Phalaborwa Complex: From Rock Drainage Characterization to Waste Revalorization

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Abstract

Mining waste characterization is a standard practice in the mining industry. A good characterization of such waste might prevent them from impacting the surroundings, mainly due to water infiltration and runoff. Since most mines generate acid drainages, current protocols are designed to detect potential acid rock drainages (ARD), overlooking the potential hazards of the mines that produce alkaline drainage, particularly frequent in South Africa. A detailed mineralogical characterization will not only improve the characterization and classification of mining waste but will also assist in the revalorization of those wastes. The recycling of tailings and waste rock dumps could lead to a circular economy model for the mining industry, which would have an economic benefit for the mines, reduction on the waste of resources and ultimately elimination of the potential source of water pollution. To achieve this, a detailed study of the waste produced at Phalaborwa Complex (PC), South Africa, was carried out by combining conventional, novel and modified ARD prediction methodologies, leachate tests, sequential extractions (SE), pseudo-total digestions and an in-depth mineralogical characterization using X-ray diffraction, petrographic and scanning electron microscope with energy dispersive spectroscopy and electron probe micro-analyzer. The results showed that there is a very low probability of ARD formation, due to the high content of calcite (25-67 wt%) and dolomite (up to 13 wt%) together with the low content or complete absence of Fe-sulfide minerals, mostly chalcopyrite and pyrite (0 to 0.5 and 0.3 wt%, respectively). These alkaline wastes would release mostly sulfate and non-toxic elements such as Ca, Mg, Na and K, not regulated but still a concern if released in high concentration. In addition, radionuclides such as U and Th, typically present in carbonatitic deposits such as PC, were found mostly in the insoluble fraction (7 and 36 mg/kg, respectively), while the leachable concentrations, as a sum of F1, F2 and F3 of the SE, were always below 0.01 and 0.005 mg/L, respectively.

Keywords: Mine Waste Characterization, Alkaline Rock Drainage, Tailing Revalorization, Rare Earth Elements, Circular Economy

Introduction

In the Ba-Phalaborwa Municipality of the Limpopo province, South Africa, there is an industrial complex where several mines and factories work synergically to extract value out of the geological formation named Phalaborwa (or Palabora) Igneous Complex (PIC). The industrial activity in this area started in the 1950s with the extraction of phosphate rocks and Cu, and it has been increasing ever since. After seven decades of production, more than 4500 Mt of waste has been accumulating in the PIC area in the form of tailings and waste rock dumps. The environmental impact of the industrial activity in PIC has been widely reported

by the scientific community as well as by pertinent governmental bodies, and the officials of the nearby Kruger National Park.

There is only one main reason for any industry to pollute the environment: it is profitable. With that thought in mind, there are two options to help the industries avoid pollution: i) Fine the companies that pollute, so that polluting is not profitable anymore. This option has been widely adopted by governments. ii) Change the industrial chain from linear to circular. The recycling of industrial waste can increase the benefits of the companies, while decreasing their environmental impact. This second option is evaluated and described in this paper for the industrial complex of Phalaborwa.

The recycling of industrial wastes is a common practice in certain sectors. That is the case of steel slag, which is an alkaline by-product of the steel industries that use the basic oxygen furnace technology (Oster, 1982). Such by-product has been used extensively in construction as road aggregates, Portland cement, roofing granules, etc. Recent studies showcase the use of this steel by-product in leach beds to neutralize acid mine drainage (AMD) (Kruse *et al.*, 2019; Simmons *et al.*, 2002). Other alkaline industrial wastes used for AMD neutralization include paper mill sludge, sewage sludge (Moodley *et al.*, 2018) and more recently overburden phosphatic carbonated wastes (Ouakibi *et al.*, 2014).

Carbonatite and phoscorite rocks compose the core of PIC. Both are present in the mining wastes making them potential alkaline materials for AMD neutralization. However, before using any industrial waste to neutralize acid water, it is necessary to perform a detailed analysis of the waste and the water-waste interaction, to ensure that no pollutants are released during the water treatment process. An example is the case of red mud, an alkaline by-product of the alumina industry, that can only be used below 10% because it increases the concentration of metals and salts when used at higher percentages (Paradis *et al.*, 2006).

On the other hand, the scarcity of economic REE deposits promoted the investigation of new REE sources worldwide. Industrial wastes such as phosphogypsum stacks (fertilizer industry), red mud (aluminium industry), coal ash (thermal power plants), wastewater streams and mining wastes (slags, tailings and rock dumps) have been described as attractive secondary REE-resources (Humsa and Srivastava, 2015; Jowitt *et al.*, 2018; Zhang *et al.*, 2014)a novel hydrometallurgy process was employed for separating and recovering RE and Nb from Bayan Obo tailings. Firstly, by sulfating roasting at 250 °C and subsequent leaching at 60°C, the RE and Nb present in the polymetallic minerals can be efficiently extracted into the leach solution. Secondly, after the reduction of Ti 4+ and Fe 3+ ions (to Ti 3+ and Fe 2+ ions. Coincidently, most carbonatites and phosphate rock deposits are REE bearing deposits. Indeed, previous petrogenetic studies examined the rare earth minerals of PIC as indicators. PIC has not been mined for REE up to now, but according to the USGS (United States Geological Survey) PIC has reserves of 652 Mt of at 0.15% REE cut-off (Orris and Grauch, 2002), which might be present in PIC's tailings.

Currently, there is no REE mining in South Africa. PIC could host the first South African REE mine if the potential of its wastes as a secondary resource of REE is proven. However, *"data and tools are needed to establish the recycling and reuse potential of these [mining waste] materials; geochemists and mineralogists have a significant role to play in this endeavour"* (Bellenfant *et al.*, 2013). Here, this study attempts to investigate in detail the waste produced at PIC by using combining conventional, novel and modified geochemical techniques in order to determine the economic potential of these wastes and their environmental impact.

Methods

Sampling

Tailing samples were collected from 16 different sectors, including six sections of recently piled tailings and 10 sections of different ages. A composite of approximately 5 kg and up to 2 m depth, were taken from each section. Each sample was homogeneously mixed and split for further chemical and mineralogical analysis.

Mineral characterization

The mineralogy and textures of tailings were investigated on polished sections by both petrographic microscope and SEM-EDS JEOL JMS-5410 equipped with a Link Oxford microanalyzer. Compositional mapping of SEM was undertaken by silicon drift detector (SDD), followed by semiquantitative mineralogical analyses by ImageJ software (https://imagej.nih.gov/ij). In addition, semiquantitative mineralogical analyses were investigated by X-ray diffraction (XRD) using a Broker D8 Advance Powder Diffractometer with Cu–Kα radiation.

Geochemical characterization

Tailing samples underwent the modified 3-steps BCR sequential extraction (Rauret *et al.*, 1999)Measurements and Testing Programme (formerly BCR. This essay was used with a double purpose: i) determine the Potential Toxic Elements (PTE) of the leachates under different environmental conditions (F1: water soluble, F2: reducible conditions, F3: oxidizing conditions), and ii) to quantify and determine the distribution of REE in the tailings offering the first insights for mining prospection. Additionally, pseudo-total digestions were performed with aqua regia (F4) in triplicate to all the samples.

The concentration of cations and S of the sequential extraction 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 State (South Africa).

Drainage prediction

The results of the mineral and textural analysis were used to determine the Modified Net Carbon Value (NCV*) as proposed in Gómez-Arias *et al.* (2021) and the textural acid rock drainage index (ARDI) as described in Parbhakar-Fox *et al.* (2011mineralogical and textural analyses. Sample screening is performed at stage-one, and a general classification given. Stage-two involves the use of routine geochemical tests in order to cross-check stage-one results, and also to quantify the acid forming/neutralising potential. Stage-three uses advanced geochemical tests and microanalytical tools to cross-check any ambiguous results from the previous stages, and for detailed characterisation of acid forming sulphide phases. Samples were obtained from two mine sites in Queensland, Australia, from which seventeen mesotextural groups were identified (A-Q).

NCV* = 0.44 × calcite + 0.48 × dolomite + 0.44 × ankerite + 0.38 × siderite – 1.37 × 0.53 pyrite – 1.37 × 0.20 arsenopyrite – 1.37 × 0.35 chalcopyrite

In addition, the samples were analysed using the Acid Base Accounting (ABA) procedure, described by Usher *et al.* (2003). The procedure includes: paste pH and conductivity, Net Acid Generation (NAG), neutralization potential (NP) and acid potential (AP). Each assay was performed in triplicate. The results of each ARD assessment has 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).

The toxicity of the leachates has been assessed using the Australian Standard method AS-4439 (Standards Australia, 1997) for solid wastes and contaminated soils. South African regulation stipulates the use of AS-4439 as leachable concentration to assess the suitability of wastes for disposal in a landfill, together with total concentration, as described in GNR 635 (Department of Environmental Affairs, 2013). The results obtained have been compared with the South African Leachable Concentration Thresholds (LCT) and total Concentration Thresholds (TCT) for landfill disposal of waste (Department of Environmental Affairs, 2013), which are similar to the Australian EPA 448.3 thresholds (Bulletin, 2007). 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 landfill disposal)

up to Type 4 (inert) following the criteria of the National Environmental Management Waste Act (59/2008) of South Africa. The chemical composition of the leachates was analysed as previously described.

Results and discussion

Environmetal characterization of tailings

The tailings generated by the copper mine are comprised by abundant alkaline minerals such as calcite and dolomite, followed by pyroxenes (diopside), magnetite, fluorapatite, olivine (mostly forsterite) and micas (mostly phlogopite) (fig. 1). On the other hand, the tailings generated by the phosphate plant are comprised of micas, pyroxene, fluorapatite and calcite. Among the minor minerals, it is worth mentioning the presence ilmenite, chalcopyrite, pyrite and monazite with relative abundance below 0.6%.

The abundant alkaline minerals and scarce Fe-sulphide minerals suggest that they do not have the potential to sustain the production acid mine drainage. Furthermore, all the samples fell under the classification of no acid forming/acid consuming for every assay performed (tab. 1). The highest neutralization potential (NP) was found in the Cu-tailing samples.

Regarding the toxicity of the leachates that they might produce, at least one of the tailings samples were above LTC0 or TCT0 for As, Ba, Co, Cu, F, Mn, Ni, Pb, Se, SO_4 and TDS, but none of them overcame LTC1 (tab. 2). Therefore, PIC's tailings classify as Type 3 waste (non-hazardous), according to the National Environmental Management Waste Act (59/2008) of South Africa.

Sequential extractions showed that they would release mostly non-toxic elements such as Ca, Mg, SO_4, Na, P, K and Fe. However, 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 the tailings, though the leachable concentrations were always below 0.006 mg/L.

To summarise, the tailings produced by the Cu mine could be used as alkaline reagents for the treatment of acid mine drainage or industrial wastewater within a circular economy strategy that would tackle at the same time the environmental impact caused by the tailings ponds and by the acid water.

Valorisation of tailings for recycling as secondary REE resource

The tailings are comprised mostly by mono-mineralic particles of calcite, dolomite, pyroxene, fluorapatite, magnetite and phlo-gopite. The mineralogical results show monazite as the main REE-mineral with an average of 60 wt% of ΣREE, while calcite and fluorapatite are the most abundant REE-bearing minerals, whose ΣREE range
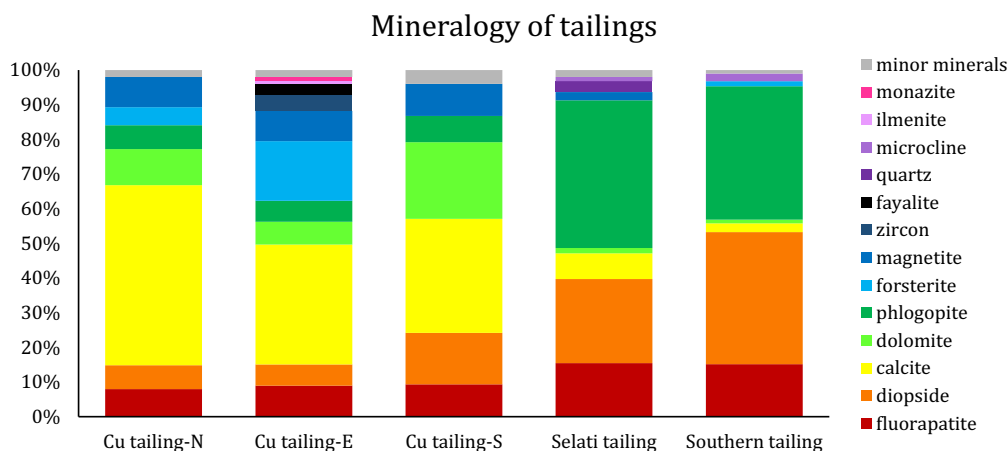
Figure 1 *Mineralogical composition of the tailings generated by the copper plant (Cu tailing North, East and West) and the phosphate plant (Selati and Southern tailings)*

Table 1 *Acid Base Account (ABA) of copper and phosphate tailings according to their paste pH, net acid generation (NAG, H_2SO_4/t), acid potential (AP in Kg $CaCO_3/t$), neutralization potential (NP, Kg $CaCO_3/t$) and net neutralization potential (NNP, Kg $CaCO_3/t$); and mineralogical characterization such as acid rock drainage index (ARDI) and the modified neutralization capacity value (NCV*)*

ABA analysis	Cu tailing S	Cu tailing N	Cu tailing W	Cu tailing E	P tailing N	P tailing S
Initial pH	8.4±0.02	8.6±0.05	8.5±0.04	8.6±0.08	9.1±0.13	9.1±0.02
Final NAG pH	7.4±0.22	8.6±1.50	8.8±0.06	8.7±1.76	6.5±0.12	5.8±0.27
NAG	0±0	0±0	0±0	0±0	0±0	0±0
AP (Open)	2.3±0.16	2.1±0.54	2.2±0.87	2.±0.43	0.3±0.11	0.3±0.09
AP (Closed)	4.6±0.32	4.2±1.08	4.5±1.63	4.2±0.86	0.6±0.22	0.6±0.18
NP	335.7±11.6	389.9±3.0	662.9±11.9	289.0±1.9	54.6±2.1	59.2±0.6
NNP (Open)	333.4±11.5	387.8±2.7	660.7±11.5	286.9±1.7	54.3±2.0	58.9±0.6
NNP (Closed)	331.0±11.3	385.7±1.9	658.4±10.2	284.8±1.0	54.0±1.9	58.5±0.4
ARDI	5.1±1.4	3.7±0.6	5.2±2.4	6.6±2.0	5.6±0.9	6.1±01.7
NCV*	25.0±3.5	27.6±4.1	21.6±2.8	18.2±3.1	3.9±1.1	1.7±0.9

Average ± standard deviation

Table 2 *Average of leachable concentration and total concentration of the analytes regulated in South Africa (Department of Environmental Affairs, 2013). Shaded in light grey are the analytes whose concentrations are below threshold 0, in dark grey are the analytes whose concentrations are between threshold 0 and 1. No analyte overcame threshold 1.*

Analyte (mg/L)	LC Cu-Tailings (mg/L)	TC Cu-Tailings (mg/kg)	LC P-Tailings (mg/L)	TC P-Tailings (mg/kg)
As	0.047±0.008	8.03±1.24	0.007±0.003	8.53±0.97
B	<0.01±0	0.025±0.01	<0.01 ± 0	0.014±0.01
Ba	6.47±0.54	472.9±18.2	2.28±0.36	219.4±11.9
Cd	0.001±0.001	0.294±0.037	0.001±0.001	0.302±0.025
Cl	43.8±5.1	n.r.	49.4±8.6	n.r.
Co	0.051±0.022	0.063±0.035	0.051±0.013	0.025±0.038
Cr	0.01±0.004	31.47±3.88	0.051±0.008	81.56±2.49
Cu	5.25±0.78	1031.6±58.8	1.71±0.37	128.6±53.8
F-	0.44±0.15	8.80±4.14	5.96±2.36	119.2±7.5
Hg	<0.001±0	<0.01±0	0.001±0.001	0.163±0.037
Mn	7.64±0.71	0.913±0.38	1.20±0.59	0.234±0.36
Mo	0.0004±0.0003	1.767±0.27	0.0003±0.0003	0.578±0.038
Ni	0.074±0.026	135.8±9.5	0.095±0.012	76.33±6.1
Pb	<0.01±0	24.97±5.51	0.101±0.076	11.3±2.2
Sb	0.0002±0.0001	0.04±0.01	0.0000±0	0.02±0.003
Se	0.101±0.026	11.27±3.48	0.003±0.001	12.34±5.71
SO4	198.2±15.2	n.r.	<40±0	n.r.
TDS	2619.1±785.3	n.r.	448.9±137.6	n.r.
V	0.0005±0.0004	0.127±0.009	0.011±0.002	0.023±0.011
Zn	<0.01±0	6.169±2.752	<0.01 ± 0	5.742±0.758

n.r. not regulated analytes

between 0.5 and 1 wt%. According to the geochemical results, the extraction of REE from monazite, fluorapatite, calcite and dolomite, from tailings produced by the Cu mine, might produce up to 5.65 kg of REE per ton. Although calcite has relatively low concentration of REE, due to its abundance, it would be the main source of REE, followed by monazite and fluorapatite (3.2, 2.0 and 1.1 kg of REE per ton of tailings, respectively). The most profitable REE are Nd, Dy, Pr and Tb which represent 87% of net value. Therefore, PIC wastes and particularly the Cu tailings, have the potential to be reclassified as secondary resources of REE. An approach to circular economy by re-processing mining waste would extend the lifetime of PIC mines and their benefits, while reducing the waste of resources and their environmental impact.

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