Quantification of Environmental Risk of U and Th in Witwatersrand Gold-Mine Tailings, South Africa

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Abstract

This study explores the most likely mineral hosts and geochemical behaviour of U and Th in Witwatersrand gold tailings facilities with the purpose of quantifying environmental risk. U occurs in the mineral uraninite of which the dissolution is enhanced by the oxidation of pyrite, primarily in the oxidation zone of the tailings facility. U concentrations in tailings pore water may be controlled by secondary U-mineral phases in the tailings zones below the oxidation zone. Th is shown to be insoluble and the phase in which it occurs to be irrelevant in terms of environmental risk of Th leaching.

Keywords: Uranium, Thorium, Acid Mine Drainage, Witwatersrand, Gold Mines

Introduction

The term risk can be defined as the probability of harm or loss and can be considered to be the product of the probability and severity of specific consequences (Watts and Teel 2005). South African law requires the assessment of the environmental risks associated with mineral waste generating mining activities for new as well as existing mining and associated activities. Geochemical modelling is increasingly becoming part of these risk assessments as a powerful tool in quantifying risks, e.g. the formation of acid mine drainage (AMD) conditions and leaching of chemical components from mineral waste material in concentrations that could be deleterious to the surrounding environment. This study focusses specifically on the source terms of the U and Th associated with the Witwatersrand tailings material as well as their geochemical behaviour in these facilities and ultimately the quantification of their environmental risk.

Methods

Material

A total of 13 fresh tailings samples were collected from tailings facilities, six from tailings in the Far West-Rand basin (FWR) and seven from tailings in the Free State (FS) basin (fig. 1). The samples were collected at the point where the tailings from the gold concentrator plants is discharged onto the tailings facilities. The samples were sent to a commercial laboratory for quantitative evaluation of minerals by scanning electron microscopy (QEMSCAN) and concentrated Aqua Regia leach followed by Inductively-Coupled Plasma Mass Spectrometry (ICP-MS) analysis.

Th data of individual uraninite grains from the Witwatersrand gold ore were sourced from literature. This data represents analyses by laser ablation inductively couple mass spectrometry (LA-ICP-MS) (Large et al. 2014, Depiné et al. 2013) and electron microprobe (Hallbauer 1986) data. The dataset used contains 91 analyses on uraninite grains. A Monte Carlo analysis was conducted on the single uraninite grain Th data with the purpose of determining whether the amount of Th in the tailings material can be explained by the Th contained in uraninite, or whether it is more likely that a separate Th-containing phase is required. The Monte Carlo analysis was conducted using the Risk Analysis Collection software plugin for the Microsoft Excel spreadsheet software. The data distribution for the Monte Carlo analysis was determined using the Mathwave Easyfit version 5.6 software.
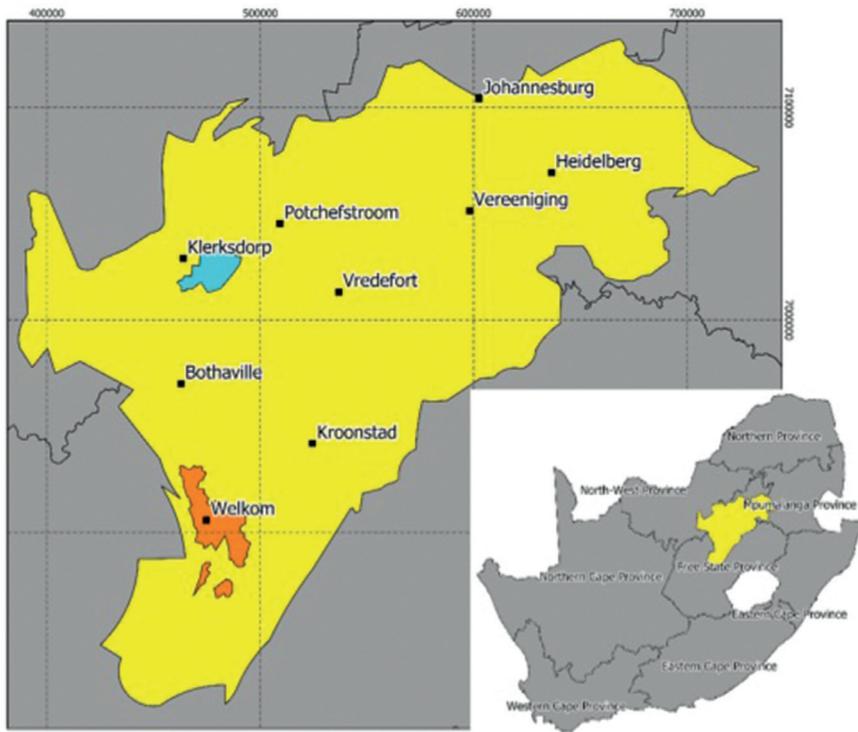
Figure 1 Locality map showing the Witwatersrand Au-mining basin as well as the Far West-Rand basin (turquoise) and the Free State basin (orange).

Conceptual framework

The conceptual framework of the Witwatersrand tailings is discussed in this section and summarised in (fig. 2). In addition to U, the Witwatersrand ore contains pyrite. As soon as pyrite is exposed to the Earth's atmosphere, it starts to oxidise according to the following reaction (Blowes et al. 2014):

Equation 1

$$FeS_{2(s)} + \frac{7}{2}O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+$$
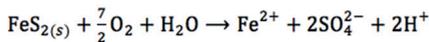
Eq. 1 indicates that the oxidation of pyrite by O_2 in the presence of water releases Fe^{2+}, SO_4^{2-} H^+ to the tailings pore water. Natural minerals are very seldom pure and pyrite can contain trace metal(loid)s which have the potential to increase the risk of environmental pollution (Hansen, 2014).

Fe^{2+} is released to the tailings pore water solution and can further be oxidised to Fe^{3+} (Blowes et al. 2014, Stumm and Lee 1961). At pH > ~3, Fe^{3+} will hydrolyse and precipitate in a range of secondary (oxy)hydroxide phases, releasing additional H^+. Ferrihydrite

generally serves as a proxy for this process (Blowes et al. 2014):

Equation 2

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_{3(s)} + 3H^+$$
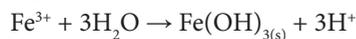
At pH values < ~3, ferrihydrite is soluble and the ferric iron ions remain in solution. Under these conditions ferric iron can replace O_2 as the main oxidant according to (Blowes et al., 2014):

Equation 4

$$FeS_{2(s)} + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{3+} + 2SO_4^{2-} + 16H^+$$
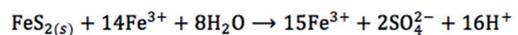
Eq. 4 indicates that for every mole of pyrite oxidised by ferric iron in the presence of water, 16 moles of H+ is produced. The acidity produced by pyrite oxidation can be neutralised by non-Fe-containing carbonates, such as calcite and dolomite according to:

Equation 5

$$CaCO_{3(s)} + H^+ \rightarrow Ca^{2+} + HCO_3^-$$

Equation 6

$$CaMg(CO)_{3(s)} + 2H^+ \rightarrow Ca^{2+} + Mg^{2+} + 2HCO_3^-$$
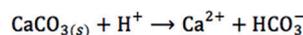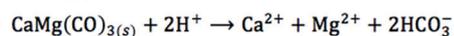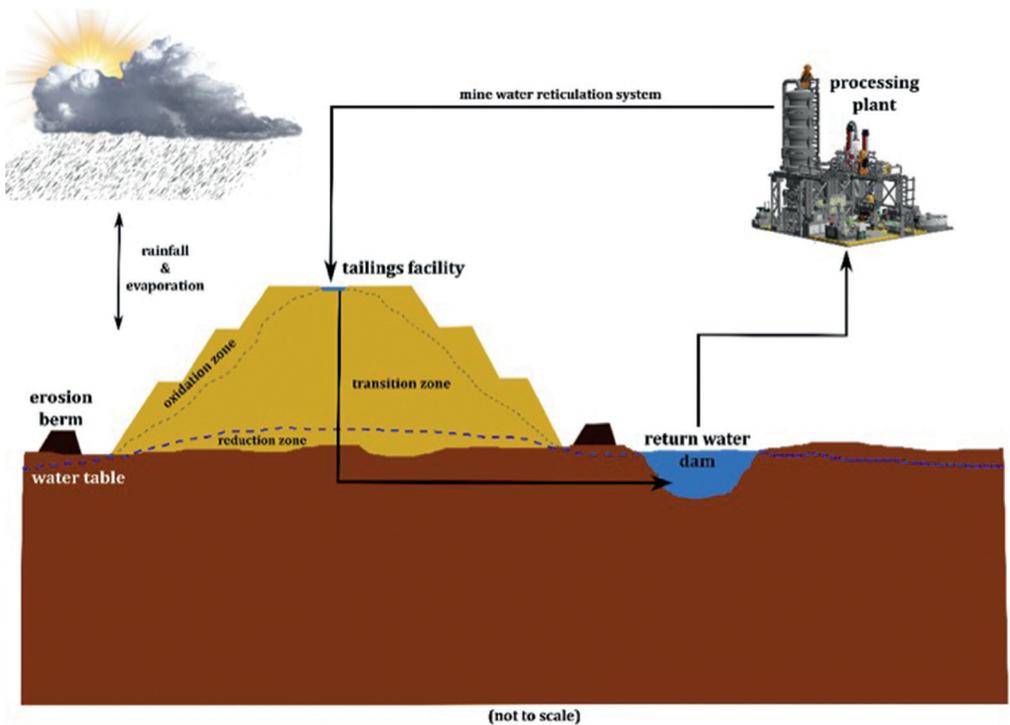
Figure 2 Conceptual model of the gold tailings facilities in the Witwatersrand gold fields showing the mine-water reticulation flow vectors as well as the geochemical zones.

The Free State and West Rand gold tailings contain small amounts of carbonates, specifically calcite and dolomite (Hansen 2018). The mass ratio of sulphides to calcite and dolomite are critical in terms of acid buffering in mine waste facilities in general (Jurjovec et al. 2002).

Most Witwatersrand tailings facilities contain the U-bearing phases uraninite and brannerite. Of the two, uraninite is the most abundant in the Witwatersrand (Fuchs et al. 2015, Lottering et al. 2008). Uraninite dissolves in low pH conditions according to:

Equation 7

$$UO_{2(s)} + 4H^+ \rightarrow U^{4+} + 2H_2O$$
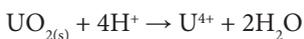
In the presence of O_2, U^{4+} can be further oxidised to U^{6+}, forming the uranyl (UO_2^{2+}) aqueous complex:

Equation 8

$$U^{4+} + \frac{1}{2}O_2 + 2H^+ \rightarrow UO_2^{2+} + H_2O$$
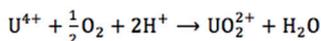
Eq. 7 and eq. 8 indicates that the dissolution of uraninite in an acidic solution in the presence of oxygen is an acid consuming process.

Thorium is less well studied in the Witwatersrand. Uraninite is a potential source for the Th (Hazen et al. 2009), although thorite has been observed (Smits 1989). However, thorite is often a product of the weathering of thorianite (Smits 1989), making the source mineral of Th in the Witwatersrand uncertain:

Equation 10

$$ThO_{2(s)} + SiO_{2(aq)} \rightarrow ThSiO_{4(s)}$$

Together with uraninite, thorite and thorianite can both weather to add Th to the tailings pore water:

Equation 11

$$ThO_{2(s)} + 4H^+ \rightarrow Th^{4+} + SiO_{2(aq)} + 2H_2O$$

Equation 12

$$ThSiO_{2(s)} + 4H^+ \rightarrow Th^{4+} + SiO_{2(aq)} + 2H_2O$$
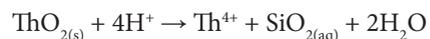
The solubility of Th in general is very low and typically occurs in solution in the order of µg/L values (Vandenborre et al. 2008, Neck et al. 2002, Langmuir and Herman 1980).

The geochemical processes described above, the hydrological regime of the tailings

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facility, and the limitations regarding the depth oxygen can diffuse in the facility, all cause the tailings facility to be stratified into three main geochemical zones (Hansen 2014, Dold and Fontbotè 2001). These three zones from the surface to the base are the oxidation zone (OZ), transition zone (TZ) and reducing zone (RZ) (Dold and Fontbotè, 2001). Recently these zones were modelled geochemically and produced results comparable to water chemistry sites already impacted by tailings material (Hansen 2014).

Numeric modelling

The numeric geochemical model of the Witwatersrand tailings was developed using three main inputs; a gas phase, a liquid phase and a solid phase. The gas phase is initially set to represent the Earth's atmosphere, containing 21% O_2 and 413 ppm CO_2. The fluid phase is set in the OZ model as pure water at pH 7. The output fluid phase at the end of the OZ calculations are used as input to the TZ model. The TZ model fluid output is in turn used as input solution to the RZ model. The output fluid from the RZ model represents the tailings pore water that has percolated through the tailings facility and reaches the substrate as well as the groundwater below the base of the tailings. The OZ and TZ are also in contact with the substrate beneath the tailings, therefore their model fluid outputs also represent tailings pore water from these specific zones, which are in contact with the substrate.

The model solid phase input is the various mineral phases as identified by the QEMSCAN results, of which the main phases are quartz, pyrophyllilte, muscovite and chlorite. Pyrite, uraninite and thorite/thorianite were also added to the model, as these are the main drivers, together with small amounts of calcite and dolomite, of the tailings geochemical system. All the minerals were described kinetically, with the exception of calcite and dolomite. Silicate mineral dissolution was modelled using the default rate equation of the software (Bethke 2008). Pyrite and uraninite reaction rates were modelled using the rate laws of Williamson and Rimstidt (1994) and Torrero et al. (1996) respectively.

There is uncertainty regarding the dominant Th mineral phases, as uraninite, thorianite and thorite are potential candidates. As the mineral phase in which Th resides may have a relevant influence on the release rates of Th and the concentration in the tailings pore waters, it is necessary to either quantify the mineral phase(s) in which Th resides, or to determine whether this quantification is important from an environmental risk assessment perspective.

A Monte Carlo analysis (Purton and Allan 2015, Ulfsbo et al. 2015, USGS 2008, EPA 1997) was conducted to determine whether Th is hosted within uraninite grains, or whether the amount of Th in the Witwatersrand ore material can only be explained by the presence of a separate Th-hosting mineral phase, i.e. in addition to uraninite. The following equation was evaluated in the probabilistic analysis:
Equation 13

$$\frac{(Ur_{whole\ rock} \times Th_{Ur\ grains})}{Th_{whole\ rock}} \times 100$$

In eq. 13, $Ur_{whole\ rock}$ represents the amount of uraninite in Witwatersrand gold ore, $Th_{Ur\ grains}$ the amount of Th in individual uraninite grains and $Th_{whole\ rock}$ represents the total amount of Th in the tailings material.

The simulation results, which are summarised in (tab. 1), indicate that 76% of 10 000 iteration data points lie below the study median of 34, while 24% lie above it. The 95th percentile simulation value is 56%. This indicates that the probability of uraninite accounting for < 56% of the Th in the basin is 95% implying that it is unlikely that uraninite is the only Th-containing phase in the Witwatersrand and that any environmental risk assessment for Th in Witwatesrand tailings needs to take this into account. The other two options are thorianite and thorite, as they are the most likely to occur together with uraninite in the Witwatersand gold ore. Model scenarios were developed for each of these minerals to evaluate their contribution to tailings pore water Th.

The model results (tab. 1) indicate that the pH is acidic in the OZ and increases to 6.02 in the TZ, where it remains relatively constant throughout the rest of the tailings facility. The OZ is oxic, while the TZ become reducing and stays so throughout the RZ.

Table 1 Model output result for the three geochemical zones of the tailings facility.

Parameters	Units	Oxidation Zone		Transition Zone		Reduction Zone	
		Thorianite	Thorite	Thorianite	Thorite	Thorianite	Thorite
pH		3.88	3.88	6.02	6.02	6.04	6.04
Eh	V	0.96	0.96	-0.02	-0.02	-0.03	-0.03
TDS	mg/L	4 372	4 372	4 584	4 584	4 552	4 552
U	µg/L	5 060	5 060	202	202	168	168
Th	µg/L	18	23	20	24	20	25

Initially in the OZ, the U concentration is elevated at 5 060 µg/L, but decreases significantly to 202 µg/L in the TZ and to 168 µg/L in the RZ. The Th concentration in the model tailings pore water remains relatively constant in both the thorianite and thorite models at ~20 µg/L.

Discussion

The geochemical models have indicated that U concentrations are likely to decrease in the tailings pore water as it percolates through the material from the OZ though the TZ and RZ to the tailings facility's base. The model has indicated that a number of secondary U mineral phases are over-saturated. They would thus be able to precipitate from the tailings pore water solution. Some of the U minerals over-saturated in the TZ and RZ include uranophane, soddyite, coffinite and uraninite itself. This indicates that the precipitation of secondary U mineral phases in the TZ and RZ may have a significant control on the concentration of U in the Witwatersrand tailings pore water.

Another control on U tailings pore water concentrations may be adsorption. Tab. 2 shows the aqueous species of U in the three geochemical tailings zones. The most important mineral phases in terms of adsorption capacity predicted by the model to be present in the tailings facility are hydrous ferric oxide (HFO) and goethite. However, the point of zero charge (PZC) of HFO is 8.1 and the PZC of goethite is between 6 to 7 (Smith, 1999). Therefore, in the OZ, with a median pH of 3.1, the negatively charged aqueous species are more likely to adsorb (Smith, 1999).

The complex $UO_2(SO_4)_2^{2-}$ occurs in the tailings OZ and can therefore potentially adsorb. The $UO_2(SO_4)_2^{2-}$ complex accounts for 14% of U in the OZ, as well as in the tailings as a whole. Therefore a maximum of 14% U can be expected to adsorb in the absence of competing ligands, which is not the case, as abundant SO42- is present in the tailings pore water, and in the presence of sufficient amounts of HFO and goethite. It is therefore unlikely that adsorption is a dominant geochemical control on the tailings pore water U concentration, although this will need to be quantified in follow-up studies.

Most of the U in the tailings pore water is introduced in the OZ. This implies a causal relationship between pyrite oxidation and uraninite dissociation. eq. 1 to eq. 4 and eq. 7 to eq. 9 indicate that pyrite oxidation introduced H+ into the tailings water, which is then utilised in the uraninite dissolution reaction in the presence of oxygen to produce soluble U(VI) as the UO_2^{2+} species. Thorium can occur in uraninite, but the Monte Carlo analysis has indicated that it is unlikely the major portion of Th in the Witwatersrand is hosted in uraninite grains.

The minerals thorianite and thorite are potential mineral hosts for Th, in addition to uraninite. The geochemical modelling results indicates that from an environmental risk perspective it does not matter in which of the two mineral phases, thorianite and thorite, Th is hosted, as the dissolution of both minerals results in equivalent model tailings pore water Th concentrations. In addition, the Th concentrations in the tailings pore water is low with a maximum of 25 µg/L.

This indicates that either the reaction rate is too slow to introduce environmentally relevant concentrations of Th into the tailings pore water, or that the solubility of the Th minerals are too low.

Table 2 Model output results of the most important U aqueous species in the various tailings geochemical zones.

Geochemical Zone	Species	Concentration molality	Concentration U molality	Proportion in tailings zone %	Proportion in whole tailings %
Oxidation Zone	$UO_2(SO_4)_2^{2-}$	6.59×10^{-6}	3.40×10^{-6}	14.0	14.0
	UO_2^{2+}	1.08×10^{-5}	9.54×10^{-6}	39.3	39.3
	$UO_2SO_{4(aq)}$	1.67×10^{-5}	1.08×10^{-5}	44.6	44.6
Transition Zone	$UO_2(CO_3)_2^{2-}$	1.12×10^{-9}	6.83×10^{-10}	83.0	< 0.1
	$UO_2(CO_3)_3^{4-}$	1.63×10^{-10}	8.64×10^{-11}	10.5	< 0.1
	$UO_2CO_{3(aq)}$	6.15×10^{-11}	4.44×10^{-11}	5.4	< 0.1
Reduction Zone	$UO_2(CO_3)_2^{2-}$	1.14×10^{-10}	6.95×10^{-11}	74.8	< 0.1
	$UO_2(CO_3)_3^{4-}$	2.61×10^{-11}	1.38×10^{-11}	14.9	< 0.1
	UO_2^+	5.96×10^{-12}	5.26×10^{-12}	5.7	< 0.1
	$UO_2CO_{3(aq)}$	4.68×10^{-12}	3.38×10^{-12}	3.6	< 0.1

Thorium minerals in general have low solubilities (Neck et al. 2003). Therefore it is likely that the low solubility of the Th mineral host phases is the main important control on tailings Th pore water concentrations.

Conclusions

Although Th does occur in the uraninite mineral structure in the Witwatersrand tailings material, it is not the most important. Most of the Th is hosted by primary Th phases, such as thorianite and thorite. From an environmental risk and geochemical modelling perspective, it does not matter which phase, thorianite or thorite, is chosen to represent Th in the Witwatersrand tailings facilities, as the solubility of both these mineral phases is too low to introduce environmentally relevant concentrations of Th into the tailings pore water.

The most elevated U concentrations in the Witwatersrand tailings facilities occur in the oxidation zone. As the pore water percolates vertically through the tailings facility, the U concentration in the pore water decreases. This is most likely due to the precipitation of secondary U mineral phases. Uranophane, soddyite, coffinite and uraninite were all oversaturated in the model tailings pore water. It is unlikely that adsorption can account for the substantial removal of U from that tailings pore water, as the U generally forms neutral and negatively charged aqueous species in the tailings pore water. This aspect will need to be quantified in follow-up studies.

As most of the U in the tailings pore water is introduced in the oxidation zone, remediation and mitigation efforts for U should be focussed on this zone. These methods can either focus on the pyrite oxidation process or on the secondary impacts, e.g. treatment of groundwater pumped from a borehole adjacent to the oxidation zone down-gradient from the tailings. The challenge with regards to engineering options for operational and post-operational tailings facilities is that funding is much more difficult to source to cover the operational expenditure of many existing technologies. New technologies will have to be developed which provide long-term low operational cost solutions or ideally sustainable passive solution. Bioremediation is a promising field.

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