Oxidation process and hydrology of tailings dams: Implication for acid mine drainage from TSFs management -The Witwatersrand experience, South Africa

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Abstract

Oxidation of sulphide minerals in the unsaturated zone of tailings dams precedes acidification process of tailings material and release of potentially toxic and heavy metals into the receiving environment. The unsaturated zone of the tailings dam is the zone where oxidation processes are active. Thus a reasonably accurate estimation of the oxidation depth and its water balance will be critical to make reliable quantification of both acidity and metal leaching as the volume and quality of the acid mine drainage (AMD) to be generated from tailings dams is directly related to the volume of the oxidized tailings.

Detailed profile mapping, mineralogical, geochemical, physical and hydrological parameters of tailings, oxygen measurements and in situ monitoring of water balance components were conducted on selected decommissioned Witwatersrand gold tailings dams.

Active oxidation zone wherein AMD formation occurs ranges from 1.5 to 5 m in depth. A further 4 m depth makes up the transitional zone where a lower level of sulphide oxidation takes place. Oxygen diffusion ranges from about 200 to 500 cm correlating well with the observed active oxidation zone. Tailings dam age did not appear to have a major impact on the ultimate depth of active oxidation zone for dams a few years old after decommissioning. Pockets of oxidized 'zones' of various shapes have been observed within the un-oxidized zone indicating that oxidation could also be triggered along preferential flow paths associated with cracks and hydraulic discontinuities. This is unlikely to be a significant volume or contributor to contaminant load when compared to the full oxidising zone available for geochemical reaction.

However it has to be noted that kinetics of oxidation processes in mine tailings is likely to vary due to the inherent variation of properties such as permeability, mineralogy and geochemistry of tailings of different mines and other factors such as climatic condition.

Investigations of hydraulic properties of the tailings showed overall decrease in grain size and residual water content; increase in hydraulic conductivity and moisture content with depth. Water retention characteristic data shows that residual water content increases with depth for most tailings.

Based on hydraulic properties and monitoring data long term analysis runoff could be approximated as 0.17*Rainfall, and for event analysis for rainfall event less than 5 mm runoff to be 0.235*Rain*(1+(API_{-7})/100) except in well vegetated areas or on steep bare side slopes.

Keywords: South Africa, Witwatersrand, oxidation zone, water balance, mine tailing dams.

Introduction

There is a regular need to undertake studies on the pollution potential of mine waste residue deposits in the gold and coal mining industry. Such studies require the integration of oxidation process and geochemical characterisation modelling as well as water balance models. The understanding of oxidation zones and phreatic water surfaces plays a very important role in the prediction of acid rock drainage (Yibas et al., 2010; 2011). The uncertainty regarding the depth and progression of the oxidation zones is one of the major drawbacks in geochemical assessment and predictive modelling and the establishment of accurate oxidation profiles and determination of phreatic surface becomes an important issue for ARD prediction (Yibas et al., 2010).

The depth of oxidation zones in tailings is site specific (e.g. Nicholson 1994; MEND 1991;) and is affected by factors such as grain sizes, sulphide consumption, water table change, oxygen diffusion rates, age, saturated or unsaturated status, enrichment in sulphide minerals, water infiltration rates, temperature and moisture contents. Due to the complexity of the oxidation and reaction process, little work has historically been done to characterise the oxidation zone kinetically. The oxidation depth is also affected by other parameters such as climatic and weather conditions and tailings dams ages after decommissioning, all of which require in depth understanding.

Methods

Fieldwork focusing on identifying and documenting all observable features relevant to understand the rate of oxidation zone development was conducted at the selected tailings dams. Sections of up to 10 m below surface, exposed by the reclamation processes were mapped and logged in detail. This was complemented by augering up to 10 m deep in the unexposed part of the dam. Representative samples along profiles and from auger holes were collected. Instrumental measurement and laboratory tests (mineralogy, geochemistry) and study of the effect of variation in hydraulic properties (porosity, permeability, water content, preferential flow pathways such as cracks/fractures, mega-pores) with depth on oxidation processes and oxygen flux measurement with depth have been performed. The oxygen content of tailings dams was quantitatively measured using a multi-level gas sampling device (MLGS) adopted from Shaw (2004) to understand the diffusion of oxygen in tailings dams with depth.

For the purpose of hydrological and water balance investigation different probes and apparatus such as tensiometers, lysimeter, WaterMark sensors, TDR probes for volumetric water content measurement, runoff plots were installed. In-situ measurements of saturated and unsaturated hydraulic conductivity at depths of 2000, 1500, 1000, 500, and 250 mm were also performed. The data generated by the instruments and laboratory analyses were collated into a database. The relationship between the datasets from the different instruments have been analysed and used in the development of the water balances. In order to evaluate the long term water balance, predictive numerical modelling has been performed using the HYDRUS2D model (Simünek et al, 2006.).

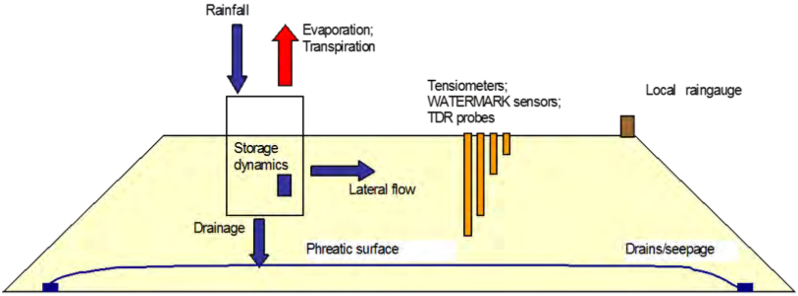

Figure1: *Schematic of instrumentation and monitoring of the water balance components of a tailings dam.*

Results and Discussion

Using the information from the detailed mapping of exposed section and auger hole data, three zones of oxidation were recognized based on differences in oxidation intensities, which varies with depth. These zones are: a) mature oxidation zone (OZ), b) Transitional oxidation zone (TZ) and c) primary or un-oxidized zone (UZ). The depth of matured oxidation zone ranges from 150 to 350 cm. The combined depth of the active oxidizing zone (transition zone) and the mature oxidized zone varies from 450 to 900 cm.

Mineralogical and geochemical evolution of tailings

Quartz, mica, and chlorite/chloritoid are the major minerals in the tailings materials, with pyrophylite and traces of K-feldspar present in some of the dams. Pyrite and jarosite ranging from 2 wt % to <0.5 wt % are also present. The effect of oxidation in the mineralogy of the tailings is apparent in that pyrite generally increases with depth and jarosite appears as an oxidation secondary mineral, thereby also increasing with depth.

Based on the paragenetic relationships (sequence in which minerals have formed) observed in sulphide-bearing mine wastes (adopted from Jambor, 2003), the oxidation evolution of the Witwatersrand Basin tailings has been established and summarised in Table 1. Accordingly, the geochemical evolution, hence the oxidation progression, is classified into early (E) mature (M) and late (L) stage of oxidation. The early stage could further be subdivided into Early 1 (E1) and early 2 (E2) sub stages.

Geochemistry

Enrichment of Al, Fe, Mg and Ca in the active oxidation zone and depletion at the mature oxidation zone is apparent from the XRF data. The percentage of Fe alone does not indicate the intensity of ARD-producing oxidation processes, because the source of Fe could be minerals other than sulphides such as chlorite and chloritoids. The concentration of trace metals such as Cr, Ni, Co, Cu, Zn and Pb depends mainly on the relative concentration of sulphide minerals. Ni, Co, Zn and at places Cu and Cr show enrichment at the active oxidation zone at the expense of depletion at the mature oxidation zone. However these patterns are not always straightforward due to interplay of factors such as relative positions of the millimetre-scale hard pans, upward capillary/osmotic actions, variations in permeability, and original geochemical variation of the tailings.

Table 1*: Relationship between progressive oxidation and mineralogy: (E1= beginning of oxidation, E2 (full early stage), M = middle stage, L= late stage, of oxidation)., Py= pyrite, Jar = jarosite, Gyp = gypsum, Chlrtd = chloritoid, Kf = K-feldspar, Qz = quartz, Pyroph. = pyrophyllite, Oxd. = oxidation, Tr = Trace*

Zone	**Py**	**Jar**	**Gyp**	**Chl-rtd**	**Kf**	**Qz**	**Mica**	**Chlo-rite**	**Pyro-ph.**	**Oxd. Stage**
TSF1-OZ	0	2	1		0	80	8	8		L
TSF1-TZ	1	1	0		1	82	9	7		E2
TSF1-UZ	1	0	0		1	80	11	7		E1
TSF2-OZ	0	1		22	0	65	4	3	5	L
TSF2-TZ	0.25	0		16	0	74	4	4	3	E1
TSF2-UZ	0	0		19	1	58	8	6	8	E1
TSF3-OZ	0	1		13	1	72	6	6	-	L
TSF3-TZ	1	0		10	Tr	75	6	6	-	E1
TSF3-UZ	0	1		22	Tr	61	7	8	-	E2-M
TSF4-OZ	-	2		7	1	74	10	6	-	L
TSF4-TZ	1	1		10	1	67	10	10	-	E2-M
TSF4-UZ	1	-		9	-	71	10	9	-	E1
TSF5-OZ	-	2		2	-	64	8	3	22	L
TSF5-TZ	1	2		3	-	66	5	3	20	M
TSF5-UZ-A	2	1		2	-	76	3	3	14	M
TSF5-UZ-B	-	1		2	-	78	6	3	10	E2-M

The pore water chemistry, summarised in Table 2, was approximated from paste pH and leachates chemistry. The overall geochemical pattern of the tailings pore water shows progressively lower pH values and high metal loading towards the top end of the dams. The geochemical evolution of the tailings pore water is governed by the combination of physical and geochemical processes that result from the products of the pH-buffering reactions combining with the products of sulphide oxidation reactions.

Table 2 *Summary of tailings pore water quality data with depth*

Dam	pH	SO_4	EC mS/m	Redox mV	Fe	Ca	Al	∑ Zn Ni Co
1	3.28-4.11	584-2934	115-314	215-255	30-157	193-265	2.4-233	10-22
2	2.5-6.2	1084-2347	190-483	324-618	<9-346	400-750	6-50	2-26
3	2.5-3.5	945-1234	204-269	452-522	2.3-119	15-340	12- 73	6-18
4	3.3	887-2149	204-344	404-546	3.4-45	174-242	18-125	16-19
5	3.2-4.1	1213-2114	237-405	454-531	2-4	364-564	19-101	9-43

The current pore water chemistry and the pH values (3-4) in the unsaturated zones of tailings dams suggest that the oxidation processes (of both sulphide and neutralizing minerals) progressed beyond the carbonates and oxyhydroxide dissolution and precipitation phases and attained the aluminosilicates breakdown stage to allow the generation of Al^{+3} and Si^{+4} in the pore waters.

The metal concentrations in the transitional zone are higher than that of the mature oxidation zone suggestive of pore water migration with soluble secondary minerals into the transitional zone. Acid neutralising reactions begin with dissolution of carbonate minerals (calcites [$CaCO_3$], siderite [$FeCO_3$], ankerite [Ca (Fe, Mg) $(CO_3)_2$, and dolomite [$CaMg(CO_3)_2$] (Jurjovec et al., 2002 and references therein). In the early stage of oxidation, carbonate dissolution can maintain the pH of the pore water near neutrality.

The dissolution of the Aluminum hydroxides and ferric hydroxides will be the primary buffers maintaining near constant pore water pH values after the dissolution of all available carbonates. The dissolution of aluminosilicate minerals becomes the principal process after the consumption of the carbonates, aluminum-hydroxides and ferric hydroxides in releasing Al and Si and buffering the pH of the pore water. The dissolution of aluminosilicates varies but generally is slow relative to the rate of groundwater flow, hence it is kinetically limited under the conditions that prevail in tailings impoundments (Blowes et al., 2003 and references therein).

The oxidation of sulphide minerals releases H^+ and $SO4^{2-,}$ and Fe^{2+}, and other metals to the tailings pore-water. The mass of metals released is controlled by the mineralogy of the tailings, the rate of sulphide mineral oxidation and by the removal of metals by secondary mineral precipitation. The pH of tailings is a good indicator of the abundance of sulphide minerals and the presence or absence of acid neutralising minerals. The extent of the acidity and the metal loads both in terms of quality and quantity, are generally lower than what would be expected if all the mass released by sulphide oxidation remained in the tailings pore water. In most tailings impoundments, the migration of low-pH conditions and the transport of dissolved metals could be limited by a series of acid neutralization reactions and metal-attenuation reactions, which occur near the zone of sulphide oxidation and beneath.

Understanding the sequence of metal mobility during the oxidation processes of tailings has been a subject of intense research. Jurjovec et al. (2002) performed a laboratory investigation and observed a predictable sequence of metal mobility, which is governed by the pH plateaus and can be tied to the times when the specific acid-neutralization reactions predominate. Zn, Ni and Co become mobile when the pH of the effluent water decreases to 5.7, whereas Al, Cr, V, Pb and Cd remains immobile until the pH decreases to 4.0. This sequence was also established for the Wits tailings studies in this project.

Oxygen concentration with depth

A decrease of O_2 gas concentration within the pore spaces of the tailings with increasing depth, as a result of O_2 consumption in sulphide oxidation reactions, is observed in the studied tailings. This relationship is also a common feature in tailings dams studied elsewhere (Smyth, 1981; Blowes and Jambor, 1990; Blowes et al., 1991). The application of O_2 gas measurements in pore spaces of tailings to locate the position and the rate and extent of sulphide mineral oxidation was adopted for this study based on previous studies of a similar nature (Blowes et al., 2003). Blowes et al. (2003) noted that the most rapid sulphide oxidation occurs shortly after tailings deposition ends, whereupon O_2-bearing gas diffuses into the tailings and the bacterial population within the tailings becomes established. As oxidation proceeds, the oxidation of sulphides becomes more extensive and oxygen migrates more deeply into the impoundment.

Blowes and Jambor (1990) have shown that there is a positive correlation between measurements of pore-gas O_2 concentrations and oxidation of sulphides in the Waite Amulet (Quebec Canada) tailings. In the shallow tailings, where sulphide minerals have been extensively depleted, gas-phase O_2 concentrations are high. Deeper in the tailings as unaltered sulphide minerals become available, gas phase O_2 concentrations decline sharply. This analogy is reflected in the tailings dams studied in this project which show a strong positive correlation between depth of mature oxidation zone and O_2 gas concentration with depth.

Accordingly, the depth of active oxidation zone as measured from the field observation ranges from about 150 cm to 350 cm. The oxygen measurement on the other hand shows that oxygen diffusion ranges from about 200 cm to 500 cm with an average O_2 diffusion depth of about 400 cm (Figure 2). This comparison highlights the potential of O_2 concentration measurement to indicate the depth of active oxidation in tailings dams.

Hydrology and water balance modelling

Investigations of hydraulic properties of the tailings showed overall decrease in grain size and residual water content and increase in hydraulic conductivity and moisture content with depth. The effect of fractures as conduits of O_2 and water into the tailings is demonstrated. The experimental study and data collection tasks have been successfully implemented. The data generated by the instruments and laboratory analyses were collated into a database for use in the project.

The relationship between the datasets from the different instruments have been analysed and used for water balance study. A tailings dam consists of variably unsaturated porous media with saturated and unsaturated zones. The proportion of the saturated zone decreases and may even disappear with time in decommissioned dams.

The hydrological system of gold tailings dams for operational and non-operational tailings dams are conceptually different and as such should be studied differently. In both decommissioned and operational tailings dams, there would be a spatial variation of the water balance components from the edge to the centre of the dam.

This is mainly attributed to the moisture available in the profile, which is governed by the presence and depth of the phreatic surface. Thus infiltration at the edge of the pool is maximum and minimum at the centre of the pool whereas evaporation would be maximum at the centre of the pool and minimum at the edge of the pool. The depth of the phreatic surface and rate of drop of this surface is difficult to estimate accurately.

Any attempt to determine the water balance of a decommissioned tailings dam should establish itself largely on the unsaturated flow processes and must account for the impacts of surface flux boundary conditions. The objectives of such studies should be to predict the actual infiltration rates and subsequently the seepage quantity from the tailings dam through, for example, dam toe drains.

The unsaturated zone in a tailings dam is characterised by significant spatial variability and relies heavily on the unsaturated flow principles. This, in turn, requires understanding and solving of the surface flux boundary problem – the result of which should be applied to predict the water balance of the entire tailings dam which is a saturated-unsaturated medium.

Full understanding of the hydrological process in a tailings dam requires knowledge of a) vertical pore water flow, b) the complex physical parameters, c) K (hydraulic conductivity) which is a complex function of volumetric water content, which varies with depth, d) Particle size distribution, e) the complicating factors such as mineralogy & preferential flow paths (fractures/cracks and partings on bedding planes) and f) the position of the phreatic surface.

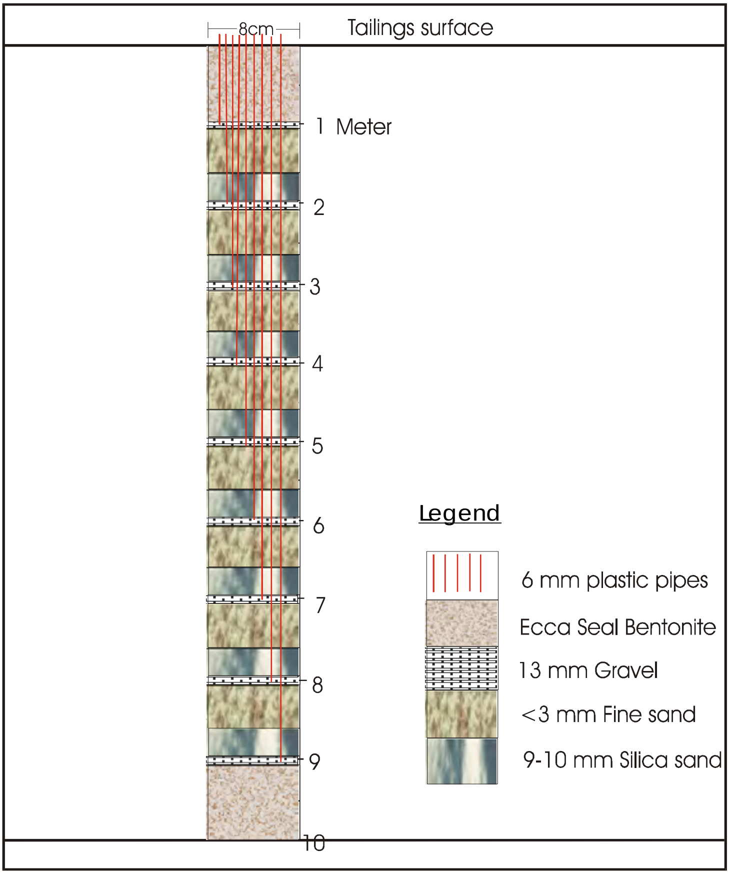

Figure 1: *Schematic diagram (not to scale) of the Multi Level Gas Sampler (MLGS) used to measure pore oxygen in tailings deposits (adopted from Shaw, 2004)*

The collected data is evaluated to extract simple 'rules of thumb' or 'general rules' that could be used to more simply determine the facility water balance when a screening-level of water balance is deemed appropriate. These general rules that have been derived are listed below.

General rule for runoff and infiltration response:

- Long term analysis: Runoff = 0.17*Rainfall, except in well vegetated areas or on steep bare side slopes
- Event analysis:No runoff for rainfall event less than 5 mm: Runoff = 0.235*Rain*(1+(API-7)/100)

General rule for evaporation from tailings surface:

- Long term analysis: Evaporation = 0.69*Rainfall,

- Event analysis: Evaporate at potential rate until 40 m pore water tension then, reduce to zero after a further 7 days without precipitation.

General rule for percolation:

- Long term analysis: Percolation = 0.17*Rainfall
- Event analysis: Derive response from pore water balance

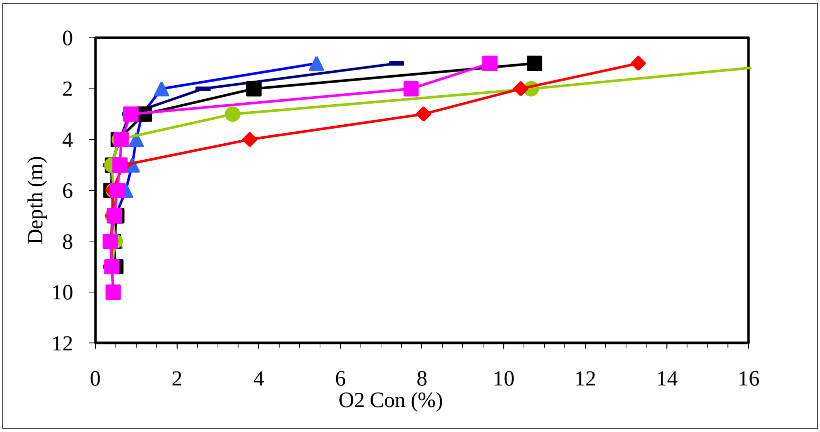

Figure 2: *O_2 gas concentration profile in the tailings deposits*

Conclusions

The active oxidation zone wherein acid rock drainage formation occurs has been found to vary between 1.5 and 5 m in depth with an average value of around 4 m in the gold tailings dams of the Witwatersrand basins. This suggests that, in the absence of more site specific data, geochemical prediction assessments for tailings dams should consider the active oxidising layer to be around 4 m thick. A further approximately 4 m of depth makes up the transitional zone where a lower level of sulphide oxidation takes place. However it has to be noted that kinetics of oxidation processes in mine tailings is likely to vary due to the inherent variation of properties such as permeability, mineralogy and geochemistry of tailings of different mines and other factors such as climatic condition.

It has been demonstrated that measurement of oxygen diffusion into the dam correlates very well with the actual observed active oxidation zone.

Pockets of oxidized ‘zone’ of various shapes have been observed, however, deeper than the established oxidation zones indicating that oxidation gets deeper down into the un-oxidized zones of the tailings dams, but mainly along preferential flow paths associated with cracks and hydraulic discontinuities. This is unlikely to be a significant volume or contributor to contaminant load when compared to the full oxidising zone available for geochemical reaction.

As a water balance is an essential precursor to a geochemical assessment, the water balance information presented herein will significantly improve the reliability of impact assessments and predictions undertaken for South African gold tailings dams. Investigations of hydraulic properties of the tailings showed overall decrease in grain size and residual water content; increase in hydraulic conductivity and moisture content with depth. Water retention characteristic data shows that residual water content increases with depth for most tailings. Based on hydraulic properties and monitoring data long term analysis runoff could be approximated as 0.17*Rainfall, and for event analysis for rainfall event less than 5 mm runoff to be 0.235*Rain*(1+(API-7)/100) except in well vegetated areas or on steep bare side slopes.

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