Applied Geochemistry 61 (2015) 217–223

Contents lists available at ScienceDirect

Applied Geochemistry

journal homepage: www.elsevier.com/locate/apgeochem

Contaminant leaching from gold mining tailings dams in the Witwatersrand Basin, South Africa: A new geochemical modelling approach

Robert N. Hansen *

University of the Free State, Department of Geology, PO Box 339, Bloemfontein 9300, South Africa

ARTICLE INFO

Article history:
Available online 10 June 2015
Editorial handling by M. Kersten

ABSTRACT

In this study a new geochemical reaction modelling methodology is used to shed light on the geochemical processes within Witwatersrand tailings impoundments and the evaluation of the geochemical impacts for future mining projects is evaluated. Information from international and local studies on tailings sulphidic tailings impoundments is used to develop a conceptual understanding on a typical Witwatersrand gold tailings impoundment. The tailings impoundments consist of 3 distinct geochemical zones: Oxidation Zone (OZ), a Transition Zone (TZ) and a Reduction Zone (RZ). Individual reaction models are developed for each of the 3 zones. The output of one model is used as an input to the next in spatial order. The results of the final model represent the tailings basal seepage characteristics, which indicate the most likely impacts on groundwater resources. The model results agree with existing information on AMD in the Witwatersrand. The results indicate that the tailings basal seepage is likely to be acidic (pH of ~3.5), containing elevated concentrations of SO_4 and trace metals (Al, Co, Cr, Cu, Mn, Ni, Zn and U). Predicted Fe concentrations are low, due to the low f_{O_2} in the TZ and RZ and the buffering effect of the precipitation of K-jarosite in the OZ and TZ. This study therefore indicates that the methodology employed produces results that can be correlated to existing information and can thus be used as a methodology in the assessments of impacts from sulphidic tailings material for future mining projects.

1. Introduction

Acid mine drainage (AMD), resulting from the gold mining activities in the Witwatersrand, South Africa, has become the focus of intense study in recent years (Naicker et al., 2003; Cukrowska et al., 2004; Coetzee et al., 2010; Nengovhela et al., 2007; Tutu et al., 2008; Peretyazhko et al., 2009). This is mostly due to fears regarding the impacts from rising mine void water in defunct gold mines and the contamination of large volumes of groundwater and of ecological sensitive surface water systems surrounding these mines (Coetzee et al., 2010). Tailings impoundments are significant contributors to AMD (Dold and Fontboté, 2001; Tutu et al., 2008) and its resultant SO_4, Fe and trace metal, including U, contamination (Tutu et al., 2008). This has placed emphasis on the need for better tools in firstly understanding the geochemical processes operational in the Witwatersrand gold tailings, but also on the assessment of the impact of tailings impoundments for planned future mining projects. Dynamic geochemical reaction modelling is such a tool.

Not one peer reviewed study on specifically geochemical models of Witwatersrand tailings impoundments could be sourced. This underscores the need for studies specifically focused on the understanding of tailings impoundments through using available tools, such as geochemical modelling. In this article a new modelling methodology is described which not only sheds light on the internal geochemical processes of the gold tailings impoundments, but which can also be used as a tool in the assessment of geochemical impacts from mine residue of future planned mining projects for e.g. environmental impact assessments.

2. Locality

The Witwatersrand gold mining basin is located in the north-eastern part of South Africa (Fig. 1). The city of Johannesburg and the towns of Klerksdorp, Potchefstroom, Vereeniging and Welkom occur within its boundaries.

3. Methods

The software package The Geochemist's Workbench® was used to develop the numeric geochemical reaction models. For the

---

* Tel.: +27 12 7512160; fax: +27 86 6072406.
E-mail address: rhansen@outlook.com

http://dx.doi.org/10.1016/j.apgeochem.2015.06.001
0883-2927/© 2015 Elsevier Ltd. All rights reserved.

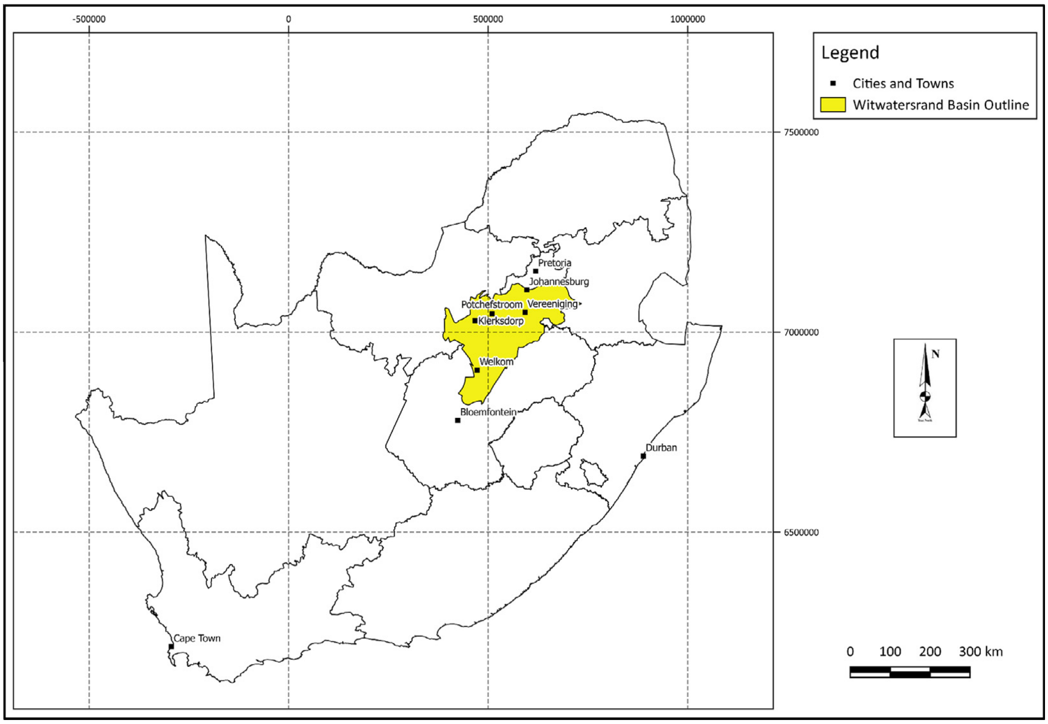

Fig. 1. Map showing the outline of the Witwatersrand Basin as well as the main towns and cities in the Basin and in South Africa. The coordinates system used is UTM and the datum used is WGS1984.

tailings geochemical models, only the operational phase is considered. The ore mineralogy of Rösner et al. (2001) and the oxygen concentration data of Nengovhela et al. (2006) were used as input to the geochemical models.

Existing data on AMD solutions and their impacts in the Witwatersrand from Naicker et al. (2003), Cukrowska et al. (2004) and Tutu et al. (2008) and tailings mineralogical data from Rösner et al. (2001) were used to evaluate the model results. A model of the tailings impoundments was built on current understanding of sulphidic tailings impoundments in general. This conceptual framework is described below.

4. Conceptual geochemical model for the Witwatersrand gold basin tailings

A review of the literature shows that the effluent from sulphide mineral containing tailings without sufficient buffer capacity, such as those resulting from the gold mining activities in the Witwatersrand are acidic in nature and contain elevated concentrations of trace metals and SO_4 (Dold and Fontboté, 2001; Gleisner and Herbert, 2002; Naicker et al., 2003; Simón et al., 2005; Nengovhela et al., 2007; Gunsinger et al., 2006; Tutu et al., 2008).

A tailings system can be considered open from a thermodynamic perspective, i.e. mass and energy can transfer across system boundaries. The main influx of water into the tailings system is water in the tailings slurry and rainfall. Evapotranspiration, interstitial lockup, seepage to groundwater and toe seepage are the main losses. It is the seepage to groundwater which is of most concern from an environmental point of view. Toe seepage is captured by the toe drains and tailings erosion paddock walls. From a dissolved mass flux perspective, the mass flux in the tailings seepage is significantly elevated above that of rainfall and evapotranspiration. Therefore for the purposes of numeric modelling the dissolved mass of rainfall and evapotranspiration can be considered as negligible.

The Witwatersrand gold–uranium ore contains an average of 3 wt% pyrite (Hallbauer, 1986). Mineralogical data of 16 tailings samples throughout the Witwatersrand collected from surface to a depth of 80 cm (Rösner et al., 2001) indicate that the major constituents, at least at surface, are quartz, mica (unspecified) and chlorite with jarosite and pyrophyllite occurring in trace amounts. Gypsum was recorded in one sample. An average mineralogical composition of the auriferous ore is presented in Rösner et al. (2001) and indicates that it consists mostly of quartz, pyrite, muscovite and chlorite. Minor components are chromite, pyrophyllite, titanite and zircon. Uraninite occurs as a trace component. The mineralogical data of the ore and tailings material indicates that the material has a sufficient sulphide content to produce AMD conditions, but that acid buffering capacity is minimal (see Fig. 2).

Pyrite can oxidised by oxygen or ferric iron according to the following reactions (Williamson and Rimstidt, 1994):

$$FeS_{2(s)} + H_2O + \frac{7}{7}O_{2(aq)} = Fe^{2+} + 2SO_2^{2-} + 2H^+ \qquad (1)$$

$$FeS_{2(s)} + 8H_2O + 14Fe^{3+} = 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \qquad (2)$$

Eqs. (1) and (2) show that for both oxidation mechanisms H^+ is produced.

For pyrite to be oxidised by ferric iron (Eq. (2)), the ferrous iron produced through the oxidation of pyrite by oxygen (Eq. (1)) needs to be oxidised to ferric iron. This occurs via the following reaction (Stumm and Lee, 1961; Jones et al., 2014):

$$Fe^{2+} + \frac{1}{4}O_{2(aq)} + H^+ = Fe^{3+} + \frac{1}{2}H_2O \qquad (3)$$

However, ferric iron is soluble at a pH value below 3 (Jones et al., 2014). Therefore, until enough acidity is produced through Eq. (1) to bring the pH down from circum neutral to <3, ferric iron will precipitate as ferrihydrite according to (Jones et al., 2014):

$$Fe^{3+} + 3H_2O = Fe(OH)_{3(s)} \qquad (4)$$

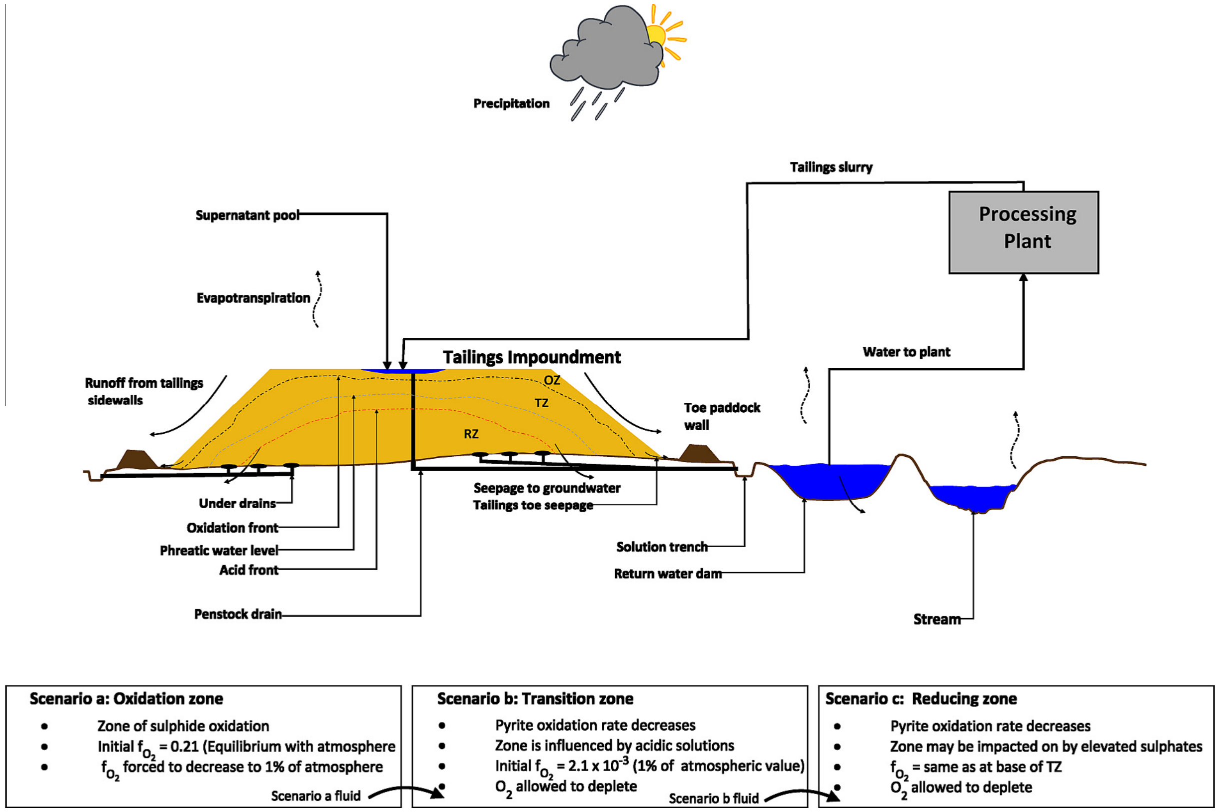

Fig. 2. Conceptual model of a typical gold tailings impoundment in the Witwatersrand. The model shows the main water flux as well as the main geochemical zones within the tailings impoundment. Main tailings system water influx is the water in the tailings slurry pumped from the plant and rainfall. Main losses are water returned to the mine reticulations system through the penstock and return water impoundment as well as evapotranspiration, interstitial lockup, seepage to groundwater and toe seepage. Toe seepage will occur when the hydraulic conductivity of the tailings material is higher than that of the substratum material to the tailings base. Seepage to shallow groundwater and base flow receiving streams adjacent to the tailings impoundment can also occur from the tailings return water dam. The main geochemical zones are: a, the oxidation zone from the tailings surface to the oxidation front; b, the neutralisation zone, between the oxidation and acid fronts and; c, the reduction zone, from the acid front to the tailings base. A concept of the modelling methodology of the numeric geochemical model is shown in the three boxes below. The upper image is the conceptual model. The boxes below indicate the individual models developed. Each model is coupled by using the output results as input to the following model. OZ is the Oxidation Zone, TZ is the Transition Zone and RZ is the Reduction Zone. The results of the final model, the RZ, represents the tailings seepage to the shallow groundwater system.

The oxidation of pyrite by ferric iron can be 2 orders of magnitude higher than oxidation by oxygen (Chandra and Gerson, 2010). However, the oxidation of ferrous to ferric iron is slow, unless the reaction is catalysed by bacteria, such as *Acidithiobacillus Ferrooxidans* (Gleisner et al., 2006). Therefore, once the pH has reached values of <3, the oxidation rate can be expected to increase. This will not occur *ad infintum*, as oxygen is still required for the bacterial catalysis of the pyrite oxidation and the oxidation by ferric iron (Williamson and Rimstidt, 1994; Gleisner et al., 2006) and the availability of oxygen is limited in a tailings impoundment with increasing depth, due to the relatively slow diffusion coefficient of oxygen into the tailings impoundment (Ritchie, 1994). In addition secondary minerals generally coat fresh sulphide mineral surfaces as oxidation progresses, thereby limiting the exposure of fresh pyrite surface to oxygen (Hansen et al., 2008). Oxidation rates therefore can be expected to reach a maximum upon the specific balancing of all these processes in the tailings impoundment. Previous studies in the Witwatersrand have shown that these processes occur sufficiently rapidly to produce acid mine drainage (AMD) conditions (Naicker et al., 2003; Cukrowska et al., 2004; Nengovhela et al., 2007).

The acidity in the tailings effluent can be mitigated if sufficient buffer capacity exists in the system in the form of especially carbonate minerals, such as calcite and dolomite or in the case where lime is added in the plant processes. Due to the ubiquitous nature of AMD conditions in the Witwatersrand gold mining region as whole, this scenario is not the norm. Thus for the purposes of this study, buffer capacity will be ignored.

Once the tailings effluent solution has become acidic the silicate minerals begin to dissolve and release trace metals stored in the silicate mineral structure. The pyrite grains themselves also contain trace metals in concentrations sufficient to account for the elevated dissolved metal content in Witwatersrand AMD solutions (Hallbauer, 1986).

The Witwatersrand gold–uranium ore contains U in the form of uraninite (Robb and Meyer, 1995). This mineral can react in acidic solutions to produce soluble U ions according to:

$$UO_{2(s)} + 4H^{+} = 2H_2O + U^{4+} \qquad (5)$$

As oxidation of sulphides and other geochemical processes occur within the tailings impoundment, water percolates through the tailings and seeps into the groundwater system in unlined facilities. In the tailings operational phase the hydrological head is due to fresh water–laden slurry being deposited on the tailings. In the post-operational phase of the facility, this water level is mostly due to precipitation on the tailings impoundment. As the water volume of precipitation on the tailings is a fraction of the water deposited in the form of slurry, the head in the tailings subsides until it reaches the groundwater table. Concentrations in the tailings pore water may become elevated due to the lower water–rock ratio, but the vertical drive of the hydraulic head is also less, leading to a decrease in seepage flux to groundwater.

Studies on the internal structure of tailings impoundments in general (Dold and Fontboté, 2001) and in Witwatersrand gold tailings (Nengovhela et al., 2007) generally agree. These studies indicate that the tailings impoundments contain three main geochemical zones. The first, which occurs from the tailings surface radially inward to the oxidation front is termed the Oxidation Zone (OZ). The oxidation front (OF) is the boundary between oxidised sulphides and unoxidised sulphides. The OZ is generally yellow to orange in colour and contains sulpho-salts, such as jarosite and gypsum and secondary iron oxy-hydroxides as sulphide oxidation products. The OZ is characterised by pore waters with high dissolved solids and low pH.

The Neutralisation Zone (NZ) occurs below the OZ. In this zone, if the tailings contains sufficient acid buffer capacity, acidity is neutralised and the pore waters are characterised by circum-neutral to alkaline pH values. However, since the Witwatersrand tailings impoundments generally do not contain sufficient buffer capacity, the NZ is actually more of a Transition Zone (TZ) between the OZ and the Reduction Zone (RZ) and will be referred to as such in this article. The oxygen content in the TZ has decreased to values <1% of the atmospheric value (Nengovhela et al., 2007). Therefore oxidation of sulphides is still possible, but the rate is a fraction of the oxidation rate in the OZ. The TZ is therefore not a zone of active reduction, but rather of very slow oxidation.

The RZ occurs below the TZ and is a zone in which reduction commonly occurs due to the low oxygen fugacity. This scenario occurs ion some sulphidic tailings impoundments from copper mines in which sulphides, such as chalcocite, actively form (Dold and Fontboté, 2001).

Although adsorption processes are conceivably operational within the tailings impoundments, its role is not taken into account during this modelling study.

The vertical structure proposed above is used to develop three numeric geochemical models, one for each of the 3 geochemical zones outlined above.

5. Numeric geochemical models

The choice of modelling methodology is important and dependent on the purpose of the model (Zhu and Anderson, 2002; Bethke, 2008; Nordstrom, 2012). One method is to treat the entire tailings impoundment as a single entity. Another method is to develop a sequence of geochemical models, one representing each of the geochemical zones within the tailings impoundment. There are some disadvantages to the first approach. The main disadvantage to this approach is spatial, in that detailed geochemical processes operational within the various geochemical zones within the tailings cannot be taken into account. However, an advantage of this type of model is relatively short model run times and time series results can be generated.

One major advantage of the latter approach is the detailed geochemical processes of each distinct zone within the tailings impoundment can be taken into account. As the modelling is conducted by using the output of one model as input to the following, the detail of the geochemical processes active in each zone is carried over to the next model, thereby maintaining holistic integrity. The disadvantages are longer model run times and time series data cannot be generated for the tailings impoundment as a whole, although it can be generated for each of the distinct geochemical zones within the tailings impoundment. The latter approach is followed in this article as the focus is on the detailed geochemical processes operational within the tailings impoundment and the characteristics of water seeping from the tailings base to the underlying soil and groundwater.

The main geochemical process in the Witwatersrand gold tailings impoundments is the oxidation of pyrite. A previous study has shown that the oxidation of pyrite by oxygen is the most important oxidation mechanism (Nengovhela et al., 2007). To model this process, the rate equation of Williamson and Rimstidt (1994) for the oxidation of pyrite by dissolved oxygen is used:

$$r = 10^{-8.19(\pm 0.10)} \frac{m_{\mathrm{DO}}^{0.5(\pm 0.04)}}{m_{\mathrm{H^+}}^{0.11(\pm 0.01)}} \tag{6}$$

In Eq. (6) above, r is the reaction rate in mol m^{-2} s^{-1}, m_{DO} is the molality of dissolved oxygen and $m_{\mathrm{H^+}}$ is the molality of hydrogen. Less important, but still significant are the reaction rates of the silicate minerals. The rates of these are constrained using the rate constants provided in Palandri and Kharaka (2004), White and Brantley (1995) and Wilson (2004). The default forward direction rate equation of the software is used to model the reactions of the alumina-silicate minerals (Bethke, 2008):

$$r = A_s k_+ \prod^{j} m_j^{P_j} \left(1 - \frac{Q}{K}\right) \tag{7}$$

In Eq. (7) above, A_s is the mineral surface area, k_+ is the intrinsic rate constant for the reaction, m_j is the concentration of the reaction's promoting or inhibiting species and P_j is those species' exponents, Q is the activity product and K is the equilibrium constant for the reaction. In the absence of promoting or inhibiting species, the product terms falls away. The minerals input in the model and governed by Eq. (7) are quartz, chlorite, muscovite and uraninite.

Mineral surface areas were not available for the study and were calculated based on a tailings grain size of >75% are <75 μm (Nengovhela et al., 2006). Idealised crystal unit size dimensions were used to calculate individual mineral surface areas (Table 1).

Modelling potential metal and metalloid contaminants not included in the model input mineral components is more challenging. If it is certain in which mineral components these potential contaminants reside, the potential contaminants can simply be added to the model and forced to dissolve at fixed rates. Such information, especially in environmental impact assessments is generally absent. To overcome this difficulty, the potential contaminants are included in the model in their ionic form and allowed to react based solely on solubility controls. Although this method is a conservative estimate of the concentration of these potential contaminants in the final tailings seepage solution, it is still more accurate than relying solely on laboratory leach tests, which do not take geochemical process over time into account. The specific metals input into the current model are of Ni, Co, Cu, Cr, Mn, Zn and U. These metals were chosen on the basis that they have been shown to be elevated in shallow groundwater and surface water resources influenced by AMD (Naicker et al., 2003; Tutu et al., 2008) and to leach from the tailings (Cukrowska et al., 2004). With the exception of uranium, which was not included in the leach tests study, the XRF data of Cukrowska et al. (2004) was used to constrain the maximum leachable quantity of these metals by simple mass balance calculations and added to the model. The 95th percentile was used as to represent the upper limits of the data distribution. U was added to the model in the form of uraninite, which has been shown to have an average concentration in the Witwatersrand ore of 47 mg/kg (Rösner et al., 2001).

Table 1
Calculated model mineral surface areas.

Mineral	Units	Surface area
Pyrophyllite	cm^2/g	356
Quartz	cm^2/g	326
Chlorite	cm^2/g	473
Muscovite	cm^2/g	562
Pyrite	cm^2/g	247
Uraninite	cm^2/g	300

In relation to the tailings impoundment pore characteristics, rainwater can be considered as distilled water. The convention of using 1 kg of liquid is used. The input fluid to the geochemical model has a pH of 6.5 in equilibrium with atmospheric oxygen. The input solids are shown in Table 2. The model represents a system with a higher mineral than water content.

The work of Nengovhela et al. (2007) indicated that 99% of the oxygen is depleted within the first few metres of the tailings impoundment. The oxygen fugacity of the OZ was therefore forced to deplete from the atmospheric value of 0.21–0.0021. The oxygen fugacity of the TZ was set to the output value of the OZ (0.0021) and allowed to deplete. The fugacity of the TZ output was used as input to the RZ model and also allowed to deplete over the simulation period.

To take the temporal dimension into account, each individual geochemical zone within the tailings needs to be viewed thermodynamically as a closed system. Although this is not strictly the case, due to the fact that the three models are coupled and thus represent the tailings impoundment as a whole, it is most likely a close approximation. The simulations are run over an operational time period of 25 years.

The default thermodynamic data base of the software was supplemented with U speciation and solubility data from Gorman-Lewis et al. (2008).

6. Results and discussion

6.1. The Oxidation Zone (OZ)

Modelling results of the tailings pore water for the OZ indicates that the solution is acidic and contains elevated SO_4, Fe, Al, Co, Cr, Mn and Ni concentrations (Table 3). Although the model U concentration in the tailings pore water is predicted to be significantly lower than that of the other trace metals, the concentration of 200 $\mu g\,l^{-1}$ is still significant.

The minerals ferrihydrite [$Fe^{3+}(OH)_3$], K-jarosite [$KFe_3^{3+}(SO_4)_2(OH)_6$], pyrolusite[MnO_2] and the clay mineral Mg-nontronite [$Mg_{0.15}Fe_2^{3+}(SiAl)_4O_{10}(OH)_2{\cdot}nH_2O$] are shown to be stable in the OZ system and precipitate from the pore water solution. Although the model shows that Mg-nontronite is likely to precipitate from the OZ pore water, this is unlikely. Although the mineral may become stable over time, its eventual stability in the OZ system will most likely follow a range of intermediate products, such as gibbsite [$Al(OH)_3$].

Initially the ferrous and ferric iron redox pair was decoupled and the oxidation reaction modelled kinetically using the oxidation rate of Nordstrom (1985). This resulted in the model precipitation of alunite [$KAl_3(SO_4)_2(OH)_6$], the Al end-member of the alunite–jarosite solid solution series, whereas K-jarosite is stable in the OZ of actual Witwatersrand tailings systems (Rösner et al., 2001). When the iron redox pair was decoupled, i.e. assuming equilibrium of the reaction, K-jarosite and ferrihydrite precipitated, but only when goethite [$Fe^{3+}OOH$] was suppressed. This implies that a process within the tailings impoundment OZ shrinks the thermodynamic stability field of goethite and expands that of K-jarosite. It is possible that the ferrous iron oxidation reaction to ferric iron can achieve equilibrium in tailings systems in which the reaction is catalysed by bacterial action. The jarosite stability at the expense of goethite in the Witwatersrand tailings systems is evidence that the ferrous iron oxidation in the OZ of the tailings is catalysed by bacterial action, which typically results in the formation of jarosite at the expense of goethite (Gleisner et al., 2006).

Table 2
Model input parameters of solid material.

Solid	Solid weight (g)	Solid concentration (wt%)
Quartz	2580	84.3
Pyrophyllite	36	1.2
Chlorite	78	2.5
Muscovite	276	9.0
Pyrite	90	2.9
Uraninite	0.5	0.016
Mn	0.36	0.012
Co	0.18	0.006
Ni	0.22	0.007
Zn	0.06	0.002
Cr	0.28	0.009
Cu	0.14	0.005
Total	3062	100.000

Table 3
Tailings impoundment pore water model results for the three geochemical zones. The results of the Reduction Zone (RZ) represent the water quality of seepage from the RZ to the shallow groundwater. The concentration of U is presented in $\mu g\,l^{-1}$.

Parameter	Units	Oxidation zone	Transition zone	Reduction zone
pH		1.8	3.4	3.5
Eh	V	1.08	0.86	0.83
TDS	$mg\,l^{-1}$	10,609	8983	8186
K	$mg\,l^{-1}$	121	<1	<1
Mg	$mg\,l^{-1}$	152	329	520
Fe	$mg\,l^{-1}$	430	<1	<1
SO_4	$mg\,l^{-1}$	7466	5084	3290
Al	$mg\,l^{-1}$	894	814	340
Co	$mg\,l^{-1}$	178	357	536
Cr	$mg\,l^{-1}$	277	555	834
Cu	$mg\,l^{-1}$	139	278	417
Mn	$mg\,l^{-1}$	356	714	1073
Ni	$mg\,l^{-1}$	218	736	656
Zn	$mg\,l^{-1}$	59	119	179
U	$\mu g\,l^{-1}$	200	484	728

6.2. The Transition Zone (TZ)

The model results of the TZ pore water indicates that the solution remains acidic as it percolates from the OZ through the TZ, although the pH does increase from 1.8 at the base of the OZ, to 3.4 at the base of the TZ (Table 3).

This is mostly due to the lack of acid buffer capacity in the Witwatersrand tailings system. Richie (1994) has indicated that the dominant transport mechanism of oxygen flux into the tailings is through diffusion, rather than as dissolved in infiltrating fluid and that the oxygen concentration can be expected to decrease with depth. Nengovhela et al. (2007) have shown that at a depth of 4 m in the particular tailings impoundment that was studies, the oxygen content had decreased to 3% of the atmospheric value. This is shown to be the case in the current results in the slow average oxidation rate of pyrite in the TZ of $4.81 \times 10^{-14}\,mol\,kg^{-1}\,s^{-1}$, compared to $5.93 \times 10^{-8}\,mol\,kg^{-1}\,s^{-1}$ in the OZ. This is a difference of 6 orders of magnitude. The increase in pH from the base of the OZ to the base of the TZ is therefore rather a function of the decrease in pyrite oxidation rate than the presence of any acid buffering capacity. In addition to a higher pH in the TZ compared to the OZ, the SO_4 concentration is lower in the TZ. This can also be ascribed to the slower rate pyrite oxidation in the TZ. The concentrations of Fe, Al, Mn, Ni and U are elevated in the TZ pore water in comparison to those in the OZ. Metal solubility is generally inversely proportional to the solution pH (Smith and Huyck, 1999), which explains why the concentrations of these metals remain elevated in the tailings pore water.

In addition to the precipitation of K-jarosite, the model also predicts the precipitation of alunite in the TZ. The decreasing pyrite oxidation rate in the TZ results in the decrease in the rate at which SO_4 and Fe is added to the tailings pore water. Therefore alunite begins to co-precipitate with K-jarosite as the thermodynamic stability field of the jarosite shrinks along the compositional axis, while that of alunite increases as the relative concentration of Al to Fe in the pore water solution increases. The ratio of Fe:Al in the TZ pore water is predicted by the model to be 1.7×10^{-7} at the base of the TZ. The model also predicts the precipitation of coffinite [$U(SiO_4)(OH_4)$], kaolinite [$Al_2Si_2O_5(OH)_2$] and Mg-nontronite. It is likely that these minerals may form eventually through intermediate products, such as gibbsite [$Al(OH)_3$].

6.3. The Reduction Zone (RZ)

The results for the RZ model are the final model results and represent the tailings seepage to groundwater (Table 3). These results do not directly represent the water quality of toe seepage from the tailings impoundment base, as the toe seepage represents an integral of drainage from a large area of the tailings base (Ritchie, 1994). It does however provide an indication of what the toe drainage would look like. The model results indicate that although the pH of the seepage (3.5) is slightly higher than that predicted for the TZ (3.4), the solution is still acidic. The sulphate concentration of 3290 mg l^{-1} predicted for the RZ is slightly lower than the 7466 mg l^{-1} predicted for the TZ.

As with the TZ, this can be ascribed to the slower average pyrite oxidation rate of 8.13×10^{-21} mol $\mathrm{kg}^{-1}\,\mathrm{s}^{-1}$ in the RZ compared to the rate of 4.81×10^{-14} mol $\mathrm{kg}^{-1}\,\mathrm{s}^{-1}$ in the TZ. The concentrations of Fe, Al, Mn, Ni and U are elevated in the RZ due to the acidic pore waters.

The model predicts the precipitation of alunite in the absence of K-jarosite. Due to the slow pyrite oxidation rate in the RZ, the rate addition of Fe to the tailings pore water in the RZ is not sufficient for the thermodynamic stability of K-jarsoite. The ratio of Fe:Al in the RZ is 2×10^{-7} at the base of the RZ. Alunite therefore precipitates as the dominant SO_4 mineral phase, as opposed to K-jarosite. This ratio is only slightly larger at a difference of 0.4, or 24%, than that of the TZ. The main difference is the predicted Fe concentration of the TZ of 1.4×10^{-4} mg l^{-1} compared to the 7.1×10^{-5} mg l^{-1} predicted for the RZ pore water. In addition to alunite, the model indicates that coffinite, kaolinite and Mg-nontronite is likely to precipitate, although this will most likely occur via intermediate products.

6.4. Model results and applicability to environmental assessments

In order to evaluate the applicability of the modelling methodology employed in this study, the results of the tailings impoundment seepage, represented by the model results of the RZ, the model results are compared to the shallow groundwater (Naicker et al., 2003; Tutu et al., 2008), seepage water (Naicker et al., 2003) and soil leachate (Rösner et al., 2001) data of studies in the Witwatersrand gold mining area (Table 4). The regulatory guideline values shown in Table 4 are used for reference purposes only. The Regulation 635 (R635) leach concentration threshold values of the National Environmental Management Waste Amendment Act (NEMWAA, Act 26 of 1998) are prioritised as these values now form the leachate assessment requirements for tailings assessments for the purposes of water use licensing as well as waste licenses. Parameters for which R635 values do not exist, the South African National Standards (SANS) 2011 drinking water standards are used. The standard error of the mean is used as a measure of the uncertainty of the mean value (Rimstidt and Vaughan, 2003).

Table 4 indicates that for the available data, with the exception of Fe and to some extent U, all the constituents, which the model predicts as being elevated in the tailings seepage, are also elevated in the shallow groundwater and soil seepage impacted by tailings impoundments. The acidic nature of the tailings seepage also compares well to the acidic nature of shallow groundwater impacted by tailings impoundments (Naicker et al., 2003; Tutu et al., 2008). Iron is generally elevated in shallow groundwater impacted by tailings impoundments in contrast to the model. Unfortunately Fe was not included in the soil study of Rösner et al. (2001) and further work is thus required to determine whether the iron is leaching from the tailings or whether it is being dissolved from soil particles. Uranium concentrations in impacted shallow groundwater are generally lower than the predicted model seepage. The soil leachate results (Rösner et al., 2001) indicates that U may be concentrated in the soil substratum to the tailings impoundments and thereby removed from the seepage solution, resulting in its absence or presence in low concentrations in tailings impacted groundwater.

It is recognised that shallow groundwater, soil seepage from affected areas and soil leachate concentrations cannot be used as a proxy of tailings seepage characteristics. This is due to the fact

Table 4
Model results including regulatory standards for comparative purposes as well as selected literature reference values.[a]

Parameter	Units	Model seepage results	Regulator guideline values		Naicker et al. (2003) – Seepage			Naicker et al. (2003) – Shallow groundwater			Tutu et al. (2008) – Shallow groundwater			Rösner et al. (2001) – Soil leachate		
		Value	Guideline value	Standard	Average	Standard error	*n*	Average	Standard error	*n*	Average	Standard error	*n*	Average	Standard error	*n*
pH	pH units	3.5	5–9.7	*SANS*	3.15	0.04	7	3.56	0.11	7	4.17	0.84	7	n.a.	n.a.	0
Eh	V	0.83	n.s.	*n.s.*	0.59	0.04	7	0.47	0.03	7	0.39	0.04	7	n.a.	n.a.	0
TDS	mg l^{-1}	8186	1000	*R 635*	n.a.	n.a.	0	n.a.	n.a.	0	n.a.	n.a.	0	n.a.	n.a.	0
K	mg l^{-1}	<1	n.s.	*n.s.*	n.a.	n.a.	0	n.a.	n.a.	0	10.51	3.94	7	n.a.	n.a.	0
Mg	mg l^{-1}	520	n.s.	*n.s.*	n.a.	n.a.	0	n.a.	n.a.	0	77.58	30.30	7	191.56	149.91	8
Fe	mg l^{-1}	<1	0.3	*SANS*	63.24	107.19	7	132.00	116.54	7	87.58	33.44	7	n.a.	n.a.	0
SO_4	mg l^{-1}	3290	250	*R 635*	1829.54	208.12	7	1791.36	214.04	7	4601.43	2139.91	7	1828.84	819.11	8
Al	mg l^{-1}	340	0.3	*SANS*	n.a.	n.a.	0	n.a.	n.a.	0	24.28	7.86	7	n.a.	n.a.	0
Co	mg l^{-1}	536	0.5	*R 635*	17.08	7.08	7	18.56	5.93	7	22.62	13.01	7	7.19	5.78	8
Cr	mg l^{-1}	834	0.1	*R 635*	9.43	3.82	7	8.78	4.10	7	n.a.	n.a.	0	0.16	0.31	8
Cu	mg l^{-1}	417	2	*R 635*	3.21	1.31	7	3.57	2.14	7	3.52	1.42	7	0.34	0.62	8
Mn	mg l^{-1}	1073	1	*R 635*	41.22	33.00	7	75.41	45.58	7	133.99	67.59	7	397.50	363.85	8
Ni	mg l^{-1}	656	0.07	*R 635*	16.17	3.27	7	16.02	3.52	7	23.46	6.30	7	27.19	22.80	8
Zn	mg l^{-1}	179	5	*R 635*	11.24	5.89	7	11.56	5.63	7	15.85	3.96	7	23.44	17.80	8
U	µg l^{-1}	728	15	*SANS*	n.a.	n.a.	0	n.a.	n.a.	0	3625.29	5154.54	7	8406.25	14792.60	8

[a] n.a. is *not analysed*, n.s. is *no standard*, SANS is South African National Standards (2011), R 635 is *Regulation 635 of the National Environmental Management Waste Amendment Act (Act 26 of 2014).*

that the seepage interacts with a soil and/or geological substrate as well as groundwater in which processes such as, amongst others, precipitation, dissolution and adsorption are active. The regolithic material underlying the majority of tailings in the Witwatersrand contains clay minerals, which have the capacity to remove contaminants from solution. Follow-up work will focus on the geochemical processes in the soil substrate that contributes to the eventual characteristics of groundwater impacted by the tailings seepage.

The effects of hydrological transport have not been taken account in this study, as to take account of detailed geochemical processes in a thermodynamic context. Follow-up work coupling the geochemical model results of this study with a detailed hydrological flow model for the tailings impoundments would provide valuable insight into the migration of pore waters through the tailings system and eventual seepage to groundwater.

The importance of adsorption processes within the tailings should also be evaluated in future work. Its role may, however, prove to be small due to the acidic nature of pore waters throughout the tailings impoundment (Smith, 1999).

7. Conclusions

The geochemical models developed for this study indicated that seepage from the tailings impoundments in the Witwatersrand are likely to be acidic and contain elevated concentrations of trace metal concentrations, specifically Al, Cr, Co, Cu, Mn, Ni, Zn and U, as well as SO_4.

The modelling methodology applied in this study treats each geochemical zone in the Witwatersrand gold mining tailings impoundments as a thermodynamic closed system and is modelled separately while coupling the models by using the output from one model as an input to the following model. Application of this methodology to the Witwatersrand tailings impoundments provided realistic results in terms of tailings seepage water quality while simultaneously providing important information in the thermodynamic processes governing contaminant mobility within the tailings impoundment itself.

Further research efforts should be focussed on the coupling of detailed geochemical models and detailed hydrologic transport models to evaluate the influence of oxygen and heat transport though the tailings impoundment on the pyrite oxidation rate and on secondary mineral precipitation. The interface between the tailings seepage and the shallow groundwater taking into account detailed geochemical processes, such as adsorption, also warrants further study to evaluate the final shallow groundwater plume characteristics.

Acknowledgements

The author would like to thank Exigo Sustainability for supplying the data required to conduct the geochemical modelling. Thank you also to Surina Esterhuyse as well as the anonymous reviewers for their critical review and constructive comments of the draft manuscript.

References

Bethke, C.M., 2008. Geochemical and Biogeochemical Reaction Modelling, second ed. Cambridge University Press, p. 543.

Chandra, A.P., Gerson, A.R., 2010. The mechanisms of pyrite oxidation and leaching: a fundamental perspective. Surf. Sci. Rep. 65, 293–315.

Coetzee, H., Hobbs, P.J., Burgess, J.E., Thomas, A., Keet, M., Yibas, B., Van Tonder, D., Netili, F., Rust, U., Wade, P., Maree, J., 2010. Mine Water Management in the Witwatersrand Gold Fields with Special Emphasis on Acid Mine Drainage. Report to the Inter-Ministerial Committee on Acid Mine Drainage, December 2010, p. 146.

Cukrowska, E.M., Govender, K., Viljoen, M., 2004. Ion mobility based on column leaching of South African gold tailings dam with chemometric evaluation. Chemosphere 56, 39–50.

Dold, B., Fontboté, L., 2001. Element cycling and secondary mineralogy in porphyry copper tailings as a function of climate, primary mineralogy and mineral processing. J. Geochem. Explor. 74, 3–55.

Gleisner, M., Herbert, R.B., 2002. Sulfide mineral oxidation in freshly processed tailings: batch experiments. J. Geochem. Explor. 76, 139–153.

Gleisner, M., Herbert, R.B., Kockum, P.C.F., 2006. Pyrite oxidation by *Acidithiobacillus ferrooxidans* at various concentrations of dissolved oxygen. Chem. Geol. 255, 16–29.

Gorman-Lewis, D., Burns, P.C., Fein, J.B., 2008. Review of uranyl mineral solubility measurements. J. Chem. Thermodyn. 40, 335–352.

Gunsinger, M.R., Ptacek, C.J., Blowes, D.W., Jambor, J.L., Moncur, M.C., 2006. Mechanisms controlling acid mine neutralization and metal mobility within a Ni-rich tailings impoundment. Appl. Geochem. 21, 1301–1321.

Hallbauer, D.K., 1986. The mineralogy and geochemistry of Witwatersrand pyrite, gold, uranium and carbonaceous matter. In: Annheausser, C.R., Maske, S. (Eds.), Mineral Deposits of Southern Africa I. The Geological Society of South Africa, pp. 731–752.

Hansen, Y., Broadhurst, J.L., Petrie, J.G., 2008. Modelling leachate generation and mobility from copper sulfide tailings – an integrated approach to impact assessment. Miner. Eng. 21, 288–301.

Jones, A.M., Griffin, P.J., Collins, R.N., Waite, T.D., 2014. Ferrous iron oxidation under acidic conditions – the effect of ferric oxide surfaces. Geochim. Cosmochim. Acta 145, 1–12.

Naicker, K., Cukrowska, E., McCarthy, T.S., 2003. Acid mine drainage arising from gold mining activity in Johannesburg, South Africa and environs. Environ. Pollut. 122, 29–40.

Nengovhela, A.C., Yibas, B., Ogola, J.S., 2006. Characterisation of gold tailings dams of the Witwatersrand Basin with reference to their acid mine drainage potential, Johannesburg, South Africa. Water SA 32, 499–506.

Nengovhela, A.C., Yibas, B., Ogola, J.S., 2007. An investigation into the availability and role of oxygen gas in gold tailings dams of the Witwatersrand basin with reference to their acid mine drainage potential. Water SA 33, 271–274.

Nordstrom, D.K., 2012. Models, validation, and applied geochemistry: issues in science, communication and philosophy. Appl. Geochem. 27, 1899–1919.

Palandri, J.L., Kharaka, Y.K., 2004. A compilation of rate parameters of water-mineral interaction kinetics for application to geochemical modeling. United States Geological Survey Open File Report 2004–1068, p. 70.

Peretyazhko, T., Zachara, J.M., Boily, J.-F., Xia, Y., Gassman, P.L., Arey, B.W., Burgos, W.D., 2009. Mineralogical transformations controlling acid mine drainage chemistry. Chem. Geol. 262, 169–178.

Rimstidt, J.D., Vaughan, D.J., 2003. Pyrite oxidation: a state-of-the-art assessment of the reaction mechanism. Geochim. Cosmochim. Acta 67, 873–880.

Ritchie, A.I.M., 1994. The waste-rock environment. In: Jambor, J.L., Blowes, D.W., (Eds.), Environmental Geochemistry of Sulfide Mine-Wastes. vol. 22, Mineralogical Association of Canada Short Course Handbook, 133–161.

Robb, L.J., Meyer, F.M., 1995. The Witwatersrand Basin, South Africa: geological framework and mineralization processes. Ore Geol. Rev. 10, 67–94.

Rösner, T., Boer, R., Reynecke, R., Aucamp, P., Vermaak, J., 2001. A Preliminary Assessment of Pollution contained in the Unsaturated Zone beneath reclaimed Gold-Mine Residue Deposits. Water Research Commission Report 797/1/01, p. 210.

Simón, M., Martín, F., Bouza, G.P., Dorronsoro, C., Aguilar, J., 2005. Interaction of limestone grains and acidic solutions from the oxidation of pyrite tailings. Environ. Pollut. 135, 65–72.

Smith, K.S., 1999. Metal sorption on mineral surfaces: an overview with examples relating to mineral deposits. In: Plumlee, G.S., Logsdon, M.J., Flipek, L.F. (Eds.), The Environmental Geochemistry of Mineral Deposits. Part A: Processes, Techniques and Health Issues, Reviews in Economic Geology, vol. 6A, pp. 161–182.

Smith, K.S., Huyck, L.O., 1999. An overview of the abundance, relative mobility, bioavailability and human toxicity of metals. In: Plumlee, G.S., Logsdon, M.J., Flipek, L.F. (Eds.), The Environmental Geochemistry of Mineral Deposits. Part A: Processes, Techniques and Health Issues, Reviews in Economic Geology, vol. 6A, pp. 29–68.

Stumm, W., Lee, G.F., 1961. Oxygenation of ferrous iron. Ind. Eng. Chem. 53, 143–146.

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. Appl. Geochem. 23, 3666–3684.

White, A.F., Brantley, S.L., 1995. Chemical weathering rates of silicate minerals. Reviews in Mineralogy, vol. 31, p. 583.

Williamson, M.A., Rimstidt, J.D., 1994. The kinetics and electrochemical rate-determining step of aqueous pyrite oxidation. Geochim. Cosmochim. Acta 58, 5443–5454.

Wilson, M.J., 2004. Weathering of the primary rock-forming minerals: processes, product and rates. Clay Miner. 39, 233–266.

Zhu, C., Anderson, G., 2002. Environmental Applications of Geochemical Modelling. Cambridge University Press, p. 300.