Acid rock drainage prediction of metalliferous soils from O’Kiep, Namaqualand, South Africa: A Humidity Cell Test assessment

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Abstract

Samples of metalliferous soils (MS) from the O’Kiep area in South Africa were evaluated for their potential to form acid rock drainage (ARD). Metalliferous soil leachates (MSL) were measured weekly for their pH, electrical conductivity, total dissolved solid, alkalinity, sulfate and Potential Toxic Elements (PTEs). Characterisation of the MS showed that the soils are rich in major oxides, i.e. $SiO_2 > Al_2O_3 > FeO_3$ with PTEs being S > Cu > F. ABA tests indicated that the MS exhibited a slightly acidic trend with a paste pH of 3.9. Furthermore, the acidity potential (28 kg $CaCO_3$/t) indicated that the MS had an acid rock drainage potential (ARDP).

Keywords: Acid Base Accounting, acid rock drainage, humidity cell tests, metalliferous soils, O’Kiep

Introduction

Metalliferous mining usually causes environmental contamination challenges due to mine waste and tailings affecting the hydrology, topography including, local vegetation; culminating in the destruction of natural habitats and degradation of soils, which essentially results in the subsequent collapse of the environment in which the mining is taking place (Moncho et al. 2017). As a result, metalliferous soils (MS) are exposed to environmental conditions in these metalliferous mining areas, culminating in a variety of biological, chemical and physical activities which could facilitate the formation of a high concentration of potentially toxic elements (PTEs) (Erdogan et al. 2018). PTEs such as; As, Ba, Cu, Pb, Se and Zn may pose potential human health risks, especially in areas with mining activities. Earlier studies showed that MS from the O’Kiep have higher concentrations of PTEs, as geochemically characterised by Moncho et al. (2017) and Erdogan et al. (2018). PTEs are usually present in MS; albeit, in concentrations that maybe high in mining overburden and tailings than in soils, a risk which has to be investigated to minimise environmental and human health implications (Portales et al. 2015). According to Erdogan et al. (2018) and Fey (2010), the soil texture and type in arid regions, consist of a different principle of soils with special sub-soil characteristics comprising of calcic and silicic constituents.

O’Kiep is a former Cu mining area with ore mineralisation being dominated by Cu-rich sulphidic ores, i.e. chalcopyrite and bornite, which are the most abundant copper bearing minerals in the area. Some of these constituents undergo oxidation, e.g. pyrite oxidation, which initiates ARD, one of the biggest environmental challenges in the mining industry. ARD enhances the dissolution of rocks, acidifies aquifers, processes which mobilises PTEs (Egiebor and Oni 2007). If the rate of acid generation due to sulphide oxidation, is in excess of acid neutralising minerals, then progression into the formation of low pH mine water may ensue. In addition to the acidity produced, the consequent mobilisation and solubilisation of mineral containing ore would result in PTEs dissolution into liquid phase, particularly at low pH, leading further into ARD thus severely affect to the receiving environment. Therefore, the ultimate goal of the research reported herein was to use ARD prediction tests in conjunction with other relevant data to assist with development of strategies for the management of mine wastes including the MS of O'Kiep. By predicting acid rock drainage potential (ARDP), environmental impacts and assessment of soils in O'Kiep especially post mining, could be done. Characterisation of the metalliferous soils and to determine weathering rates using the humidity cell tests (HCTs) and the variation in leachate quality, was conducted.

Methods

Sample collection and MS analyses

Sandy-silt-clay MS samples (n = 10, 5 kg each) with limited agricultural potential were collected in August 2017 from O'Kiep, Namaqualand, South Africa. Each MS sample was collected using polypropylene buckets washed with dilute 0.5 M HCL and sterile distilled water to minimise environmental and physical alteration. Sampling locations were cleared of litter and surface rocks prior to sample collection. These sub-soil samples were collected based on field examination to account for physical weathering and surface conditions. All sample buckets were labelled and transported to the laboratory. Figure 1 enlists sampling locations (marked using a GPS), i.e. highland (OCM1, OCM2, OCM3); midland (OCM4, OCM5, OCM6) and lowland (OCM7, OCM8, OCM9, OCM10), with each sample being collected at a depth of 1 to 1.5m from the surface, using a Draper

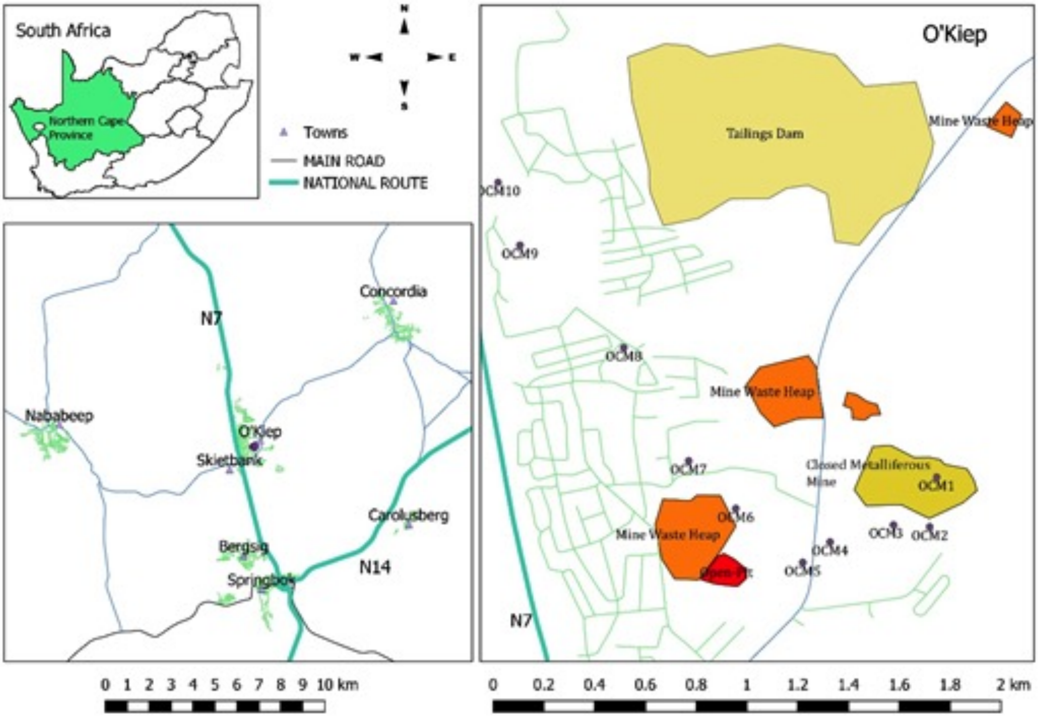

Figure 1 Location of study area and sampling points drawn using Quantum GIS software (v. 2.18.11) and data from the National Geo-Spatial Information (NGI) system, a component of the Department of Rural Development and Land Reform, South Africa.

24414 steel auger (Schoeneberger 2012).

All samples were air dried at ambient temperature, and subsequently screened using a 2-mm sieve prior to further analyses. A portion of each MS sample was used for soil mineralogical characterisation and an acid-base accounting test. Further more, analytical analysis were performed including quantitative mineralogical assessment of the soil using X-ray diffraction (XRD) and X-ray fluorescence (XRF). The details of sample preparation and analytical instrumentation analyses are as described by Beckhoff et al. (2007).

Acid Generation Potential and Humidity Cell Tests

The potential ARD sources in O'Kiep are the partially rehabilitated metalliferous mine, mine tailings and mine waste heap (-see Figure 1). O'Kiep soils also have a potential to generate ARD due to the soils physico-geochemical characteristics. A modified field and laboratory test method for acid-base accounting (ABA) was used for each MS sample. Additionally, a prediction test was performed using a paste for pH testing, to assess individual samples' acid forming characteristics. Furthermore, the acidity potential (AP) was quantified on the basis of total sulphur content, with the neutralisation potential (NP) being determined using a titration experiment whereby NaOH (0.1 N) and HCl (1 N) were used for each sample. Subsequently, the determination of AP and NP allowed for the computation of the net neutralisation potential (NNP) including the neutralising potential ratio (NPR) - a criteria used for the determination of ARDP of the MS samples. On-going Humidity Cell Tests (HCTs) of each homogenised MS samples (1 kg) were performed in a capped Percpec cylindrical chamber (203 mm height X 102 mm diameter) and ASTM:D2216-10 (2010). The MS samples were placed at the bottom of the humidity cell. Then, 750 mL of sterile deionised water was added to each test chamber for the initial immersion of the MS samples. The HCTs were run for twenty one weeks, with each week cycle consisting of the following procedure: leach cycle (1 day), dry air cycle (3 days) and moist air cycle (3 days). After each week cycle, metalliferous soil leachates (MSLs), i.e. 750 mL were collected in to flasks. Subsequent to filtration (45 µm filter into polyethylene bottles of 500 mL capacity; the MSLs produced were analysed for quality characteristics to account for alkalinity, electrical conductivity (EC), pH, total dissolved solids (TDS), sulphate (SO_4) and for PTEs using Inductively Coupled Plasma - Mass Spectrometry (ICP-MS) as per 6020B method described in EPA (2014).

Results and Discussion

Mineralogical composition and Acid base accounting (ABA) of the metalliferous soils

In the O'Kiep region, several secondary minerals have been observed at the surface. These minerals occur as extremely fine-grained particles described as efflorescent salts (Fosso-Kankeu et al. 2017). The presence of these minerals in large quantities is indicative of rapid acidification potential, particularly if ARD formation processes are initiated. Therefore, PTEs generated by dissolution and oxidation of the primary minerals, may lead to the incorporation of secondary minerals into the local environment by either adsorption and/or ion exchange. There was a variation among the MS mineralogical composition based on the XRD results obtained. However, the dominant mineralogical constituents (Table 1), were quartz and albite while the major elements included S and Cu. Quartz (80.1%) is reported to be less reactive in oxidising conditions and has minimal acid neutralising potential. The presence of albite (2.92 %) and Muscovite-IM (0.19%), is indicative of an ore body bearing granite and gneisses (Singh 2005), a characteristic attributed to the geology of the study area. Furthermore, the presence of Halloysite-10A, also known as kaolinite (0.26%), was indicative of constituents that normally occur in arid soils (Ziegler et al. 2003). The MS samples were characterised by a high SiO2 (67.6%) and Al (12.4% as Al_2O_3), Fe (7.3% as Fe_2O_3), K (4.0% as K_2O), Na (1.9% as Na_2O) and Ca (1.6% as CaO). The major PTEs (mg/kg) were S (2437) > Cu (1192) > F (1079) > Ba (674) > Mn (457) > Cl (131).

The paste averaged pH of 3.9 indicated that the MS of O'Kiep are slightly acidic, which is an indication of the presence of sulphides that could react to form acid. This was also confirmed by the total sulphur content of up to 0.89% for samples tested, with a further lowly (0.14) NPR value. This suggested a considerable percentage of sulphur and a greater potential of ARD production. The total acidity was attributed to dissolved PTEs, which are generally dominant in ARD. The AP was approximated to be high (28 kg $CaCO_3$/t), which corresponded to a negative NNP average of -32 kg $CaCO_3$/t. By using a criteria as described in Miller et al. (1991) in combination with the NP to AP ratio criteria of Adam et al. (1997), the MS of O'Kiep can therefore be classified as having an ARDP.

Weathering of metalliferous soils

HCTs are long-term (20 to >300 weeks) leach tests considered to be among the most reliable geochemical characterisation methods for ARDP (Maest and Nordstrom 2017). Similarly, the ABA test can be used to determine the ARD chemistry, PTEs release rates and generic MS behaviour when exposed to environmental conditions suited for ARD formation. The geochemical analyses of the MSL using ABA tests, exhibited slightly acidic leachates characterised by AP of ≈3.9; results which were similar to those obtained using the paste pH. There was no clear indication as to the influences of pH changes, as this parameter can be affected by several environmental mechanisms including specie retention in the solid phase of the MS which can culminated in MSL characteristic variation during HCTs.

As such, the MSL generation and its quality characteristics could be directly associated with factors such as simultaneous oxidation of sulphide species and the dissolution of major oxides and calcite, which would in turn minimise the acidification of the MS. The slightly acidic values observed

***Table 1** Averaged mineralogical composition and XRF analysis of metalliferous soil samples*

	Composition	
Mineral	Formulae	(%)
Quartz	SiO_2	80.1
Albite, ordered	$NaAlSi_3O_8$	2.92
Muscovite-IM, syn	$KAl_2(AlSi_3O_{10})(OH)_2$	0.19
Halloysite-10A	$Al_2Si_2O_5(OH)_4.2H_2O$.	0.26
Illite	$(K,H_3O)(Al,Mg,Fe)_2(Si,Al)_4O_{10}[(OH)_2, (H_2O)]$	0.13
	XRF analysis	
Major Oxide (wt. %)	PTEs	mg/kg
Al_2O_3 (12.4)	Ba	674
CaO (1.6)	Cl	131
Fe_2O_3 (7.3)	Co	25.6
K_2O (4.0)	Cr	83.9
MgO (1.0)	Cu	1192
MnO (0.1)	F	1079
Na_2O (1.9)	Mn	457
P_2O_5 (0.2)	Mo	5.9
SiO_2 (67.6)	Nb	15.0
SO_3 (0.3)	Ni	39.9
TiO_2 (0.8)	Pb	61.5
LOI (1.7)	Rb	197
Totality (99.3)	S	2437
H_2O^- (0.4)	Sc	14.7
	Sr	152
	Th	57.5
	U	5.5
	V	76.2
	Y	33.6
	Zn	97.7
	Zr	279

for MS samples of O’Kiep, indicated that the generated H^+ ions were to some extent, being consumed by the dissolution of the identified aluminosilicate minerals. This was evidenced by the total alkalinity of the MSL, determined to be <5 mg/kg $CaCO_3$. Furthermore, the EC and TDS values of the MSL were initially averaged at 376 mS/m and 5046 mg/kg, respectively, with a sequential steady decline of up to 109 mS/m and 964 mg/kg, being observed. Similarly, the SO_4^{2-} concentration of the MSL declined from 2682 to 574 mg/kg. Therefore, the variation in EC and TDS profiles was analogous to the observed SO_4^{2-} trend, indicating that the EC and TDS are predominantly associated with SO_4^{2-} concentration and MS sample decomposition thus weathering, which was an indication of ARD formation. Additionally, PTEs presence in the MSLs, indicated dissolution in the liquid phase; an observation supported by the increase of Si in the MSL from 5.9 to 11.5 mg/kg; albeit,with minimal decrease of Ca from 204 to 186 mg/kg – a phenomena associated with complexation of the Ca with other oxide species to form a precipitate.

The principal carbonates observed in MS were calcite and quicklime at1.6%. The rate of PTEs release was initially rapid during the initial stages of the HCTs with subsequent decreases thereafter. The highest average of the major PTEs in the MSL were observed during the first week of the test at the following concentrations (mg/kg): Ca (167) > Mg (46.9) > Al (26.1) > Cu (17.5) > Cl (12.3) > Si (10.6) > Na (7.83) > Mn (4.73) > K (1.02) > Ni (0.5) > Zn (0.92) > Fe (0.42). Other PTEs occurred at low concentrations, e.g. F < 2 mg/kg, in the MSL. The highest decline in the release of PTEs was observed over time (mg/kg): Al (8.1), Cu (5.9) and Mg (5.1) followed by Na (2.02), Mn (0.6) Fe (0.02), K (0.54), Pb (0.1), Co (0.02), Ni (0.14) and Zn (0.3). Although slight variations were observed in the MSL for some PTEs, a steady decline over the period of experimentation (n = 3 weeks) was observed. The MSL contained higher sulphur content and was rich in PTEs. The Na in the MSL is related to albite while K is associated with muscovite in the MSL as the sulphides were assumed to have been partly altered due to oxidation to secondary minerals (i.e. goethite and hematite). Primary minerals, such as chlorite and quartz grains, might be covered in iron sulphate, with the Fe leaching being low in the MSL due to reduced oxidation rates. After the first week of the experiment, the concentrations of the Fe in the MSL started to decrease. However, lowly dissolved Fe in the leachate does not indicate the absence of pyrite oxidation (Gleisner and Herbert Jr 2002). Additionally, the reduction of Ca, Mg and Mn was likely due to the products of neutralisation reactions in the MS. Therefore, the dissolution and leaching of these elements is caused by acid generation related to pyrite oxidation (Mäkitalo et al. 2016). The observed leaching of Al, K and Na is most likely due to aluminosilicate dissolution of MS constituents such as albite, which was also observed in the MS.

Conclusion

In the present study, ABA tests suggested that the MS had a high acid producing potential. This was confirmed by the results of ongoing HCTs, which revealed a potential of acid rock drainage formation. Low $CaCO_3$ in the MS, contributed to the decline in the neutralising potential of the metalliferous soil studied. Monitoring of the leachate quality showed that the MS sample started producing acid very early in the test, i.e. in the first week of experimentation. The results suggested that there is a risk for ARD formation in the metalliferous soils of O’Kiep under pryrite oxidation conditions. Results of this study also suggeststed that there was accelerated PTEs leaching from the metalliferous soils which would result in uninhibited formation of PTEs thus contamination of the surrounding groundwater bodies. PTEs contamination in MS in O’Kiep may pose health and environmental risks. The acidic nature of MS of O’Kiep would thus be unsuitable for growth of agricultural commodities.

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