Chemical Transformations of Metals Leaching from Gold Tailings

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ABSTRACT

Chemical reactions that follow the release of metals from gold mine tailings in the Witwatersrand Goldfields were assessed through a combination of analytical techniques and geochemical modeling. A flow path for metal pollutants which consisted of a tailings storage facility (TSF), a rainwater runoff pond, a pollutant control dam and a wetland was considered. Water and solid samples from these features were collected and analyzed. Sequential extractions of solids were conducted to assess the chemical partitioning of metals within them. Metal content was partitioned into water and acid-soluble (readily soluble salt phases), reducible (associated with iron and manganese oxides), oxidizable (bound to organic or sulfide minerals) and residual (silicate minerals) fractions. The change in metal partitioning with increasing distance from the tailings storage facilities was found to be correlated to changes in the chemistry of water which in turn was correlated to the change in the geochemistry of solids along the flow path. Speciation-solubility, inverse and forward modeling using the PHREEQC modeling code were combined with sequential extractions and used to characterize the chemical reactions that transform the metals.

Keywords: Chemical partitioning, sequential extraction, geochemical modeling, inverse modeling

INTRODUCTION

Environmental impacts of the decant of metal-rich, sulfate-rich, low pH water from gold mine tailings around Johannesburg, South Africa have been a cause for concern for some time now (Förstner & Wittmann, 1979; Naicker, Cukrowska & McCarthy, 2003; Tutu, McCarthy & Cukrowska, 2008).

The release of metals from gold mine tailings into the environment is dependent on the mineralogy of the tailings and the association of metals with that mineralogy. Knowledge of bulk mineralogy alone does not provide an accurate indication of the potential release of metal pollutants from the tailings. Metal pollutants could exist in minor minerals that are below standard powder X-ray diffraction (PXRD) detection limits. The chemical behavior of the minerals hosting metal contaminants affects their release and mobility. A metal ion of interest, for instance, can be associated with a single mineral phase or a combination of mineral phases. Such mineral hosts include water-soluble salts, ion-exchange sites on clay minerals, carbonate minerals, adsorption on or inclusion into amorphous or crystalline iron (Fe) oxides, sulfide minerals and silicate minerals (Leinz et al., 2000). Leaching and sequential extraction techniques have been used to characterize the phase association of metals in contaminated sediments and solid waste (Rao et al., 2008). The most commonly used sequential extraction methods have been the Tessier method (Tessier, Campbell & Bisson, 1979) and the Communities Bureau of Reference method (BCR) (Rauret et al., 1999).

In this paper, the use of sequential extractions was combined with speciation-solubility and inverse modeling in order to better understand the partitioning and transport of metals emanating from gold mine tailings at a site in the West Rand of the Witwatersrand Goldfields, South Africa.

METHODOLOGY

Sampling and analysis

The study site comprised a tailings storage facility (TSF) that was undergoing reprocessing; a tailings pond which collected rainwater runoff from the TSF; a pollution control dam that encroached partially onto a reprocessed TSF and collected water from the TSF in the study; and a wetland which is adjacent to the pollution control dam wall.

Water samples were collected during the rainy season (January and March 2014). Water sampling was conducted using acid-washed and deionised water rinsed polypropylethylene bottles. Measurements of temperature, pH, Eh, electrical conductivity (EC) and dissolved oxygen were conducted in the field using calibrated field electrodes. A portion of each sample was filtered in the field using a syringe mounted with 0.45 μm polytetrafluoroethylene (PTFE) filters and acidified prior to metal analysis using inductively coupled plasma-optical emission spectrometry (ICP-OES). A separate portion was filtered in the same manner without acidification and analyzed for anion content using chemically-suppressed ion chromatography (IC). The remaining portion of sample was not filtered and was used for alkalinity determination. Alkalinity was determined using titrations with standard HCl solutions to pH 4.5 using bromocresol green and a calibrated pH electrode to detect the end-point (ASTM International, 2010).

Sediment samples were collected at the same time as water samples in March 2014. Samples with a high water content were centrifuged to extract pore water. Sediment samples were collected at the same points where water samples were collected. In the pollution control dam, there were two distinct layers in the shallow sediments that were sampled as separate samples.

The samples were dried at 35 °C. Samples were ground using a mortar and pestle to particle size <10 μm. Sequential extractions to determine metal partitioning were performed using the Communities Bureau of Reference method (BCR) (Rauret et al., 1999). Leaching solutions were shaken on an elliptical shaker for the duration recommended by the method. The BCR-701 certified reference material was used for assessment of leaching accuracy. The leaching protocol was used to determine the following environmentally important or environmentally extractable metal fractions: 1) water soluble, acid soluble and exchangeable; 2) reducible (metals associated with Fe and manganese (Mn) oxyhydroxides); 3) oxidizable (metals associated with organic matter or sulfide minerals). Acidic microwave digestion of the residues after the third leach step and of the unleached material was conducted using hydrochloric, nitric and hydrofluoric acids to dissolve the silicate matrix. Inductively coupled plasma-optical emission spectrometry was used to determine metal content in the resulting leachates and acidic solutions.

Geochemical modeling

Speciation-solubility, inverse and forward modeling were conducted using the United States Geological Survey (USGS) software PHREEQC combined with the Lawrence Livermore National Laboratory database (llnl.dat) (Parkhurst & Appelo, 1999; Charlton & Parkhurst, 2002). Speciation-solubility models are used to define the distribution of stable species in the system and to determine the saturation states of minerals within the system. In forward modeling, the final composition of a solution after a reaction or equilibration is calculated. Inverse modeling is also known as mass balance modeling and can provide a set of possible reactions that occur between two known solutions along the same flow path (Zhu & Anderson, 2002).

RESULTS AND DISCUSSION

Overview of water analysis

Table 1 summarizes the electrode measurements of the water samples taken during the two sampling sessions. The first sampling took place in the middle of the rainy season, before major thundershowers. The tailings pond samples had lower pH, elevated Eh and EC than samples taken from the same pond two months later towards the end of rainy season. The effect of pH on metal mobility was obvious for the tailings pond samples collected in January that had an average Fe concentration of 54 mg.L^{-1} whereas samples collected in March had an average of 4.2 mg.L^{-1}. The same dilution effects are less evident in the pollution control dam samples. The results for percentage electrical charge balance (calculated using PHREEQC) are also presented in Table 1. The charge balance is a common indication of the quality of water analysis (Zhu & Anderson, 2002). Large percentage errors can indicate that a cation or anion was not analyzed for, analyzed incorrectly or that the sample was altered during transport or storage (for example, precipitation of analytes can occur). The charge balances presented in Table 1 are below 20%, with the largest deviations observed in the pollution control dam. The dam has a number of tributaries that could be contributing to various chemical processes occurring in it. Cyanide and organic matter were not

quantified in this study, but their contribution to charge balance may be significant if they are present in high concentrations. Even though the samples were filtered with 0.45 μm filter paper, several colloids are smaller than this and would be analyzed as dissolved species. This would contribute to a positive error. Colloidal aluminum (Al) is known for such behavior and the studied samples contained elevated Al concentrations.

Table 1 Summary of field measurements and PHREEQC-determined charge balance for water samples.

Location	Sample	Month	Temperature	pH	Eh	Conductivity	Dissolved oxygen	Charge Balance
			(°C)		(mV)	(mS/cm)	(mg/L)	(%)
	TP 1	January	23.8	2.68	625	3.14	6.53	-9.9
	TP 2	January	23.8	2.67	611	3.17	6.51	-7.5
Tailings Pond	TP 3	March	25.6	3.43	448	1.67	5.60	9.6
	TP 4	March	23.8	3.36	454	1.74	6.96	1.0
	TP 5	March	22.4	3.36	461	1.78	7.17	-8.0
	PCDI 1	March	25.8	3.50	550	3.79	3.64	1.4
Pollution Control Dam Inlet	PCDI 2	March	25.1	3.02	538	2.79	4.69	-7.5
	PCDI 3	March	24.3	2.72	607	3.11	6.41	6.3
	PCD 1	January	24.4	2.31	660	7.37	6.73	-18.8
	PCD 2	January	24.4	2.31	667	7.55	6.82	-18.5
Pollution Control Dam	PCD 3	March	26.5	2.67	682	3.21	6.69	-3.8
	PCD 4	March	26.6	2.70	672	3.17	6.75	10.6
	PCD 5	March	25.8	2.74	642	3.19	6.58	-14.7
Wetland	W 1	March	28.1	2.59	648	6.76	4.00	1.3

Sequential extractions and speciation-solubility modeling

Water and sediment samples from the rainwater runoff pond adjacent to the TSF were analyzed. Speciation-modeling was conducted on water samples in Table 1. Saturation indices (SI) are an indication of a solution's saturation with respect to a mineral (Zhu & Anderson, 2002). A positive SI indicates that the mineral is supersaturated in the system and a negative SI indicates that the mineral is undersaturated. Generally, the water samples showed that most minerals dissolved in them are undersaturated with the exception of gypsum, alunite and jarosite. Gypsum ($CaSO_4.2H_2O$) was close to saturation in TP 1 and TP 2 (SI of -0.03), close to saturation in PCD 1 (SI of 0.02),

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supersaturated in PCD 1 and PCD 2 (average SI of 0.10) and supersaturated in W 1 (SI of 0.11). In all other samples, gypsum was undersaturated (SI of < -0.20). Jarosite ($KFe_3(SO_4)_2(OH)_6$) was undersaturated in all of the tailings pond samples and PCDI 2, was close to saturation in PCDI 3 (SI of -0.06) and was supersaturated in all of the pollution control dam samples, PCDI 1 and wetland sample. Alunite ($KAl_3(SO_4)_2(OH)_6$) was undersaturated in all of the samples except for PCDI 1 (SI of 1.5).

The results for BCR extractions of the tailings pond sediments are presented in Figure 1. Over 90% of the total Al, calcium (Ca), potassium (K), magnesium (Mg) and sodium (Na) content is held within silicates that are in the residual phase of the extraction protocol. The residual fraction has been omitted from Figure 1 in order to clarify the partitioning of the environmentally extractable fraction (Figure 1). A significant proportion of Ca and sulfur (S) is held in the water soluble, acid soluble or exchangeable phase. This relates well with the gypsum being near to saturation within the pond (from modeling results). The environmentally extractable Al (from the first three leach steps) is equally distributed in the sediment. Most of the environmentally extractable Fe is present as a reducible phase, that is, ferric oxyhydroxides. The majority of Fe in the tailings pond water samples was speciated as dissolved ferrous iron (Fe(II)). The water samples were found to be close to saturation with atmospheric oxygen. This meant that Fe(II) in solution was oxidized by atmospheric oxygen and converted to Fe(III) which is insoluble and precipitates from solution as ferric hydroxide. The partitioning of trace elements is presented in Figure 1. Cobalt (Co), copper (Cu), Mn and zinc (Zn) were found to be largely held in the water soluble, acid soluble or exchangeable phase. This phase is likely associated with sulfate salts owing to the abundance of sulfates due to AMD. From modeling results, the sulfate salts of these elements were undersaturated in the pond water samples. The saturation indices are calculated for pure end members (Zhu & Anderson, 2002). The minerals present in the system are likely to be solid solutions and will have different thermodynamic properties. Less than 10% of the environmentally extractable fraction of Cd, Co, Mn, U and Zn was associated with reducible Fe oxyhydroxides. There was a strong association of Cr, Cu and Li with the reducible Fe oxyhydroxides (greater than 18%), likely through adsorption on the surface or through incorporation of solid solutions within the lattice. A significant proportion (> 40%) of the trace metals cadmium (Cd), Co, Cu, uranium (U) and Zn extracted from the first three leaches were associated with oxidizable phases. These phases could include organic material, sulfide minerals and possibly strong cyanide complexes.
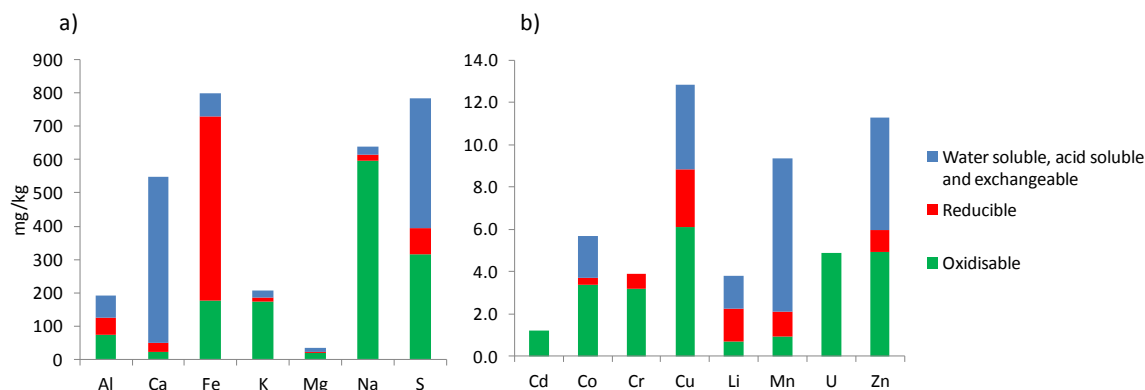

Figure 1 a) Major metal and sulfur partitioning within tailings pond sample. b) Minor metal partitioning within tailings pond sample.

Sequential extractions and inverse modeling

The pollution control dam will be used an example of how the use of sequential extractions can help in mineral selection for inverse modeling.

Modeling results showed that water sample PCD 3 was almost saturated with gypsum (SI of -0.27). Iron was found to be in ferrous (85%) and ferric (15%) form at the measured Eh. The presence of soluble ferric phases led to higher saturation indices of these phases. For instance, $Fe(OH)_3$ had an SI of -2.2; goethite was supersaturated; Na jarosite ($NaFe_3(SO_4)_2(OH)_6$) was saturated (SI of 0.0); and K jarosite ($KFe_3(SO_4)_2(OH)_6$) was supersaturated (SI of 3.4). The results for partitioning of elements in sediments collected at the pollution control dam are presented in Figure 2. The results showed elevated concentrations of Fe in the reducible phase (largely Fe oxyhydroxides), and this corresponded with the characteristic reddish-orange color of the sediments. A large proportion of Cd, Cr, Cu and Mn were associated with the reducible phase in these sediments (Figure 2). In the rainwater runoff pond, Mn and Cu were associated with the water soluble acid soluble or exchangeable phase; Cd, Co and a small proportion of Cu were associated with the oxidizable phase; and Cr was associated with the residual phase (Figure 1). These results suggest that the metals could be readily released from the runoff pond, adsorbing onto Fe oxyhydroxides along the flow path and deposited in the pollution control dam. The contribution of leachates from a municipal waste site is not apparent as sampling at that site could not be conducted.
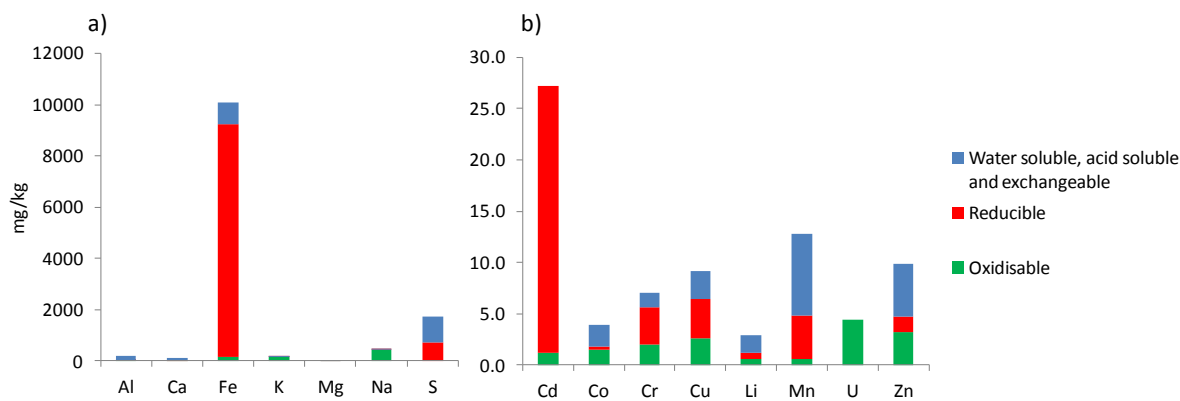

Figure 2 a) Major metal and sulfur partitioning within upper pollution control dam sediments. B) Minor metal partitioning within upper pollution control dam sediments.

To gain further insight into metal partitioning in the sediments, some inverse models were used. One such model generated the pollution control dam sample (PCD 3) from mixing the three incoming water types. The main aim was to identify minerals that would precipitate from this process and correlate these to the phases observed in sequential extractions. The minerals that were chosen as phases of interest were selected from the sequential extraction results of the upper sediments sample presented in Figure 2. The following minerals were selected as phases: $Fe(OH)_3$, gypsum ($CaSO_4.2H_2O$), $Mn(OH)_2$, epsomite ($MgSO_4$), $NiSO_4$, $ZnSO_4$ and bieberite ($CoSO_4.7H_2O$). Chloride and Na were regarded as conservative elements while water vapor was used in the simulation to allow for the impact of evaporation. Several potential models were generated. The

general trend in the models was a large contribution from PCDI 3, a smaller contribution from PCDI 1 and a negligible contribution from PCDI 2. A minimal phase model is presented in Table 2. The solution mixing fractions were: PCDI 1 (0.340), PCDI 2 (0.069) and PCDI 3 (0.840). The mixing of the different solutions generated a solution with a mass of 1.25 kg. An amount of 250 g of water vapor was allowed to exit the system, resulting in 1.00 kg remaining. The negative sign for gypsum in Table 2 indicates that the mineral precipitated out of the solution while a positive sign as in the case of $Fe(OH)_3$ indicates that the mineral dissolved into the solution. Thus, the pollution control dam sample was undersaturated with respect to $Fe(OH)_3$. Given the high concentration of ferric oxyhydroxide in the upper sediments of the dam, it is possible that $Fe(OH)_3$ was in the process of being released from the sediments.

Table 2 Phase mole transfers between a mixture of pollution control dam inlet streams and pollution control dam water.

Phase	Mole transfer
$Fe(OH)_3$	3.04×10^{-4}
Gypsum	-2.35×10^{-3}
$Mn(OH)_2$	-4.01×10^{-4}
Epsomite	-3.43×10^{-3}
$NiSO_4$	-6.56×10^{-5}
$ZnSO_4$	-3.38×10^{-5}
Bieberite	-2.61×10^{-5}
$H_2O(g)$	-138

Since inverse models are based on mass balance principles only and do not take into account mass action principles, forward modeling can be used to test whether the results from an inverse model are thermodynamically possible. The inverse model presented above was tested using non-equilibrium and equilibrium approaches. The non-equilibrium approach forces the precipitation and dissolution of minerals (by disregarding their saturation indices). The equilibrium approach only dissolves minerals that are undersaturated in solution and only precipitates minerals that are supersaturated. A comparison of the final modeled results with the experimental solution is presented in Table 3. In the equilibrium model, no minerals precipitated as they remain undersaturated in solution. Therefore, there are higher elemental concentrations and a correspondingly higher ionic strength than for the other two solutions.

Table 3 Comparison of an experimental solution, non-equilibrium and equilibrium forward-modeled solutions.

Parameter	Experimental solution	Non-equilibrium model	Equilibrium model
pH	2.7	2.78	2.92
pe	11.4	12.5	12.4
Ionic strength	0.065	0.068	0.079
Elemental concentrations (mol.kg^{-1})			
Al	6.68×10^{-3}	5.58×10^{-3}	5.57×10^{-3}
Ca	1.02×10^{-2}	0.90×10^{-2}	1.14×10^{-2}
Cl	1.02×10^{-3}	1.14×10^{-3}	1.14×10^{-3}
Co	6.49×10^{-5}	6.48×10^{-5}	9.09×10^{-5}
Cu	3.38×10^{-5}	2.85×10^{-5}	2.85×10^{-5}
Fe	2.30×10^{-3}	1.95×10^{-3}	1.94×10^{-3}
K	2.49×10^{-4}	3.02×10^{-4}	3.02×10^{-4}
Mg	3.60×10^{-3}	3.47×10^{-3}	6.90×10^{-3}
Mn	3.30×10^{-4}	3.30×10^{-4}	7.31×10^{-4}
Na	1.27×10^{-3}	1.28×10^{-3}	1.28×10^{-3}
Ni	1.27×10^{-4}	1.27×10^{-4}	1.92×10^{-4}
S	2.47×10^{-2}	2.91×10^{-2}	3.50×10^{-2}
U	5.63×10^{-6}	4.61×10^{-6}	4.60×10^{-6}
Zn	1.19×10^{-4}	1.19×10^{-4}	1.53×10^{-4}

CONCLUSION

This study has shown that partitioning of metals within various mineralogical phases in gold mine wastes exerts control over their release and transport to the surroundings. From sequential extraction and geochemical modeling, processes such as dissolution, precipitation, ligand complexation, adsorption and desorption were shown to be important. These processes were apparent when metals in the runoff pond were shown to be essentially in oxidizable phases while a short distance further in the pollution control dam they were found to be held in reducible phases. Combining sequential extractions with geochemical modeling provides insight into the water-solid interactions. Model simulations depicted elemental speciation (through speciation-solubility models) and the likely partitioning within the mineral phases (through inverse models). The simulations were also useful in predicting minerals that would precipitate when various water types are mixed.

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REFERENCES

ASTM International (2010) D1067-06: Standard test Methods for Acidity or Alkalinity of Water. In Annual Book of ASTM Standards Section 11 Water and Environmental Technology (Vol. 11.01), Baltimore: ASTM International.

Charlton, S & Parkhurst, D (2002) PHREEQCI—A Graphical User Interface to the Geochemical Model PHREEQC, Retrieved May 20, 2012, from ftp://brrftp.cr.usgs.gov/pub/dlpark/geochem/pc/phreeqc/PhreeqcI.FactSheet.pdf

Förstner, U & Wittmann, G (1979) Metal accumulations in acidic waters from gold mines in South Africa, Geoforum , 7 (1), 41-49.

Leinz, R, Sutley, S, Desborough, G & Briggs, P (2000) An Investigation of the Partitioning of Metals in Mine Wastes Using Sequential Extractions, In Proceedings from the Fifth International Conference on Acid Rock Drainage (pp. 1489-1499). Littleton, Colorado: The Society for Mining, Metallurgy, and Exploration Inc.

Naicker, K, Cukrowska, E & McCarthy, T.S (2003) Acid mine drainage arising from gold mining activity in Johannesburg, South Africa and environs, Environmental Pollution , 29-40.

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.

Rao, C, Sahuquillo, A & Lopez Sanchez, J. (2008) A Review of the Different Methods Applied in Environmental Geochemistry For Single and Sequential Extraction of Trace Elements in Soils and Related Materials, Water, Air & Soil Pollution (189), 291–333.

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.

Reeder, R, Schoonen, M & Lanzirotti, A (2006) Metal Speciation and Its Role in Bioaccessibility and Bioavailability, Reviews in Mineralogy and Geochemistry , 64, 59-113.

Tessier, A, Campbell, P & Bisson, M (1979) Sequential Extraction Procedure for the Speciation of Particulate Trace Metals, Analytical Chemistry , 51 (7), 844-851.

Tutu, H, McCarthy, T. S & Cukrowska, E (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.