

Biological Influence on the Mobility of Metals from Mine Tailing Dump Located in Krugersdorp Area

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Abstract: *Anthropogenic activities such as mining and smelting of metals ores have increased the prevalence of heavy metals which mobility in the tailing dumps or solid wastes is increased following deposition of the later in the environment. In nature, microbes are involved in weathering of rocks, in the mobilization of metals from minerals, in the reduction and oxidation of metals, and in metal precipitation and deposition. A six steps sequential extraction method, according to the 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) a residual fraction. The results showed higher concentrations of heavy metals such as Fe, Pb and Zn, which were dominant in various fractions of the different sampling points (top, middle and bottom of the tailing dump). The DNA sequencing was carried out on tailing samples to identify the microorganisms likely to promote the mobility of metals. Among the host of microorganisms identified, autotrophic species such as *Leptospirillum* sp and *Sulfobacillus*, as well as heterotrophic species such as *Bacillus* sp and *Pseudomonas* sp are those frequently reported in bioleaching processes. The binding groups identified by FTIR attest of the presence of organic matters which are likely to be involved in the entrapment of metals in the organic fraction of the tailing dumps. With most of the metals being attached to the exchangeable and the organic fractions of the tailing dumps, coupled with the presence of active microorganisms, the susceptibility of metal release from the tailings is more probable overtime.*

Keywords: Tailing dumps, sequential leaching, microorganisms, mobility of metals, pollution

1. Introduction

Human activities such as mining, and smelting of metal ores have increased the prevalence and occurrence of heavy metal contamination of the earth's surface [1].

Mining activities usually produce many types of mine wastes, which include mine tailings, waste rock and slag [2]. Mine tailings are finely crushed rock particles and mineral wastes remaining after extraction of valuable components that are produced and deposited in slurry form on tailing dumps [3]. Mine tailings can be referred to as a mine soil. Wastes from gold mines constitute the largest single source of waste and pollution in South Africa as can be seen from the Witwatersrand mining basin, which is the world largest gold and uranium mining area [4]. Wastes generated by the mining industry contain high concentrations of metals and metalloids which can be mobilized, resulting in leaching of such metals into groundwater and surface water. Most of these heavy metals are highly toxic and are not biodegradable [5]. The presence of high concentration of toxic metals make the tailings among other mine wastes the largest environmental impact and the most susceptible to wind dispersal and water erosion, which are the main mechanisms for the loss of metals from mine tailings [6]. The mine wastes contain large amounts (between 10 and 30kg/ton) of sulphide minerals, such as pyrite (FeS₂), which are prone to generate acid mine drainage (AMD). AMD is generated when erosion of poorly managed tailings dumps occurs, and the tailings subsequently washed away by rain water [3]. For example, enormous amounts of mine tailing found in the abandoned mines in the Krugersdorp area have contaminated the soil and groundwater in that area, as such mine wastes have eroded and mobilized to the bottom of the dump and neighboring area. The mine tailing contamination of soil and water might lead to a high level of toxicity from heavy metals such as Zn, As, Pb, Ni, Cr and Cu which are

mostly found in contaminated areas. Arsenic is commonly found in high concentrations in mine tailings because of its natural occurrence in Ag and Au ores and the surrounding bedrock [7]. Some studies have investigated the availability of metals in the soil and tailings; according to the study reported by Wu et al. [8], an estimation of metal availability is more useful, since it is related to specific bioavailability, reactivity and mobility. The mechanisms concerning metal accumulation in soil lead to the existence of five major geochemical forms [8]: (i) exchangeable; (ii) bound to carbonate phase; (iii) bound to iron manganese oxides; (iv) bound to organic matter; and (v) residual metal phase.

Biological influence processes can contribute to a large extent to future technologies which includes mine wastes treatment; in this case the microorganisms are accepted to be the natural way of solving the environmental issues [9]. According to such studies microorganisms can influence the mobility of the metals in the mine waste in several ways [10]. Microorganisms can be able to mobilize metals through autotrophic and heterotrophic leaching, chelation by microbial metabolites and siderophores and methylation, which can result in volatilization [11].

Most naturally occurring bacteria and fungi accomplish numerous physiologically important reactions that enable them to grow and reproduce [12]. Mineralytic effects of bacteria and fungi on minerals are based on four mechanisms namely: (i) acidolysis, (ii) complexolysis, (iii) redoxolysis, and (iv) alkylation [9,12]. Microorganisms are able to mobilize metals through the following processes: Formation of organic and inorganic acids (proton formation), excretion of complexing agents (ligand formation), oxidation and reduction reactions [12]. The organic acids are produced by heterotrophic microorganisms, whereas the inorganic acids are produced by autotrophic organisms. The autotrophic microorganisms

require atmospheric CO₂ as a carbon source and obtain energy for growth from the process of oxidizing ferrous (Fe²⁺) to ferric (Fe³⁺) which creates acidic conditions favorable for metal removal from soil [13]. Autotrophic bacteria can also be called sulphur-oxidizing bacteria, as are capable of oxidizing the metal sulphides to sulphates and thus releasing the metals in cases where respective sulphates are soluble [14]. Those sulphur oxidizing bacteria are considered to be among the most useful microorganisms for the bacterial leaching of sulphide ores [14]. Non sulphidic ores such as oxides, carbonates and silicates which contain no energy source for chemotrophic microorganisms may however be leached by heterotrophic bacteria and fungi, which require an organic carbon source as a source of energy and carbon for their growth [15]. The autotrophic bacteria used in bioleaching process to mobilize metals include *Chemolithotrophic* bacteria of genus *Acidithiobacillus* and *Thiobacillus*, such as *T. ferrooxidans* and *A. thiooxidans* and *thiobacillus thioparus* [16,13]. The *Chemolithotrophic* bacteria are also called the acidophilic bacteria. Heterotrophic bacteria include *Bacillus licheniformis* and *Bacillus polymyxa*, and fungi species such *Aspergillum niger* and *penicillium simplissimum*. Fungi species such as *Penicillium simplissimum* and *Aspergillum niger* are some of eukaryotic bioleaching microorganisms that are applied in metal recovery from the industrial wastes particularly the non sulphides [17,9,12]. The main objectives of this study is to investigate the susceptibility of metals release from tailing dumps with a specific focus on the influence of biological matters on the mobility of metals.

2. Methodology

Materials

Mine tailings were collected from a mine area located in the Krugersdorp, Gauteng, South Africa. The tailings samples were taken from the top 30 cm of the surface at 14 locations spread between the top, the middle and the bottom of the dump, using an auger drill. All samples were air dried in the laboratory for 2 days, sieved through 75 µm of mesh, homogenized before characterization and sequential leaching analysis, the remaining of samples were kept in plastics bags prior to use in the rest of experiment.

Characterization of mine tailings by XRD, XRF and FTIR

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 particle sizes. Non-oriented powders were examined on a Philips X'pert MPD diffractometer, at a power of 1.6 kW 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. For the identification of the functional groups in the tailings and for the evaluation of the surface activation, the FTIR (Fourier transform infrared) spectroscopy was recorded using the IR-Affinity-IS FTIR spectroscopy from Shimadzu. The resolution was set to a 4 cm⁻¹ and the operational range was 4000-400 cm⁻¹.

Sequential leaching

The mobility of metals is strongly dependent on their specific chemical forms and methods of binding [18]. Sequential leaching can provide information about the fractionation of metals in the different lattices of the solid sample [18]. To better understand the transportation and retention mechanism of elements, 14 tailings samples were selected for sequential leaching: 6 samples were collected on top of the tailing dump, 5 in the middle and 2 at 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 Arwidsson and Allard [19]. 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 hydroxysulfates. 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 1600 rpm for 20 minutes. The supernatant was stored for analysis of released 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. Hydrous 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.

DNA sequencing

Fresh samples from the abounded mine in Krugersdorp area was used for DNA sequencing. The samples were divided into 3 according to the site of collection as follows: top, middle and bottom of the dump. Genomic DNA was extracted from 1g of each of the 14 tailings samples using ZR soil microbe DNA Mini Prep Kit™ according to the manufacturer's instruction. DNA concentrations were determined spectrometrically with a Nano-Drop spectrophotometer (Thermo scientific). Then extracted DNA samples were sent to a commercial biotechnical laboratory for sequencing using Next Generation Sequencing (NGS)

Determination of Organic Carbon

- 1) The organic carbon in the tailings was determined by the use of the Walkley-Black chromic acid wet oxidation method. The moisture content of the air-dry tailings which has been ground to pass a 75 µm sieve was determined. A mass of 2 g of tailing was weighed accurately into a dry tared 250 mL conical flask to determine the organic carbon content.
- 2) 10 mL of 1 N K₂Cr₂O₇ was accurately added and the flask swirled gently to disperse the soil in the solution. 20 mL concentrated H₂SO₄ was added, directing the stream into the suspension. The flask was swirled immediately until the tailing and the reagent were mixed. A thermometer was inserted in the flask which was heated on a hot plate while swirling the flask and the contents, until the temperature reached 135 °C.
- 3) To cool the flask slowly, it was set aside in a fume cupboard. Two blanks (without soil) were run in the same way to standardize the FeSO₄ solution.
- 4) When cooling the mixture in the flask (for 20 minutes), it was diluted to 200 mL with deionized water and

preceded with the FeSO₄ titration using a "ferroin" indicator. The ferroin titration was conducted as follows:

"Ferroin" Titration

3 or 4 drops of Ferroin indicator was added and titrated with 0.4 N FeSO₄. As the end point approached, the solution took on a greenish colour and then changed to a dark green. At this point, the ferrous sulphate was added drop-by-drop until the colour changed sharply from blue-green to reddish-grey. When the end point was overshoot, 0.5 or 1.0 mL of 1 N K₂Cr₂O₇ was added and the end point was re-approached drop-by-drop. For the extra volume added, it was corrected for. When over 8 mL of the 10 mL dichromate was consumed, the determination was repeated with a smaller tailing sample.

3. Results and Discussion

Characterization of mine 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 the Krugersdorp mining area was determined by X-ray diffraction (XRD). The XRD pattern showed the dominance of quartz (SiO₂) minerals in the top and middle of the tailing dump, while other minerals, such as iron catena-silicate & ferrosilite, sillimanite, and aluminium iron (III) oxide were only detected in high concentration in few samples. A similar trend about the dominance of quartz in the tailings was reported in the study by Novhe et al.[20].

Table 1: 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	79	85	92.3			97	73.2	91	-	-
Iron catena-silicate, ferrosilite	-	96	-	-	-	-	-	-	-	-	-	-	-	-
Aluminium iron(III) oxide	-	-	-	-	-	-	-	60	-	-	-	-	-	-
Sillimanite	-	-	-	-	-	-	-	-	-	-	-	-	85	-
Dialuminum silicate oxide, kyanite	-	-	95	-	-	-	-	-	-	-	-	-	-	-
Dicalcium silicate	-	-	-	-	-	-	-	-	-	-	-	-	-	87

XRF

The major, minor and trace elements were determined by using XRF analysis, represented in Table 2. SiO₂ is the dominant oxide in all samples collected from the Krugersdorp mining area, which ranges from 40.49% to 89.15%. This confirms the result obtained using the XRD technique. SiO₂ was also found by others to have dominion over other oxides in mine tailings [20]. 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 almost all the samples and were therefore considered as main focus in the rest of the study.

Table 2: Major and trace elements in tailing samples

Samples	Mass %				
	Cr ₂ O ₃	Fe ₂ O ₃	PbO	ZnO	SiO ₂
1	0.1	7.08	0	0.01	69.7
2	0.05	2.68	0.02	0	81.4
3	0.08	3.03	0	0	78.1
4	0.07	1.79	0	0.01	80.7
5	0.08	2.9	0.01	0.01	78
6	0.06	2.7	0.07	0.01	78.6
7	0.11	1.89	0.02	0.01	86.5
8	0.11	5.58	0.03	0.01	72.8
9	0.08	38.2	0.33	0.03	40.5
10	0.06	6.18	0.21	0.01	69.7
11	0.02	10.5	0.04	0	70.2
12	0.07	6.76	0	0.01	75.3
13	0.05	1	0	0	89.2
14	0.07	7.24	0	0.1	42

FTIR

The FTIR results for the samples taken at the top of the dump (S1-S7), middle (S8-S12) and bottom of the tailing dump (S13-S14) are shown in Figure 1A, B and C respectively. Generally, the spectra which depict the top and the middle of the dump were very similar and exhibited same peak pattern. However most samples from the top of the dump do not show the broad peak identified in the samples from the middle of the dump, which is about 2400cm^{-1} due to stretching hydrogen bonded OH group. Samples from the middle of the dump also exhibit a peak which range between 1609.85 and 1424.70cm^{-1} which corresponds to the H-CH bond, as well as a peak in the range $1124-1000\text{cm}^{-1}$, which is attributed to C-O stretching, i.e esters and ethers. Samples from the bottom of the dump reveal peaks at $3029.03-2917.65\text{cm}^{-1}$, $2393.33-2240.33\text{cm}^{-1}$ and $1083.31-1014.25\text{cm}^{-1}$, which are attributed to H-C-H asymmetric and symmetric/ H-C-H asymmetric stretching, C=H-H asymmetric, C=N and C-O stretching. All the

groups identified on the spectra are able to bind to metals. The organic matters normally are likely to complex as a ligand and release the metals. In that regard Brandl and Faramarzi, [9] have explained the mechanism of complexolysis (ligand-induced metal solubilization) in which the microbial formation of complexing or chelating agents leads to an increase of metal mobility, these complexes are formed on the metal surfaces by ligand exchange polarizing bonds and facilitating the detachment of metals from the surface. Although these metals can mobilize or release metals from tailings, the availability of metals in solution can be affected by the binding group identified by FTIR, all the C2 report can bind to the metals and prevent the release of metals. The groups observed by FTIR analysis are similar to the groups causing metal mobility as reported by Brandl and Faramarzi[9], namely carboxyl, sulfonate, phosphate, hydroxylamino or imino residues.

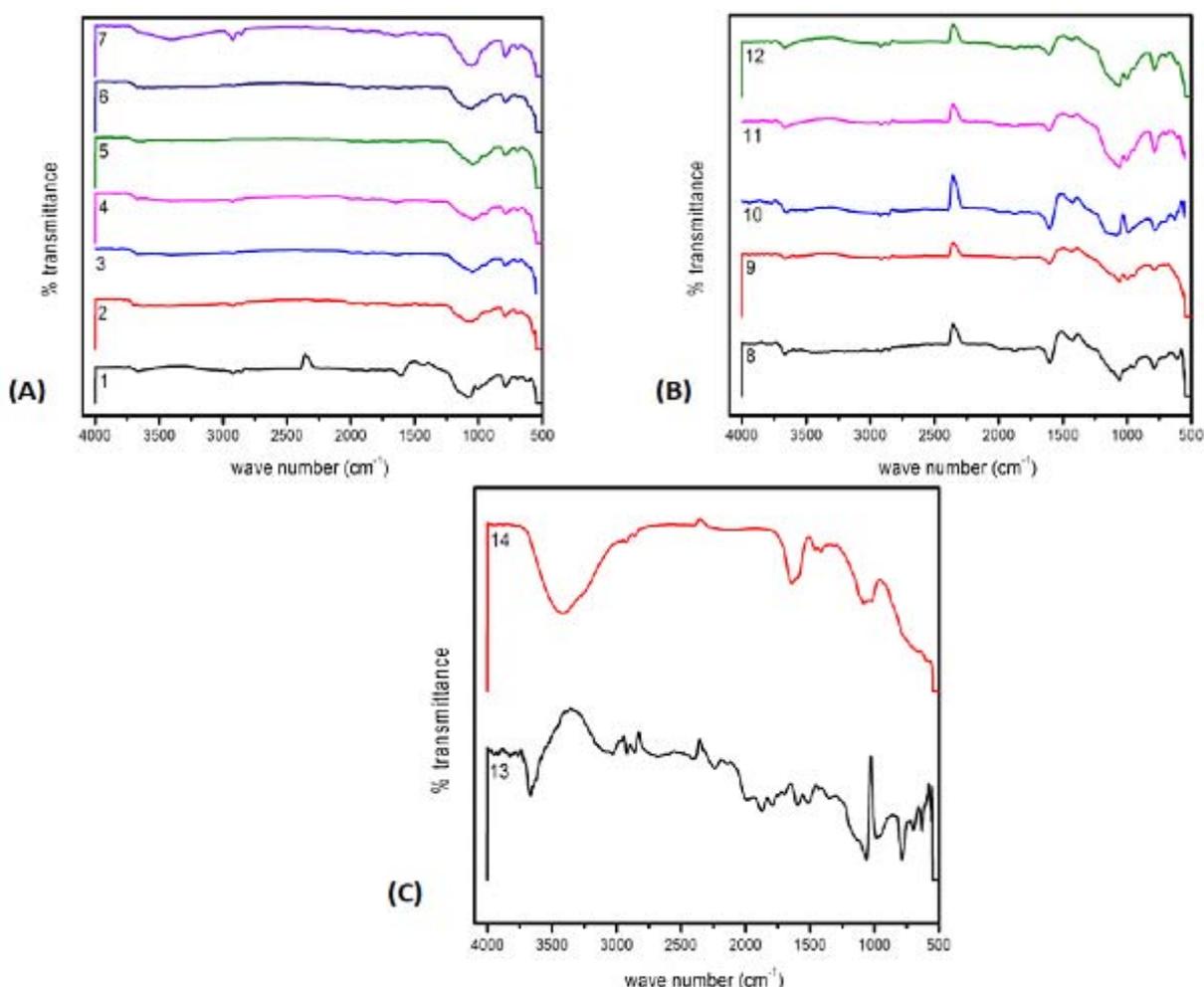


Figure 1: FTIR spectra of (A) top samples 1-7, (B) middle samples 8-12 and (C) bottom samples 13-14 of the tailing dump

Microorganisms in the tailing dumps

In the DNA sequencing results shown in Table 3, the acidophile bacteria of genus *Leptospirillum ferroxidans* where found in all the three sampling sites and represented 0.14%, 0.36% and 0.01% of all the microorganisms in samples from the top, middle and bottom of the dump, respectively. The acidophile bacteria of genus *Sulfobacillus* sp was also found in the middle of tailing dumps. According to the literature these microorganisms

often occur in dumps of mine waste rock and tailings from sulfide ore processing plants. Acidophilic iron(II)- and sulfur-oxidizing bacteria are responsible for the release of sulfuric acid which are able to promote the release of metals from the tailing dumps [21]. Heterotrophic bacteria were represented by *Bacillus* sp and *Pseudomonas* sp which are among the bacteria species most likely to degrade the organic matter to form organic acids; these species were found at all the sampling sites.

Table 3: Selected species from blast output results

Sampling Site	Autotrophic bacteria		Heterotrophic bacteria	
	Species	%	Species	%
Top	<i>Leptospirillum</i>	0.14	<i>Bacillus</i>	1.6
			<i>Pseudomonas</i>	1.91
Middle	<i>Leptospirillum</i>	0.36	<i>Bacillus</i>	1.33
	<i>Sulfobacillus</i>	0.1	<i>Pseudomonas</i>	1.1
Bottom	<i>Leptospirillum</i>	0.01	<i>Bacillus</i>	0.06
			<i>Pseudomonas</i>	1.22

Mobility of metals

The results obtained in the various steps of the fractionation technique are shown in Table 4. In the water soluble fraction (F1), Zn is the most abundant metal and ranges between 0-60.7% for samples taken from the top of tailing dump (S1, S2, S3, S4, S5, S6, S7), whilst it ranges between 0 to 62.5% for the sample taken from the middle of the dump (S8, S9, S10, S11, S12) and it shows a low percentage for samples collected from the bottom of the dump, in the range between 0-2.7%. The abundance of Zinc in the residual fraction (F6) ranges from 0 to 30.8% for the tailing samples collected from the top of the tailing dump and for sample taken from the bottom of the dump it ranges 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 is much likely to occur in the exchangeable 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 [22]. This fraction consists of elements that are easily soluble, e.g. as chlorides and sulphates [22]. 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 [22].

The highest recovery of Pb bound to the carbonate fraction (F3), was 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 and the other four fractions in which its concentration ranged from 0 to 34.37%. Pb in the fraction collected at the top of the tailing dump has a relatively higher mobility and potential bioavailability than the residual fraction and the other phases (F4 and F5). The reducible or bound to organic fraction has a higher

concentration of Pb than the other geochemical phases, which means that Pb is less likely to be release under environmental conditions. According to the XRF results there was no Pb in the samples collected at the bottom of the dump, which explains why no recovery was achieved through sequential leaching.

Fe was mainly recovered at the bound to organic fraction for the sample taken from the middle of the dump, ranging from 0 to 88%. In this fraction the Fe recovery % is higher than in the residual and all other fraction for samples collected from the same site, which means that this metal is mostly located in the organic fraction. Metals present in the residual fraction are a measure of the degree of environmental pollution[23]. The higher the metals present in the residual fraction, the lower the degree of pollution [23].

Fe is more abundant if bound to a carbonate fraction (F3) and for the sample found at the top of the dump the Fe recovery % is higher than in the other fractions for the samples collected from the same site. The Fe recovery % is high for samples taken from the bottom of the dump in the fraction bound to a carbonate, and ranged from 8.34 to 10.09%. The recovery % of Cr is relatively low in all fractions, however the water soluble fraction (F1), exhibits a high concentration for the 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, considering samples collected from the same site. For the samples collected in the middle of the tailing dump Zn was the metal 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 sites, which 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 (weathering)of the top surface of the tailing which is more exposed to atmospheric conditions contributes to increase the mobility of metals.

Table 4: 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	0.4	1.04	1.58	0	0.19	0.22	0.54	7.23	2.76	0	0.45	0.98	0.08
Fe	0.2	5.15	7.17	0.07	0.34	0.1	0	2.62	20.37	0.08	0.01	0.1	0.02	0.06
Pb	3.59	0	27.5	0	0	19.91	6.85	0.93	0	4.1	0.84	0	0	0
Zn	60.7	0	17.14	57.18	36.7	13.37	18.35	22.77	30.81	62.51	0	57.44	0	2.65
Fraction 2	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Cr	0.34	0	0	0.05	0.33	0	0.46	0.03	0.1	0.12	0.06	0	0	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	0	0	0	34.15	6.05	6.2	0	0	4.2	62.28	0	0
Zn	10.38	0	8.34	0	24.37	0	7.98	11.77	0	0	0	0.48	0	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	0.05	0	0.89	0.1	0	0.15	0.09	0.81	0.07	0.12
Fe	0.17	0.14	20.93	8	0.04	0.14	0.23	3.21	16.85	3.48	0.03	0.09	8.34	10.09
Pb	0.07	0	85.62	0	0	0	0	0	0	14.69	2.93	0	0	0
Zn	47.91	0	19.97	26.75	32.42	0	9.58	8.07	5.53	11.07	0	40.91	0	0.81
Fraction 4	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Cr	0.15	0.05	0	1.02	0	0.06	0.19	0	0.08	0.15	0.09	0	0	0
Fe	2.21	2.64	62.11	11.74	49.45	0.52	0.23	5	1.52	0.03	0.85	5.56	0.09	2.5
Pb	17.11	0	0	0	0	39.4	6.25	5.32	1.46	12	3.7	73.04	0	0
Zn	8.7	0	23.13	0	50.67	3.85	11.9	0	44.26	7.46	0	19.12	0	3.62
Fraction 5	1	2	3	4	5	6	7	8	9	10	11	12	13	13
Cr	0.43	0.4	0.3	0.44	0.19	0.59	0.55	0.42	0.39	0.37	0	0.61	0.33	0
Fe	2.03	3.68	7	0.54	0.05	1.89	1.34	0.28	88.1	2.64	0.73	4.02	0.02	4.4
Pb	8.13	0	68.02	0	0	0	0	0	0	13.82	0	70.56	0	0
Zn	7.47	0	10.41	0	24.41	0	12.21	6.76	13.91	0	0	23.92	0	2.51
Fraction 6	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Cr	0.14	0.5	0.52	0.75	0.62	0.71	0.8	0.69	0.73	0.11	0.04	0.55	0.6	0.14
Fe	0.2	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	0	0	0	0	34.37	9.78	2.07	0.38	0	2.84	50.91	0	0
Zn	11.99	0	14.25	24.93	30.78	2	6.43	0	6.82	13.97	0	23.02	0	0

Organic carbon (OC) content

The organic carbon results are summarized in Table 5. Organic carbon was present in all samples, i.e. collected on the top of the tailing dump (S1, S2, S3, S4, S5, S6, and S7); in the middle of the dump (S8, S9, S10, S11 and S12) and also at the bottom of the tailing dump (S13 and S14). The top and the middle of the tailing dump contained OC in the range of 0.06% to 1.44% while the bottom of the tailing dump exhibited a relatively lower concentration of OC in the range of 0.09% to 0.18%. However the organic carbon was mainly found in sample S7 which is the sample collected at the top of the dump and S12 which taken at the middle of the dump. The organic carbon acts as the source of nutrients for microorganisms [24], so the presence of organic carbon in all three sampling sites may contribute to the mobility and/or bioavailability of metals, as the microorganisms are capable of degrading the organic carbon to form organic acids which promote the dissolution of metals from tailing dumps[25].

Table 5: Organic carbon (OC), top of the dump (S1-S7), middle of the dump (S8-S12) and bottom of the dump (S13-S14)

Samples site	OC (%)
1	0.19
2	0.2
3	0.06
4	0.09
5	0.06
6	0.06
7	1.44
8	0.13
9	0.09
10	0.08
11	0.06
12	1.44
13	0.09
14	0.18

4. Conclusion

The mineralogical structure showed that the top and middle layers of the tailing were mostly made up 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 tailings had a significant impact on the mobility of the 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 up 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, carbonate fraction and organic fractions than from the residual fractions, which indicate that these metals are likely to be mobilized in the environment. Autotrophic and heterotrophic microorganisms identified in the tailing dumps have the potential to mobilise metals through mechanisms such as acidolysis or complexolysis; considerable amount of organic carbon was measured in the tailings which can sustain the growth of heterotrophic microorganisms while forming organic acids as byproducts. Binding groups such as H-C-H, C=H-H, C≡N and C-O found in the tailings are likely to be involved in the entrapment of metals in the organic fraction. The susceptibility of metal release from the tailing dumps is therefore likely to be stimulated by chemical and biological mechanisms that can occur naturally in the environment.

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