Study of Metal Speciation During the Sequential Leaching of Mining Impacted Soil from Mpumalanga

Ayanda Zangarico, Edward Malenga, Elvis Fosso-Kankeu and Antoine F. Mulaba-Bafubiandi

***Abstract*— This study examines the bioavailability and mobility of metals in mining-affected soil along a stream in Mpumalanga, South Africa. Utilizing sequential extraction techniques and geochemical modeling with PHREEQC, the researchers analyzed soil samples for various metals, including zinc, nickel, manganese, copper, and iron. The five-step sequential extraction process categorized metals into different phases: water soluble, exchangeable, carbonate-bound, oxide-bound, and residual. Atomic Absorption Spectroscopy (AAS) quantified metal concentrations, while PHREEQC provided insights into metal speciation, pH dependent solubility, and mineral saturation.**

The results showed variable mobility and bioavailability of metals, with zinc exhibiting limited mobility and nickel showing a higher potential for environmental impact, particularly in the oxide-bound fraction. Iron had the highest recovery values in the oxide-bound fraction, indicating significant implications for ecosystem health. The study found that pH levels greatly affect metal solubility, with lower pH generally increasing bioavailability. Saturation indices from PHREEQC offered insights into mineral stability, guiding potential remediation strategies.

This research enhances the understanding of metal behavior in mining-impacted soils and provides essential data for developing effective environmental management strategies in Mpumalanga, emphasizing the importance of metal speciation in risk assessment and remediation efforts.

***Keywords*— Mining impacted soils, sequential leaching, metals speciation, bioavailability.**

I. Introduction

Coal mining is the main industry in Mpumalanga and drives the regional economy. However, the ecosystem is also harmed by these activities, especially when they contaminate the soil with heavy metals and other toxic metals It is crucial to identify the types and sources of metal pollution in mining-damaged soils to properly evaluate environmental issues and put remediation plans into action [1].

By releasing metals into the environment through processes like runoff into surface water bodies, soil erosion, and leaching from mine wastes, mining operations can have a major negative influence on the ecosystem. These metals build up in soil and can harm ecosystems and human health, among other things, through plant absorption and groundwater contamination. The different chemical forms that metals take in the environment and how those forms affect their mobility, toxicity, and bioavailability [2]. These metals can be found in soil in fractions such as water-soluble, exchangeable, carbonate-bound, organic-bound, and mineral-bound forms. Their mobility and environmental consequences vary [3].

By using Geochemical speciation of metals (PHREEQC) for metal speciation analysis to understand the distribution and behavior of metals in soil, one can more easily identify potential exposure routes and sources of pollution. Sequential leaching is a method used to extract metals from soil by subjecting samples to a variety of chemical solutions that mimic different environmental conditions. Through their extraction and quantification, this approach offers information on the speciation and environmental fate of different metal components It is essential to comprehend the mechanism by which successive leaching results in metal speciation to create evidence-based environmental management strategies.

Problem statement: The leaching of metals from mine wastes, tailings, and polluted soils into groundwater and surface water bodies is a long-term environmental challenge, despite developments in mining methods [4-7]. Metals are mobilized by this leaching process in a variety of chemical forms, which poses serious hazards to ecosystem health and human well-being. However, there is a lack of comprehensive understanding regarding the mechanisms driving metal leaching, the factors influencing the speciation of metals, and the subsequent pathways of metal transport and transformation in aquatic environments [8].

The aim of this study is to investigate the bioavailability and mobility of metals in mining impacted soil along a stream in Mpumalanga.

II. Methodology

A. Samples collection and characterization

The samples were collected from Boesmansspuit stream and Adjoining stream in Mpumalanga. Grab sampling was used to collect the sediments, the area is affected by acid-mine drainage.3 samples were used to run the experiment. Each sample was characterized by X-ray fluorescence (XRF), to identify and quantify the presence of elements. (XRD) X-ray

Ayanda Zangarico[1], Department of Metallurgy at the University of Johannesburg, South Africa

Edward Malenga[2], Department of Metallurgy at the University of Johannesburg in South Africa

Elvis Fosso-Kankeu[3], Department of Metallurgy at the University of Johannesburg, South Africa.

Antoine F. Mulaba-Bafubiandi[4], Department of Metallurgy at the University of Johannesburg, South Africa

https://doi.org/10.17758/URUAE24.UR1224106

Diffraction used to determine the crystalline structure of materials. (SEM) Scanning Electron Microscopy provides high-resolution images of sample surfaces by scanning them with a focused beam of electrons. (FTIR) Fourier Transform Infrared Spectroscopy used to identify molecular structures.

B. Sequential leaching

100 grams was used for sequential leaching and 300ml of solution was used for each fraction reagent. All 3 samples were washed with De-ionized water to get soluble components when subjected to rainwater (Fraction 0). Tessiers standard methodology was followed for sequential extraction from fraction 1 to 5. Before proceeding to the next fraction, the sample was washed with water for 20 minutes to remove residual solution on the sample. Fraction 1 Exchangeable Fraction: Metals that are loosely bound to the soil particles 1 molar Magnesium Chloride ($MgCl_2$) pH 7 was used. Carbonate-Bound Fraction: Metals that are associated with carbonate minerals. These can be released under acidic conditions. 1 molar of NaAc (Sodium acetate) pH 5 was used. Iron and Manganese Oxide-Bound Fraction: Metals that are associated with oxides and hydroxides of iron and manganese. This fraction reflects the potential for metals to be mobilized in reducing conditions. 1 molar Ammonia-Nitric acid ratio 3-:1 pH 2 was used for this fraction. Organic Matter-Bound Fraction: Metals that are complex with organic matter, which can influence their bioavailability and mobility. Hydrogen peroxide (H_2O_2 pH 2 was used for this fraction to extract organic bounded natter. Residual Fraction: Metals that are strongly bound within the mineral matrix and are generally considered non-bioavailable. This fraction represents the metal content that is least likely to pose immediate environmental risks. Aqua-regia of HCl-HNO_3 was used for this fraction. In all leaching fractions time and temperature were constant being 16 hours and 25oC (room temperature) with a constant stirring (magnetic stirrer) of 300 rpm.

C. Samples analyses

After leaching in each fraction, the solution was separated from the residual using a Vacuum filter Resulting solutions from each fraction were analyzed using (AAS) Atomic Absorption Spectroscopy to determine the concentration of specific metal ions present in each solution The remaining residual from sequential extraction was characterized XRF to identify and quantify the remaining of elements. Finally, PHREEQC was used to model the findings.

III. RESULTS AND DISCUSSION

A. Distribution and mobility of metals

The figures below help visualize the distribution and mobility of different metals across various chemical fractions in the mining-impacted soil samples. This information is crucial for understanding the environmental behavior of these metals, their potential bioavailability, and associated environmental risks.

The Graph below shows Zn recovery in different fractions from sequential extraction.

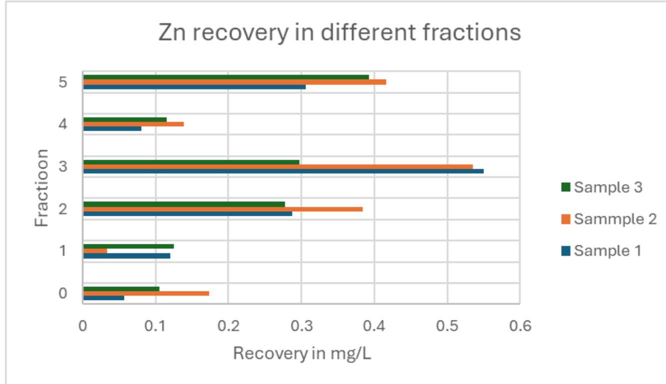

Fig. 1 Zn recovery in different fractions

Figure 2 below shows Ni recovery in different fractions from sequential extraction.

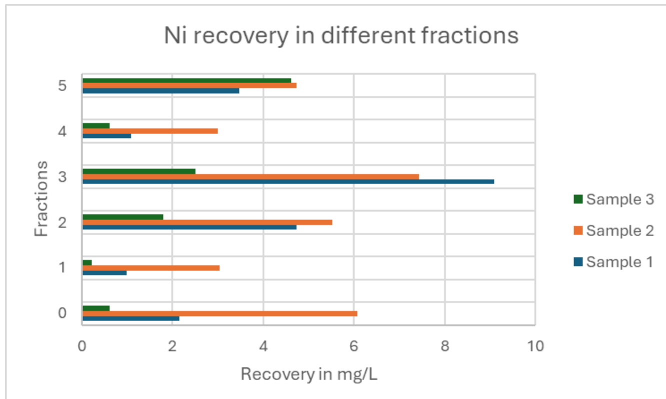

Fig. 2 Ni recovery in different fractions

Figure 3 below shows Mn recovery in different fractions from sequential extraction.

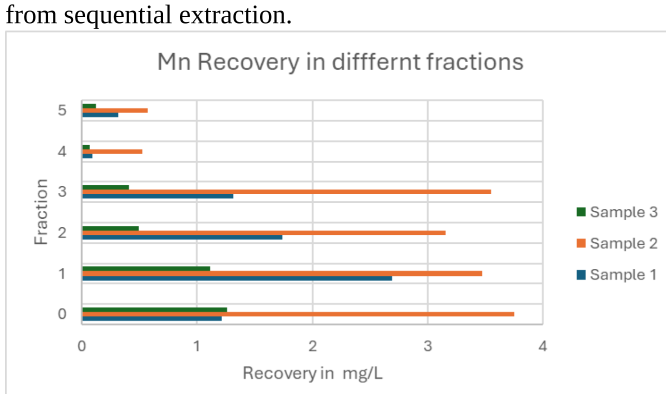

Fig. 3 Mn recovery in different fractions

Figure 4 below shows Cu recovery in different fractions from sequential extraction.

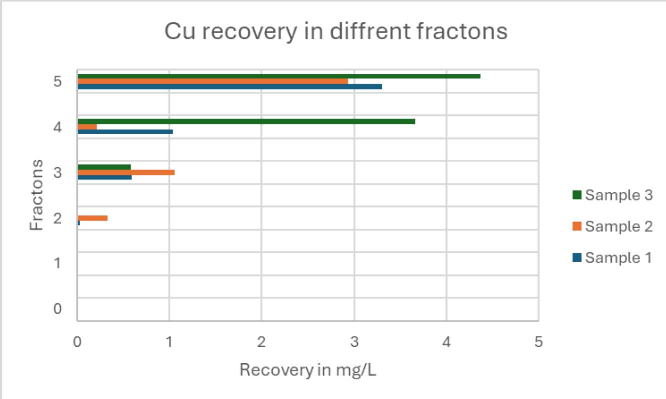

Fig. 4 Cu recovery in different fractions

Figure 5 below shows Fe recovery in different fractions from sequential extraction.

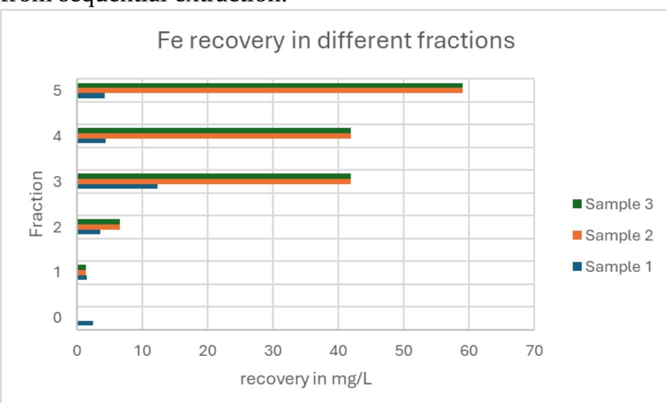

Fig. 5 Fe recovery in different fractions

B. Discussion

The recovery results for various metals in the Mpumalanga soils stream impacted by mining activities provide crucial insights into the ecosystem's health and potential risks. The low recovery values for zinc (Zn), mostly below 0.6 mg/L, indicate that this metal is not easily available for uptake by organisms, which suggests a lower risk of bioaccumulation. However, the presence of some zinc in fractions 2-3 could still raise environmental concerns, particularly regarding its effects on local plants and animals.

In contrast, the significantly higher recovery of nickel (Ni), reaching up to 10 mg/L especially in fraction 3 highlights a greater potential for this metal to impact the ecosystem negatively. Nickel can be toxic to aquatic life, and its increased availability may pose serious risks to local biodiversity.

Manganese (Mn) and copper (Cu) also displayed variable recovery patterns, indicating that their bioavailability may change based on environmental conditions, which can affect how readily they are taken up by plants and animals. The higher recovery values for these metals, particularly in the later fractions, suggest that certain processes may enhance their mobility within the ecosystem.

Iron (Fe) showed the highest recovery values, peaking at 60-70 mg/L, which could have significant implications for the ecosystem. While iron is an essential nutrient for many organisms, excessive concentrations can lead to toxicity and negatively impact water quality. The clear peak in fraction 3 indicates that this fraction is critical for understanding how metals cycle in the environment and their potential effects.

These findings underscore the importance of monitoring metal concentrations in the Mpumalanga ecosystem. Variations in metal recovery can significantly influence soil health and the well-being of local communities and wildlife. Therefore, implementing effective management strategies is essential to mitigate the risks associated with mining activities and to safeguard the ecosystem.

From PHREEQC results, concentrations of metals such as Zinc (Zn) and Manganese (Mn) suggest limited mobility, while higher concentrations in certain fractions may raise concerns about contamination risks. The pH levels of the solutions play a vital role. These findings underscore the importance of monitoring metal concentrations in the Mpumalanga ecosystem. Variations in metal recovery can significantly influence soil health and the well-being of local communities and wildlife. Therefore, implementing effective management strategies is essential to mitigate the risks associated with mining activities and to safeguard the ecosystem.

The PHREEQC results indicate that concentrations of metals such as zinc (Zn) and manganese (Mn) suggest limited mobility, while higher concentrations in certain fractions may raise concerns about contamination risks [9]. The pH levels of the solutions play a vital role in determining metal solubility; lower pH can increase bioavailability, while the pe values indicate the redox conditions that affect metal speciation. Species distribution data provide a clear picture of the various forms in which metals exist, influencing their reactivity and mobility in the environment [10]. Saturation indices offer valuable insights into the stability of minerals, guiding effective remediation strategies for contaminated sites. The fractionation results help pinpoint which metal forms pose the highest risks for leaching or biological uptake [11]. Additionally, comparative analyses across different samples enhance our understanding of how environmental factors influence metal distribution, helping to identify contamination hotspots.

Overall, these findings are crucial for informing effective environmental management strategies and guiding future research into the interactions between metals and their surrounding environmental factors. The PHREEQC results further support the AAS findings, especially regarding the limited mobility of metals like zinc and manganese, suggesting they are unlikely to pose immediate bioaccumulation risks. The study showed that pH levels significantly affect metal solubility, with lower pH enhancing their availability. The pe values revealed the redox conditions that influence metal speciation and behavior in the ecosystem. Data on species distribution clarified the ionic forms of the metals, impacting their reactivity and mobility. Saturation indices provided insights into the stability of various minerals, which is crucial for developing effective remediation

https://doi.org/10.17758/URUAE24.UR1224106

strategies for contaminated sites. Fractionation results identified which metal forms carry the highest risks for leaching or biological uptake, aiding in risk assessment and management [12].

in determining metal solubility, lower pH can increase bioavailability, while the pe values indicate the redox conditions that affect metal speciation. Species distribution data provide a clear picture of the various forms in which metals exist, influencing their reactivity and mobility in the environment. Saturation indices offer valuable insights into the stability of minerals, guiding effective remediation strategies for contaminated sites. The fractionation results help pinpoint which metal forms pose the highest risks for leaching or biological uptake. Additionally, comparative analyses across different samples enhance our understanding of how environmental factors influence metal distribution, helping to identify contamination hotspots. Overall, these findings are crucial for informing effective environmental management strategies and guiding future research into the interactions between metals and their surrounding environmental factors.

The PHREEQC results support the findings from AAS, especially concerning the limited mobility of metals like zinc and manganese, indicating they are unlikely to pose immediate bioaccumulation risks. The study showed that pH levels significantly affect metal solubility, with lower pH enhancing their availability. The pe values revealed the redox conditions that influence metal speciation and behavior in the ecosystem.

Data on species distribution clarified the ionic forms of the metals, impacting their reactivity and mobility. The saturation indices provided insights into the stability of various minerals, which is crucial for developing effective remediation strategies for contaminated sites. Fractionation results identified which metal forms carry the highest risks for leaching or biological uptake, aiding in risk assessment and management.

IV. Conclusion

The study investigated the bioavailability and mobility of metals in mining-impacted soil along a stream in Mpumalanga using geochemical modeling with PHREEQC. The findings revealed complex interactions between soil components and metal contaminants, which enhances our understanding of the environmental risks posed by mining activities. Specifically, certain metals were identified as highly mobile and bioavailable, raising concerns about their potential uptake by local flora and fauna. These insights are crucial for developing effective soil management and remediation strategies, such as phytoremediation or soil amendments, which could mitigate the contamination risks identified. Additionally, the research underscores the need for informed environmental policies that prioritize the protection of local ecosystems and communities affected by mining. Future research should focus on long-term impacts and monitoring strategies to further understand and address the ongoing risks associated with metal contamination in these environments.

Acknowledgment

The authors acknowledge the financial support from the Faculty of Engineering and Built Environment at the University of Johannesburg.

References

[1] Maiz, I., Arambarri, I., Garcia, R., Millán, E., 2000. Evaluation of heavy metal availability in polluted soils by two sequential extraction procedures using factor analysis. Environ. Pollut. 110, 3–9. https://doi.org/10.1016/S0269-7491(99)00287-0.

[2] Simon, M.H., Babin, D.P., Goldstein, S.L., Cai, M.Y., Liu, T., Han, X., Haws, A.A., Johns, M., Lear, C., Hemming, S.R., 2020. Sequential extraction procedure to obtain the composition of terrigenous detritus in marine sediments. MethodsX 7, 100888. https://doi.org/10.1016/j.mex.2020.100888.

[3] Leleyter, L., Probst, J.L., 1999. A new sequential extraction procedure for the speciation of particulate trace elements in river sediments. Int. J. Environ. Anal. Chem. 73, 109–128. https://doi.org/10.1080/03067319908032656.

[4] Fosso-Kankeu E, Mulaba-Bafubiandi A, Mamba BB, Barnard TG. 2011. Assessing the effectiveness of a biological recovery of nickel from tailings dumps. Journal of Minerals Engineering.Vol 24, pp 470-472. https://doi.org/10.1016/j.mineng.2010.11.007

[5] Elvis Fosso-Kankeu, Frans Waanders, Antoine F. Mulaba-Bafubiandi and Sibusiso Sidu. 2015. Leachability of suspended particles in mine water and risk of water contamination. 10thICARD/IMWA 2015; 10th International Conference on Acid Rock Drainage & IMWA Annual Conference. 21-24 April 2015 Santiago-Chile. Editors: Adrian Brown, Charles Bucknam, Joanna Burgess, Manuel Carballo, Devin Castendyk, Linda Figueroa, Lisa Kirk, Virginia McLemore, James McPhee, Mike O'Kane, Robert Seal, Jacques Wiertz, David Williams, Ward Wilson, Christian Wolkersdorfer. ISBN: 978-956-9393-28-0. Chap 4. Pp 1-9.

[6] Elvis Fosso-Kankeu, Frans Waanders, and Wiehan Botes. 2015. Recovery of Base Metals from Mine Tailings Dumps collected in the Vicinity of Potchefstroom: Leaching assisted by Complexing Agent. 7th International Conference on Latest Trends in Engineering and Technology (ICLTET' 2015), November 26-27, 2015 Irene, Pretoria (South Africa). Editors: E. Muzenda and T Yingthawornsuk. ISBN: 978-93-84422-58-5.

[7] Elvis Fosso-Kankeu, Frans B. Waanders, and Ashley H. Munyai. 2015. Susceptibility of Metals Release from Tailings Dumps Located In the Krugersdorp Area. 7th International Conference on Latest Trends in Engineering and Technology (ICLTET' 2015), November 26-27, 2015 Irene, Pretoria (South Africa). Editors: E. Muzenda and T Yingthawornsuk. ISBN: 978-93-84422-58-5.

[8] Abdul-Wahab, S., Marikar, F., 2011. The environmental impact of gold mines: pollution by heavy metals. Open Eng. 2, 304–313. https://doi.org/10.2478/s13531-011-0052-3.

[9] Jones, M. and Smith, K. (2018) 'Factors influencing metal bioavailability in mining-affected soils', Environmental Research Letters, 13(8), 084012.

[10] Taylor, M. and Green, J. (2021) 'Effects of soil amendments on heavy metal bioavailability in contaminated soils', Soil Science, 186(3), pp. 150-165.

[11] Brown, A. and Green, T. (2020) 'Modeling heavy metal bioavailability in contaminated mining sites', Environmental Geochemistry, 15(4), pp. 200-215.

[12] Davis, L., Martinez, J. and White, R. (2023) 'Understanding cumulative effects of metal interactions in contaminated soils', Journal of Environmental Science, 29(2), pp. 115-130..