Environmental and Geochemical characterization of alkaline mine wastes from Phalaborwa (Palabora) Complex, South Africa

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Abstract

A detailed characterization of alkaline tailing ponds and waste rock dumps from Phalaborwa Igneous Complex (PIC) South Africa, has been accomplished. The study goes beyond the environmental characterization of mining wastes, offering the first insight towards the recycling of the wastes as alkaline reagent to neutralize acid industrial wastewater. To achieve these aims, tailings and waste rocks were characterized using a combination of conventional, novel and modified Acid Rock Drainage (ARD) prediction methodologies, as well as South African leachate tests, sequential extractions and pseudo-total digestions. The scarcity of Fe-sulphide minerals and the abundance of alkaline minerals indicated that PIC wastes are not ARD producers. The highest neutralization potential was found in the carbonatite rocks and East tailing samples (range between 289 – 801 kg $CaCO_3$ eq/t). According to the National Environmental Management Waste Act (59/2008) of South Africa, tailing ponds and waste rock dumps from PIC classify as non-hazardous (Type 3 waste). The sequential extractions showed that the different fractions from most of the samples would mostly release sulphate and non-toxic elements, such as Ca, Mg, Na and K, which might be a concern if leached in high concentration. In addition, relatively high concentrations of radionuclides, such as U and Th (average of 6.7 and 36.3 mg/kg, respectively) are present in the non-labile fraction of PIC wastes, while the leachable concentrations were always below 0.006 mg/L. Among PIC wastes, East tailing would be the best option as alkaline reagent to neutralize acid wastewater because of its high neutralization potential and non-harmful leachate composition. In general, this study exposes the shortcomings in mine waste characterization, particularly for alkaline mine wastes and introduces the assessment of potential revalorization as a novel practice in mine waste characterization that, if extended as a regular practice, would facilitate a circular economy approach to the mining industry with its consequent economic and environmental benefits.

Keywords: mining waste recycling, carbonatite tailing; waste rock dump; acid-base accounting; leaching test; sequential extraction;

1 Introduction

Alkaline mine wastes are usually classified as inert material because this type of waste has the capacity to neutralize acid leachates leading to the immobilization of cations and anions (e.g., metal precipitation as hydroxides or oxyhydroxy-sulphates). However, the near neutral–slightly alkaline pH reached in leachates generated from this type of waste may not be enough to induce the complete precipitation and removal of divalent metals such as Zn and Mn, as well as anions such as sulphate, phosphate, fluoride and chloride (Hiller et al., 2013). In addition, the alkali metals (e.g. Na and K) and alkaline earth cations (e.g. Ca, Mg and Ba) commonly released from alkaline mine wastes, which are not considered as toxic elements, might drastically affect the aquatic environments if they are leached in high concentrations.

The potential environmental problems caused by alkaline wastes have not been well-investigated (Kauppila et al., 2008; Kirby and Cravotta 2005; Pettit et al. 1999). Several studies have attempted to describe the negative environmental impact caused by alkaline mine tailings in aquatic systems of Finland and Tunisia (Heikkinen et al., 2009; Souissi et al., 2013), while other studies denied its impact (Hiller et al., 2013; Moukodi, 2008) based on current standards and protocols that indicate that samples classified as non-acid forming (e.g. sulphide absent, neutral paste pH and positive net neutralization potential) do not require further testing (e.g., Usher et al., 2003 and references therein). This assumption has provoked that the environmental impact of large alkaline tailings such as those from Bayan Obo Deposit in China and Phalaborwa igneous complex (PIC) in South Africa, among others, have been overlooked. In the case of PIC is worrisome because of its proximity to the renowned Kruger National Park (KNP) and the negative impact that it might have on its biodiversity.

On the other hand, most of the regulations for mine wastes are currently aimed to predict only acid mine drainage (AMD) generation and their toxicity, focusing on chemical test such as ABA (acid base accounting) and leachate test (Parbhakar-Fox and Lottermoser, 2015a; Usher et al., 2003). However, recent studies agree that a detailed mineralogical approach should be included to improve the interpretation and prediction of leachates (Becker et al., 2015; Dold, 2017) not only to prevent the generation of AMD, but also the generation of neutral/alkaline mine drainage (NAMD). In the case of South Africa, NAMD occurrence is particularly high (Castillo et al., 2015). Although no specific regulation for extractive waste disposal has been developed in South Africa, the general landfill disposal regulation, which includes mining wastes, is stricter than elsewhere regulations (e.g., Australia and USA) including the elements commonly present in alkaline mine drainage. For instance the South African protocols and threshold stablished that are based on the USA standard for Toxicity Characteristic Leaching Procedure (1311-TCLP) test (USEPA, 1998) and the Australian Standard method AS-4439 (Standards Australia, 1997), with similar Leachable Concentration Thresholds (LCT) and Total Concentration Thresholds (TCT) (Department of Environmental Affairs, 2013), certain parameters such as B, Ba, Cl, Co, Mn, Sb, V, sulphate (SO_4) and total dissolved solids (TDS) have been included. Despite these efforts, conventional protocols overlook the speciation, and thereby mobility and long term bioavailability of the leachate compounds (Rodgers et al., 2015). Thus, although sequential extraction procedures (SEP) (Rauret et al., 1999) are not part of the protocol for landfill disposal, it has been included herein since it is a more comprehensive tool to address the leachates that wastes may produce under different circumstances; weathering (bioaccessible fraction (F1)), anaerobic conditions (reducible fraction (F2)) and aerobic conditions (oxidizable fraction (F3)).

On the other hand, alkaline mine waste from PIC might have the potential to be used as neutralizing reagent to remediate acid industrial wastewater (AIW). Other alkaline wastes such as fly ash, paper mill waste and bauxite tailing (red mud), among others, have been widely studied as a substitute for alkaline materials to neutralize AIW (Paradis et al., 2006; Pérez-López et al., 2011; Surender, 2009). Even though these alkaline wastes are a cheaper option and they may contribute to the neutralization process, quite often these wastes contain toxic elements that could be released into the treated water. Before recycling any alkaline waste as neutralizing reagent, or for any other purpose, a preliminary characterization of the leachates that a waste may produce, such as those suggested herein, should be addressed.

Therefore, this study goes beyond conventional environmental characterization of mine wastes and seeks to achieve two aims; i) overcome the limitations of traditional protocols that are aimed to predict AMD by including novel and modified procedures, and ii) provide the first insight about the potential revalorization of PIC wastes based on its environmental characterization. The latter approach would enhance a circular economy strategy for the mining industry with its consequent economic and environmental benefits.

2 Study area

Phalaborwa Igneous Complex (PIC), South Africa, is an alkaline complex comprised by pyroxenite, phoscorite and the only carbonatite primarily mined for Cu in the world (**Error! Reference source not found.**; Giebel (2019)). Mining activities commenced in PIC between 1930s and 1960s to recover apatite, vermiculite and copper, among other by-products (Southwood and Cairncross, 2017). After 60 years of intensive mineral extraction and processing, more than 4500 Mt of mining wastes (rocks and tailings) have been disposed of on several dumps and ponds (FOSKOR, 2018; Moukodi, 2008). Indeed, PIC host one, if not, the largest tailing in the southern hemisphere (approx., 2830 Mt). This tailing, hereinafter referred to as Selati tailing (Fig. 1), consists of the processed material from the phosphate plant (FOSKOR, 2018) and is located in the southern most area of PIC. Smaller tailings grouped in the easternmost part of PIC, collect the carbonatite froth-flotation from the Cu beneficiation (Hu et al., 2017; Moukodi, 2008), hereinafter referred to as East tailing. In addition, PIC also host more than 1085 Mt of waste rocks piled in dumps and comprised of mainly barren carbonatites, phoscorites and pyroxenites (Brink, 2011; Moukodi, 2008). These mining wastes exposed to the rainwater leachate alkaline drainages that have deteriorated the water quality of surrounding aquatic ecosystems (i.e. surface and groundwater). In that sense, the Kruger National Park (KNP), which is the biggest natural reserve of South Africa (19,485 km^2) and declared a biosphere reserve by UNESCO in 2001 (K2C, 2014), is of especial concern, due to its proximity to the mining wastes of PIC (Fig. 1). Indeed, the Department of Environmental Affairs (2009) reported that “Olifants River, from the Selati [River] confluence to downstream border in the Kruger National Park … is negatively impacted by poor water quality of the Selati River as a result of mining activities at Phalaborwa”.

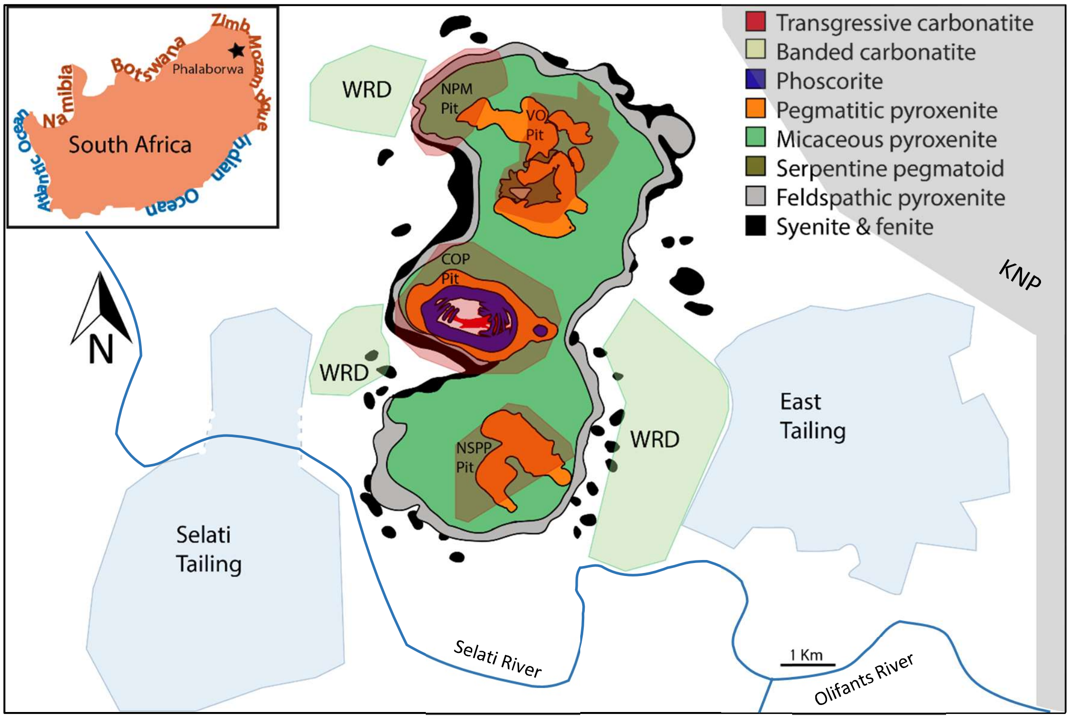

Fig. 1. Simplified geological map of Phalaborwa Igneous Complex and industrial facilities (modified from Giebel et al., 2019). Red shadows represent the Cu open pit (COP), the North Pyroxenite Mine (NPM) pit, the New South Pyroxenite Pit (NSPP) and Vermiculite Open (VO) Pit; Blue shadows represent the East and Selati tailing dams; shaded in green are represented the waste rock dumps (WRDs); and shaded in grey is the Kruger National Park (KNP).

3 Methodology

3.1 Sampling and samples preparation

The sampling of mining waste from PIC includes 60 rock samples collected from the WRDs (approx. 1 to 12 kg/each) and tailing samples from up to 2m-deep trench (approx. 5 kg/each) from 16 sampling points, collected with shovels and soil samplers (Fig. 1, sample geolocation data in supplementary material Annex 1 and Table A.1). Polished thin sections and polished blocks were prepared at the University of Huelva from each rock and tailing sample for further mineralogical and textural determinations. For the sake of clarity, the results discussed herein are the average of mineralogical and textural determinations of each of the seven main lithologies, i.e. phoscorite, banded carbonatite (B-carbonatite), transgressive carbonatite (T-carbonatite), pegmatoidal pyroxenite (P-pyroxenite), micaceous pyroxenite (M-pyroxenite), feldspathic pyroxenite (F-pyroxenite) and syenite; as well as of each of the six tailing sectors, i.e. Selati tailing S, Selati tailing N, East tailing S, East tailing N, East tailing E and East tailing W.

Half of each sample collected was milled and split in representative subsamples for geochemical analyses at the University of the Free State. Out of the milled samples, 13 composite samples were prepared for the acid rock drainage (ARD) study. These included a composite of each of the seven main PIC's lithology, as well as, a composite of each of the six sectors of PIC tailings. In addition, leachate tests and sequential extractions were also performed to each of the seven main lithologies of PIC, as well as to a composite of Selati tailing samples and to a composite of East tailing samples.

3.2 Mineralogical and textural analyses

Mineralogical determinations on both WRDs and tailings samples were carried out at the University of Huelva (Spain) and the University College Dublin (Ireland). Detailed mineralogical and micro-textural analyses on polished thin section were performed by both petrographic microscope and scanning electron microscope coupled with energy dispersive spectroscopy and SEM-EDS JEOL JMS-5410 equipped with a microanalyzer Link Oxford.

Semi-quantification of main mineralogy on WRD samples were estimated using the X-powder software on X-ray diffraction (XRD) analyses using a Broker D8 Advance Powder Diffractometer with Cu–Kα radiation. In addition, an estimation of minor minerals abundances in the tailing samples was carried out by petrographic observations. Silicon drift detector (SDD) were used for elemental mapping of tailing samples, followed by semiquantitative mineralogical analyses by ImageJ software (https://imagej.nih.gov/ij). A summary of mineralogical analysis result is given in supplementary material, Table A.3.

3.3 Acid rock drainage (ARD) prediction

Over the last decades different ARD protocols have been developed to assess the potential of mine waste to produce acid drainage. Current protocols are imprecise and they tend to differ among themselves in the prediction of the potential of mine waste to produce or neutralize acidity. The Water Reasearch Commission (WRC) of South Africa (WRC, 2011) recommends to follow the acid-base accounting (ABA) procedure described by Usher et al. (2003). This protocol includes, paste pH, net acid generation (NAG), net neutralization potential (NNP) and neutralization potential ratio (NPR), and uses a spreadsheet tool named ABACUS to standardise the interpretation of the results. In order to increase the accuracy of the predictions, mineralogical methods such as the traditional net carbon value (NCV, Bucknam, 1997) and the novel textural acid rock drainage index (ARDI, Parbhakar-Fox et al., 2011) are included in this study.

The results of the mineral and textural analysis were used to determine the **Net Carbon Value** (NCV) (Bucknam, 1997) and the textural acid rock drainage index (ARDI) as described in Parbhakar-Fox et al. (2011). NCV is based in the percentage of CO_2 of common carbonates, which is 44, 48, 44 and 38 CO_2% for calcite, dolomite, ankerite and siderite, respectively. These, multiplied by their abundance (in %), account altogether as the neutralization potential. The acid potential of a given sample is determined by the stoichiometric equivalence of one mole of sulphide being oxidised to sulphuric acid, consuming one mole of carbon dioxide, times -1.37 the percentage of sulphide present in each mineral, which is 53 and 20% for pyrite and arsenopyrite, respectively (eq. 1).

$$\text{NCV} = 0.44 \text{ x calcite} + 0.48 \text{ x dolomite} + 0.44 \text{ ankerite} + 0.38 \text{ x siderite} - 1.37 \text{ x } 0.53 \text{ pyrite} - 1.37 \text{ x } 0.20 \text{ arsenopyrite} \qquad \text{eq. 1}$$

Since the most abundant Fe-sulphide in PIC waste was expected to be chalcopyrite (Giebel et al., 2017; Russell et al., 1955), a modified NCV (NCV*) is proposed herein, which includes the percentage of sulphide present in the chalcopyrite (eq. 2).

$$NCV^* = 0.44 \text{ x calcite} + 0.48 \text{ x dolomite} + 0.44 \text{ ankerite} + 0.38 \text{ x siderite} - 1.37 \text{ x } 0.53 \text{ pyrite} - 1.37 \text{ x } 0.20 \text{ arsenopyrite} - 1.37 \text{ x } 0.35 \text{ chalcopyrite} \quad \text{eq. 2}$$

The results are expressed in CO_2%. Negative values are indicative of the acid generation potential, while positive values are indicative of the acid neutralization potential (ARD classification displayed in Table 2). It is worth noticing that this method does not take into account the reactivity of each mineral.

On the other hand, the **textural ARDI** uses five parameters (A-E) to evaluate the acid generation potential of a given rock. Parameter A refers to the contents of acid forming phases (Fe-sulphides); parameter B is related to the degree of alteration of those sulphide minerals; parameter C evaluates the morphology of sulphides according to the available surface area for sulphide oxidation; parameter D is the amount of neutralizing minerals that surrounds the sulphides; and parameter E evaluated the spatial relationship between acid forming and acid consuming phases. Each parameter is evaluated in both mesoscale (using eq. 3) and microscale (using eq. 5) for each WRD sample. However, the tailing samples only allow microscale evaluation. Therefore, ARDI for WRD samples has been calculated as the average of meso- and microscale (eq. 7), while ARDI for tailing samples correspond to the microscale evaluation (eq. 4). Negative ARDI results are indicative of acid consuming capacity, while positive values are indicative of acid generating capacity (ARD classification displayed in Table 2).

$$Me = [A_{0-10} + B_{0-10} + C_{0-10} + D_{-5-10} + E_{-5-10}] = X \quad \text{eq. 3}$$

$$X^1 = \sum X / \text{no. of Me phases} \quad \text{eq. 4}$$

$$Mi = [A_{0-10} + B_{0-10} + C_{0-10} + D_{-5-10} + E_{-5-10}] = Y \quad \text{eq. 5}$$

$$Y^1 = \sum Y / \text{no. of Mi phases} \quad \text{eq. 6}$$

$$ARDI = (X^1 + Y^1) / 2 \quad \text{eq. 7}$$

On the other hand, representative pulverized composite samples ($ø < 75$ µm) from tailings and WRD (13 samples in total) were analysed using the **Acid Base Accounting** (ABA) procedure, described by Usher et al. (2003). Each assay was performed in triplicate. The procedure includes:

- Paste pH-Conductivity 1:1 (w/w) assess the readily available acidity/alkalinity of a sample. This procedure provides no indication of the sample's total acidity/alkalinity, but determines the immediate pH and electrical conductivity (EC) of the drainages produced by the wastes during the initial stage of the waste-water interaction. Each paste was stirred for 5 seconds and then pH and EC were measured after 10 minutes, 12 h, 24h and 48h.

- Net Acid Generation (NAG) tests the reactivity of minerals, particularly Fe-sulphides, using hydrogen peroxide (H_2O_2) to determine the final NAG pH. Afterward, sodium hydroxide (NaOH) is used to titrate the solution up to pH 4.5, in order to determine the potential acidity of the samples as kg of sulphuric acid per tonne (kg H_2SO_4/t). Initial paste pH and final NAG pH are compared and discussed as an estimation of the evolution of the alkalinity or acidity of the drainage released from the wastes (Weber et al., 2006).

- Sobek procedure was used to determine both the neutralization potential (NP) and the acid potential (AP) of each sample (eq. 8 and 9, respectively). NP is related to the abundance of carbonates, bases and alkaline earth metals that are available to neutralize acidity, while AP is related to the abundance of sulphides, main precursor of acidity in mine residues (Usher et al., 2003). Due to the complexity of the samples, the acid potential (AP) has been calculated using the S% obtained from the fraction 3 of the sequential extraction as sulphide S% (Pérez-López et al., 2007). The results of both NP and AP are expressed as kg of $CaCO_3$ equivalent per ton (kg $CaCO_3$/t).

$$NP\ (kg\ CaCO_3/t) = \frac{(N\ x\ vol\ of\ HCl) - (N\ x\ vol\ NaOH)\ x\ 50}{Weight\ of\ sample} \qquad eq.\ 8$$

$$AP\ (kg\ CaCO_3/t) = S\%\ x\ 31.25 \qquad eq.\ 9$$

AP and NP values were used to calculate the net neutralization potential (NNP) and the neutralization potential ratio (NPR) of each sample (eq. 10 and 11, respectively). The results are expressed as kg of $CaCO_3$ equivalent per ton.

$$NNP\ (kg\ CaCO_3/t) = NP - AP \qquad eq.\ 10$$

$$NPR = NP / AP \qquad eq.\ 11$$

The results of each ARD assessment have been interpreted using the Acid Base Accounting Cumulative Screening Tool (ABACUS) developed by the Institute for Groundwater Studies of the University of the Free State, South Africa (Usher et al., 2003). ABACUS is a tool that provides consistency in the application and interpretation of the diverse ABA procedures used worldwide. Also, the program takes into consideration the presence or absence of gas phases. When carbon dioxide is present, the solubility of calcite increases. This occurs in "open systems" such as surface water bodies or pore water in contact with a gas phase. If the water is not in contact with a gas phase, which is the case of groundwater below the water table or the bottom of tailing ponds, it is considered as a "close system" with lower dissolution rate of calcite. Therefore, ABACUS offers two verdicts for each sample analysed based on the values of NNP close system and NNP open system.

3.4 Prediction of drainage's elemental composition

The toxicity of the leachates has been assessed using 0.5N acetic acid, as described in the Australian Standard method AS-4439 (Standards Australia, 1997) for solid wastes and contaminated soils. South African regulation stipulates the use of AS-4439 to assess the suitability of wastes for disposal in a landfill, including extractive waste. The results have been compared with the South African Leachable Concentration Thresholds (LCT) for landfill disposal of waste (Department of Environmental Affairs, 2013), which are similar to the Australian EPA 448.3 thresholds (EPA Victoria, 2007) (Table A.2 of supplementary material). In addition, the total concentration (TC) of the pollutants present in the solid wastes have been assessed and compared with South African total concentration thresholds (TCT) as described in GNR 635 (Department of Environmental Affairs, 2013). Each element has four LTC thresholds; LTC0 (inert), LTC1 (non-hazardous), LTC2 (hazardous) and LTC3 (extreme hazardous), and three TC thresholds; TCT0 (inert), TCT1 (hazardous) and TCT2 (extreme hazardous). Each waste can be classified according to the highest threshold overcame by any of the elements assessed from Type 0 waste (unsuitable for land fill disposal) up to Type 4 (inert) following the criteria of the National Environmental Management Waste Act (59/2008) of South Africa (DEA, 2013) (more details in supplementary material, Annex 2 and Table A.2).

In addition, the potentially toxic elements (PTEs) contained in PIC's wastes were assessed using sequential extractions following the BCR procedure described by Rauret et al. (1999). This methodology has been previously applied to assess metal mobility in mining wastes (e.g. Álvarez-

Valero et al., 2009; Pérez-López et al., 2008). However, a recent study (Caraballo et al., 2018) has recommend to be precautious at the time of interpreting the results, because the high metallic concentrations of the mine residues frequently induce oversaturation of the leaching solutions and the concomitant inefficiency of the extraction step. The sequential extraction includes three steps or fractions; each fraction represents a different mobile phase of the waste (Table 1, more details in supplementary material annex 3). Fraction 1 (F1) or bioavailable refers to metals associated with phosphate and sulphate evaporitic salts. Fraction 2 or reducible refers to metals bound to Fe and Mn oxides; and Fraction 3 or oxidizable refers to metals associated to sulphides and organic matter (Pérez-López et al., 2007). In addition, the residual fraction (F4) represents the phase of non-mobile metals, which has been digested with aqua regia. The sum of each fraction (F1, F2, F3 and F4) comprises the pseudo-total composition. To verify reproducibility of the experiment, a pseudo-total digestion of each sample has also been performed using aqua regia. The high dissolution rate of alkaline materials in the pseudo-total digestions favours its comparison with total concentration thresholds (TCT), as described in GNR 635 (Department of Environmental Affairs, 2013).

Table 1. Simplified BCR-sequential extraction procedure (Pérez-López et al., 2011)

Step	Fraction	Reagents	Procedures
F1	Easily soluble	0.11 M CH_3COOH	40 mLCH_3COOH + 1 g sample shaken for 16 h
F2	Reducible	0.5 M $NH_2OH{\cdot}HCl$ (pH 2)	40 mL $NH_2OH{\cdot}HCl$ + residue from step 1 shaken for 16h
F3	Oxidizable	8.8 M H_2O_2 1 M $NH_4C_2H_3O_2$ (pH2)	10 mL H_2O_2 + residue from step 2 at 85˚C to almost dryness 50 mL $NH_4C_2H_3O_2$ shaken for 16 h
F4	Residual	Aqua Regia 3:1 (12 M HCl:15.8 M HNO_3)	10 mL aqua regia + residue from step 3 (first 20 h and then 1 h at 100˚C)

The concentration of cations and S of the leachates, as well as the sequential extraction and the pseudo-total digestion were analysed by inductively coupled plasma optical emission spectroscopy (ICP-OES) Teledyne Prodigy; P and F were analysed by the discrete analyzer Easy Chem 200; and Cl was analysed using the spectrophotometer HACH DR3900. All the analyses were performed by an accredited laboratory at the Institute for Groundwater Studies at the University of Free Sate (South Africa) (Analytical details can be found in supplementary materials, Annex 4).

4 Results

4.1 Mineralogy

The mineralogical characterization is focused in those minerals with known acidification or neutralization potential, such as sulphides and carbonates, among others. Sulphide minerals in the waste rocks and tailings are scarce. Semi-quantified analysis by elemental mapping show contents below 1 wt% (supplementary material Table A.3). Sulphide phases are mainly concentrated in both carbonatite rock fragments (Fig. 2c-f) and East tailing (Fig. 2j-l). The main acid-forming-sulphide minerals found in PIC wastes were chalcopyrite ($CuFeS_2$) and, to a lesser extent, pyrite (FeS_2) (Fig. 2d-f and 2j-l). Both sulphides are strongly associated with calcite ($CaCO_3$), dolomite ($CaMg(CO_3)_2$), magnetite (Fe_3O_4), ilmenite ($FeTiO_3$) (Fig. 2a, b and g-i) and other minor sulphide minerals such us bornite (Cu_5FeS_4), covellite (CuS), chalcocite (Cu_2S), cubanite ($CuFe_2S_3$), millerite (NiS) and vallerite ($(Fe,Cu)_4(Mg,Al)_3S_4(OH,O)_6$) (Fig. 2c, d, e, f, j and l), as well as newformed Cu-sulphate (Fig. 2k).

Alkaline minerals in both, the waste rocks dumps and tailings, are highly abundant (supplementary material Table A. 3). Among them, calcite and dolomite are the most abundant (Fig. 2a, b and h), followed by diopside ($MgCaSi_2O_6$), phlogopite ($KMg_3AlSi_3O_{10}(F,OH)_2$), microcline ($KAlSi_3O_8$) and apatite ($Ca_5(PO_4)_3(Cl/F/OH)$ group minerals (Fig. 2a, b, g and h). Calcite contents in carbonatite fragments and East tailing range between 25 and 67 wt%, determined by XRD and elemental mapping, whereas dolomite is particularly abundant in the East tailing (average value of 13 wt%). Diopside concentration in pyroxenite fragments ranges from 10 to 30 wt%. Selati tailing exhibits the highest concentration of diopside with mean values of 31 wt%, particularly enriched on its southernmost area (38 wt%, on average). Phlogopite content in pyroxenite fragments ranges between 5 and 55 wt%, and is particularly abundant in Selati tailing (with mean value of 40 wt%). Microcline is particularly abundant in F- pyroxenite (55 wt%) and represents 2 wt% of the Selati tailing. In addition, apatite mean content in phoscorite fragments are 70.5 wt%, whereas in both tailings (East and Selati) are 9 and 15 wt%, respectively.

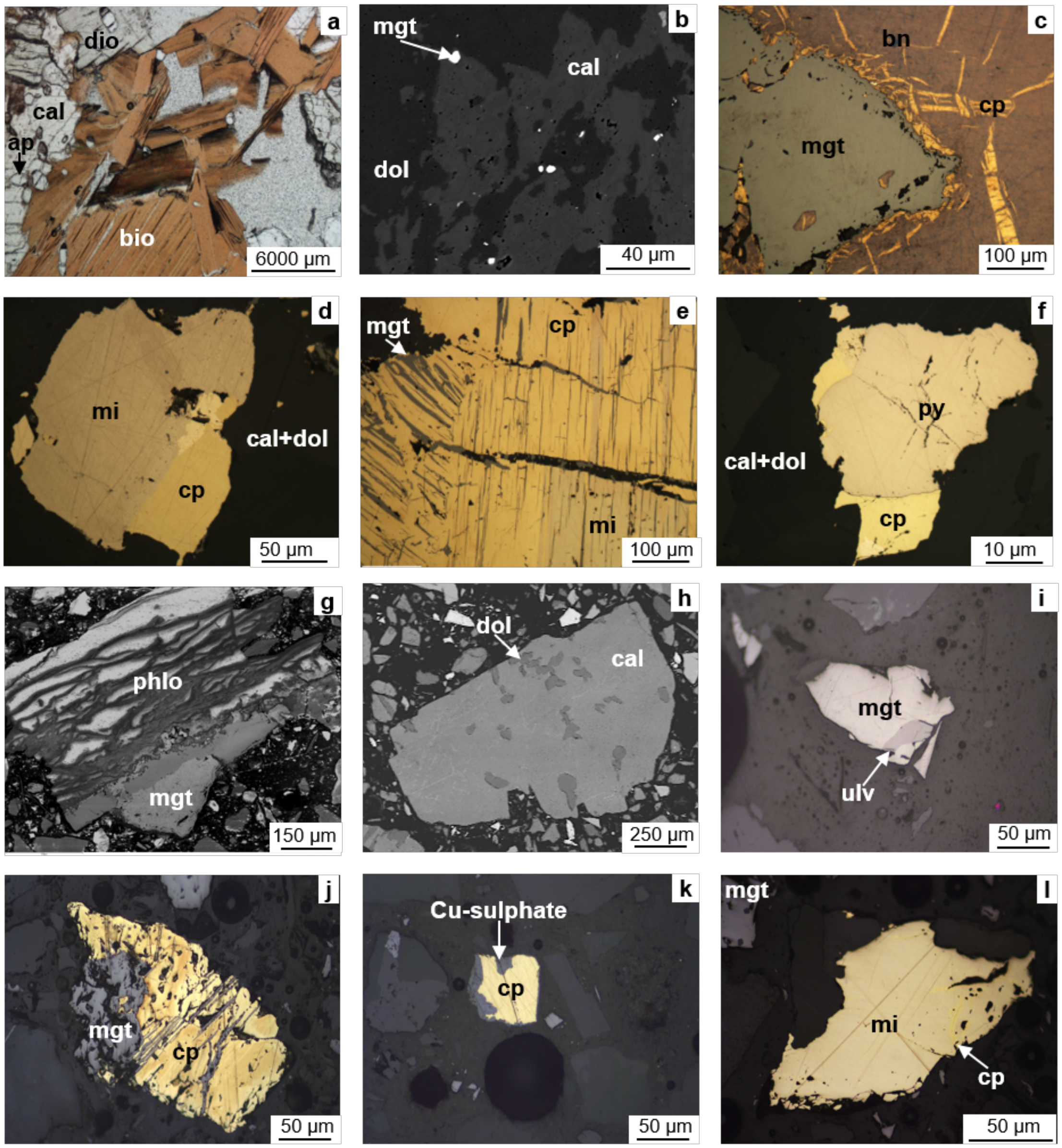

Fig. 2. Transmitted, reflected light and backscattered electron (BSE) images from the Palabora WRD (images a to f) and tailings (images g to l). a) biotite (bio) aggregate associated with calcite (cal), diopside (dio) and apatite (ap); b) calcite and dolomite (dol) including fine grained magnetite (mgt); c) chalcopyrite (cp) and bornite (bn) filling open space and replacing in magnetite; d) Interstitial millerite (mi) and chalcopyrite included in calcite and dolomite; e) Magnetite replaced by chalcopyrite and millerite; f) pyrite and chalcopyrite locked in cal and dolomite; g)mixed-fragment forms of phlogopite (phlo) and magnetite (mgt); h) Calcite (cal) grain showing fine grainded dolomite (dol) inclusions; i) magnetite grain including ulvospinel (ulv); j) Grain comprises of chalcopyrite (cp) and magnetite; k) mixed-fragment formed by chalcopyrite and a newly-formed Cu-sulphate; l) Millerite (mi) and chalcopyrite forming a mixed grain.

4.2 Acid rock drainage (ARD) prediction

4.2.1 Mineralogical approach

Both ARDI and NCV mineralogical approaches indicate that none of the PIC wastes have potential to generate acid drainage (ARDI < 10, NCV > 0) (Table 2). According to ARDI, all the waste rock samples ranged between 5 and 10, reflecting non-acid forming to acid consuming conditions (more details in supplementary material, Table A.4), while NCV of carbonatites, phoscorite and East tailing fall under the classification of high potential for acid neutralization (NCV > 5).

Table 2. ARD tests using traditional chemical procedures and novel mineralogical approaches. Units for NAG rate (pH 4.5) are given in kg H_2SO_4/t; AP, NP, NNP are in kg $CaCO_3$ eq/t; units for NCV are in %CO_2. Potential acid rock drainage (ARD) thresholds adapted from previous studies (Bucknam, 1997; +Parbhakar-Fox et al., 2011; ^Usher et al., 2003).*

	CHEMICAL^								**MINERALOGICAL**	
Samples	Initial pH (24h)	Final pH (NAG)	NAG rate	S%	AP	NP	NNP	NPR	ARDI+	NCV*
T-carbonatite	8.69	9.83	0	0.25	7.7	680	671.9	88	8.2	17.01
B-carbonatite	8.24	9.37	0	0.37	11.6	801	789.0	69	9.7	17.21
East tailing S	8.39	7.35	0	0.07	2.3	336	333.4	145	5.1	25.01
East tailing N	8.58	8.64	0	0.07	2.1	390	387.8	184	3.9	27.62
East tailing W	8.53	8.78	0	0.07	2.3	663	660.7	295	5.2	21.58
East tailing E	8.65	8.67	0	0.06	2.1	289	268.0	138	6.6	18.16
Selati tailing N	9.10	6.50	0	b.d.l	–	54.6	54.6	–	5.6	3.90
Selati tailing S	9.11	5.83	0	b.d.l	–	59.2	59.2	–	6.1	1.66
F-Pyroxenite	9.32	4.05	1.5	b.d.l	–	12.3	12.3	–	7.6	3.12
P-pyroxenite	9.27	7.35	0	0.47	12.5	72.0	43.9	5	7.7	2.94
Syenite	9.48	4.95	0	b.d.l	–	10.2	10.2	–	7.8	2.20
M-Pyroxenite	9.72	5.39	0	b.d.l	–	25.4	18.1	–	7.6	1.99
Phoscorite	8.82	5.38	0	b.d.l	–	113	112.8	–	6.3	7.04
ARD Classification										
Potential acid forming-High	< 3.5	< 3.5					< (-20)		41–50	< (-5)
Potential acid forming			> 0	> 0.3				< 1	31 – 40	(-5) – (-1)
Potential acid forming-Low	3.5 – 5	3.5 – 4.5					(-20) – 0	1 – 2	21 – 30	(-1) – (-0.1)
Not acid Forming/ acid consuming	> 5	> 4.5	0	< 0.3			0 – 20	2 – 4	-10 – 20	(-0.1) – 5
High acid Consuming							> 20	> 4		> 5

The NAG threshold for not acid forming was stablished at pH 4 by Miller et al. (1990) and at 5.5 by Usher et al. (2003). An intermediate value of 4.5 is used herein for ARD classification.

4.2.2 Paste pH/EC

The ultrapure water used for the paste pH/EC tests and as a control (dH_2O in Fig. 3) had an initial pH of 8.26 and no significant variations were observed throughout the experiment. In general terms, all the lithologies assessed showed a similar behaviour; they increased their pH within 10 minutes, but they decreased gradually over time without reaching the initial pH. The exception is B-carbonatite that showed a slight decreased of pH after 10 min, but it increased thereafter recovering initial values. In particular, the highest pH was achieved by syenite and pyroxenites (Fig. 3).

On the other hand, the EC of the ultrapure water increased in every test performed. Among lithologies, the highest EC was produced by B-carbonatite (5.02 mS/cm), while sections west and south of the East tailing showed the highest EC (6.96 and 4.74 mS/cm, respectively) among the assessed tailing samples.

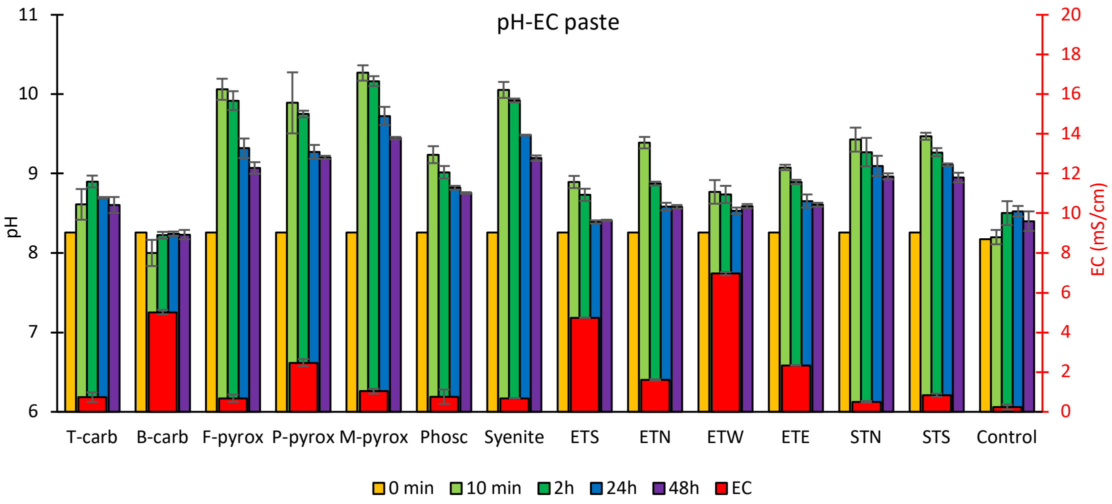

Fig. 3. Graphic of paste pH-EC. pH measured after 10 min, 2 h, 24 h and 48 h. Electrical conductivity measured after 48 h. Samples analysed; transgressive carbonatite (T-carb), banded-carbonatite (B-carb), feldspathic pyroxenite (F-pyrox), pegmatoidal pyroxenite (P-pyrox), micaceous pyroxenite (M-pyrox), phoscorite (Phosc), syenite, East tailing S (ETS), East tailing N (ETN), East tailing W (ETW), East tailing E (ETE), Selati tailing N (STN), Selati tailing S (STS) and ultrapure water as control. Errors bars correspond to standard deviations of triplicates.

4.2.3 Net acid generation

According to the net acid generation (NAG) procedure both tailings would be classified as material with non-acid-generation capacity (final pH > 4.5). Also, the WRDs are composed of non-acid-generating rock fragments, with the exception of F-pyroxenite that represents low risk to generate acid drainage, as shown by a final pH of 4.05 and NAG rate of 1.5 kg H_2SO_4/t (Table 2).

4.2.4 Net neutralization potential and neutralization potential ratio

The average of the neutralization potential (NP) of each lithology and tailing samples are shown in table **Error! Reference source not found.**2. B-carbonatite resulted in the highest NP range, followed by T-carbonatite and East tailing samples (801, 680 and 663 kg $CaCO_3$/t, respectively), while F-pyroxenite and syenite had the lowest NP range (10.2 and 12.3 kg $CaCO_3$/t, respectively).

Most lithologies contained less than 0.3 S%, resulting in an acidification potential (AP) ≤ 9.4 kg $CaCO_3$ eq/t. In contrast, some B-carbonatite and P-pyroxenite samples showed average values of 0.4 and 0.5 S% (11.6 and 12.5 kg $CaCO_3$ eq/t), respectively. The tailing samples also had low concentration of S, and therefore low AP, particularly the Selati tailing whose S content was below detection limit.

The high NP of all the samples analysed, together with their relatively low AP, confer positive values of NNP, hence falling under the classification of acid consuming material. Most NNP values are far above 20 kg $CaCO_3$ eq/t, hence they have high acid consuming capacity, except for syenite, F- and M-pyroxenites (10.2, 12.3, 18.1 kg $CaCO_3$ eq/t, respectively). In addition, all NPR values are also above high acid consuming threshold (4 kg $CaCO_3$ eq/t), with P-pyroxenite showing the lowest NPR value (4.9 kg $CaCO_3$ eq/t).

4.3 Prediction of elemental composition

4.3.1 Leaching tests as per waste disposal regulation

Every leaching test performed on tailing samples and waste rocks showed values below TCLP limits (US standard for Toxicity Characteristic Leaching Procedure, Table A.2 of supplementary material). They were also below LTC0 (South African threshold for inert waste, Table A.2 of supplementary material) for B, Cl, Co, Cr, Mo, Sb, V and Zn (Fig. 3, top graphs). However, some of the samples from the WRDs reached or exceed LTC0 for As, Ba, Cd, Cu, F, Hg, Mn, Ni, S, and TDS (Fig. 3). East tailing samples were above LTC0 for As, Ba, Cu, Mn, Ni, Se and TDS, while Selati tailing exceeded LTC0 for Ba, F, Ni, and Pb. It is worth noting that none of PIC wastes overcame LTC1 (threshold for non-hazardous material).

In addition, all the wastes surpassed TCT0 for at least 1 analyte. For example, Cu was above TCT0 at every waste characterized, except for M-pyroxenite (Fig. 4, bottom left graph). Other elements above TCT0 were, in order of occurrence, Ba, As, Se, F, Ni and Pb (Fig. 4, bottom graphs). However, TCT1 thresholds were never exceeded.

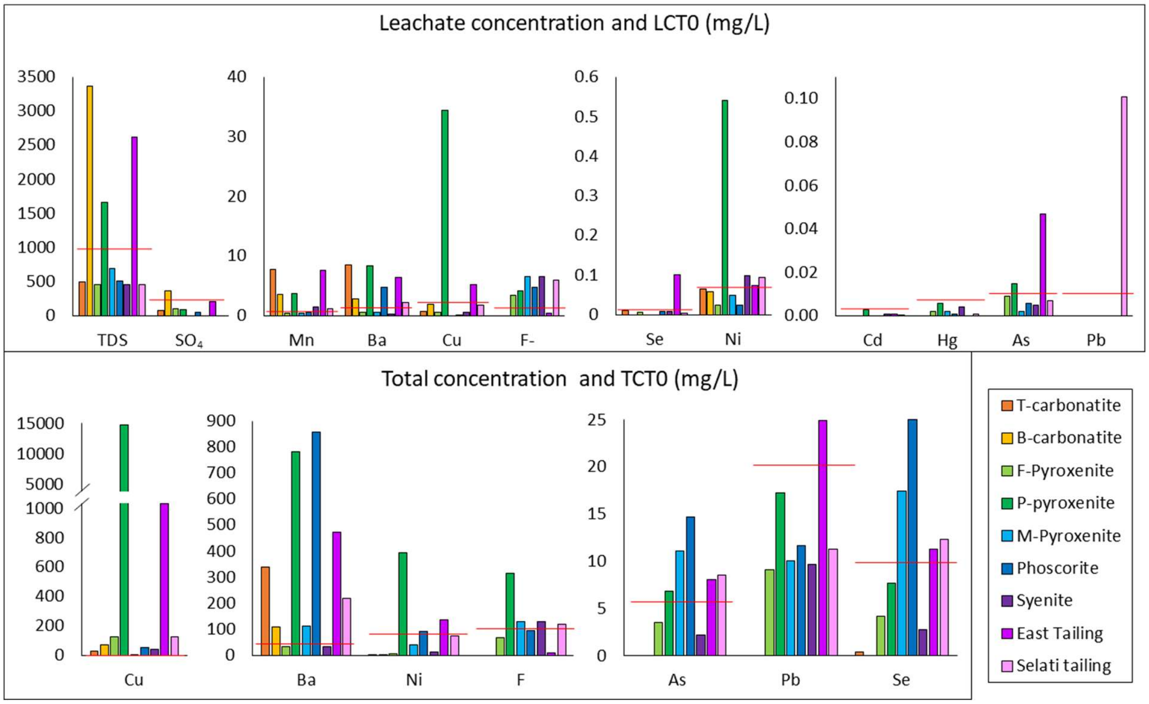

Fig. 4. Leachable elemental composition after submitting the mine residues to the Australian Standard method AS-4439 following the South African procedures for leaching tests (top), Leachable Concentration Thresholds for inert material (LTC0) are marked in red, and total concentration of elements in solid wastes (bottom) obtained from the sum of fractions 1, 2, 3 and 4 of the sequential extraction, Total Concentration Thresholds for inert material (TCT0) are marked in red. Only elements that are closed or above LTC0 or TCT are shown.

4.3.2 Sequential extraction

In general, mean concentrations of S and Cu were predominant among the leachates of PIC wastes (waste rocks and tailings), particularly in fraction 3 (Fig. 5) where the oxidative dissolution of Cu-sulphides (Fig. 2) take place. However, none of the samples overcame the threshold LTC0 in any of the fractions for S, as well as for B, Cd, Co, Cr, F, Mo, Sb, V and Zn, while Mn was above LTC0 but below LTC1 for every fraction.

In the bioavailable fraction (F1), S, Mn and Ba were predominant in most waste rocks and East tailing, while no S was bioavailable for syenite, M-pyroxenite and Selati tailing. In this fraction, only Ba, Cu and Mn overcame LCT0. The reducible fraction (F2) also showed high concentrations of S for T- and B-carbonatite, F-pyroxenite and phoscorite samples, as well as for both tailings. However, Cl was predominant in F2 for syenite, P- and M-pyroxenite. In F2, As was above LTC0 in all the samples analysed; Ba and Mn were above LTC0 for some tailing samples, as well as for phoscorite, T- and B-carbonatites. Pb and Se were above LTC0 for all three pyroxenites, syenite and Selati tailing. The oxidizable fraction (F3) was characterized by high concentrations of S, Cu and Mn and, to a lesser extent, Ba, Ni, Pb, Se and As. Cu was above LTC0 for T- and B-carbonatite, F-pyroxenite, and East tailing, while one of the pyroxenites analysed (P-pyroxenite) reached up to 210 mg/L, which is above LTC2. Only carbonatites released Mn concentrations above LTC0 in F3. Although most Ba were released during F1 and F2, in F3 the concentration of Ba also overcame LTC0 in phoscorite, carbonatites and P-pyroxenite, together with Ni. In addition, As was also above LTC0 in all the pyroxenites, phoscorite and Selati tailing samples. Se was above LTC0 for all the samples except syenite. Concentrations of Pb were above LTC0 for all the rocks analysed, except for T-carbonatite.

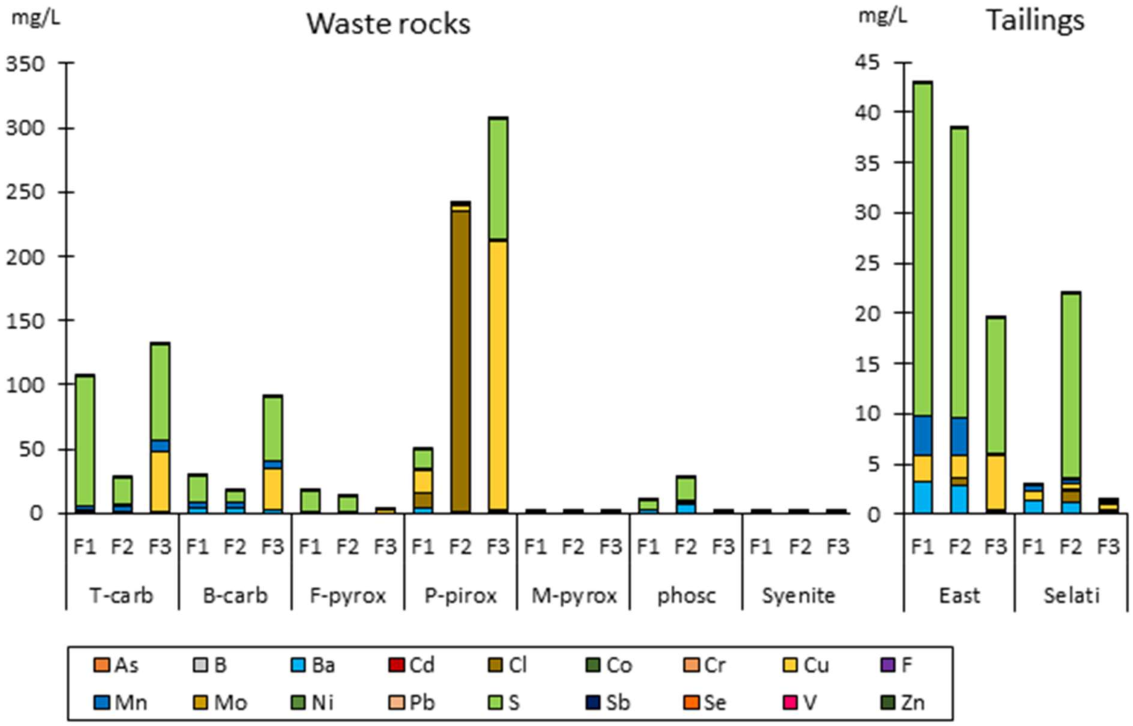

Fig. 5. Leachates elemental composition of the bioavailable (F1), reducible (F2) and oxidizable (F3) fractions of the sequential extraction of PIC's waste rocks (left) and tailings (right). The results showed herein correspond to the average of the elements regulated by the South African Department of Environmental Affairs (2013).

The occurrence of no regulated elements such as Ca, Mg, Na and K were high in the labile fraction of most waste rocks and tailing samples (Table 3). The highest concentration of Ca and Mg were released from carbonatite samples, while their concentrations of Na and K were particularly low. The concentration of trivalent metals such as Fe and Al were also relatively high, particularly in the labile fraction of P-pyroxenite and syenite. In addition, the total concentration of radionuclides such as U and Th reach up to 46.7 and 159.7 mg/kg, respectively (supplementary material, Table A.6), although the labile fractions of all PIC samples were always below 0.031 and 0.013 mg/L, respectively (Table 3).

Table 3. Mean concentration of non-regulated elements in the labile fraction of the sequential extraction (F1+F2+F3) performed to PIC wastes.

Analyte (mg/L)	B-carb	T-carb	F-pyrox	P-pyrox	M-pyrox	phosc	syenite	East tailing	South tailing
Ca	5273	5111	90.1	182	136	274	18.9	434	194
Mg	461	970	33.1	214	154	1127	33.6	380	283
Na	44.5	44.3	89.9	108	85.8	114	87.8	105	87.1
K	8.06	4.14	15.8	214	69.3	37.6	18.1	3.73	61.6
Fe	48.4	36.3	13.1	52.9	20.0	22.1	54.5	20.0	33.1
Al	2.91	4.65	12.2	21.8	19.9	28.6	24.7	1.28	19.9
Th	0.000	0.000	0.004	0.002	0.003	0.002	0.001	0.005	0.013
U	0.000	0.000	0.008	0.013	0.013	0.011	0.002	0.004	0.031

5 Discussion

Alkaline mine wastes are not well understood and the scarce investigation on these wastes is traduced in lack of specific regulation and assessment for its disposal and its potential reuse worldwide. That is the case of the South African Phalaborwa Igneous Complex (PIC) where more than 4500 Mt of alkaline mining wastes have been disposed in tailing dams and waste rock dumps (FOSKOR, 2018; Moukodi, 2008). This study uses current protocols designed typically for sulphidic mine wastes and alternative methods that might enhance the characterization of alkaline mine wastes, the prediction of alkaline mine drainage composition and, at the same time, shed some light about its potential reuse as alkaline reagent.

5.1 Assessment of alkaline mine wastes.

The acid-base account (ABA) is one of the most commonly used methods in the assessment of sulphidic mine wastes to characterize acid-forming materials (INAP, 2009). However, this method also evaluates acid-neutralizing processes (dissolution of carbonates, displacement of exchangeable bases, and weathering of alkaline silicates). Therefore, somehow it can be useful when evaluating alkaline wastes. Nevertheless, the ABA method present significant limitations such as; a) the neutralization potential of a waste is measured according to rapidly dissolving sources of neutralisation, such as carbonates, and do not take into account the long term neutralisation capacity of other sources of neutralization, such as silicates (Gerson et al., 2019); and b) the acid potential (AP) calculation assumes that all sulphur measured by the total S method can be oxidized to produce 1 mol of sulphuric acid per mole of sulphur (Bouzahzah et al., 2015; Lawrence and Wang, 1996; Sobek et al., 1978; Usher et al., 2003), which occurs during the oxidation of pyrite. However, this assumption is invalid for many mine wastes whose main sulphide minerals are not pyrite and/or the sulphur is present in other phases such as sulphates.

The sequential extraction has been used herein to partially resolve the overestimation of AP (Fig. 4); the sulphates present in the samples were extracted in the first step of the sequential extraction (F1), the sulphur contained in oxide minerals were extracted in the second step (F2) and finally, in the third step (F3) hydrogen peroxide/ammonium acetate (H_2O_2/NH_4OAc) mixture was able to oxidize sulphides (Du Laing, 2010), even though it is still not able to distinguish among sulphide species that are acid-forming or not. For example, for T-carbonatite and East tailing above 60% of total S belonged to sulphate and oxide species (Fig. 5). Previous study (Caraballo et al., 2018) stated that the fractions could be oversaturated when used in sulphidic mine waste, which means that part of the sulphates, S-oxides and sulphide species could remain undigested after F1, F2 and F3, respectively, and get digested thereafter. Therefore, the concentration of S digested in F4, which ranged 10 to 30% of the total S for PIC wastes, add uncertainty to the sulphide S results obtained from F3. It should however be noted that the concentration of sulphide in PIC wastes is low, compared to the sulphidic mine wastes and, therefore unlikely to oversaturate the F3 of the sequential extraction. Other authors have stressed the importance of mineralogical characterization in the prediction of ARD (Dold, 2017; Parbhakar-Fox and Lottermoser, 2015). In this study, the mineralogical characterization showed the presence of 7 different sulphide minerals, as well as sulphate compounds, (Fig. 2) from which only two of them, i.e. chalcopyrite and anecdotic pyrite are identified as acidity producers (e.g. Dold, 2017; Stumm and Morgan, 1981). In general, the PIC wastes contain below 0.3% pyrite and 0.6% chalcopyrite (Table A3 of supplementary material), which supports the findings of the sequential extraction. Thus, the PIC wastes do not have enough Fe-sulphide minerals to sustain acid drainage generation.

In order to further improve ABA method, a mineralogical approach has been introduced in this study using NCV and textural ARDI (Bucknam, 1997; Parbhakar-Fox et al., 2011). This approach, together with semiquantitive mineralogical analysis give a more realistic information about the constituents of the samples and foster a better understanding of the minerals that are able to produce acidity or generate alkalinity. In that sense, abundant alkalinity-producing minerals were found throughout PIC wastes, including fast-dissolving minerals such as calcite and dolomite, as well as long term alkalinity-producing minerals such as diopside, phlogopite and microcline (Sverdrup, 1990). According to Kwong, (1993), there is an effective neutralizing capacity if the abundance of diopside and biotite exceeds 5 and 10%, respectively. Such is the case of all the pyroxenites and Selati tailing samples analysed (Table A3 of supplementary material). In addition, the high concentration of Si in fractions 2 and 3 (Table A6 of supplementary material) suggest that relatively-easy soluble silicates are present in PIC wastes. Therefore, the long-term neutralization potential may be higher than the results determined by ABA (Table 2). The combination of BCR and mineralogical characterization undeniably enhanced the characterization of alkaline wastes and the prediction of NAMD.

Although both tailings and WRDs from PIC have neutralization potential, the magnitude of the neutralization potential obtained differed depending on the procedure used. For example, according to NCV and NPR, East tailing has the highest neutralization potential (23.1 %CO_2 and 190.5, respectively), followed by both carbonatites and phoscorite (Table 1). This differs from NNP results, which indicate that both carbonatites have the highest neutralization potential, followed by East tailing and phoscorite (Table 1). The discrepancies between the methods are mostly because both carbonatites have the highest concentration of sulphide and carbonate minerals. Therefore, those methods in which AP values weight more than NP will underestimate the neutralization potential of the carbonatite, and vice versa.

Similar discrepancies were observed in the analysis of syenite and pyroxenite samples. The highest paste pH values were achieved by those lithologies (Table 1). However, according to NNP and NCV, they are not classified as high acid consuming materials. Furthermore, F-pyroxenite would fall under low-potential of acid forming, according to NAG (Table 1). Such discrepancies might be related to the low concentration of carbonate and sulphide minerals, except for P-pyroxenite (Fig. 2 and table 2). This resulted in an initial alkaline pH due to minor fast-dissolving alkaline minerals (paste-pH above 9, table 2, Fig. 3), followed by a pH dropping after carbonates are consumed and the sulphides start been oxidized (NAG pH 4-7, table 2). Once the scarce sulphides are consumed, no acid mine drainage would be produced, and low alkalinity is expected to be generated afterwards (NP and NCV classification, table2), which is consistent with the alkaline mineral content (Fig. 2 and table A.3 of supplementary material). The most abundant alkaline minerals of these lithologies are diopside and phlogopite whose NP are below 10 kg $CaCO_3$ eq/t and their reactivity at pH 5 range between 10 and15 Keq/ha/year, which is 40-60% of the carbonate 25 Keq/Ha/year (Blowes et al., 2003; Brough et al., 2013; Global Acid Rock Drainage, 2014; Sverdrup, 1990).

ABACUS verdict, according to the NNP values, is that most of the samples probably have an excess of neutralizing minerals (Tables A.7 and A.8 of supplementary material), which suggests the potential of PIC wastes to generate NAMD. Although the comparison between NPR and S% leaves P-pyroxenite and B-carbonatite in the uncertainty area (Fig 6b), only P-pyroxenites could produce acidity under certain conditions, according to the S% and NPR values for both, open and closed systems (Fig. 6a). Taking into account that the S% is an overestimation because it does not discern among sulphur species, and the neutralization potential is underestimated because it only assesses rapidly dissolving sources of neutralization, the ABACUS veridic can be considered as a conservative evaluation of the potential generation/neutralization of acid rock drainage. The limitations of ABA procedures and ABACUS tool affect both acid and alkaline mine waste characterizations.

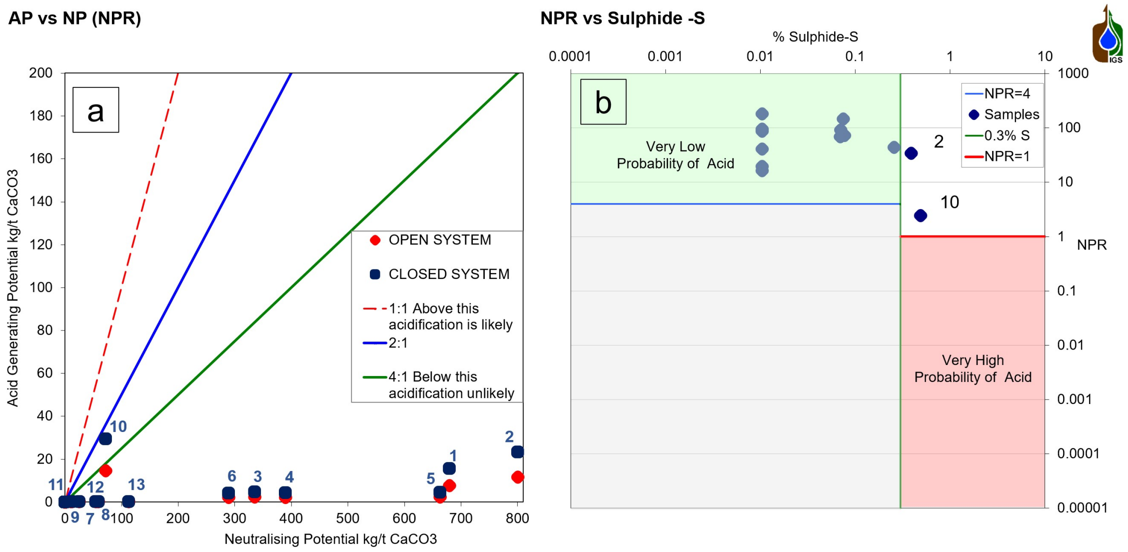

Fig. 6. Abacus charts showing the average of each lithology (1: T-carbonatite, 2: B-carbonatite, 9: F-pyroxenite, 10: P-pyroxenite, 11: Syenite, 12: M-pyroxenite and 13: Phoscorite) and each tailing sector (3: East tailing S, 4: East tailing N, 5: East tailing W, 6: East tailing E, 7: Selati tailing N and 8: Selati tailing S); a) Acid Potential (AP) versus Neutralization Potential (NP) and b) Neutralization Potential Ratio (NPR) versus sulphide content expressed as S% under closed conditions. Note that in order to represent the samples with S% below detection limit (0.01 S%), the value of 0.01 S% has been used.

EC values does not play a role in the ABACUS verdict. However, it indicates the elemental load in the leachate, which is crucial when predicting the AMD or NMD formation. Current tests highlight the problems related to heavy metals present in AMD ignoring the high concentrations of alkali and alkaline metals in solution. It is worthy of mention that the leachable concentration test of the South African regulation is stricter in this regard and it includes TDS and SO_4^{2-} Cl, B, Ba, Co, Mn, Sb and V thresholds for the classification of the waste (Department of Environmental Affairs, 2013). In this study, high concentrations of no regulated elements such as Ca, Mg, Na and K are released from the labile fraction. This corresponds with the high EC values of the leachates, and altogether indicates the potential of these type of wastes to generate saline NAMD.

On the other hand, the leaching tests show that all the rocks and tailing samples have at least one element above LTC0 and/or TCT0 (Thresholds for inert material), but none of them overcame LCT1 nor TCT1 (thresholds for non-hazardous waste). Therefore, the drainages produced by PIC wastes would classify as non-hazardous. However, the sequential extractions indicate that under oxidizing conditions (F3) P-pyroxenite have the capacity to release concentration of Cu above the limit LTC2, assigned for harmful material. This exposes the limitations of the leachate test to predict the release of toxic elements in the long term, as the F3 of the sequential extraction simulates the complete oxidation of sulphide minerals, in this case mostly chalcopyrite.

Even though pseudo-total digestion is compared with total digestion thresholds, all the elements regulated were far below TCT1 for all the samples analysed, being the closest Se, Cu and Ba whose concentrations were, on average, 5, 8 and 18 times smaller than TCT1 threshold (Table A6 in supplementary material). Therefore, all the mining residues classify as non-harmful material (type 3 waste) according to the National Environmental Management Waste Act (59/2008) of South Africa, in spite of their capacity to generate saline NAMD.

5.2 Alkaline mine wastes reuse.

These non-harmful wastes, and in particular the tailings, can substitute the limestone sand typically used in passive water treatments such as DAS (dispersed alkaline substrate; Caraballo et al., 2011). Even though carbonatite rocks have more calcite, their relatively high content in Fe-sulphide minerals (mainly chalcopyrite) might be a concern. However, the mineral processing of the carbonatites to concentrate Cu sulphide minerals, including chalcopyrite, has produced a tailing (East tailing) rich in carbonates and poor in sulphides. Indeed, all the methods described herein concur on classifying East tailing as high acid consuming material (table 2 and Fig 6). Therefore, it is reasonable to assume that wastes from East tailing have the capacity to neutralize acid industrial wastewater and is a better option than Selati tailing and WRD. However, the released of Ca>Mg>Na>SO_4>K>Fe could be detrimental to the treatment´s efficiency because they can interfere with the precipitation of the mineral phases responsible for the metal removal within the treatment (i.e., schwertmannite, hydrobasaluminite and gypsum). These elements (with the exception of SO_4 and Fe) are not typically included in any regulation for landfill or extractive waste disposal around the world, but they are present in water regulations, as they would increase hardness and ionic strength of the water, which could have a detrimental impact on the surrounding environment.

Furthermore, the radionuclides, such as U and Th, do not belong to the routine of elements to screen for in waste characterization protocols. However, carbonatitic deposits are known to often concentrate them (13% of carbonatite deposits have thorite and 12% have thorianite and/or U-thorianite (Berger et al., 2009). On average, the pseudo-total concentrations of U and Th in PIC wastes were 6.7 and 36.3 mg/kg, respectively (supplementary material, Table A.6). Nevertheless, the labile fractions of those radionuclides were, on average, 0.003 and 0.006 mg/L for Th and U, respectively

(Table 3), which is far below the limit stablished by the World Health Organization (WHO) for drinking water (0.03 mg of U/L; WHO, 2017). The low leachability of the U and Th might be because the main source of these radionuclides in PIC are silicates, such as thorite, and therefore they belong to the non-labile fraction of the residues. Both thorite and thorianite have been identified in PIC as micrometric inclusion in apatite and strongly associated with magnetite (Dawson et al., 1996; Giebel et al., 2017; Milani et al., 2017). Therefore, if the material from East tailing is used as alkaline reagent, the concentration of U in the treated water would presumably comply with drinking water standards (WHO, 2017).

In addition, the characteristics of East tailing are better in comparison with other alkaline wastes used to neutralize acid industrial wastewater such as fly ash and red mud (Table 4). The neutralization potential of East tailing (662.9 kg $CaCO_3$/t) are 2 to 30 times higher than fly ash (20 – 275 kg $CaCO_3$/t) (Qureshi et al., 2016) and 7 times higher than red mud (~91.6 $CaCO_3$/t) (Paradis et al., 2006). On the other hand, the highest concentrations of potentially toxic elements in East tailing are only represented by Fe, Al and Mn, while in red mud and fly ash, in addition to those metals, high concentrations of Cr, Zn, Pb, and As, are present (Table 4).

Table 4. Neutralization potential (NP, expressed in kg $CaCO_3$), paste pH and the pseudo-total concentration of toxic elements (mg/kg) of several red mud and fly ash studies are compared with PIC waste from East tailing.

Waste	NP	pH	Fe	Al	Mn	Cr	Zn	Pb	As	Location	References
Red mud	~91.6 (Doye and Duchesn, 2003)	10.00-12.56 (Taneez and Hurel, 2019)	261,000	65,700	406,000	1350,000	80,000	50,000	1,000	**Alcoa (Spain)**	(Rubinos and Barral, 2013)
Red mud			560,000	200,000	1180,000	1120,000	n.r.	230,000	213,000	**Ajka (Hungary)**	(Milačič et al., 2012)
Red mud			550,000	106,000	3,850,000	580000	300000	230,000	75,000	**BB Alumina (Bosnia and Herzegivina)**	(Smiciklas et al., 2015)
Fly ash	20 – 275 (Qureshi et al., 2016)	9.5-13.48 (Qureshi et al., 2016)	312,000	179,000	700	168	218	18.9	7.49	**Power plant-West Bengal (India)**	(Qureshi et al., 2016)
Fly ash			132,153	33,394	232.34	20.5	46.7	110	44.2	**Atikokan Thermal Power (Canada)**	(Yeheyis et al., 2009)
Fly ash			22,503	147,918	309	n.r	42.09	56.56	49.1	**Eskom power station (South Africa)**	(Maingany e et al., 2013)
Tailing	662.9	8.53	116,204	6,578	913	31.5	6.2	24.9	8.1	**East tailing**	This study

n.r.=not reported

The determination of the mobility of metals plays an important role in the mine waste characterization. In that sense, the sequential extractions brough benefits to both the characterization of the alkaline mine waste and the assessment of its revalorization potential; i) the determination of the bioavailable fraction (F1) is similar to conventional leachate test, and ii) determines the pollutants that might be released under reducing (F2) and oxidative (F3) conditions. Such information is also relevant for the preliminary evaluation of any alkaline material subject to be used as a reagent for water treatments in either anaerobic or aerobic reactors (F2 and F3, respectively). In addition, kinetic experiments such as column percolation tests, suggested for extractive waste management measures by EU regulations (Commission Decision 2009/360/CE), could be used to simulate short-term geochemical behaviour of the alkaline waste, which combined with geochemical modelling could enhance long term prediction.

6 Conclusions

The combination of traditional technique such as ABA with mineralogical analyses, as well as the combination of leachate test with BCR-sequential extractions enhanced the characterization and led to have a better understanding of the alkaline waste, from its neutralization capacity to its toxicity, shedding some light on its recycling potential.

Despite the discrepancies between methods, it was concluded that the residues produced by the mining activity in PIC have no potential to sustain acid drainage generation due to the scarcity of Fe-sulphide and the abundance of alkaline minerals. Indeed, the identification of soluble carbonates and relatively fast-dissolving silicates (diopside, phlogopite and microcline) in the samples suggests long term generation of NAMD.

Although the sequential extractions demonstrated that under oxidizing conditions some waste rocks (P- pyroxenites) have the capacity to release concentrations of Cu above the limit assigned for harmful material, all the samples would classify as non-harmful material according to national and international regulations for solid waste and contaminated soil, which demonstrates its limitations for alkaline mine waste characterization. In addition, current regulations do not include alkali/alkaline elements (Ca, Ba, Na, Cl, among others) and radionuclides, which are present in both waste rocks and tailings. Indeed, these elements are present in water regulations, as they would increase hardness and ionic strength of the water, which could have a negative impact on the aquatic environment. Therefore, this study highlights the need to include them in current regulations in order to consider the potential risk of alkaline mine waste to the environment.

The environmental characterization of PIC wastes also offered the first insight toward their recycling potential as alkaline reagent to neutralize AIW. Among PIC wastes**,** East tailing is the most feasible alternative to neutralize acid industrial wastewater because of its high neutralization potential and its low concentrations of potentially toxic elements. Despite the high concentrations of some alkali/alkaline elements, which could be detrimental to the final quality of the treated water.

In conclusion, this study stresses the need to enhance mine waste characterization procedures and set the ground for the inclusion of options of revalorization as part of the protocols for mine waste characterization, which would decrease the environmental impact of mine waste, and is aligned with the global circular economy strategy.

7 Acknowledgment

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