Determination of cyanide and potentially toxic elements in gold tailings at Barberton, Mpumalanga, South Africa

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Abstract

This paper addresses critical environmental, health, regulatory, and scientific concerns related to gold mining activities in the specific area of Barberton, Mpumalanga, South Africa. The paper thus calls for informed decisions to be made by the authorities to safeguard both the environment and people's health.

The novelty of this study is based on its comprehensive nature of the simultaneous assessment of both cyanide and potential toxic elements (PTEs) in tailings, while taking into account their composition variability over time. By combining these aspects, it is then possible to provide a holistic understanding of the contamination risks associated with mining tailings and thus justify the need for regular monitoring and supervision to ensure compliance against regulatory limits. Additionally, this paper considered investigating the dynamic nature of tailings, which are subject to changes in their chemical composition due to exposure to weathering by various agents.

In this study, the determination of weak acid dissociable (WAD) and free cyanide in tailings was performed using a validated method employing the South African Council for Mineral Technology (MINTEK) Laboratory Cynoprobe. The PTEs in tailings were determined by an inductively coupled plasma optical emission spectrometer (ICP-OES).

The results revealed that the tailings contained primarily substantial amounts of PTEs, including Fe (87,566 to 37,800 mg/L), Cu (271 to 110 mg/L), Mn (2,100 to 680 mg/L), Ni (400 to 390 mg/L), Zn (180 to 68 mg/L), Cr (645 to 510 mg/L), As (450 to 128 mg/L), and Pb (up to 35 mg/L).

The cyanide concentrations in tailings varied between 0.20 mg/L and 0.26 mg/L for free CN (with a mean of 0.23 mg/L in water leaching), 0.23 mg/L to 0.28 mg/L for free CN (with a mean of 0.25 mg/L in alkali leaching), 0.24 mg/L to 0.35 mg/L for WAD CN (with a mean of 0.28 mg/L in water leaching), and 0.31 mg/L to 0.39 mg/L for WAD CN (with a mean of 0.35 mg/L in alkali leaching).

The measured concentration of cyanide and the PTEs was compared to the minimum permissible levels enforced by the South African Department of Water and Sanitation (DWS) and the Water Research Commission (WRC) regulations that govern the disposal of hazardous constituents into the environment. Additionally, it was observed that the concentrations of contaminants in the tailings exceeded the acceptable minimum limits for hazardous waste exposure, posing risks to the environment and human health.

Keywords: ICP-OES, tailings, cyanide, potentially toxic metals, environmental monitoring

Introduction

Tailings are the waste materials left over after the valuable components of ores have been extracted during mining and mineral processing operations. In areas where mining and mineral processing of metal ores take place, the anticipation of pollution by potentially toxic elements (PTEs) and chemicals, such as cyanide, is particularly high. Some of the elements and chemicals in tailings are non-biodegradable and extremely persistent and accumulate thus leading to substantially adverse environmental and health risks for living beings. Waste tailings in particular are of concern, as they are often left without proper management and are characterized by high potential emissions and high contaminant concentrations (Soltani et al. 2017). When tailings are disposed of in large quantities, they can potentially lead to sedimentation in rivers, lakes, and other water bodies. This can disrupt aquatic habitats, reduce water quality, and alter the natural flow patterns of watercourses. Additionally, chemical substance such as cyanide can volatilize under natural light to form hydrogen cyanide, especially under acidic conditions. The toxic fumes and fine particles from dry tailings released into the atmosphere can become airborne, potentially leading to air quality degradation and health concerns for nearby communities. These particles and fumes can contain contaminants that pose risks to human health and wildlife when inhaled (Hinds & Zhu 2022).

Many countries have established regulations and guidelines to control and limit the hazardous constituent disposal including the potentially toxic elements and cyanide disposal. These regulations aim to protect both the environment and public health. In the case of South Africa hazardous constituent disposal has been regulated by the guidelines published by the Department of Water and Sanitation (DWS) and the Water Research Commission (Brice et al. 2006).

While previous studies have often focused solely on (semi-)metals or cyanide, this study aimed to bridge this gap by investigating both contaminants simultaneously. Additionally, the study investigated the dynamic nature of tailings which may be attributed to the combination of physicochemical and microbiological mechanisms. These mechanisms include volatilization, adsorption, precipitation, chemical oxidation, chemical hydrolysis, transport of dissolved species and bacterial degradation (Zagury et al. 2004). These in turn can lead to changes in their chemical composition and the consideration of the long-term perspective justified the study to assess the potential gradual increase or decrease of the effects of contaminants over time.

Therefore, the investigation and evaluation of cyanide and PTEs in the tailing storage facility (TSFs) in gold tailings in Barberton, Mpumalanga is intended to provide a deep understand of the pollution status of the surrounding environment, which plays an important role in the treatment and ecological restoration of the tailing dumps. In this research, the weak acid dissociable (WAD) and free cyanide and eight PTEs, namely, Fe, Cu, Mn, Ni, Zn Cr, As and Pb, in the Barberton TSFs, were studied to determine their concentrations, to provide a scientific basis for the subsequent comprehensive treatment of TSFs.

Materials and Methods

Study Area

The study area involved four TSFs: Rimmer's, Brommer's, Extension 14, and Extension 10, all located in Barberton in the Mpumalanga Province of South Africa (Fig. 1).

Sample collection

The portable power auger drilling rigs were utilized for drilling and sample extraction in TSFs (Fig. 2). Samples were drawn in 1-metre increments and directly placed in plastic bags sealed using cable ties and immediately stored in a dark at 4 °C, with approximately 2–3 kg of sample per metre drilled.

Mineralogical analysis

The determination of the mineral phase and mineral elemental composition of the tailing samples was carried out using advanced analytical techniques including, X-ray diffraction (XRD) analysis which was employed to accurately identify the mineral phases present in the samples. Additionally,

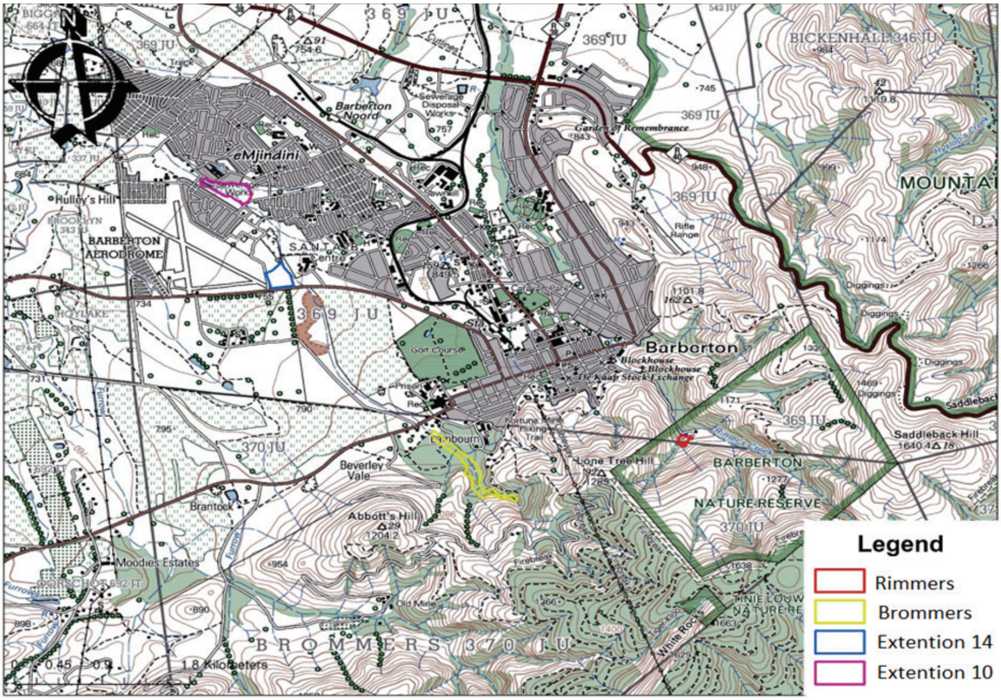

Figure 1 Location map of study areas in Barberton Town, Mpumalanga Province of South Africa

X-ray fluorescence (XRF) spectroscopy was employed to determine the mineral elemental composition of the tailings. These comprehensive analytical approaches provided a detailed understanding of the tailings' mineralogical and elemental characteristics, essential for evaluating their potential environmental impact.

Analysis of elemental concentrations and chemical compositions

Elemental concentrations and chemical compositions within the tailing samples were determined using an inductively coupled plasma optical emission spectrometer (ICP-OES) (Agilent Technologies 5100 ICP-OES), Prior to the analysis, the tailings samples underwent a thorough digestion process, adhering to the established methods described in previously published scientific literature (Zhao et al. 2023; Ying et al. 2022).

Cyanide contents analysis

A Mintek Laboratory cynoprobe was utilized for the determination of WAD and free cyanide in tailings samples. The developed method was validated as per US Food and Drug Administration (FDA) guidelines for its linearity, limits of detection and quantitation, precision, accuracy, and stability. All calibration curves obtained were found to be within the range (0.05 to 0.4 mg/mL) and were linear (R2 > 0.99). The percentage relative standard deviation (% RSD) for both intraday and interday validation was ≤ 5%. Before the analysis, the tailings samples underwent a cyanide leaching test in both deionized water and NaOH (10% w/v) solution. All cyanide forms were assumed to be extracted by the caustic solution since very alkaline conditions make even strongly complexed cyanides, soluble (Zagury et al. 2004). The leaching using de-ionised water is such that very weak adsorbed and the water-soluble cyanide are recovered.

Results and Discussion

Process Mineralogy of Tailings

Chemical Composition of Tailings

The results of the ICP-OES chemical compositional analysis of tailing samples revealed that the tailings contained SiO_2,

Figure 2 *Morphology and sample map of sampling sites in tailings dump*

MgO, Fe_2O_3 and Al_2O_3 which accounted for the largest proportion, with the mass fractions of 52.40, 9.63, 8.09 and 7.69%, respectively. This analysis confirmed that SiO_2 was the predominant mineral in the tailings, a finding that was consistent with X-ray Diffraction (XRD) results. The other metal oxides present in the tailings accounted for a mass fraction of less than 5%.

Mineral Composition and Content of Tailings

The XRD results (Fig. 3) indicated that in tailings the main minerals were quartz, dolomite, magnesite, chlorite, mica, albite and pyrophyllite, however, the XRD pattern did not show other minerals with lower concentration. The XRD results showed that SiO_2 was the main mineral composition of tailings, as indicated by the ICP-OES chemical compositional results. This might be because the tailings in the study area come from the whole slime materials, which are directly produced after the process of cyanide leaching by gold flotation (Li et al. 2022). The improper management of minerals like quartz, dolomite, magnesite, chlorite, mica, albite, and pyrophyllite can cause environmental impacts, including land degradation and water pollution (Mishra et al. 2004). The minerals can potentially alter the pH levels in nearby water bodies, adversely affecting aquatic ecosystems. Furthermore, dust containing these minerals can pose health risks to communities close to mining and processing sites (Stovern et al. 2014).

Elemental Compositions in Tailings

The results of the ICP-OES elemental compositional analysis of tailing samples revealed that the tailings contained Fe, Cu, Mn, Ni, Zn, Cr, As and Pb with concentrations of (37,800–87,566 mg/L), (110–271 mg/L), (680–2,100 mg/L), (390–400 mg/L), (68–180 mg/L), (510–645 mg/L), (128–450 mg/L) and (<10–35 mg/L) respectively. Moreover, the results obtained from the ICP correlate with the semi-quantitative results obtained from the XRF analysis (Table 1), which showed that the tailings contained Fe, Cu, Mn, Ni, Zn Cr, As and Pb. This also validates both methods used for the analysis of the elemental concentrations in the tailing samples. The PTEs under examination can indeed pose substantial risks to both ecosystems and human health when concentrations exceed established safety thresholds (Giao & Minh 2022). This study references guidelines from

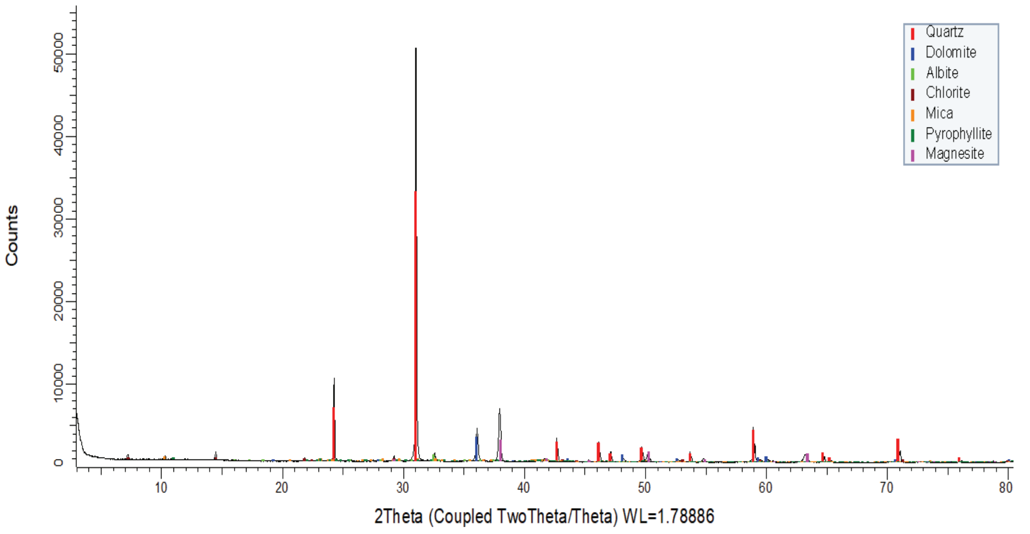

***Figure 3** XDR patterns of tailings*

the U.S. Environmental Protection Agency (EPA), the World Health Organization (WHO), the South African Department of Water and Sanitation (DWS), and the South African Water Research Commission (WRC) as benchmarks for assessing the environmental and health safety of PTEs (Brice et al. 2006). Excessive PTE levels in the environment can lead to several adverse effects. For instance, iron (Fe) can induce eutrophication, triggering harmful algal blooms that deplete oxygen and adversely affect aquatic life (Orihel et al. 2015). Copper (Cu) impairs the sensory abilities of fish, manganese (Mn) disrupts their reproductive systems and growth (Wood 2009), and nickel (Ni) and zinc (Zn) are toxic to aquatic organisms, affecting their growth and reproduction (Santore et al. 2021). Furthermore, chromium (Cr(VI)) and arsenic have been identified as highly toxic and carcinogenic, posing serious health risks including cancer (Pan et al. 2018). Additionally, lead (Pb) is known to affect the nervous system, representing a considerable health threat (Kumar et al. 2020).

Cyanide Contents in Tailings

The cyanide contents results obtained from Mintek lab Cynoprobe indicated that cyanide

***Table 1** Elemental composition of tailing, XRF scan*

Element	Fe	Cu	Mn	Ni	Zn	Cr	As	Pb
Dimension	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
Brommers_1	59,800	104.7	1109	367.8	123.7	1152	140.6	7.4
Brommers_2	55,200	210.6	1012	568.4	66.7	1857	285.2	8.1
Brommers_3	50,400	146.4	842.4	337.8	371	1143	129.9	14.3
Rimmers _1	93,600	246.2	2142	387.5	246	1167	601.1	18.1
Rimmers _2	79,600	193.5	2131	364.5	246.5	1173	538.2	32.7
Rimmers_3	85,800	181	1157	204	166.1	846.7	420.8	20.1
EXT10_1	46,000	200.8	781	387.9	76.2	1294	147.6	10
EXT10_2	48,000	148.5	807.4	524.3	83.3	1813	267.8	12.8
EXT10_3	48,400	199	790.4	422	166.7	1342	131.7	9.9
EXT14_1	43,300	181.5	740	340.2	81.1	1184	123.8	8.5
EXT14_2	41,200	157.5	724.8	334.5	69.2	1123	131.4	10.6
EXT14_3	45,900	198.3	793.9	424.2	74.3	1271	211.4	11.3

concentrations in tailings varied between 0.20 mg/L and 0.26 mg/L for free CN (with a mean of 0.23 mg/L in water leaching), between 0.23 mg/L and 0.28 mg/L for free CN (with a mean of 0.25 mg/L in alkali leaching), between 0.24 mg/L and 0.35 mg/L for WAD CN (with a mean of 0.28 mg/L in water leaching) and between 0.31 mg/L and 0.39 mg/L for WAD CN (with a mean of 0.35 mg/L in alkali leaching). The Free and WAD cyanide seems to exceed the minimum limits of acceptable hazardous waste exposure (Brice et al. 2006). Both WAD cyanide and free cyanide can indeed pose threats to both surrounding ecosystems and human health if their concentrations exceed certain thresholds. Free cyanide can inhibit cellular respiration by interfering with the electron transport chain in aquatic organisms, leading to asphyxiation at the cellular level (Eisler 1991). When cyanide in tailings can leach into the soil, it can alter soil chemistry and potentially harm plant life by inhibiting seed germination and root growth (Donato et al. 2007). Moreover, contamination of surface and groundwater by cyanide can pose direct health risks to humans, including poisoning and long-term health effects such as neurological damage (Ravindiran et al. 2023). Thus, managing cyanide in mining operations is critical to preventing its adverse effects on the environment and human health.

Conclusions

The mineralogical and cyanide investigation conducted on the tailings in Barberton, Mpumalanga, was crucial to accurately evaluate the pollution level and potential ecological risks posed by the gold tailing storage facilities (TSFs). According to our detailed analysis and results, it was evident that the tailings demonstrated a substantial pollution potential and ecological risks to the surrounding environment. Notably, all the eight identified potentially toxic elements (PTEs), along with the cyanide contents found in the tailings, exceeded the established standard value limits. These exceedances are concerning, as they surpass the acceptable minimum limits for hazardous waste exposure, posing risks to both the environment and human health.

The primary applications and implications of this comprehensive work are multifaceted. They include providing essential data to inform environmental impact assessments, enabling more effective and accurate risk assessments and monitoring, ensuring strict regulatory compliance, and promoting sustainable mining practices. Additionally, this research plays a crucial role in enhancing public awareness and understanding of the relevant environmental challenges associated with mining and mineral processing operations. By highlighting these issues, our study aims to contribute to the development of more environmentally responsible and sustainable approaches in the mining sector.

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