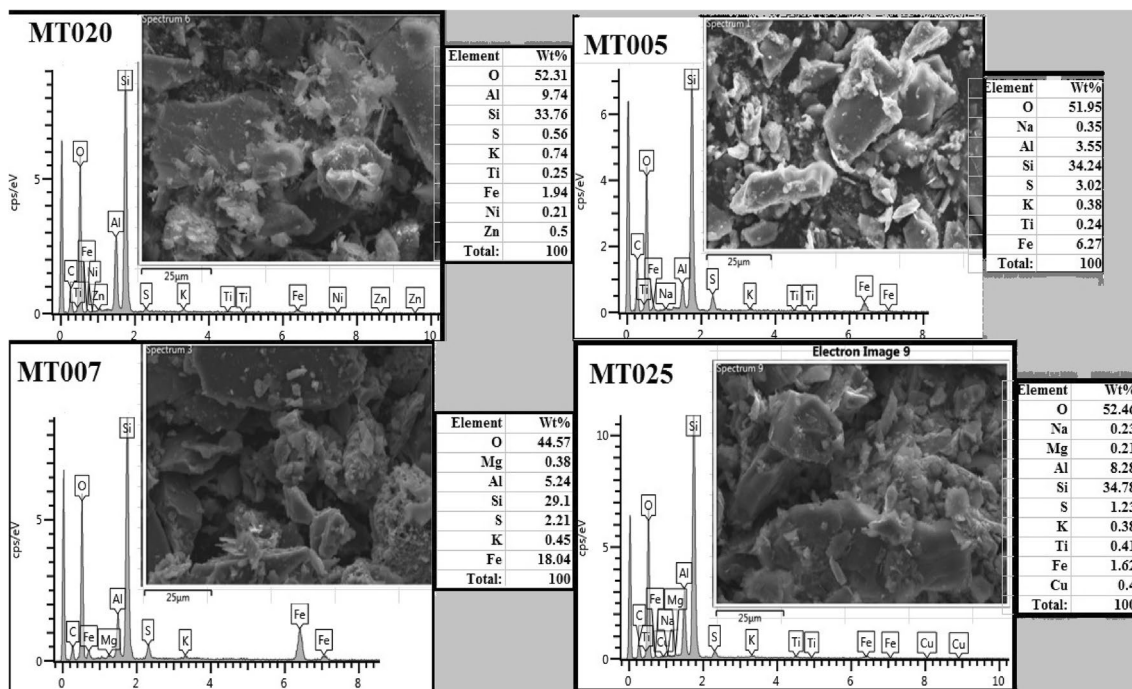
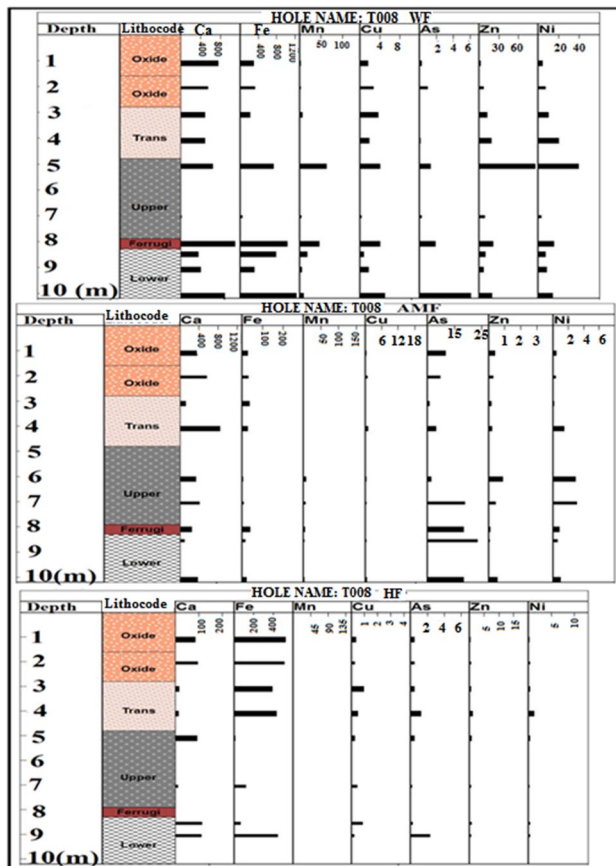
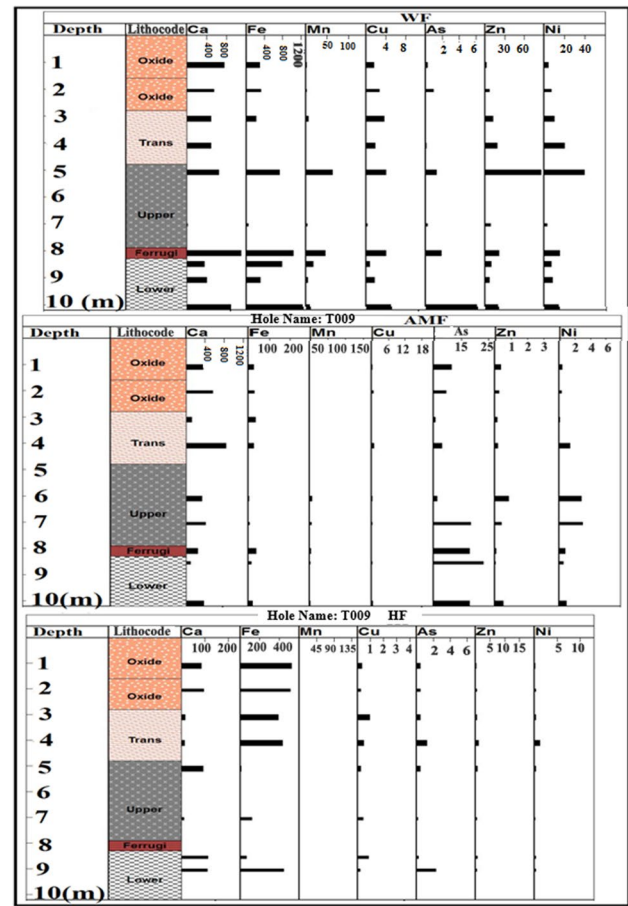


Fig. 3 SEM-EDX analysis of selected samples representing peculiar horizon within the Mogale tailings dam



**Fig. 4** Downhole plots of selected elements from each SEP fraction in borehole T008. *WF* water fraction, *AMF* ammonium acetate fraction, *HF* hydroxylamine fraction



**Fig. 5** Downhole plots of selected elements from each SEP fraction in borehole T009

### Downhole description of the SEP results

Samples from boreholes T008 and T009 were further analysed by using SEP coupled with statistical analysis as presented in Fig. 4 and 5. All the values in Figs. 4 and 5 are presented in mg/kg. Generally, the water leach showed that more trace elements such as Zn, Cu, As, and Ni were leached out by water compared to the other leachants showing their high solubility and mobility. For the major elements (Fe, Ca, and Mn), the concentration leached out in the water-leach phase increased downhole. This could be due to the available leachable material and initial elemental concentration of the tailings, which increases downhole. However, a considerable amount of calcium was leached out in the water phase. This could be attributed to the presence of secondary minerals, which are the product of redox reduction derived from the oxidation and weathering of overlaying layers.

Further observations deduced showed that a general increase in leached content downhole was observed in the water phase, while more Ca was released in the ammonium acetate leachant compared to other phase(s).

For T008, the concentration of Ca increased downhole, but was more prominent at the base of the upper zone, whereas for T009 it increased downhole and later decreased by demonstrating uneven weathering. The presence of high Ca in AMF indicated the presence of carbonate materials or neutralising minerals. No specific trend was observed for other major elements, except for a very low amount leached out in all sample concentrations of Mn from T009 compared to borehole T008. For the trace elements (Cu, Zn, As, and Ni), there was no particular trend downhole, although the topmost layer showed low concentrations indicating extreme downhole. Among the toxic trace elements, As leaching was most prominent from the two boreholes.

For the hydroxylamine fraction (HF), Fe was prominently leached compared to other major elements. Low values were observed for Mn and Ca in both boreholes. There is no particular downhole trend in the concentration of the trace elements as shown in Figs. 4 and 5. In borehole T009, Fe showed a high concentration between oxidised and transition zone.



## Statistical analysis

### Factor analysis

Principal component analysis was used to extract factors based on varimax with the Kaiser normalisation rotation method, with eigenvalue  $> 1$ . Values lower than  $\pm 0.3$  were not considered because of their significance (Table 1). In the water fraction, four factors extracted are given as: factor 1 indicates positive components for Ni, Zn, Mn, Mg, Pb, Fe, and K; factor 2 indicates positive components for Mn, Mg, As, P and Fe, but negative component for Na; factor 3 shows positive components for Mg, Pb, Ca, Fe and K, while, factor 4 indicates a positive component for Cu.

Based on eigenvalues greater than one, factor 1, 2, 3 and 4 represent 32.685%, 18.087%, 16.037%, and 13.976% of the sample, respectively. These estimates denote the order of relevance of the four factors. Clearly, this accounts for a cumulative sum of 80.8% of the sample. Out of the four factors, Fe contributed to three factors that indicate the presence of Fe ions (assuming  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ ) responsible for the acidity increase of the tailings.

In the effect, factor 1 represents the most labile elements that can be easily leached and factor 3 shows neutralising agents such as Ca and Mg carbonates, which do not play a prominent role as Fe, and thereby provided insufficient neutralisation potential.

In the case of the ammonium acetate fraction, three factors were identified. Based on eigenvalues greater than one, Factors 1, 2, and 3 represent 33.130%, 20.055%, and 16.897% of the sample, respectively. These estimates denote the order of relevance of the factors. This accounts for a cumulative sum of 70.082% of the sample. Factor 1 indicates positive values for Ca, Mg, Na, Zn, Ni, Mn, and Fe, but negative values for As; factor 2 indicates positive values for Ca, K, Pb, and Mn; and factor 3 indicates positive values for Cu, As, and Fe. In factor 1, the effect of the carbonates present on the acidity was observed when Ca associated with Fe. This denotes that the tailings contained a considerable amount of neutralising potential. Therefore, as leaching conditions become stronger, there is a tendency for an increase in alkalinity within the tailings.

For the hydroxylamine phase, there were a greater number of factors of more complexity. In this case, only five factors were identified. Based on eigenvalues greater than 1, factors 1, 2, 3, 4, and 5 represent 38.788%, 14.620%, 10.542%, 8.794%, and 8.475% of the sample, respectively. More so, factor 1 indicates positive values for Ni, Zn, Pb, Cu, Mg, Fe, and Mn; factor 2 indicates positive values for As and Fe; factor 3 indicates positive values for Ca and Mg, followed by factor 4 with a positive value for K and a negative value for Fe; and lastly, factor 5 showed a positive value

for Na and a negative value for Mn. This means that most trace elements such as Ni, Zn, Pb, and Cu are associated with the Fe/Mn oxides, and easily transported with the acid-generating ions.

### Acid generation potential

Acid base accounting (ABA) on various Witwatersrand gold tailings samples showed AP:NP ratios from 1:0.5 to 1:2.78 (Bezuidenhout and Rousseau 2006). Measured S concentrations varied between 0.17% and 0.45% S, thus placing the tailings within the uncertain range, in terms of its potential to generate AMD (Bezuidenhout and Rousseau 2006). However, AMD generation is really a complex encompassing chemical, biological, and electrochemical reactions affected by fluctuating environmental conditions, in which pyrite and marcasite remain the predominant acid producers (Simate and Ndlovu 2014). Despite the fact that weathered tailings samples indicated a lower average of %S (1.21%) as compared to the fresh tailings (2.60%), the acid neutralisation potential of the weathered samples was higher than that of the fresh samples. From the geochemical data, the total %S for these samples ranged from 0.26 to 2.75% (Abegunde et al. 2016) in all samples. However, from the analysis of total percentage of sulphide-sulphur, the available oxidizable sulphide ranges from 0.15 to 2.11% of selected borehole samples (see Table 1). A prominent association between Ca and Mg (as established by factor analysis) indicated that they both contribute to the neutralising potential of the tailings, and the use of Mg in calculating cumulative net acid producing potential (NAPP) is justified. From Eqs. 1 to 3, the net acid producing potential is calculated separately as NAPP and cumulative NAPP. This is calculated as NP/MPA and cumulative NP/MPA, respectively, and the results are displayed in Table 2.

If NAPP or C. NAPP is less than one, then it indicates that mine tailings are acid generating. Otherwise, if these values are greater than one, it indicates that the mine tailings have the potential to be acidic. Likewise, if these values are greater than two, this means that the mine tailings are not acid generating. From Table 2, the NAPP (NP/MPA) for total sulphur is less than one for all samples. Literally, this means that the mine tailing is acid generating at all layers. Most samples that fall within layer 1 have values greater than 0.5, while other samples indicate low value of NAPP. The NAPPs (NP/MPAs) for total sulphide-sulphur is less than one for all samples, except for MT038 and MT010 samples from the top most layers.

Also, in Table 3, samples at the top layer indicate values greater than 0.5 for NAPPs. This indicates that the mine tailings considerably contain high acidity-generating potential despite the presence of neutralisation materials.

**Table 2** Factor analysis result for all SEP fractions (extraction method: principal component analysis. Rotation method: varimax with Kaiser normalisation)

Rotated component matrix <sup>a</sup> (WF)					Rotated component matrix <sup>a</sup> AM-F			Rotated component matrix <sup>a</sup> HH-F					
Component					Component			Component					
1	2	3	4		1	2	3	1	2	3	4	5	
Ni	<b>0.931</b>				Ca	<b>0.61</b>	<b>0.618</b>	Ni	<b>0.976</b>				
Zn	<b>0.929</b>				Mg	<b>0.797</b>		Zn	<b>0.951</b>				
Mn	<b>0.691</b>	<b>0.55</b>			Na	<b>0.756</b>		Pb	<b>0.946</b>				
Mg	<b>0.668</b>	<b>0.341</b>	<b>0.437</b>		K		<b>0.904</b>	Cu	<b>0.925</b>				
Pb	<b>0.53</b>		<b>0.525</b>		Pb		<b>0.732</b>	As		<b>0.914</b>			
As		<b>0.804</b>	<b>0.337</b>		Cu			Ca			<b>0.908</b>		
Fe	<b>0.469</b>	<b>0.7</b>	<b>0.394</b>		As	<b>-0.472</b>	<b>0.69</b>	Mg	<b>0.517</b>		<b>0.587</b>		
Na		<b>-0.543</b>			Zn	<b>0.835</b>		K				<b>0.878</b>	
Ca			<b>0.884</b>		Ni	<b>0.814</b>		Fe	<b>0.357</b>	<b>0.353</b>		<b>-0.502</b>	
K	<b>0.405</b>		<b>0.772</b>		Mn	<b>0.581</b>	<b>0.581</b>	Na					<b>0.813</b>
Cu				<b>0.957</b>	Fe	<b>0.304</b>	<b>0.659</b>	Mn	<b>0.363</b>				<b>-0.61</b>

<sup>a</sup>Rotation converged in five iterations ( $n=38$ ) 11 variables

For the cumulative NAPP, all core samples were less than one except for MT001, MT002, MT018-1 and MT038, which were greater than one but less than two. In this case, all other samples were topmost layers except for MT018-1. Moreover, the values for C. NAPP imply that if both CaO and MgO were present in the tailings as a buffer, they could only neutralise AMD generated in the top layer 1. This shows that the tailings contained sulphides and insufficient buffering minerals, which made it susceptible to acid generation, because the finely ground material had a large accessible reactive surface area. Neutralisation potential evaluation with mineralogical assessment is not largely used, since it is challenging to accurately estimate the sample mineralogy (Bouzahzah et al. 2014) using qualitative XRD analysis.

However, most trace elements were released due to acidity. After the alkalinity of the tailing increased, more Fe oxides were released that produced more H<sup>+</sup> ions. This reduced the alkalinity. But as the acidity increased, several toxic metals were released.

### Relationship between leachates and acid generation potential

The statistical deductions attained established that pH or acidity, Fe ions, Ca<sup>+</sup>, and Mg<sup>2+</sup> played a major role in the released metals. The variation in the Fe and Ca leached out in each phase indicates the presence of oxidizable sulphide and neutralising minerals. The water phase releases the bulk of the elements leached compared to other phases. Also, the water phase denotes the natural environment. If the tailings are exposed to the natural leaching agent (WF), elements such as oxidised Fe, Ca ions and associated trace elements are released (Grover et al. 2016). This indicates

that the tailings are susceptible to weathering under normal condition (Grover et al. 2016). More Fe ions released are responsible for the increased acidity that Ca ions generated, because it could not completely neutralise it. As the leaching environment becomes harsh (AMF) and more carbonates are released, then more Ca ions are released. In the end, the available Fe ions react to produce more acidity (HF), which leads to a greater amount of trace elements to be released. Due to this, zones of accumulation showed increased pH compared to the topmost and the bottommost layers. From the acid base accounting (ABA) results, the NAPP and cumulative NAPP showed that overall, the tailings would generate acidity due to the high presence of leachable sulphides. The trends observed in the carbonate phase indicated that despite the posit of acidity, the tailings contain a considerable amount of neutralising agent to serve as a buffer. However, the trend observed in the Mn and Fe phase showed that in the long run, the Fe ions released will overcome the buffer system within the tailings and more acidity will be produced and thereby release toxic metals.

From the results, the acid generation potential of the system relates to the speciation of elements. In addition, the presence of more oxidizable sulphides makes these gold tailings a threat to the environment due to the release of toxic metals.

### Conclusions

In this study, the inhomogeneous characteristics of the mine tailings particles from the SEM image were revealed, while surface samples showed the presence of reactivity. However,

**Table 3** The acidic potential, neutralisation potential (NP), and the maximum potential acidity (MPA) of the samples in all drilled holes

S. No	T008			T009			T010			T004					
	C.NP/MPA	NP/MPA	NP/MPAs	S.no	C.NP/MPA	NP/MPA	NP/MPAs	S. no	C.NP/MPA	NP/MPA	NP/MPAs	S. no	C.NP/MPA	NP/MPA	NP/MPAs
MT001	1.70	0.44	0.74	MT010	0.73	0.63	1.06	MT020	0.40	0.09	0.12	MT038	1.52	0.57	0.86
MT002	1.36	0.47	ND	MT011	0.59	0.24	ND	MT021	0.62	0.34	0.71	MT039	0.50	0.16	0.37
MT003	0.26	0.05	0.10	MT012	0.55	0.17	0.32	MT021-1	0.70	0.42	0.48	MT040	0.50	0.13	0.08
MT004	0.47	0.09	0.15	MT013	0.37	0.11	0.21	MT023	0.73	0.50	1.30	MT041	0.47	0.15	0.11
MT005	0.42	0.13	0.13	MT014	0.57	0.17	0.73	MT024	0.15	0.06	0.32	MT042	0.66	0.25	0.24
MT006	0.65	0.23	0.24	MT015	0.44	0.14	0.12	MT025	0.38	0.17	0.18	MT042-1	0.49	0.19	0.35
MT007	0.66	0.40	0.50	MT016	0.39	0.14	ND	MT026	0.27	0.09	0.13	MT043	0.42	0.14	0.48
MT007-1	0.64	0.38	0.96	MT017	0.36	0.15	0.19	MT027-1	0.39	0.14	0.22	MT044	0.42	0.19	0.21
MT008	0.50	0.22	0.28	MT018	0.26	0.10	0.39	MT028	0.39	0.18	0.20	MT045	0.20	0.07	0.11
MT008-1	0.14	0.04	0.04	MT018-1	1.28	0.25	ND					MT046	0.30	0.11	0.26
MT008-2	0.65	0.53	ND	MT019	0.33	0.10	ND								
MT009	0.43	0.17	ND												

NP neutralisation potential, MPA (for total sulphur) maximum potential acidity, C.NP cumulative neutralisation potential, MPAs maximum potential acidity for sulphide-sulphur

findings attained indicate that pH or acidity, Fe ions, Ca<sup>2+</sup> and Mg<sup>2+</sup> played a major role in the released metals. Out of the four factors identified in factor analysis results for water fraction (WF), Fe contributed to three factors that showed the presence of Fe ions (assuming Fe<sup>2+</sup> and Fe<sup>3+</sup>) responsible for the increased acidity of the tailings. A more prominent Fe effect showed positive acidic potential despite the presence of Mg and Ca. For the water phase, the release of Fe ions into the surroundings can be associated with the gradual mobility or releases of toxic metals. Factor 1 represents the most labile elements that can be easily leached, while factor 3 represents the presence of neutralising agents such as Ca and Mg carbonates. However, this particular factor did not play a more integral role than Fe, and thus could not provide enough neutralisation potential. For WF, Fe has values for ocomponent 1, 2, 3 indicating that the presence of Fe assist in the release of most elements. Ni (0.931), Zn (0.929), As(0.804), Ca(0.844) and Cu (0.957) show high positive values indicating that they are highly susceptible to water leach. Only Cu (0.957) has no association with Fe, indicating that it is leached non Fe-containing minerals.

In the case of the ammonium acetate fraction (AMF), findings indicated that Ca(0.61) & Mg(0.797) are was associated with Fe. This demonstrates the effect of the carbonates found on the acidity, and the tailings contain a considerable amount of neutralising potential. Therefore, as the leaching conditions become stronger, there is a tendency for an increase in alkalinity within the tailings and the carbonate minerals play a major role in releasing more buffer. Further findings showed that the positive value of Fe reflected the potential release of Fe ionic species into the environment, which can increase the acidity of the tailings. Most trace elements, such as Ni, Zn, Pb, and Cu with values > 0.9, are associated with the Fe/Mn oxides phase leachable. Thus, easily transport with the acid-generating ions. Potentially, more carbonates are released with more Ca ions as the leaching environment harsh (AMF). Eventually, the available Fe ions react to produce more acidity (HF), which caused a greater amount of trace elements to be released. That is why zones of accumulation showed increased pH compared to the topmost and the bottommost layers. The trends observed in the carbonate phase showed that, despite the posit of acidity, the tailings contain a considerable amount of neutralising agent to serve as a buffer. The trend observed in the Mn and Fe phase showed that in the long run, the Fe ions released will overcome the buffer system within the tailings and more acidity will be produced, thereby releasing toxic metals.

Generally, the NAPP and cumulative NAPP showed that overall, the tailings would generate acidity due to the high presence of leachable sulphides. The use of sulphur-sulphide as compared to total sulphur in calculating neutralisation potential help to avoid considerable assumption in estimating amount of acid produced.

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