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The Release and Transport of Metals Arising from Gold Mining Tailings Storage Facilities in the Witwatersrand, South Africa

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Abstract The evolution and transport of metals arising from active gold mining tailings storage facilities (TSFs) within the Witwatersrand Basin were assessed through a combination of analytical techniques and geochemical modelling. Sequential extractions were conducted to provide insight into the partitioning of metals in tailings. Speciation and solubility geochemical modelling of water samples indicated the controlling minerals of interest in the tailings. Combining these two approaches allowed for the transformation of metals and their subsequent attenuation to be better understood.

Keywords sequential extractions, geochemical modeling, metals

Introduction

Extensive gold mining of the Witwatersrand reefs in South Africa has produced wide spread surface tailings waste. Unprocessed ore minerals remain in the waste material. Oxidation of the tailings results in acid mine drainage (AMD) that leads to the release of metals into surface and ground water systems. The presence and extrapolation of sulphate plumes are often used to map the predicted affect of acid mine drainage. High sulphate concentrations arising from acid mine drainge are often associated with low pH conditions, except in cases where lime treatment has occurred (Tutu, McCarthy & Cukrowska 2008). In this work, the release and transportation of metals from tailings were assessed through the combination of analytical techniques and geochemical modelling.

Methodology

The study site has an active TSF. Plumes emanating from the TSF were sampled in order to determine changes in metal content of the groundwater. For the purpose of this paper, only two sampling sites will be discussed. The first site lies adjacent to the TSF. A trench was dug and solid material from above and within the water table was sampled. Water from a borehole approximately 10 m away from this trench was sampled (borehole A). The second site was approximately 500 m from the TSF site, but within reach of the plume. Solid material from a newly sunk borehole was obtained at the start of the dry season and water from this borehole was sampled at the end of the dry season (borehole B).

Sequential leaching offers an improvement in specific phase targeting as compared to batch leaching (Pueyo et al. 2001). The same material is subjected to progressively stronger leaching solutions in order to extract metals bound to specific phases. The solutions as proposed by the Standards, Measurements and Testing Programme of the European Commission in their sequential leach protocol, the BCR leach, were used (Rauret et al. 1999). Leaching conditions and volumes were varied from the protocol and are detailed in table 1. Validation of the leaching protocol was done using the BCR certified reference material (BCR-701). Leaching experiments were carried out in triplicate. The sum of metals in steps

A, B, C and D were within 10% of the total concentration determined after total digestion by microwave of the material.

***Table 1** Sequential leaching protocol for the solid material*

Step	Targeted Phase	Leaching solution	Volume (mL)	Leaching conditions
A	Water soluble, exchangeable and acid soluble	0.11 M acetic acid	40	Overnight at room temperature
B	Reducible (associated with iron and manganese oxides)	0.5 M hydroxylamine hydrochloride	40	Overnight at room temperature
C	Oxidisable (associated with organic material and oxides)	1) H_2O_2	10	1 hour at room temperature, 1 hour at 85℃ and then reduced to 3 mL
		2) H_2O_2	10	1 hour at 85℃ and then reduced to 3 mL
		3) 1 M ammonium acetate	40	Overnight at room temperature
D	Residual (associated with silicates)	1) Hydrochloric acid	5	Microwave assisted complete digestion with acid regia and hydrofluoric acid (approximately 1.5 hours)
		Nitric acid	2	
		Hydrofluoric acid	1	
		2) Deionised water	<100	Volume made up to 100 mL

Water samples were filtered in the field using 0.45 µm syringe filters. A filtered aliquot of each water sample was acidified for metal content determination. Metal content of leachates and water samples were analysed using inductively coupled plasma-optical emission spectroscopy (ICP-OES, Spectro). Anion content of water samples was analysed using chemically suppressed anion chromatography. Field parameters (pH, Eh, temperature, conductivity and dissolved oxygen) were measured in the field shortly after sample collection using appropriate, calibrated field meters. Triplicate alkalinity titrations to bromocresol green end point were completed within 24 hours of collecting the samples.

Speciation-solubility models were used to define the distribution of stable species and saturation states of minerals in the system (Zhu & Anderson,2002). PHREEQC was used to compile speciation-solubility models of the sampled borehole water (Parkhurst & Appelo, 1999). The WATEQ4F database was used with no adjustments.

Results

Water analysis

The water sample obtained from a borehole adjacent to the TSF at a depth of 2.5 m had a pH of 4.01 at 21.0 ℃, Eh of 391 mV and conductivity of 8.33 mS/cm. The water sample obtained from the borehole situated 500 m away from the TSF at a depth of 7.6 m had a pH of 6.67 at 22.1 ℃, Eh of 400 mV, conductivity of 3.93 mS/cm and alkalinity of 148 mg/L $CaCO_3$. Results for anion and metal concentrations are summarised in table 2. The metal content was higher at sites close to the TSF than at borehole B. In particular, aluminium, cobalt, iron, manganese, sodium and nickel concentrations are notably lower away from the TSF.

***Table 2** Analytical results for water samples from a plume emanating from a TSF(Concentrations in mg/L)*

Sample	Cl^-	SO_4^{2-}	Al	Ca	Co	Cu	Fe	K	Mg	Mn	Na	Ni	Pb	Zn
Borehole A	425	5065	52	605	6.2	0.4	7.5	52.2	640	322	705	8.0	2.7	3.6
Borehole B	230	2202	nd	640	0.3	0.1	0.0	12	393	2	63	nd	nd	nd

“nd” means not detected

Sequential leaching results

The solid material collected from the freshly dug pit adjacent to the TSF and from borehole B were analysed. The results for iron and sulphur are presented in fig. 1 and 2, respectively. Iron was found to be distributed largely in the reducible and oxidisable phases. The reducible phase is iron present as ferric oxyhydroxides. The amount of Fe in this phase was found to increase with distance from the TSF. The assessment of Fe in the oxidisable fraction is still under investigation. The sulphur content (fig. 2) leached in Step C was found not to be correlated to the iron content (fig. 1), thus it is unlikely to be sulphide minerals. Sulphur is mostly present as a water and acid soluble sulphate phase. Two potential explanations are proposed. Firstly, the iron could be held in a more crystalline phase that requires the harsher conditions of the oxidisable leach step in order to dissolve. Secondly, iron could be associated with cyanide phases. Step D revealed that most of the iron in the samples is present in the residual phase and is not mobile. For example, in the 10 m sediment sample from borehole B, there was no readily soluble iron, 6.1 mg/kg reducible iron, 7.4 mg/kg oxidisable iron and 91.6 mg/kg residual iron. Aluminium exhibited a leaching trend similar to iron. In the wet sediments collected close to the TSF, calcium was found to be predominantly water soluble, acid soluble or exchangeable. Further away from the TSF, the amount of calcium that is leached from the solid remained almost the same, but with approximately one third of it readily soluble and two thirds associated with the reducible phase.

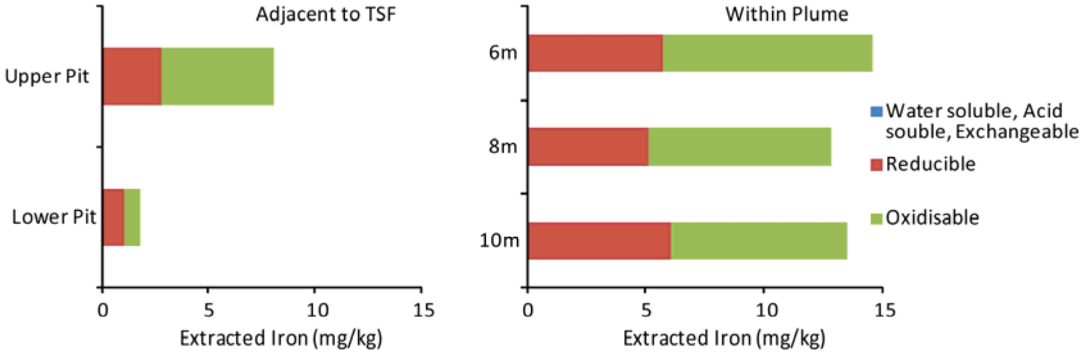

Fig. 1 *Iron partitioning in sediments as determined using sequential extraction*

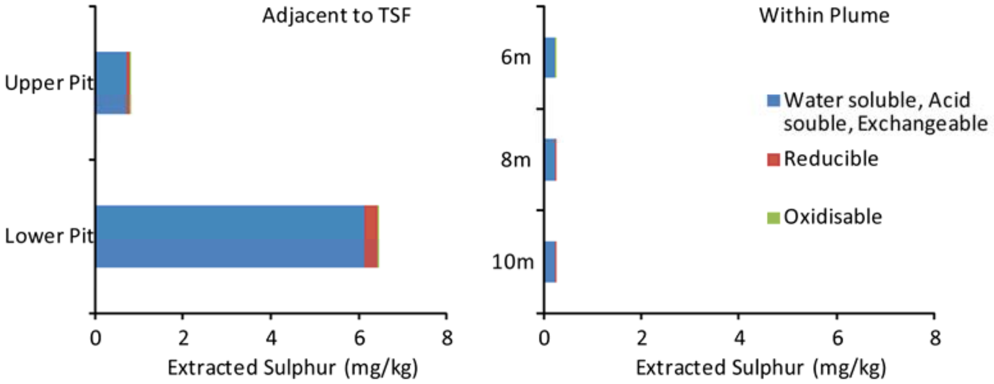

Fig. 2 *Sulphur partitioning in sediments as determined using sequential extraction*

Geochemical Modelling and Discussion

Input data for the speciation-solubility models of the borehole water samples included: alkalinity, field parameters, and anion and metal contents. At the measured Eh values of the samples, the iron is predominantly present in ferrous form near the TSF. The distribution of ferrous to ferric decreases further away from the TSF and at borehole B, the soluble ferric hydroxide species is the dominant iron species. Amorphous iron hydroxide is undersaturated in the groundwater close to the TSF (saturation index of -3.89). In borehole B, the groundwater is close to saturation with amorphous iron hydroxide (saturation index of 0.93). As seen in the leaching, the amount of iron oxide leached in Step B increases with distance from the TSF thus suggesting the precipitation of iron hydroxides during transport. In borehole A, aluminium oxyhydroxide, diaspore, had a saturation index of 0.55 while aluminium hydroxide, gibbsite, had a saturation index of -0.67. The aluminium concentration in borehole B was too low to be determined. In the solid material, aluminium was associated with the reducible phase. The combination of these factors leads to the conclusion that aluminium emanating from the TSF is precipitated as (oxy) hydroxides. The calcium content at the two sites did not differ greatly. The saturation index of gypsum for the two borehole samples was 0.05 and -0.02, implying that close to the TSF, gypsum precipitates and the solution remains in equilibrium with gypsum during transport. The inclusion of alkalinity into the model for borehole B, allowed for the determination of the saturation indices for calcite (-0.22) and dolomite (-0.35). The proximity of the saturation indices of gypsum, calcite and dolomite to zero implies that these minerals are also responsible for the maintenance of the calcium concentration. The dissolution of carbonates increases pH and the precipitation of gypsum aids in the removal sulphate and calcium from solution. The increased pH renders several metals insoluble, making them precipitate out of solution. The adsorption of contaminants onto freshly precipitated iron hydroxides also influences their concentration in solution as demonstrated for copper through forward adsorption geochemical modelling.

Conclusions

The study has shown that metals are not conservatively transported away from the TSF. Natural attenuation, largely through precipitation and adsorption, during interaction with soil occurs during transportation. The extent of this attenuation should be further assessed. Combining analytical protocols with geochemical modelling has provided insight into the reactions that occur during metal transport. These results will be further used to build comprehensive inverse and forward models to augment understanding of the release and transport of metals.

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References

Parkhurst D, Appelo C (1999) User's guide to PHREEQC (Version2)—A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations

Pueyo M, Rauret G, Luck D, Yli-Halla M, Muntau H, Quevauviller P, Lopez-Sanchez J (2001) Certification of the extractable contents of Cd, Cr, Cu, Ni, Pb and Zn in a freshwater sediment following a collaboratively tested and optimised three-step sequential extraction procedure. Journal of Environmental Monitoring 2(3):243-250

Rauret G, Lopez-Sanchez J, Sahuquillo A, Rubio R, Davidson C, Ure A, Quevauviller P (1999) Improvement of the BCR three step sequential extraction procedure prior to the certification of new sediment and soil reference materials. Journal of Environmental Monitoring 1(1): 57-61

Tutu H, McCarthy TS, Cukrowska EM (2008) The chemical characteristics of acid mine drainage with particular reference to sources, distribution and remediation: The Witwatersrand Basin, South Africa as a case study. Applied Geochemistry 3666-3684

Zhu C, Anderson G (2002) Environmental Applications of Geochemical Modeling. Cambridge, United Kingdom, The Press Syndicate of the University of Cambridge