

# Bioavailability of Metals from Mine Impacted Soils along AMD Receiving Stream in Mpumalanga Province, South Africa

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**Abstract**—The biological availability of metals from three soil samples collected near a mining area in Mpumalanga Province, South Africa was studied using sequential leaching. Data were collected according to the standard sequential extraction procedure.

The X-ray fluorescence, scanning electron microscopy and atomic absorption spectrometer were used to investigate metal deportation in the solid matrix as well as the solution generated at different steps of the sequential leaching.

The morphologic analysis revealed that larger particle of contaminants, captured contaminants, and are subject to incasement. While the sequential leaching showed that most of the metals were from the exchangeable fraction implying that they are more prone to bioavailability and release in the environment

**Keywords**—About four key words or phrases in alphabetical order, separated by commas.

## I. INTRODUCTION

Mining activities around the world were reported to produce at least 3500 tonnes of tailing storage facilities in 2012. These tailings are often loaded with relatively large amount of residual metals that could be released into the environment upon weathering of the tailing. The possible release of these metals into the environment poses a considerable risk for the aquatic life and degradation of agricultural lands [1-5]. A study by Kim et al. [6] reported that industrial activities contributed to the contamination of agricultural lands around fifteen industrial complexes by Zn, Cu and Pb. The uptake of metals by plants can affect their development as well as the contamination of foods resulting in intoxication of human. Metal distribution in soils has been the subject of many studies and it has been observed that they often partition between the oxides, carbonates, sulphides and hydroxides on the soil [7]. The physico-chemical forms in which metals are partitioned is a determining factor in their distribution, mobility, and bioavailability in the environment. The European Communities of Bureau References (BCR) developed a four-stage sequential extraction procedure which has been successfully used by researchers to determine the partitioning of metals in the soils [8]. The objectives of this study were to determine the impact of acid mine drainage generated from a coal mine on the contamination of soils downstream.

The study was carried out near a coal mine in the province of Mpumalanga which is located in the Eastern part of South Africa.

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Most of the mining companies in the province mine coal, contributing to about 60% of the whole production in the country. Mining activities have resulted in the deposition of mountains of tailings in the area and subsequently production of acid mine drainage. The impact on the environment is therefore obvious, but should be assessed and documented accordingly.

## II. METHODOLOGY

### A. Soil sample preparation

Three different samples were collected from different areas around the dam as follows: one was before the dam, after the dam and on the zoom dam. These sample were analysed using the XRF and were having the characteristic displayed in table and the morphology in Figure 1.

### B. Characterisation procedure

Extracted and digested liquor generated during the investigation were analyzed using atomic spectrometry, Thermo Scientific™ iCE™ 3300 AAS Atomic Absorption Spectrometer. Before the analysis of the analytes, corresponding standards were prepared for elements found after XRF analysis while using single-element standards.

The XRF analysis was performed to determine the chemical composition of the solid samples at different condition using Rigaku ZSX Primus II with SQX analysis software. 10 g of a well-pulverized sample was mixed with the Sasol wax and poured into an aluminum cup. All mixture was pressed into a pellet using a dill under the pressure of 15ton and oven dried to about 50 °C for 30min before analysis to remove all moisture and loaded in the spectrometer for element determination. Data was collected through the EZ-Scan interface while the sample was scanned under vacuum using P10 gas.

Scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDS) analysis was performed to determine the phase distribution using the TESCAN instrument type Vega 3X having a tungsten filament as an electron source of energy. The sample was mounted in the polish section in resin and then coated with the carbon layer to promote conductivity. The analysis was performed using the secondary or backscatter detectors at a voltage of 20 kV. Images were collected at different magnifications using Vega

software to allow the visualization of phase mineral distribution in the bulk sample. The analysis was performed gradually on the sample generated from the raw to the optimum to observe the changes. The energy-dispersive X-ray spectroscopy (EDS) analysis was used to determine the chemical composition of target spots based on the difference in contrast while the mapping will be performed using INCA software from Oxford.

### C. Reagents

High-grade reagents provided by Merck were used during the experiment. Here is the list of different reagents used during the investigation: Nitric and acetic acids, Hydrogen peroxide, Ammonium acetate, and hydroxylammonium chloride. Calibrant solutions selected based on identified elements from the XRF were prepared by dilution of 1000 ppm in the corresponding series.

### D.3.4 Sequential Extraction Procedures

The sequential extraction method applied in the current investigation was performed in four different steps to evaluate in which way different metals and metalloids are associated in the collected soils from different sites on the abord of a dam. The following steps were applied.

The first step consisted of the evaluation of possible exchangeable metals in the selected soil. Therefore, about 200 mL of acetic acid of 0.11 M was prepared and added to 10 g of dry sample. The pulp was placed on the magnetic stirrer at a speed of 250 rpm for 16 h while leaching at a temperature of 25°C. After the required dissolution time was riched, the solution was separated from the residues. The leachate was collected and analyzed using the AAS. It should be noted that the residues were further washed with deionized water up to the equilibrium of the pH (equal to the water pH). Only the solution from the immediate dissolution was considered while the other generated after further washing was discarded. Care should be taken during the solid/liquid separation to avoid loss of material.

The second step refers to the determination of the metals bound to iron and manganese oxides. To investigate this, 200 mL of a freshly prepared solution of 0.1 M of hydroxyl ammonium chloride (NH<sub>2</sub>OH.HCl) was added to the residue generated from the first leaching step. Before performing the leaching, the pH of the pulp was adjusted to 2 using diluted nitric acid. The mixture was agitated at a speed of 250 rpm using the magnetic stirrer for a duration of 16 h at a temperature of 25°C. After the time was riched, the residues were separated and washed with deionized water to the water equilibrium pH. The solution was collected and analyzed using the AAS.

The third step consisted of the evaluation of metals bound to organic matter and sulfides. In this stage, 200 mL of 8.8 M hydrogen peroxide was added to the residues from the second step while adjusting the pH in the range of 2-3. The mixture was first digested for 1 h at 25°C, thereafter at 85°C for 30 min using a shaker water bath. The solution was collected for

analysis, while the residues were washed, dried, cooled and subjected to further leaching in the presence of 200 mL of 1.0 M ammonium acetate. The pulp pH was adjusted to 2 by adding HNO<sub>3</sub> and stirring for 16 h at 25°C at 250 rpm. After completing the required time, the liquor was collected and separated from the solid phase and analyzed using AAS.

The fourth step consisted of digesting residues from step three using aqua regia (HNO<sub>3</sub> + 3HCl) to evaluate insoluble metals in the previous steps. Therefore, 200 mL aqua regia solution was added to residues while leaching at 60°C for 8 hours. After leaching, the solution was collected and analyzed using the AAS. The remaining residues were water-washed and subjected to XRF analysis and SEM analysis.

It should be noted that during the investigation elements such as Ca, Co, Cr, Cu, Fe, K, Mg, Mn, Na and Zn were selected based on the XRF results.

## III. RESULTS AND DISCUSSIONS

### A. Characterization of the as-received samples

The X-ray fluorescence, scanning electron microscopy and atomic absorption spectrometer were used to investigate metal deportation in the solid matrix as well as the solution generated at different steps of the sequential leaching (Table 1).

The morphologic analysis revealed that larger particle of contaminants, captured contaminants, and are subject to incasement (Figure 1 and Figure 3).

### B. Mobility of metals

The collected samples from the mining area content relatively high amount of metals due to contamination by mining effluents (Table 1 and Table 2).

The metals were mostly recovered from the exchangeable fraction (Figure 2). Metals such as Ca, Mn and Na were the most labile in all the samples. The bioavailability of these metals from soil samples collected near a dam in a mining area increase in the following order: Ca>Mn>Na. The variety of metals recovered decreased from the following order in the various fraction: Exchangeable fraction>oxidizable fraction>reducible fraction>residual fraction. Implying that most metals were likely to be mobilized under relatively soft conditions.

Table 1: chemical composition of the as received samples

	Na <sub>2</sub> O	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	SO <sub>3</sub>	Cl	K <sub>2</sub> O	CaO	TiO <sub>2</sub>	V <sub>2</sub> O <sub>5</sub>	Cr <sub>2</sub> O <sub>3</sub>	MnO	Fe <sub>2</sub> O <sub>3</sub>	ZnO	Rb <sub>2</sub> O	SrO	ZrO <sub>2</sub>
After dum	0,04	0,16	0,71	3,45	0,07	7,39	0,01	0,19	1,17	0,08	0,04	0,07	0,02	86,58	0,00	0,00	0,01	0,02
Zoom dum	0,04	0,18	8,60	23,79	0,12	5,59	0,02	1,02	0,32	0,78	0,05	0,13	0,05	59,11	0,02	0,02	0,04	0,11
Nex dum	0,11	0,09	3,22	7,29	0,06	9,70	0,02	0,72	0,55	0,24	0,04	0,06	0,03	77,80	0,00	0,00	0,04	0,03

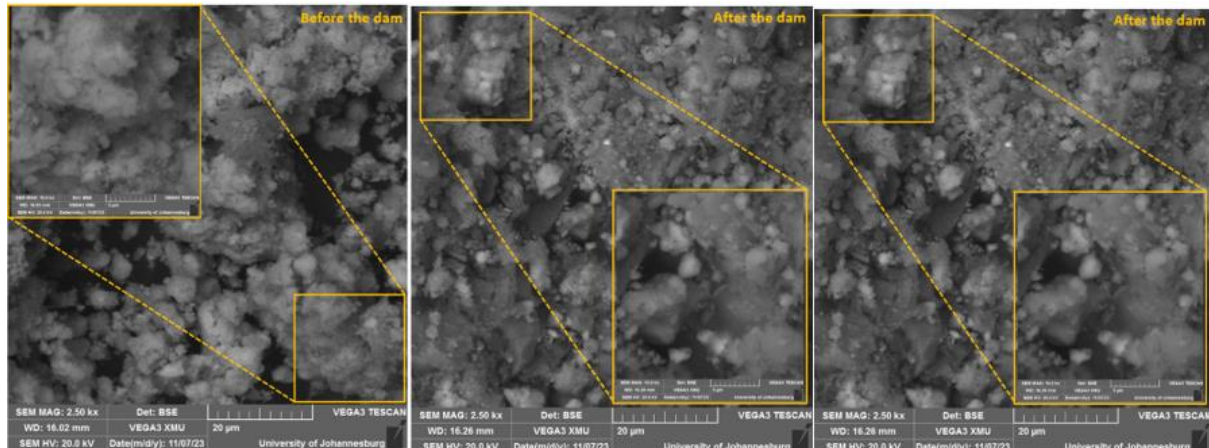


Figure 1: SEM of the as-received samples

Table 2: Comparison of the chemical composition of the sample before and after sequential extraction

	As received sample			Residue After SEP		
	After dum	Zoom dum	Nex dum	residue After dum	Resudue Zoom dum	Resudue Nex dum
Na <sub>2</sub> O	0,039	0,042	0,111	0,000	0,072	0,018
MgO	0,157	0,177	0,093	0,000	5,894	0,197
Al <sub>2</sub> O <sub>3</sub>	0,708	8,602	3,224	0,347	40,247	2,065
SiO <sub>2</sub>	3,448	23,788	7,293	13,637	0,077	26,712
P <sub>2</sub> O <sub>5</sub>	0,073	0,121	0,063	0,046	1,117	0,076
SO <sub>3</sub>	7,391	5,591	9,698	0,824	4,452	2,075
Cl	0,013	0,024	0,016	3,640	1,698	5,263
K <sub>2</sub> O	0,188	1,016	0,723	0,232	0,133	1,158
CaO	1,169	0,323	0,547	0,083	1,946	0,178
TiO <sub>2</sub>	0,076	0,777	0,241	0,354	0,337	1,157
V <sub>2</sub> O <sub>5</sub>	0,037	0,055	0,035	0,000	0,000	0,000
Cr <sub>2</sub> O <sub>3</sub>	0,071	0,130	0,060	0,110	0,062	0,371
MnO	0,019	0,049	0,029	0,000	43,220	0,000
Fe <sub>2</sub> O <sub>3</sub>	86,583	59,108	77,799	80,238	0,000	60,104
Co <sub>2</sub> O <sub>3</sub>	0,000	0,000	0,000	0,000	0,051	0,000
ZnO	0,000	0,022	0,000	0,000	0,065	0,051
Rb <sub>2</sub> O	0,000	0,019	0,000	0,000	0,000	0,000
Br	0,000	0,000	0,000	0,053	0,052	0,090
Rb <sub>2</sub> O	0,000	0,000	0,000	0,000	0,139	0,059
SrO	0,010	0,045	0,042	0,054	0,440	0,152
ZrO <sub>2</sub>	0,019	0,111	0,026	0,384	0,000	0,277

Table 3: Dissolved fraction of different element after sequential extraction procedure in different medium in %

	Acetic acid									
	Ca	Co	Cr	Cu	Fe	K	Mg	Mn	Na	Zn
Nex dum	1,504	0,006	0,000	0,003	0,000	0,002	0,519	0,254	0,204	0,019
After dum	0,192	0,002	0,000	0,001	0,002	0,012	0,311	0,445	0,555	0,005
Zoom dum	1,864	0,003	0,002	0,000	0,003	0,006	0,248	0,130	0,593	0,016
	Hydroxyl ammonium chloride									
	Ca	Co	Cr	Cu	Fe	K	Mg	Mn	Na	Zn
Nex dum	0,011	0,000	0,000	0,000	0,006	0,026	0,013	0,000	0,274	0,000
After dum	0,007	0,000	0,000	0,000	0,011	0,057	0,014	0,008	0,609	0,000
Zoom dum	0,020	0,000	0,000	0,000	0,012	0,008	0,026	0,008	0,530	0,002
	Hydrogen peroxide									
	Ca	Co	Cr	Cu	Fe	K	Mg	Mn	Na	Zn
Nex dum	0,003	0,000	0,000	0,006	0,001	0,011	0,004	0,000	0,269	0,003
After dum	0,002	0,000	0,005	0,006	0,002	0,033	0,003	0,000	0,728	0,005
Zoom dum	0,011	0,000	0,000	0,019	0,002	0,007	0,004	0,000	0,709	0,012
	Ammonium acetate									
	Ca	Co	Cr	Cu	Fe	K	Mg	Mn	Na	Zn
Nex dum	0,002	0,000	0,002	0,072	0,016	0,012	0,025	0,000	0,212	0,031
After dum	0,001	0,000	0,005	0,023	0,029	0,046	0,013	0,005	0,611	0,000
Zoom dum	0,004	0,000	0,001	0,018	0,028	0,004	0,013	0,000	1,045	0,000
	Aqua regia									
	Ca	Co	Cr	Cu	Fe	K	Mg	Mn	Na	Zn
Nex dum	0,024	0,003	0,008	0,120	0,170	0,206	0,030	0,052	8,374	0,079
After dum	0,012	0,000	0,009	0,045	0,059	0,236	0,016	0,057	0,952	0,004
Zoom dum	0,078	0,002	0,004	0,099	0,282	0,032	0,012	0,019	0,842	0,062

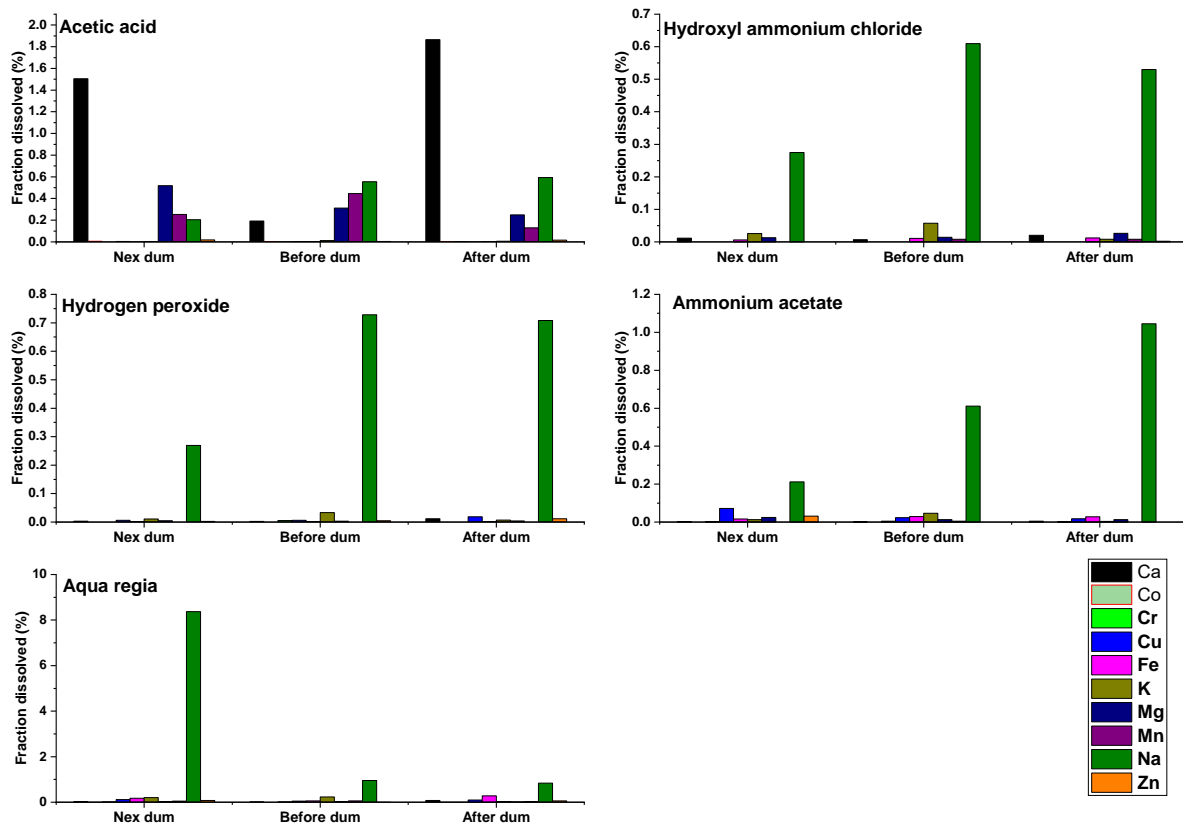


Figure 2: Dissolved fraction of different element after sequential extraction procedure in different medium

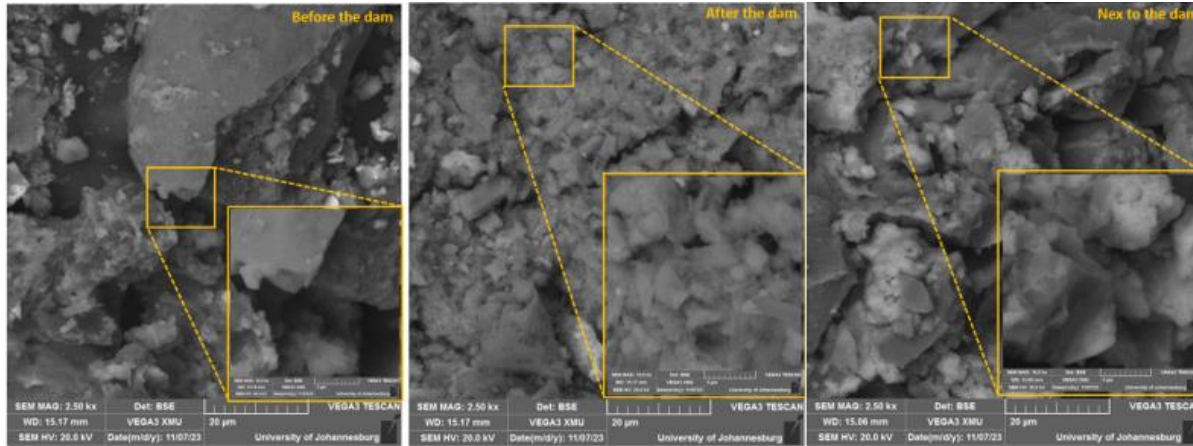


Figure 3: SEM of the final residues after sequential extraction process

#### IV. CONCLUSION

The release of untreated mine water in the environment results in the contamination of soils which accumulate large amount of metals. The bioavailability of such metals from the soils near a mining area has been demonstrated in this study. These metals are likely to be released spontaneously and seriously impair the nearby aquatic life.

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