Possible Value Recovery from Abundant Gold Mine Dumps and Waterbodies in Krugersdorp, South Africa

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Abstract

The current study focused on identifying valuable elements that can be recovered from Lancaster Dam and gold mine dumps in Krugersdorp, a city in Gauteng Province, South Africa. The mine dumps considered are from closed and abandoned mines and have been existing for many decades. The area is also known for high volumes of acid mine drainage. The concentrations of valuable and base elements were measured. Rare earth elements (REEs), Ni, Co, Ag, Li, Cu and Cr among others were detected and found to be in concentrations that can be recovered to help meet their demand. Salvaging REEs and other valuable elements from mine waste can help improve the economies of many countries since, the elements are in demand due to improving technologies and growing population. Other elements including those that are toxic at very low concentrations were also detected. Thus, suitable techniques for the recovery of valuable elements in the study area, are those that have high selectivity and efficiency.

Keywords: Mine dumps, mine waste, contaminated waterbodies, rare earth elements, valuable elements

Introduction

Krugersdorp, a city in South Africa, located on the western ridge margin of the Witwatersrand Basin is known as the territory of gold mining (Shapi *et al.* 2021). The closed, abandoned and operating mines in this region have led to serious air, soil and water pollution due to large amount of waste in the form of solid (mine dumps) and liquid (wastewater, acid mine drainage) released into the environment either directly or indirectly (Fig. 1). High amount of waste in this region was left untreated by the previous mine owners, who cannot be identified since mining laws and regulations have only been implemented in recent years. Thus, the responsibility now rests with the local government to protect local residents from the negative effects of mining waste (Mabaso 2023). The rehabilitation of mining areas is often expensive, however, without it, mining has long lasting negative impact on the environment and on living organisms. Without rehabilitation, toxic elements will continue to migrate to waterbodies (e.g., groundwater and surface water) which should be protected, especially in countries with waters shortages (Lusilao-Makiese *et al.* 2013). Some of the toxic elements can be transported through the air and reach residential areas, nature reserves, agricultural areas and waterbodies, leading to ease of access to living organisms including humans, livestock and wild animals. Residents in the vicinity of mining areas have been found to suffer from serious health effects due to continuous ingestion of toxic elements (Munyai *et al.* 2016). Thus, there is an urgent need to rehabilitate closed and abandoned mines.

Precious and valuable elements including rare earth elements (REEs), gold, platinum group elements, nickel and cobalt among others, have been found in some mining waste (Watson and Beharrell 2006). The profit from the recovery of these elements using cheap and efficient methods and techniques can boost the economies of many countries and assist the government with the funds required for rehabilitation. This is because, the natural resources of these precious elements have been depleting, but their demand is increasing due to population growth and improving technologies (De Boer and Lammertsma 2013).

This study is based on identifying precious and valuable elements in Krugersdorp and concluding on their potential for recovery. The concentrations of toxic elements were also measured in order to determine the urgency of rehabilitation in the area.

Methodology

Study area and sampling

The study was conducted in Krugersdorp (S 26°07.8321', E 027°46.6774'), a city in Gauteng Province, South Africa. Krugersdorp is known as a mining city due to large amount of gold reserves which were discovered in 1887. The study site is in the vicinity of an abandoned gold mine, which is characterized by a number of mine dumps and acid mine drainage (Fig. 1a). There are also illegal artisanal miners in the area, who have been operating for decades, indicating that there is still gold in the area (Fig. 1b). Lancaster Dam, which is situated in the study area, was considered for the collection of liquid samples. Samples were collected from five sites which include the Lancaster Dam (Fig. 2). GPS coordinates were recorded using GPSMAP 65 TopoActive Af (Garmin, USA). A multiparameter was used to measure temperature, pH, conductivity, redox potential and total dissolved solids (TDS) in the Dam and wetlands. Both solid and liquid samples were collected and their colours were recorded. The containers used for the samples were acid washed, following a cleaning protocol. Liquid samples were collected in triplicates using polypropylene containers with caps and immediately preserved in a cooler at 4 °C. Solid samples including tailings and plant stems were collected. Tailings were collected at a depth of between 10 and 50 cm below surface using an auger. The parameters recorded in the field were also recorded in the laboratory after transportation, to account for any changes.

Analysis of samples

The solid samples collected were dried at room temperature for a week and digested using Multiwave GO Plus microwave digester (Anton Paar, Germany). 0.25g of the ground sample was digested with 10 ml HNO_3 and 2.5 ml H_2O_2 for 45 minutes at 180 °C. The collected liquid samples were filtered using 0.22 µm microfilters and stored in the refrigerator until required. Inductively coupled plasma optical emission spectroscopy (ICP-OES) (Spectro Genesis, Germany) was used to measure the concentration of elements (REEs and other elements). The anions were measured using ion chromatography (IC) (Metrohm, South Africa). Fourier transform infrared spectroscopy (FTIR) was used to determine the functional groups on the collected samples.

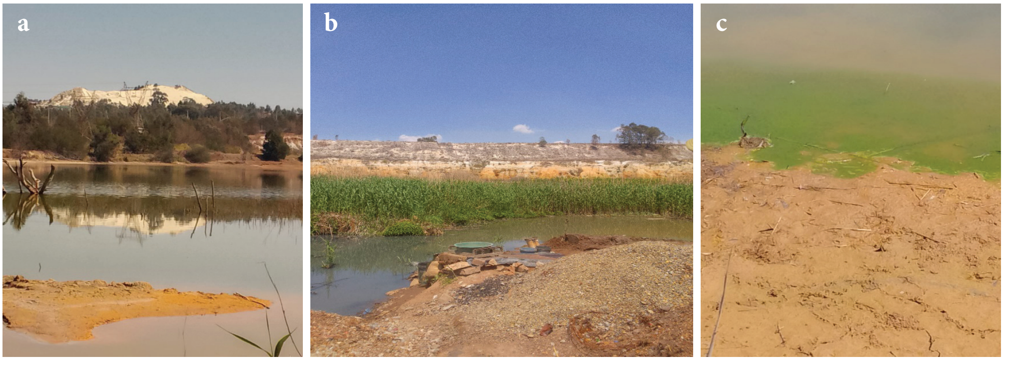

***Figure 1** Solid and liquid waste in Krugersdorp.*

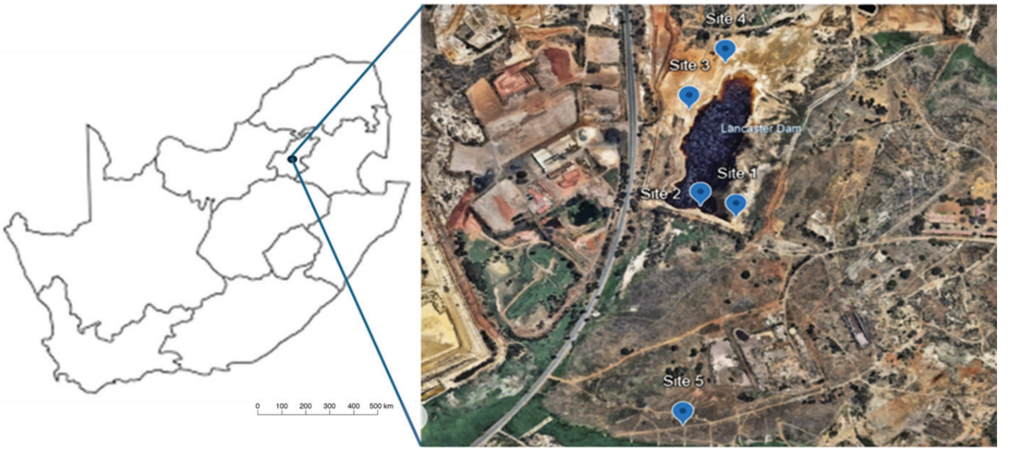

Figure 2 *The study area and sampling sites.*

Results and discussions

The results of the samples collected from different sites in the study area are presented in Table 1. Liquid samples were collected around the Dam in sites 1-3 (Fig. 2). The Dam was found to be acidic with a pH of less than 3. Moreover, the Dam was characterized by high content of dissolved inorganic and organic substances, as indicated by the high TDS (Table1). High TDS means that water cannot be used for supporting biodiversity, ecosystem services, recreation, agriculture and farming among others (Adjovu *et al.* 2023). High TDS can also result in harmful green algae and eutrophication, which was observed in the Dam (Fig. 1c). The redox potential in the Dam was greater than 200 mV, which indicates that there are more oxidizing species in the water. Some of the solid and liquid samples had greenish blue colour, which might be due to the cyanide which was used during mineral processing. Moreover, the operations of illegal miners in the study area (site 5) (Fig. 2) can negatively affect the environmental quality of the area.

The results indicating the concentrations of REEs from the study site are presented in Fig. 3. Samples indicated by site 1a-3a were collected from the dam. The concentrations ranged between 0 and 2 mg L^{-1}. Ce and Tb were the dominant REEs in the Dam (Fig. 3a). Other REEs i.e., Y, La, Nd and Dy were also detected in higher concentrations. It is highly likely that high concentrations of REEs have settled at the bottom of the dam. The concentrations of REEs were also determined in the vicinity of artisanal mining in the area, however, the concentrations were very low. REEs found in the dam were also detected in nearby mine dumps but, at significantly ($p<0.05$) higher concentrations (0- >300 mg L^{-1}) (Fig. 3b). This indicates that there is a higher chance that the REEs migrated from the mine dumps to the dam, through the air and the soil.

There is a wetland around the artisanal mining site (site 5), and some plants were tested for the concentrations of REEs. Certain REEs (Sc, Er, Pr and Tb) were detected in higher concentrations (>3 mg L^{-1}) in the stems

Table 1 *Colours observed and parameters measured in the field.*

Site Name	Temperature (°C)	pH	Conductivity (mS cm^{-1})	Redox potential (mV)	TDS (mg L^{-1})	Colour
1	25.9	2.7	4	220.15	>2000	Dark brown
2	21.4	2.9	4	219.77	>2000	Light brown
3	22.2	2.8	4	219.90	>2000	greenish blue

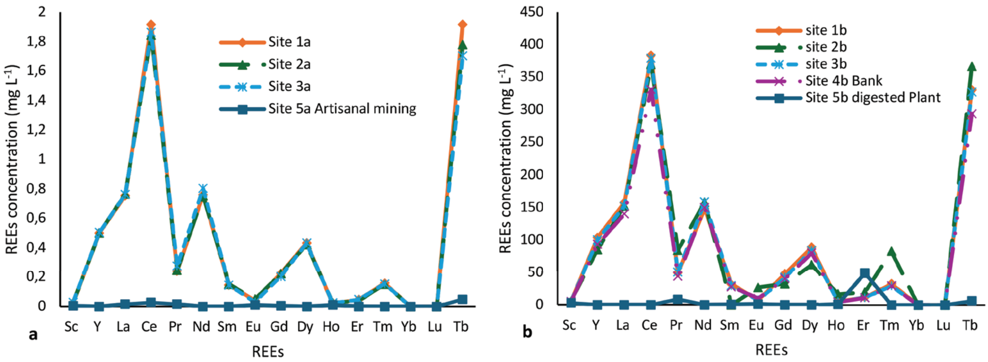

Figure 3 *Concentrations of REEs in the (a) liquid and (b) solid samples (n = 3, RSD < 5%).*

of the plants. Thus, REEs can be taken up by plants. The results indicated that the REEs around Krugersdorp are in concentrations which can be considered for recovery and can help meet their demand. REEs can be found in many parts of the world but large REEs reserves are found in few countries including China, USA and Brazil (De Boer and Lammertsma 2013). As a result, the price of REEs has been increasing over the years. This is also heightened by their demand. Thus, mining waste and waterbodies in the vicinity of mining sites rich in REEs can be considered as potential secondary sources of REEs to help meet demand and help improve the economies of many countries including South Africa.

The concentrations of other elements including Ag, Al, Ca, Co, Cu, Zn, Ni, Fe, Li, Na, K, Mg and Mn were also measured, and the results are shown in Table 2. It is important to know the presence and concentrations of some of these elements as they can negatively impact the recovery of precious elements. Ag, Zn, Co, Cu, Li and Ni are known as some of the most valuable elements used in different technologies including batteries, catalysts and pharmaceuticals (Li *et al.* 2019). The concentrations of these elements were high in solid samples, and good enough for recovery. Al, Na, K, Mg and Fe were observed to be the most dominant elements in the study area.

To recover REEs and other valuable elements from waterbodies, adsorbents and ion exchange techniques might be beneficial due to efficiency and less time required. However, recovery could be challenging due to the high content of other elements which can act as competing ions. To successfully recover the valuable elements, functionalized and highly selective techniques should be used. Cheap and efficient bio-surfactants, flushing, microbial leaching and phytoremediation can be used to recover valuable elements in the areas (Lima and Ottosen 2021).

Very toxic elements including Pb, Cd and Tl were also found in the solid and liquid samples. Their concentrations were low (<0.5 mg L^{-1}), however, their toxicity and effect to living organisms can be severe at low levels (≈1 µg L^{-1}) (Nava-Ruíz and Méndez-Armenta 2013). When ingested by humans, these elements can lead to cancer and liver, kidney and nervous system failure (Aloke *et al.* 2019). Their presence in both solid and liquid samples, means that they can be easily accessible to local residents as they travel through the air, especially in windy seasons. Depending on environmental conditions, Cr can be oxidized to Cr^{6+} which is very toxic in small concentrations. The oxidation process is very likely to occur in the Dam which was characterized by positive redox potential. Thus, the dam and the mine dumps are not safe for local residents. Moreover, these elements can migrate to groundwater through the soil profile, which increases their accessibility to humans and livestock dependent on groundwater. South Africa is a water scarce country; therefore, the available natural water resources should be protected from pollution. Rehabilitation may be the best process to apply immediately after the recovery techniques in order to prevent further environmental

Table 2 Concentrations of other elements found at different sites in the study area ($n = 3$, RSD < 5%).

Sample	Ag	Al	Ca	Co	Cu	Zn	Ni	Fe	Li	Na	K	Mg	Mn
Site 1a	0.184	170.005	0	4.127	1.696	11.236	9.406	28.601	0.92	105.617	63.365	63.245	24.637
Site 2a	0.186	118.594	0	3.196	1.034	7.985	7.089	28.775	0.894	72.95	57.907	63.913	18.479
Site 3a	0.186	101.07	0	2.602	0.881	6.684	5.869	25.265	0.821	60.056	50.577	57.619	15.558
Site 5a	0.189	0.361	15.562	0.098	0.237	0.069	0.071	0.15	0.602	46.407	12.773	15.11	2.746
Site 1b	35.4	16905.6	974.6	26	108.2	64.6	48	3057.6	142.4	235.8	684.6	301	40.2
Site 2b	35.2	22498.6	1071.6	40.4	191.2	132.4	96.4	46701	574	531	3232.6	1222.6	173.4
Site 3b	35.4	3314	109.6	17.2	69.2	19	18.4	4136.6	143.4	319.4	660.8	141	24
Site 4b	35.2	5819.8	2255.6	41	51.4	43	19.4	11384.6	184.4	600.8	507	1806	157.2
Site 5b	37	39750.6	1571.6	54.2	251	1942.4	1735.6	7102.2	196.2	19463.8	13612.2	13031.4	329.6
Site 5b Plant	36.4	1666.2	2659.4	25	47	80.8	14.8	30.4	120.6	10278	2889	3203	2306.4
Site 5b stem	37	129.8	2314	18.2	75	214.4	128.6	1760.2	121	2389.4	244498	9314	392.2

Site 1a-3a = Lancaster Dam Site 5a = artisanal mining wastewater Site1b-3b = Mine dump (>500 m from Lancaster Dam) (solid waste)
Site 5b = artisanal mining site (solid waste)

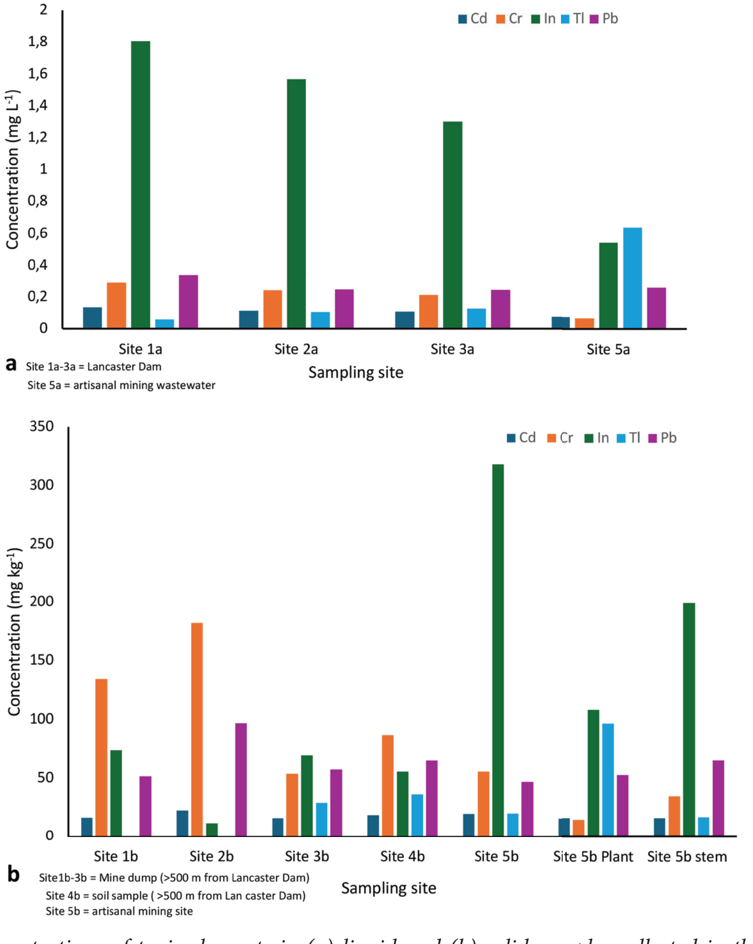

Figure 4 Concentrations of toxic elements in (a) liquid and (b) solid samples collected in the study area ($n = 3$, RSD < 5%).

pollution. The profit from the recovery of valuable elements including REEs can help with the implementation of rehabilitation in Krugersdorp.

Conclusions

Krugersdorp, a city in South Africa is known for gold mining. The area is characterised by numerous closed and abandoned mine sites due to depleted reserves. There are also a number of mine dumps and large volumes of acid mine drainage. This study focused on identifying and quantifying valuable elements that can be recovered from mine dumps and a dam in the area. The dam was characterised by low pH, high conductivity, high total dissolved solids and positive redox potential. Rare earth elements and other valuable elements (Ni, Co, Mn, Li and Ag) were detected in the dam and mine dumps. The study area can be considered as a potential place for the recovery of valuable elements to meet their global demand. The conditions of the mine dumps and the dam which were determined in this study, will help select the best recovery techniques for valuable elements. Selective ion exchange resins, membranes and functionalised adsorbents can be used as cost-effective and efficient recovery techniques in the study area. Other elements including Al, Na, K, Mg and Fe were detected in high concentrations and can be considered as potential competing ions when recovery techniques are applied. Moreover, toxic elements were detected, and their concentrations indicate that the residents and other living organisms in the area might not be safe. Thus, there is an urgent need for rehabilitation, which can be quickened by using the profits made from the recovery of valuable elements.

Acknowledgements

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