

Susceptibility of Metals Release from Tailings Dumps Located In the Krugersdorp Area

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Abstract—Six steps sequential extraction according to Tessier method was used to fractionate heavy metals into the following fractions: (F1) water soluble Fraction (H₂O), (F2) exchangeable metals, (F3) easily reducible fraction (CO₃), (F4) Moderately reducible fraction (Oxide), (F5) metals associated with organic matter and secondary sulphides (organics) and (F6) residual fraction. The results showed the higher concentration of heavy metals from different sampling points (top, middle and bottom of the tailing dump), which were dominating in various fractions such as Fe, Pb and Zn. The tailings samples were characterized by the use of x-ray diffraction (XRD) and X-ray fluorescence (XRF). According to the XRD results, the top of the tailings dumps was dominated by the oxide minerals while the bottom of the tailings dumps mostly contained sulphide minerals. The toxic heavy metals considered in this study exhibited higher concentrations in the mobile and labile phases (reducible/bound to carbonate, water soluble and bound to organic fractions) and lower concentrations in the immobile fraction (residual), which shows that these metals will mobilize and pollute the environment around Krugersdorp mine.

Metals mobilization is therefore likely to occur in these tailings dumps under environmental conditions and may affect the quality of surface and ground waters.

Keywords—Tailings dumps, sequential leaching, bioavailability, metal mobility, complexation

I. INTRODUCTION

MINING activities usually produce many types of mine wastes, which include mine tailings, waste rock and slag.

South Africa produced an estimated 468 million tons of mineral waste per annum [1], most of the mining waste is produced by gold mines as it was estimated to account for 221 million tons or 47 % of all mineral wastes produced, making it the largest, single source of waste and pollution. Specifically, opencast mining activities have a serious environmental impact on soils and water streams, having generated millions of tons of sulfide-rich tailings [2]. Mine tailings can cause a problem to an environment because they release toxic heavy metals, when these trace elements or heavy metals accumulate to a soil, they will create a hazard when transferred to water or plants [3]. The toxic heavy metals which are mostly found in

contaminated areas and sites are lead (Pb), chromium (Cr), arsenic (As), zinc (Zn), cadmium (Cd), copper (Cu), mercury (Hg), and nickel (Ni) [4]. The mine tailings which cause the environmental pollution or contamination are mainly those which are found in abandoned mines or in active mines which were left unmanaged or rehabilitated. South Africa consist of many abandoned tailing dams, some of which were dumped many years ago [5; 6], example is the abandoned mine in Krugersdorp area, which represent a great hazard. The mine tailings dam in that area has been eroded and mobilized to the bottom of the dump and neighboring area. Pyrite bearing mine tailings disposed of at neutral or slightly alkaline conditions can weather and continue to leach metals through acid mine drainage (AMD) for decades or even centuries after the mining activity has ceased, ultimately contaminating the surface and subsurface environment, not only in the adjacent areas, but often over much more extended areas [7]. In South Africa, examples of AMDs are found in Krugersdorp, West rand and also Witwatersrand in Gauteng province [1]. In 2002, near town of Krugersdorp, AMD also welled up and began pouring out of surface, since then about 15 million liters a day of AMD have been spilling out [8]. The release of toxic metals from the solid waste dump rely on the mobility of the elements within the tailing dump, and they further shown that the transformations in the chemical form of such toxic substances in the solid dump will affect their mobility and bioavailability [9]. Metal mobility in soil systems depends on the chemical form of soil-metal interactions: metals immobilised by adsorption and precipitation, can be released when the metal retention capacity is overloaded or there is a particular change in soil environmental conditions, enhancing metal mobility (degradation of organic compounds, change in pH, redox potential, soil solution composition) [10]. In this study the attempt was made to predict the susceptibility of metals release from tailings dumps in the Gauteng Province of South Africa.

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II. METHODOLOGY

A. Materials

Mine tailings were collected from a mine area located in Krugersdorp, Gauteng province. The tailings samples were taken from the top 30 cm of the surface at 14 locations using an auger. All samples were air dried in the laboratory for 2 days, sieved through 75 μm of mesh, homogenized before XRD and XRF and sequential leaching analysis, the remaining of samples were kept in plastics bags prior to use in the rest of experiment¹.

B. Characterization of mine tailings by XRD and XRF

The mineralogical study of the tailings samples were carried out by means of X-ray diffraction (XRD) analysis. The bulk composition was determined using the powder diffraction method, after grinding and homogenization of the samples to 75 μm , nonoriented powders were examined on a Philips X'pert MPD diffractometer, at a power of 1.6 operating at 40KV. Major and trace elements of the tailings were analysed using the X-ray- fluorescence spectrometer (XRF) which was done on the magiX PRO SuperQ Version 4. A rhodium (Rh) anode was utilized in the X-ray tube and operated at 50 kV and current 125 mA; at power level of 4 kW.

C. Sequential leaching

The mobility of metals is strongly dependent on their specific chemical forms and methods of binding [11]. Sequential leaching can provide information about the fractionation of metals in the different lattices of the solid sample [11]. To better understand the transportation and retention mechanism of elements, 14 tailings samples were selected for sequential leaching: 6 samples were collected on the top of tailing dump, 5 on the middle and 2 on the bottom of the dump. The binding and chemical state of the metals in the tailings was characterized by a sequential leaching procedure which has six fractions (F1–F6), the leaching method was adapted from that of Tessier et al. (1979; modified) as cited by [12]. Fraction 1 (F1) consisted of water soluble metals. Fraction 2 (F2) consisted of exchangeable metals and/or those soluble in slightly acidic conditions. Fraction 3 (F3) (easily reducible fraction) represents metals bound to short range-order Fe, Al and Mn (oxy) hydroxides and poorly-crystallised ferric hydroxylsulfates. Fraction 4 (F4) (moderately reducible fraction) represents metals bound to long-range-order Fe, Al and Mn (oxy) hydroxides and well-crystallised ferric hydroxylsulfates. Fraction 5 (F5) represents metals associated with organic matter and secondary sulphides. Fraction 6 (F6)

consists of metals bound to primary sulphides. The following leaching scheme was used:

Fraction 1. Water-soluble (H₂O). One gram of dry tailings was added to 20 ml of water; the mixture was agitated continuously for 15 min at 20°C using a shaker. After shaking the mixture was centrifuged at 500 rpm (3000 gravity) for 20 minutes. Then the supernatant was stored for the analysis of release elements using the inductively coupled plasma optical emission spectrometry (ICP-OES), the same procedure of centrifugation and analysis was used in each fraction after shaking.

Fraction 2. Cation exchangeable. The residue from F1 was added to 20 mL of 1.0 M NH₄Ac that was adjusted to pH 7.0 with acetic acid; the mixture was agitated continuously for 1 h at 20°C.

Fraction 3. Carbonates and hydroxides (CO₃). The residue from F2 was added to 20 mL of 1.0 M NH₄Ac that was adjusted to pH 5.0 with acetic acid; the mixture was agitated intermittently for 5 h at 85°C.

Fraction 4. Hydrated oxides of Fe and Mn (oxide). The residue from F3 was added to 20 mL of 0.043 M NH₂OH–HCl in 25% (v/v) acetic acid; the mixture was agitated intermittently for 5 h at 85°C.

Fraction 5. Labile organics and amorphous metal sulphides (organic). The residue from F4 was added to 12 mL of 0.02 M HNO₃ and 30% H₂O₂ (3:5 v/v) that was adjusted to pH 2.0 with HNO₃; the mixture was agitated intermittently for 3 h at 85°C, followed by addition of 7.5 ml of 3.2 M NH₄Ac in 20% HNO₃ + 10.5 mL of distilled water; this mixture was agitated continuously for 30 min at 20°C.

Fraction 6. Consolidated organics and metal sulfides, (residual). The residue from 5 was digested in 10 mL of concentrated HNO₃ + 10 mL of distilled water.

IV. RESULTS AND DISCUSSION

A. Characterization of tailings XRD

The mineralogical composition of the 14 representative samples used in this study is summarized in Table 1. The mineralogical composition of tailing samples from Krugersdorp mine was determined by X-ray diffraction (XRD). XRD pattern showed the dominance of the quartz (SiO₂) minerals in the top and middle of the tailing dump, while other minerals, such as iron catena-silicate & ferrosilite, sillimanate, and aluminium iron (III) oxide were only detected in high concentration in few samples. Similar trend about the dominance of quartz in the tailings was reported in the study by Novhe et al. [13].

TABLE I
MINERALOGICAL COMPOSITION OF TAILING SAMPLES

Minerals	Weight percentage in each sample													
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Quartz	84.8		-	91.0	79.0	85.0	92.3			97.0	73.2	91.0	-	-
Iron silicate, catena-ferrosilite	-	96.0	-	-	-	-	-	-	-	-	-	-	-	-
aluminium iron(III) oxide	-	-	-	-	-	-	-	60.0	-	-	-	-	-	-
Sillimanite	-	-	-	-	-	-	-	-	-	-	-	-	-85.0	-
dialuminium silicate oxide, kyanite	-	-	95.0	-	-	-	-	-	-	-	-	-	-	-
dicalcium silicate	-	-	-	-	-	-	-	-	-	-	-	-	-	87.0

XRF

The major, minor and trace elements were determined by using XRF represented in Table 2. SiO₂ is a dominant oxide in all samples collected from the Krugersdorp mine, which range from 40.49% to 89.15%. This confirms the result obtained using the XRD. SiO₂ was also found by others to have dominion over other oxides in mine tailings [13]. Heavy

metals such as Al, Fe, Cr, Ni, Zn, Cu, As, Pb and Co were also identified in the tailings samples; however, only Cr, Fe, Pb and Zn were present in all the samples and were therefore considered as main focus in the rest of the study.

TABLE II
MAJOR AND TRACE ELEMENTS IN TAILING SAMPLES

Samples	Cr ₂ O ₃ Mass%	Fe ₂ O ₃ Mass%	PbO Mass%	ZnO mass %	SiO ₂ Mass%
1	0.1003	7.0757	0	0.0141	69.6826
2	0.0539	2.6767	0.0152	0	81.3664
3	0.0825	3.0261	0	0	78.1389
4	0.0699	1.7918	0	0.006	80.7074
5	0.0807	2.9005	0.009	0.0055	78.024
6	0.0633	2.7017	0.0648	0.0066	78.5499
7	0.1091	1.8939	0.0165	0.0072	86.4781
8	0.1127	5.58	0.0304	0.0079	72.7715
9	0.0745	38.2009	0.331	0.0282	40.4851
10	0.0545	6.1833	0.2112	0.0137	69.7409
11	0.0186	10.4723	0.0387	0	70.1661
12	0.0656	6.7607	0	0.0064	75.3456
13	0.0481	0.9971	0	0	89.1518
14	0.0691	7.2354	0	0.1029	41.977

B. Sequential leaching

The results obtained in various steps of the fractionation technique have been exhibited in Table 3. In the water soluble fraction (F1), Zn is the most abundant than any other metals, which range between 0-60.7% for sample taken from the top of tailing dump (S1, S2, S3, S4, S5, S6, S7), range between 0 to 62.5% for sample taken from the middle of the dump (S8, S9, S10, S11, S12) and show the low percentage for samples collected from the bottom of the dump, which exhibited

concentrations in the range between 0-2.65%. The abundance of Zinc in the residual fraction (F6) range from 0 to 30.78% for the tailing samples collected from the top of the tailing dump and for sample taken from the bottom of the dump which range from 0 to 23%. The lower recovery from the samples collected at the bottom layer was likely due to the fact that these samples were mostly sulfide minerals which do not dissolve easily. The recovery percentage of Zinc in other fractions was low, which means that the mobility of Zn in the tailing may result in the easy release of a fraction while the rest

is more likely to remain in the tailing for a long time. The metals leached in ultrapure acidified water—“water-soluble” fraction (i.e. leaching stage 1)—are relatively labile and thus may be potentially bioavailable [12]. This fraction consists of metals that are easily soluble, e.g. as chlorides and sulphates [14]. This fraction is the most readily available one from the point of view of the environment, and thus the leaching of metals in this fraction is a major environmental concern [14].

The highest recovery % of Pb bound to the carbonate fraction (F3), were found in samples collected at the top of the tailing dump and ranged from 0-85.65%, which was higher as compared to the residual fraction which ranged from 0 to 34.37% and other four fractions. Pb in this fraction for tailing collected at the top of the tailing dump has relatively high mobility and potential bioavailability than the residual fraction and other phases (F4 and F5). Reducible or bound to organic fraction has high concentration of Pb than the other geochemical phases, which means that Pb is more mobile in this phase than the other metals. However, Pb was not mobile in the samples collected at the bottom of the tailing dump as it remained undetectable in all the fractions. These further confirm the fact that sulfide minerals are refractory and hardly dissolve, therefore making difficult the recovery of metals.

Fe was mainly recovered at the bound to organic fraction for the sample taken from the middle of the dump, which range from 0.28-88.10%, in this fraction Fe recovery % is higher than in the residual and all other fraction for samples collected from the same site, this means that this metal is more mobile from the organic fraction. Metals present in the residual fraction are a measure of the degree of environmental pollution [15]. The higher the metals present in residual fraction, the lower the degree of pollution [15]. The high mobility and

bioavailability of this metal make the tailings to have potential hazardous effect on the environment.

Fe is more abundant at bound to carbonate fraction (F3) for sample found at the top of the dump, in this fraction Fe recovery % is higher than in the other fractions for the samples collected from the same site. Fe recovery % is high for samples taken from the bottom of the dump at the fraction which bound to carbonate, which range from 8.34 to 10.09%. The recovery % of Cr is relatively low in all fractions, however at water soluble fraction (F1), it exhibit high concentration for sample found on top of the dump as the recovery ranges from 0- 1.58%, thus this recovery % is the highest compared to all the other phases, for samples from the same site. For the samples collected in the middle of tailing dump Zn was the metal most easily removed in all the fractions; however higher recovery of Zn was achieved in fraction 1 where the recovery percentage ranged between 0 and 62.51 %; implying that under environmental conditions, Zn will be very mobile from the middle layer of the tailings. The order of recovery of the other metals mostly varied according to the specific sites in the middle layer; however, according to the general trend, the following order Fe > Pb > Cr could be considered. The recovery of metals in the samples from the bottom of the tailings was poor compared to the other samples; this furthermore confirms the fact that the refractory structure or mineralogy of the samples from the bottom of the tailings is a limiting factor to the mobility of the metals. It is therefore clear that the oxidation moving from the top of the tailing to the bottom contribute to the mobility of the metals.

TABLE III

SEQUENTIAL LEACHING RESULTS SHOWING SIX FRACTIONS IN A THREE SAMPLING SITES: TOP OF THE TAILING DUMP (S1-S7), MIDDLE OF THE TAILING DUMP (S8-S12) AND BOTTOM & FOOT OF DUMP (S13 AND S14)

Fractions and elements	% Recovery of metals per sample													
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Fraction 1														
Cr	0.97	0.40	1.04	1.58	0	0.19	0.22	0.54	7.23	2.76	0	0.45	0.98	0.08
Fe	0.20	5.15	7.17	0.07	0.34	0.10	0.00	2.62	20.37	0.08	0.01	0.10	0.02	0.06
Pb	3.59	0.00	27.50	0.00	0.00	19.91	6.85	0.930	0.00	4.10	0.84	0.00	0.00	0.00
Zn	60.70	0.00	17.14	57.18	36.70	13.37	18.35	22.77	30.81	62.51	0.00	57.44	0.00	2.65
Fraction 2	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Cr	0.34	0.00	0.00	0.05	0.33	0.00	0.46	0.03	0.10	0.12	0.06	0.00	0.00	0.08
Fe	0.02	0.03	0.13	0.02	0.03	0.12	0.04	0.27	2.98	0.02	3.75	9.25	0.02	0.14
Pb	4.19	0.00	0.00	0.00	0.00	34.15	6.05	6.20	0.00	0.00	4.20	62.28	0.00	0.00
Zn	10.38	0.00	8.34	0.00	24.37	0.00	7.98	11.77	0.00	0.00	0.00	0.48	0.00	5.31
Fraction 3	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Cr	1.19	0.05	0.11	0.00	0.05	0.00	0.89	0.10	0.00	0.15	0.09	0.81	0.07	0.12
Fe	0.17	0.14	20.93	8.00	0.04	0.14	0.23	3.21	16.85	3.48	0.03	0.09	8.34	10.09
Pb	0.07	0.00	85.62	0.00	0.00	0.00	0.00	0.00	0.00	14.69	2.93	0.00	0.00	0.00

Zn	47.91	0.00	19.97	26.75	32.42	0.00	9.58	8.07	5.53	11.07	0.00	40.91	0.00	0.81
Fraction 4	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Cr	0.15	0.05	0.00	1.02	0.00	0.06	0.19	0.00	0.08	0.15	0.09	0.00	0.00	0.00
Fe	2.21	2.64	62.11	11.74	49.45	0.52	0.23	5.00	1.52	0.03	0.85	5.56	0.09	2.50
Pb	17.11	0.00	0.00	0.00	0.00	39.40	6.25	5.32	1.46	12.00	3.70	73.04	0.00	0.00
Zn	8.70	0.00	23.13	0.00	50.67	3.85	11.90	0.00	44.26	7.46	0.00	19.12	0.00	3.62
Fraction 5	1	2	3	4	5	6	7	8	9	10	11	12	13	13
Cr	0.43	0.40	0.30	0.44	0.19	0.59	0.55	0.42	0.39	0.37	0.00	0.61	0.33	0.00
Fe	2.03	3.68	7.00	0.54	0.05	1.89	1.34	0.28	88.10	2.64	0.73	4.02	0.02	4.40
Pb	8.13	0.00	68.02	0.00	0.00	0.00	0.00	0.00	0.00	13.82	0.00	70.56	0.00	0.00
Zn	7.47	0.00	10.41	0.00	24.41	0.00	12.21	6.76	13.91	0.00	0.00	23.92	0.00	2.51
Fraction 6 (residual)	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Cr	0.14	0.50	0.52	0.75	0.62	0.71	0.80	0.69	0.73	0.11	0.04	0.55	0.60	0.14
Fe	0.20	0.85	2.43	0.41	0.96	0.39	0.54	0.16	10.16	0.34	0.12	0.23	0.11	0.47
Pb	0.00	0.00	0.00	0.00	0.00	34.37	9.78	2.07	0.38	0.00	2.84	50.91	0.00	0.00
Zn	11.99	0.00	14.25	24.93	30.78	2.00	6.43	0.00	6.82	13.97	0.00	23.02	0.00	0.00

III. CONCLUSION

The susceptibility of toxic heavy metals and trace elements in tailing samples collected from the Krugersdorp mine were examined, in that regard mobility and the bioavailability of toxic metals in tailing dump were determined. The samples were analysed by XRD, XRF and further examined by modified Tessier method of sequential leaching. The mineralogical structure showed that the top and middle layers of the tailing were mostly made of oxide minerals while the bottom layer contained sulphide minerals. Metals of commodity values but also with potential of toxicity were found in the tailing dump irrespective of the layer. It was found that the mineralogical structure of the tailing had a significant impact on the mobility of metals as they were mostly mobile in the top and middle layers, which were made of oxide minerals while they show poor mobility in the samples from the bottom layer made of sulphide minerals. The speciation results have shown that most of metals considered in this study were released in large amount from the mobile fractions such as water soluble, bound to carbonate and bound to organic fractions than from the residual fractions, which indicate that these metals are likely to be mobilized in the environment.

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