Oxidation Processes and Formation of Acid Mine Drainage from Gold Mine Tailings: A South African Perspective

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Abstract

Detailed multidisciplinary investigation of selected tailings storage facilities (TSFs) from the Witwatersrand gold mines generated datasets of mineralogy, chemistry, hydraulic properties, oxygen content with depth and leachate pore water chemistry. Three oxidation zones, namely mature oxidation (MOZ), transitional oxidation (TZ) and unoxidized (UZ) are recognized and mapped.

Pyrite, the major primary sulfide mineral, generally increases with depth, whereas jarosite appears at shallow depth at the expense of pyrite and decreases with depth, consistent with the progression of the oxidation front. Slight modifications of grain size distribution due to oxidation is evident. Hydraulic conductivity and moisture content increases and residual water content decreases with depth. Oxygen diffusion varies from 2 to 5 m with an average of about 4 m depth, correlating well with the measured oxidation zone thicknesses.

Sulfide minerals paragenesis, relative depletion and enrichment of certain major and trace elements in the MOZ and the TZ, respectively, and the pore water pH in the OZ, all indicate oxidation process reached "Late Stage" in the TSFs.

This study indicates that integrated investigation provides insights in the kinetics of oxidation processes and establishes a relationship between the volume of oxidized part of a TSF and the volume and quality of generated AMD.

Keywords: Tailings storage facilities, oxidation process, oxidation zone, mine drainage, oxygen diffusion, pore water chemistry

4.1 Introduction

Mine residue deposits are substantial contributors of pollution that adversely affects water resources, soil, and the surrounding ecosystem. As a result, studies to investigate the potential of mine residue deposits to generate pollution and its qualities and quantities are frequently conducted. Tailings storage facilities (TSF) generate voluminous, mining-affected

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water of varying quality and metal concentrations. The quality and chemical composition of the drainage from a TSF is directly related to the volume of the tailings portion subjected to oxidation processes.

Although the oxidation zone thickness in a TSF is site specific, geochemical prediction of drainage from a TSF is in most cases based on extrapolations from other sites. The oxidation processes and the resultant oxidation zone thickness is governed by the interplay of various factors such as particle size distribution, mineralogy and chemistry, water and oxygen availability, temperature and infiltration, and diffusion rates, as well as the age of the TSF after decommissioning.

South Africa has been mining gold for over 130 years and was the largest gold mining country for over a century. This gold mine operation created of over 270 mine residue deposits such as TSFs and waste rock deposits over an area of 400 km^2 (Figures 4.1 and 4.2). It is estimated that billion tons of mine residues are contained in these mine residue deposits [1].

This chapter presents and discusses data such as oxidation zone thickness, physical, mineralogical, geochemical, and geohydrological characteristics of tailings, as well as oxygen diffusion with depth based on the findings of two research projects to investigate kinetic oxidation processes and water balance methodologies on mine residue deposits [2, 3]. The interplay of the factors critical to oxidation processes of tailings material and advances in understanding the quality and quantity of the resultant effluent from the Witwatersrand mine TSFs is discussed here.

4.2   Weathering and Oxidation of the Witwatersrand Gold Tailings

The oxidation processes and oxidation profiles of selected TSFs from the Witwatersrand gold mines were studied [2]. These TSFs were selected using criteria such as operational status (operational, closed, decommissioned, reclamation), age after decommissioning, geographic distribution, and geological variation. Available historical information such as design and construction, physical dimension and volume, seepage volume and quality, phreatic surface level data for the selected TSFs were collected [2]. Detailed site investigation of several TSFs and cross section mapping of exposed tailings due to reclamation were undertaken to investigate the lateral and vertical extent of oxidized and unoxidized zones [2, 4, 5]. Geochemical,
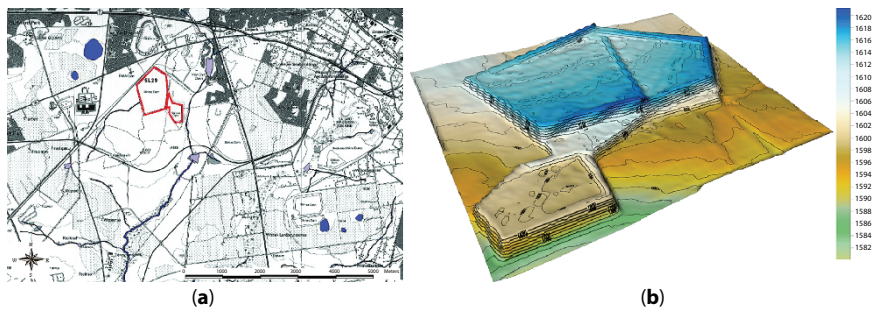

Figure 4.1 (a) Local topography map for TSF1; (b) 3D visualisation of TSF1, representative of the investigated TSFs (from [2], courtesy Anglo Gold Environmental).

Figure 4.2 Exposed mature oxidation zone (MOZ) with underlying Transitional Zone (TZ) (TSF5) with a vegetation cover on top.

mineralogical, and hydraulic properties such as grain size distribution, porosity, permeability, and water content and water retention characteristics of the tailings' samples were conducted on representative samples collected from the exposed cross sections and from auger holes [3]. The occurrence and effect of secondary permeability inducing phenomenon such as preferential flow pathways (e.g., cracks, fractures, mega-pores, bedding parallel flows) on oxygen and water infiltration and therefore on oxidation processes of tailings materials were investigated. A multilevel oxygen flux measurement with depth in selected TSFs was conducted following the methodology of [6] as discussed in detail in [2, 5, 7].

Most of the Witwatersrand gold mine TSFs are deposited in bench configuration of variable areal extent and height. The height of the investigated TSFs ranges from 1.1 to 34 m (Figures 4.1 and 4.2) with benches ranging from 1 to 4 (Figures 4.3 and 4.4). Cross-sections of profiles exposed during reclamation together with logging of several auger holes up to 10 m depth each were used to characterize variations of oxidation and identify three depth dependent oxidation zones (Figure 4.4). The lateral extent, thicknesses, and relative position of these zones are governed by the number and configuration of depositional benches (Figure 4.4). These three oxidation zones are: the mature oxidation zone (MOZ), transitional or active oxidation zone (TZ), and primary or unoxidized zone (UZ). The MOZ is amorphous with its most part and is characterized by leached buff gray top layer that grades into a light brown bottom layer. Itis interlayered with dark gray organic thin layers. The TZ is characterized by alternation of oxidized and partially oxidized or entirely unoxidized layers which are in most cases parallel to the depositional layers. However, irregularly shaped oxidation layers grading into partially oxidized and unoxidized parts of the zone are not uncommon. The MOZ thickness ranges from 1.5 to 3.5 m and the TZ thickness ranges from 3.0 to 4.5 m. The combined depth of the MOZ and TZ represents the total oxidation zone thickness and ranges from 5.5 to 9 m. The UZ is the thickest zone in all the TSFs forming
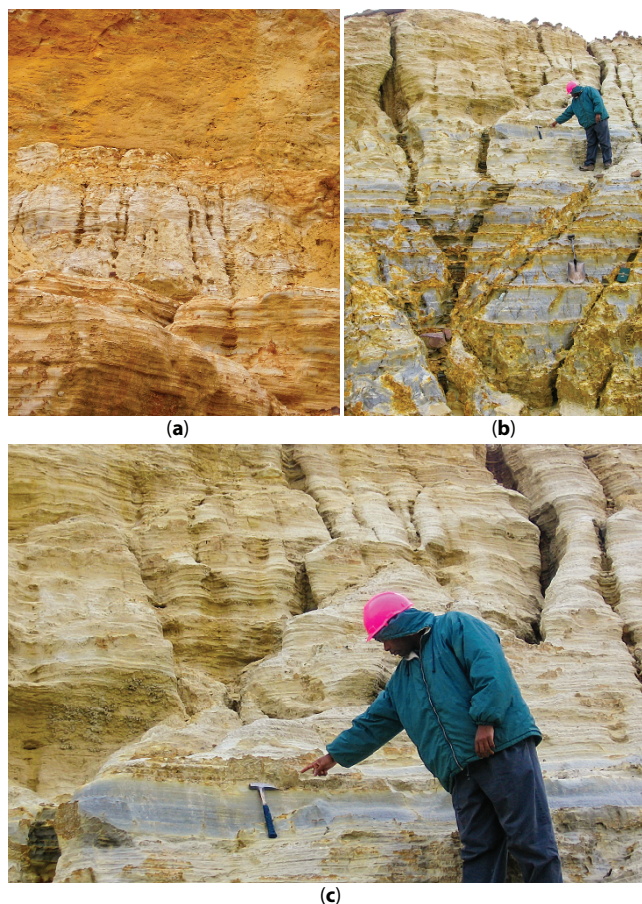
Figure 4.3 Detailed views of exposed tailing sections: (a) oxidation zone profile (≈8-m high) with oxidation zone (OZ) thickness of about 4.5 m; (b) exposed section of TSF5 (≈9-m thick) with about 3.5-m thick MOZ and over 5-m thick TZ with alternating oxidized and unoxidized layers reflecting compositional and textural variations, (c) exposed section showing the gradational contact between the MOZ and the TZ.

up to 70 % of the thickness of the TSFs. It is gray to dark gray and moist with little or no visible oxidation.

4.3   Water Infiltration and Oxygen Diffusion *vs* Oxidation Processes

4.3.1   Hydrogeology of Tailings Storage Facilities

4.3.1.1   Introduction

Tailings storage facilities are variably unsaturated porous media consisting of an unsaturated upper part and saturated lower part separated by a phreatic surface. The proportion of the saturated zone decreases and may even disappear with time in non-operational/decommissioned TSFs.
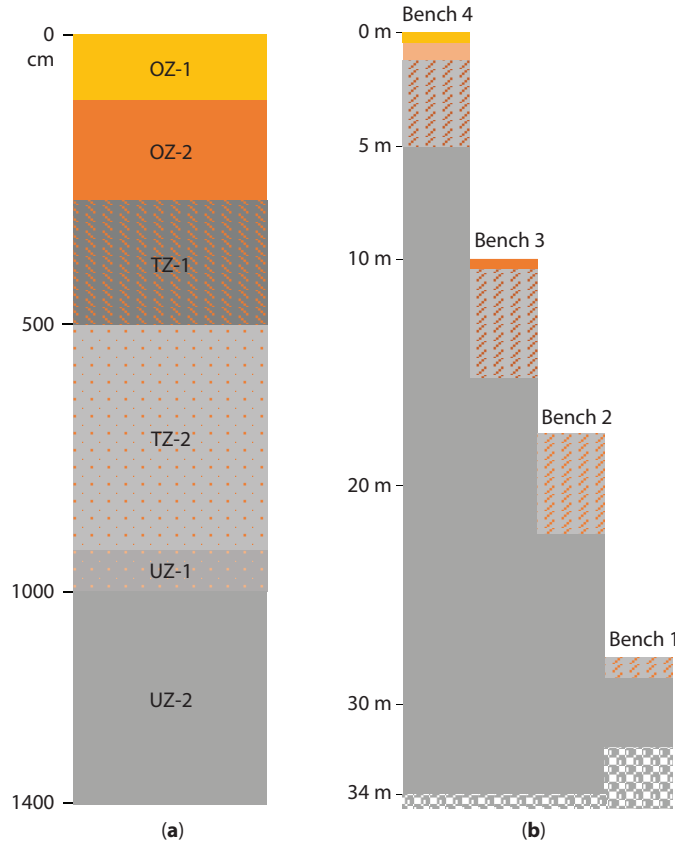
Figure 4.4 Oxidation profiles (a) OZ (MOZ), TZ, and UZ and subdivisions within the oxidized zones due to internal variation in oxidation intensity in TSF1, (b) oxidation zone development mimicking the depositional bench configuration wherein the vertical positions of the MOZ, TZ, and UZ are different in the different benches.

The saturated zone water balance components of a TSF are relatively well understood and can be estimated or calculated with relative ease. However, the estimation or calculation of the surface flux components above the phreatic surface is not well understood. Measurement of these surface flux components is expensive and time consuming and complicated further by the lateral thickness variation of the unsaturated zone from the edge to the center of a TSF due to the bell-shaped curve of the phreatic surface (Figure 4.5). This results in the spatial variation of the water balance components from the edge of the pool to the center of the TSF [8].

In operational TSFs, infiltration is maximum at the edge of the pool and minimum at the center of the pool, while evaporation is maximum at the center of the pool and minimum at its edge. Decommissioned TSFs have spatially varying unsaturated zones with the position of the phreatic surface and rate of drop of this surface difficult to estimate accurately which makes simple physical water balance calculations inappropriate (Figure 4.5). The main hydraulic properties that govern water flow paths in a porous unsaturated medium are particle size distribution, moisture content, bulk density, permeability/hydraulic conductivity, and water retention characteristics.
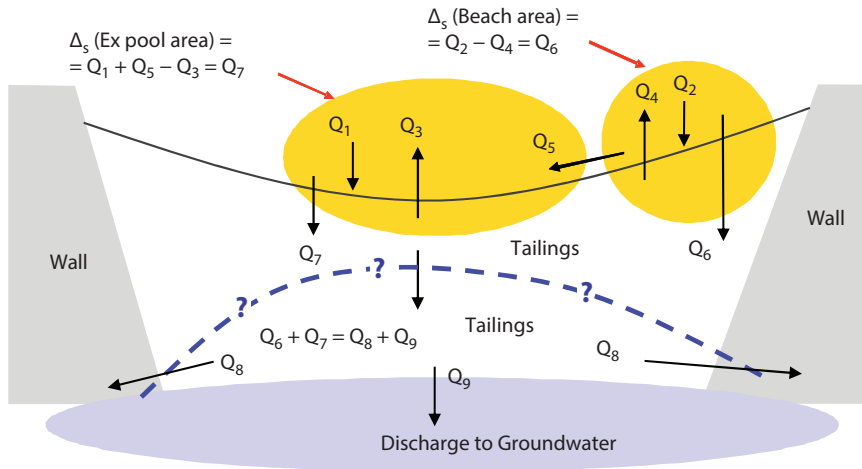
Figure 4.5 Schematic of water balance components for decommissioned TSF: Q_1, Q_2: precipitation on ex-pool and beach areas, respectively; Q_3, Q_4: potential evaporation from the ex-pool and beach area, respectively; Q_6, Q_7: infiltration from the beach and ex-pool areas, respectively; Q_8, Q_9: sideway seepage and discharge into groundwater, respectively (after [2]).

Numerical modeling is the only option available to determine the water balance components of the unsaturated zone (e.g., [8]). The existence of the spatial distribution of the surface fluxes (infiltration and evaporation) along the TSF profile could be used to establish a methodology to calculate these fluxes, which paves the way to formulate a more rigorous multidimensional unsaturated/saturated flow water balance modeling [8, 9].

4.3.1.2   Primary Hydraulic Characteristics

The depositional particle size distribution of the Witwatersrand gold mine tailings was relatively uniformly graded and dominantly sandy silt and rarely silty sand. In operational TSFs, particle size distribution tends to be finer from the edge to the center (pond or pool area) of the TSF during deposition forming alternate layers of relatively finer and coarser tailings vertically as the TSF grows in thickness and areal extent. Such alternate layers create capillary break, which complicates flow of water in tailings materials [3].

The particle size distribution of the tailings material in the different oxidation zones does not show substantial differences. However, detailed observation of the hydrometer analyses shows that the TZ materials are slightly coarser than that of the MOZ and both are coarser than the underlying UZ, the latter may reflect the original depositional particle size distribution (Table 4.1 and Figure 4.6). The slight grain size increase at TZ compared to the MOZ indicates the reworking of grain size distribution due to the weathering and oxidation processes.

Commonly, the water content of the original slimes and slurries of gold mines during deposition are approximately 1:1 [1]. Moisture content of tailings material then becomes variable in time and space. Measured moisture content data range from 7 to 20 wt. % with an overall increase of moisture content with depth. The lowest water content recorded

Table 4.1 Summary of the particle size distribution and water content data of selected Witwatersrand gold mine TSFs.

TSF1			
Zone	**OZ**	**TZ1**	**TZ2**	**UZ**
Depth (m)	0–2	2–5	5–9	9–10
% Clay	0	0	0	0
% Silt	68	63	68	61
% Sand	32	37	32	39
% Gravel	0	0	0	0
Material	Sandy silt	Sandy silt	Sandy silt	Sandy silt
Moisture (%)	15	16.7	14.1	19.5
TSF2				
Zone	**OZ**	**TZ**	**UZ-A**	**UZ-B**
Depth (m)	0–1.5	1.5–4.5	4.5–8	8–10
% Clay	0	0	0	2
% Silt	45	45	47	55
% Sand	55	55	53	43
% Gravel	0	0	0	0
Material	Silty sand	Silty sand	Silty sand	Silty sand
Moisture (%)	13.9	18.9	16.4	19.1
TSF3				
Zone	**OZ1**	**OZ2**	**TZ**	**UZ**
Depth (m)	0–2	2–4	4–5	5–10
% Clay	0	0	0	0
% Silt	59	60	43	64
% Sand	41	40	57	36
% Gravel	0	0	0	0
Material	Sandy silt	Sandy silt	Silty sand	Sandy silt
Moisture (%)	7.3	8.2	13.2	10.8

(*Continued*)

Table 4.1 Summary of the particle size distribution and water content data of selected Witwatersrand gold mine TSFs. (*Continued*)

TSF5				
Zone	**OZ1**	**OZ2**	**TZ**	**UZ**
Depth (m)	0–2	2–4	4–5	8.5–10
% Clay	0	0	0	0
% Silt	59	56	56	56
% Sand	41	43	44	44
% Gravel	0	1	0	0
Material	Sandy silt	Sandy silt	Sandy silt	Sandy silt
Moisture (%)	10.6	7.6	13.5	15.3
TSF4				
Zone	**OZ2**	**OZ1**	**TZ**	**UZ**
Depth (m)	1.5–2.5	0–1.5	2.5–5	5–8
% Clay	0	2	2	2
% Silt	76	66	75	74
% Sand	24	31	23	24
% Gravel	0	1	0	0
Material	Sandy silt	Sandy silt	Sandy silt	Sandy silt
Moisture (%)	16.1	19.1	20.3	27.9

is from the TSF3 tailings and ranges from 7 to 13 wt. %, whereas TSF4 shows the highest moisture content which ranges from 19–28 wt. % (Table 4.1). Water retention capacities and residual water content decreases with depth consistent with the general particle size distribution pattern (Figure 4.7). Residual water content ranges widely from 5.5 to 20 wt. % consistent with increasing bulk densities and decreasing porosities with depth. The hydraulic conductivities of samples from the TSFs ranges from 7.1×10^{-5} to 1.2×10^{-2} cm/s consistent with uniformly graded and well sorted nature of the tailings and the formation of hardpans leading to the formation of relatively flat beaches and hence relatively uniform permeability.

4.3.1.3   *Geological Structures as Preferential Flow Paths*

Discontinuous oxidized layers and irregular bodies were observed within UZ far below the boundaries of the UZ and the TZ (Figure 4.8a). The oxidation process that formed
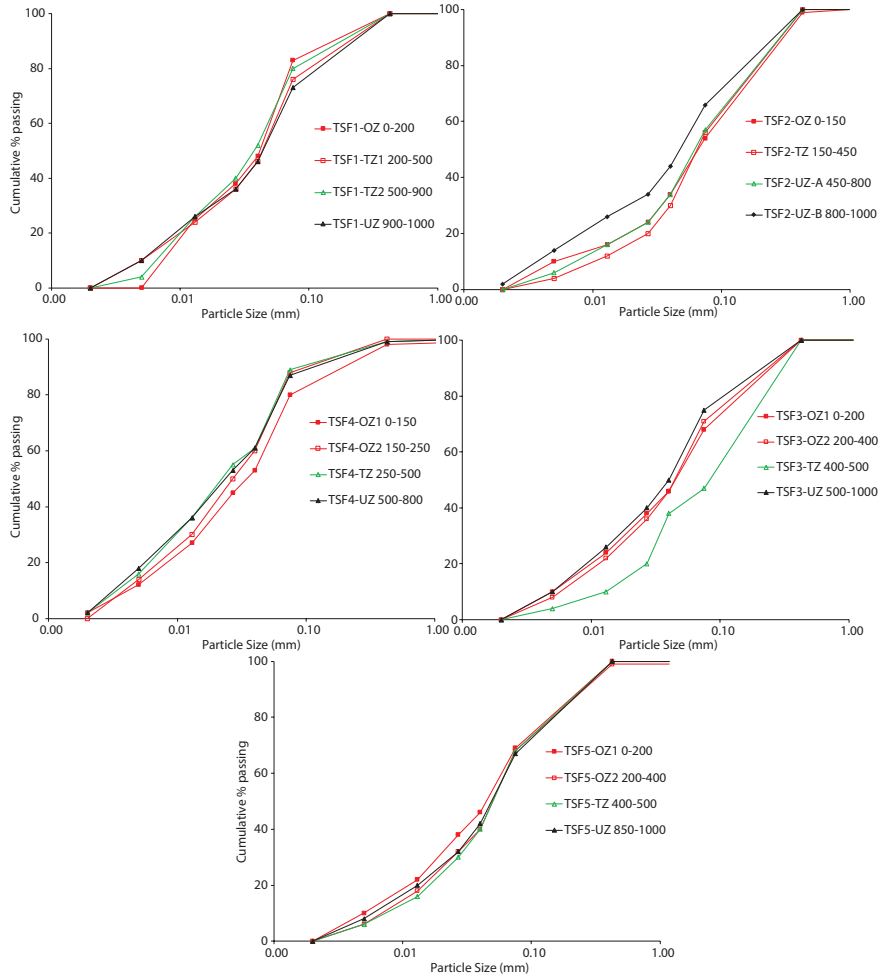
Figure 4.6 Particle size distribution of the different TSF oxidation zones.

these bodies is attributed to the existence of geological structures such as fractures, desiccation cracks, and bedding planes which acted as preferential flow paths to water and oxygen below the normal oxidation fronts (Figure 4.8b).

Although, generally, gold tailings are not the best growth medium due to their mineralogical composition which dominated by quartz and due to their low pH after weathering and oxidation, the effect of vegetation in the formation of preferential flow paths was evident in rare cases in TSFs where proper rehabilitation using soil cover and grass growth was effective for the growth of dense grass cover. The development of up to 20 cm of organic rich dark gray soil with grass roots penetrating up to 15 cm into the TSF were observed in these TSFs. In rare cases, where trees are planted (e.g., TSF3), root induced cracks are evidenced which could be used as preferential flow paths for water and oxygen infiltration in these TSFs.
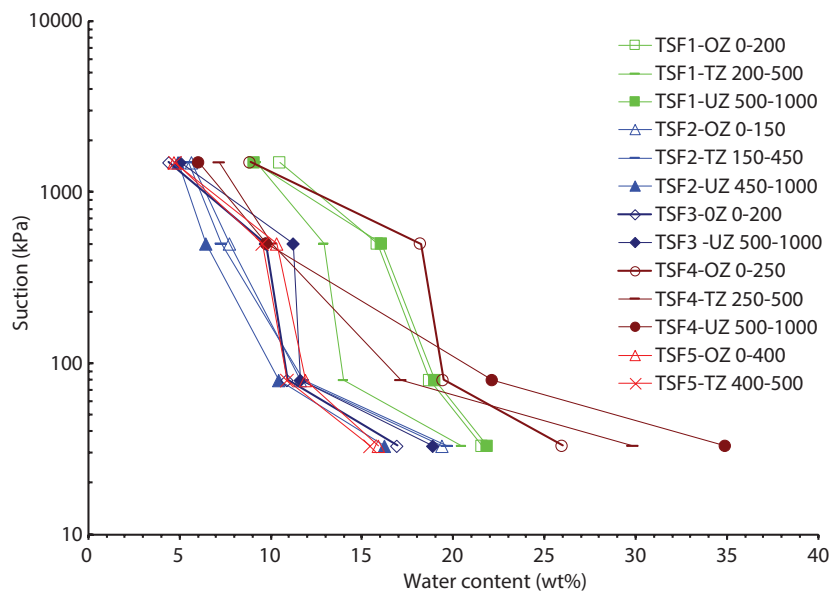
Figure 4.7 Water retention characteristics of the TSFs with depth as measured on four pressures (after [3]).
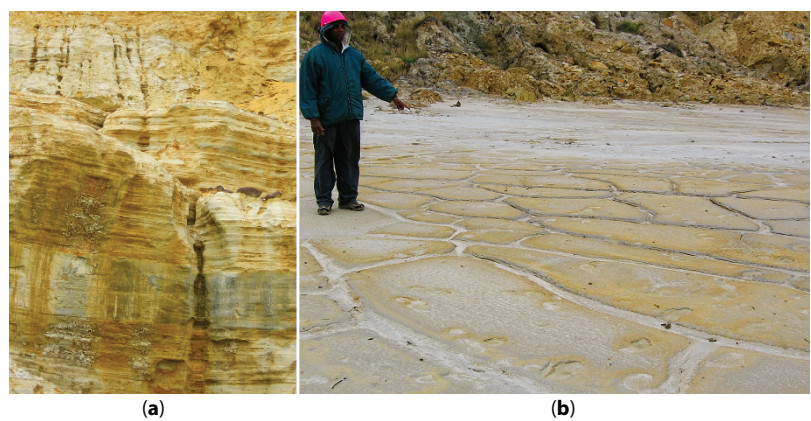
Figure 4.8 (a) Heterogeneity in oxidation intensity in a transitional oxidation zone (TZ); (b) Desiccation crack formation, which might lead to preferential flow paths for water and oxygen when interlayered and interconnected with other planar features.

4.3.2   Oxygen Diffusion

Oxidation in TSFs can occur in an aqueous or sub aqueous system where water content and oxygen flux will govern the rate of oxidation of minerals such as pyrite. As the phreatic surface above the saturated zone migrates downwards, the oxidation system will change from

subaqueous to sub aerial, whereby the partial pressure of oxygen and vapor pressure are the main factors controlling oxidation processes.

Transportation of oxygen into the tailings deposit could occur in one of three mechanisms: (1) advective transport with water that contains oxygen, (2) free or forced air convection through the top layer of the tailings deposit, and (3) diffusion in the gaseous and aqueous phases through pores in the material [10]. Diffusion is the dominant mechanism for transporting atmospheric oxygen from the surface of the tailings to the depth where oxidation takes place [11, 12, 15, 22]. Mechanisms (1) and (2) could be applicable in operational TSFs and at the top thin layers of all TSFs, whereas the atmospheric oxygen transport in the subaerial and aerial system of most TSFs is dominantly by diffusion in the gaseous and aqueous phases.

Inside a TSF, the degree of water saturation, the rate of water infiltration, the rate of oxygen consumption and temperature govern variations in oxygen concentration. The shape of an oxygen profile is controlled by the rate and the way oxygen diffuses into the TSF and the rate at which the oxygen is consumed within the TSF. The evolution of oxygen profiles as oxidation process progresses is the function of the consumption of oxygen [14].

Field studies conducted on uncovered unsaturated tailings deposits in Canada, has shown that the pore gas oxygen concentration decreased from atmospheric concentrations (21 vol. %) to less than 5 vol % within the upper 60 cm of the TSFs [15]. This showed that oxygen gradients exist in unsaturated upper part of TSFs. At water-saturated conditions, i.e., below the ranges widely from 5.5 to 20 vol. % (phreatic surface), the oxygen concentration is limited to the solubility of oxygen in water (i.e., $\approx$ 21 vol. %). In general, however, the dissolved oxygen concentrations are very low in the saturated part of TSFs. Measurement of oxygen concentration in a TSF and establishment of oxygen profiles have become part of mine residue characterization studies. Earlier studies of TSFs have demonstrated that the consumption of pore-gas O_2 through *in situ* reactions results in decreasing O_2 concentrations with depth where transport is controlled by vertical diffusion of O_2 to the atmosphere [16].

In situ pore gas oxygen concentration with depth was measured at 1 m interval up to 10 m depth in the selected TSFs and the results are discussed in detail elsewhere [2, 4, 9]. The TSFs exhibit variable diffusion rates with an averaging oxygen concentration of 10.62 vol. % at 1 m depth and decreases substantially to an average concentration of 0.49 vol. % at 6 m depth and drops to 0.41 vol. % at 9 m depth. The oxygen diffusion depth ranges from about 2 to 5 m with an average of about 4 m (Figure 4.9), in agreement with the observed depth of oxidation front [2, 4, 9].

O_2 concentrations in all the TSFs show a negative correlation with porosity, permeability, and percentage of sand size grains and moisture content and a positive correlation with increasing silt percentages. High positive correlations exist between O_2 concentration and vegetation density. The apparent negative correlation with porosity, permeability, and moisture content may indicate that the dominant diffusion mechanism in the upper 3 to 4 m of these TSFs is not diffusion through pores in the gaseous and aqueous phases but rather by free or forced air convection through the top layer of the deposit following oxidation progression.

A decrease of O_2 concentration within the pore spaces of the tailings with increasing depth is consistent with findings of similar studies elsewhere [17–19]. The most rapid sulfide oxidation occurs shortly after tailings deposition ends, whereupon O_2 diffuses into
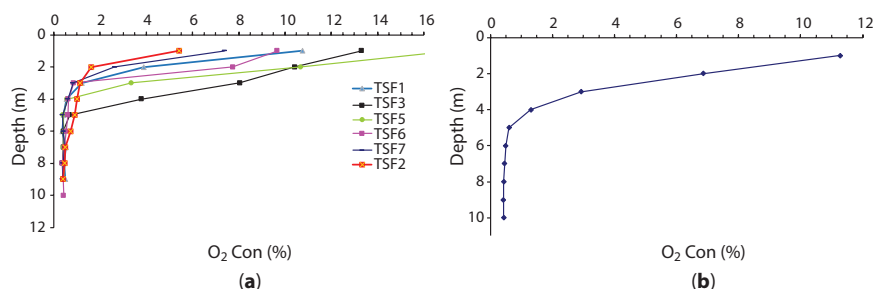
Figure 4.9 O_2 gas concentration profile in the Witwatersrand gold mine TSFs: (a) oxygen concentration with depth for all the TSFs; (b) average oxygen concentration with depth; Note the depth where all the curves converge which marks the active oxidation front.

the tailings and the bacterial population within the tailings becomes established [20]. As oxidation proceeds, more (di-)sulfide will be consumed, and oxygen migrates deeper into the tailings [4]. Blowes and Jambor [18] have shown that there is a positive correlation between pore-gas O_2 concentrations and oxidation of sulfides in the Waite Amulet (Quebec, Canada) tailings. In the shallow tailings, where sulfide minerals have been extensively depleted, gas-phase O_2 concentrations are high and decline sharply deeper in the tailings, as unaltered (di-)sulfide minerals become available. This is reflected in the Witwatersrand TSFs showing a positive strong correlation between depth of MOZ and O_2 gas concentration with depth (Figure 4.9). This comparison highlights the potential of O_2 concentration measurement with depth to decipher the depth of active oxidation in TSFs [2].

4.4   Geochemical and Mineralogical Evolution

4.4.1   Tailings Geochemistry and Mineralogy

Chemistry and mineralogy are the two main principal factors together with availability of oxygen and water that govern the rate and intensity of oxidation. Generally, the UZ shows high SiO_2 contents for all the TSFs, suggestive of the high quartz content of the mined ore. Enrichment of Al, Fe, Mg, Ca, in the TZ and depletion in the MOZ is evident. Ni, Co, Zn, Cu, and Cr show enrichment in the TZ at the expense of depletion in the MOZ. The concentration of trace metals such as Cr, Ni, Co, Cu, Zn, and Pb depends mainly on the relative concentration of sulfide minerals.

The characteristics principal minerals of the Witwatersrand gold mine tailings are quartz, mica, and chlorite/chloritoid with pyrophyllite and traces of K-feldspar present in some. In addition, 2 wt. % to <0.5 wt. % of pyrite and jarosite are common. The effect of oxidation in the mineralogy of the tailings is shown by the appearance of jarosite as a secondary mineral and increases whereas pyrite decreases and then disappears as oxidation process intensified. Pyrite then reappears in the UZ (Table 4.2).

The oxidation evolution of the Witwatersrand gold TSFs shows that: 1) oxidation is intense and reached "Late stage" in all the MOZ as evidenced by absence of sulfide minerals

Table 4.2 Mineralogical profile across the three oxidation zones of the investigated TSFs.

Zone	Pyrite	Jarosite	Gypsum	Chloritoid	K-Feldspar	Quartz	Mica	Chlorite	Pyrophyllite
TFS1-OZ	0.00	2	1		0	80	8	8	
TSF1-TZ	1.00	1	0		1	82	9	7	
TSF1-UZ	1.00	0	0		1	80	11	7	
TSF2-OZ	0.00	1		22	0	65	4	3	5
TSF2-TZ	0.25	0		16	0	74	4	4	3
TSF2-UZ	0.00	0		19	1	58	8	6	8
TSF3-OZ	0.00	1		13	1	72	6	6	–
TSF3-TZ	1.00	0		10	Trace	75	6	6	–
TSF3-UZ	0.00	1		22	Trace	61	7	8	–
TSF4-OZ	–	2		7	1	74	10	6	–
TSF4-TZ	1.00	1		10	1	67	10	10	–
TSF4-UZ	1.00	–		9	–	71	10	9	–
TSF5-OZ	–	2		2	–	64	8	3	22
TSF5-TZ	1.00	2		3	–	66	5	3	20
TSF5-UZ-A	2.00	1		2	–	76	3	3	14
TSF5-UZ-B	–	1		2	–	78	6	3	10

Table 4.3 Schematic representation of the progressive oxidation of a mine residue containing sulfides pyrite (py) and pyrrhotite (po) (after [24]).

Early (1)	Early (2)	Maturing	Late
Oxidation of Fe sulfides	Acceleration	Slowing	Consumed
Native sulfur	–	–	–
Marcasite	–	–	–
Fe oxyhydroxides	Fe oxyhydroxides	Geothite	Goethite
Fe sulfates	Fe^{2+} sulfates to Fe^{2+}, Fe^{3+}	Fe^{3+} sulfates	–
–	Jarosite	Jarosite	Jarosite
Po + Py	Py > Po	Py	–

and concomitant presence of jarosite, 2) the presence of both pyrite and jarosite in the TZ in all the TSFs show "Early-2 stage" to "Mature Stage" of oxidation in TZ, and 3) most of the UZ show a varying degree of oxidation dominantly "Early-1" and "Early-2" stages and rarely the "Maturing Stage" (Table 4.4) following the classification of Jambor [21] based on the paragenetic relationships in the oxidized mine residue deposits (Table 4.3).

4.4.2 Pore Water Geochemistry

The pH and paste pH of the pore water increase with depth. SO_4 and total metals concentrations, EC, and redox values are consistently high in the TZ, intermediate in the MOZ, and low in the UZ (Table 4.5 and Figure 4.10). This trend indicates pore water migration with soluble secondary minerals from MOZ into the TZ. The quality of the pore water depicts the mature stage of the oxidation process attained in the TSFs when considered in terms of the total oxidation (MOZ + TZ) thickness. This trend is distinct in terms of pH, sulfate, and total metals concentrations which are high in the oxidized zone (MOZ + TZ) and consistently low in UZ (Figure 4.11).

The low pH values (2.5–4.1) of the pore water are indicative of the final stage of oxidation whereby weathering of both sulfide and neutralizing minerals progressed beyond the carbonates and oxyhydroxides, having reached the aluminosilicates buffer range with Al^{3+} and Si^{4+} in the pore water. Zn, Ni, and Co become mobile when the pH decreases to below 6, while Al, Cr, V, and Pb remain immobile until the pH decreases to 4.0, consistent with results of laboratory investigation [13]. This sequence of mobility is governed by the pH plateaus and can be tied to the times when the specific acid-neutralization reactions predominate.

The pore water chemistry therefore mirrors the acid mine drainage that would have been discharged from these TSFs subjected to extensive "Late Stage" oxidation processes and provides useful information on the progress, depth, and rate of oxidation consistent with the mineral paragenesis discussed earlier.

Table 4.4 Progressive oxidation mapping based on the mineralogical classification in the three oxidation zones for the investigated TSFs.

Zone	Pyrite	Jarosite	Gypsum	Chloritoid	K-Feldspar	Quartz	Mica	Chlorite	Pyrophyllite	Oxidation stage
TFS1-OZ	0.00	2	1		0	80	8	8	8	Late
TSF1-TZ	1.00	1	0		1	82	9	7	7	Early (2)
TSF1-UZ	1.00	0	0		1	80	11	7	7	Early (1)
TSF2-OZ	0.00	1		22	0	65	4	3	5	Late
TSF2-TZ	0.25	0		16	0	74	4	4	3	Early (1)
TSF2-UZ	0.00	0		19	1	58	8	6	8	Early (1)
TSF3-OZ	0.00	1		13	1	72	6	6	–	Late
TSF3-TZ	1.00	0		10	Trace	75	6	6	–	Early (1)
TSF3-UZ	0.00	1		22	Trace	61	7	8	–	Early (2)–Maturing
TSF4-OZ	–	2		7	1	74	10	6	–	Late
TSF4-TZ	1.00	1		10	1	67	10	10	–	Early (2)–Maturing
TSF4-UZ	1.00	–		9	–	71	10	9	–	Early (1)
TSF5-OZ	–	2		2	–	64	8	3	22	Late
TSF5-TZ	1.00	2		3	–	66	5	3	20	Maturing
TSF5-UZ-A	2.00	1		2	–	76	3	3	14	Maturing
TSF5-UZ-B	–	1		2	–	78	6	3	10	Early (2)–Maturing

Table 4.5 Pore water chemistry of the three oxidation zones for the investigated TSFs, BDL: below detection limit.

| Sample ID	pH	Paste pH	EC, mS/m	Redox, mV	SO_4	Al	Ca	Fe	Mg	Mn	ΣBase metals*
TSF1-OZ	3.28	3.6	314	218	2,934	233	265	157	101	4	22
TSF1-TZ	3.92	4.1	204	235	1,215	46	237	49	60	6	19
TSF1-UZ	4.11	6.4	115	217	584	2	193	30	24	5	11
TSF2-OZ	3.06	3.2	345	456	1,791	25	750	9	23	3	3
TSF2-TZ	2.56	2.8	483	606	2,347	50	643	226	26	30	24
TSF2-UZ-A	2.52	2.8	469	618	2,280	43	571	346	36	24	29
TSF2-UZ-B	6.16	7.0	190	324	1,084	6	400	BDL	23	3	1
TSF3-OZ	3.32	3.5	241	505	1,234	73	239	3	47	2	9
TSF3-TZ	2.52	2.9	269	522	945	50	15	119	3	2	16
TSF3-UZ	3.50	4.0	204	452	1,138	12	340	2	33	6	19
TSF4-OZ	3.31	3.5	323	475	1,770	125	188	3	112	6	20
TSF4-TZ	3.28	3.6	344	404	2,149	78	242	45	138	9	22
TSF4-UZ	3.25	3.8	204	546	887	18	174	4	43	5	19
TSF5-OZ	3.41	3.6	315	454	1,576	81	401	4	85	4	11
TSF5-TZ	3.22	4.1	405	531	2,114	101	564	4	71	7	45
TSF5-UZ	3.27	4.0	237	529	1,213	19	364	2	52	8	18

*ΣBase metals = Zn + Pb + Ni + Cu + Co.
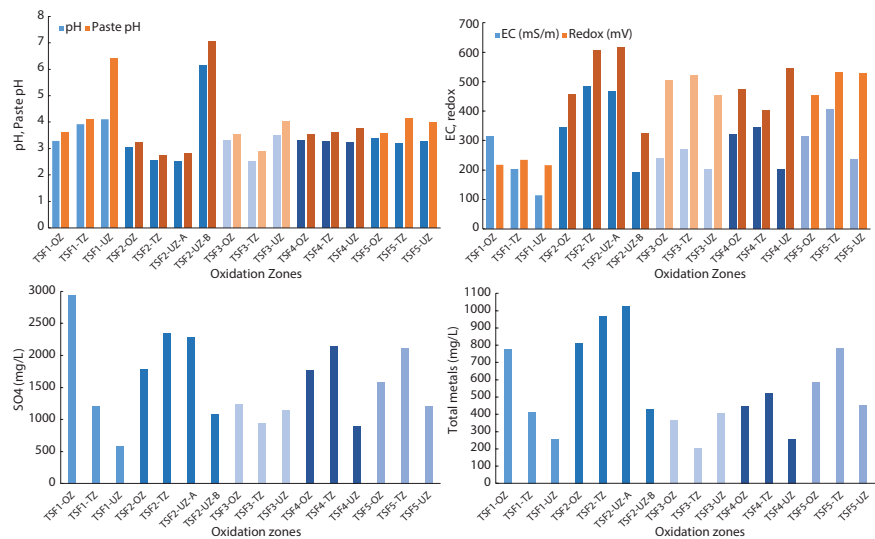
Figure 4.10 Pore water chemistry in the three oxidation zones.
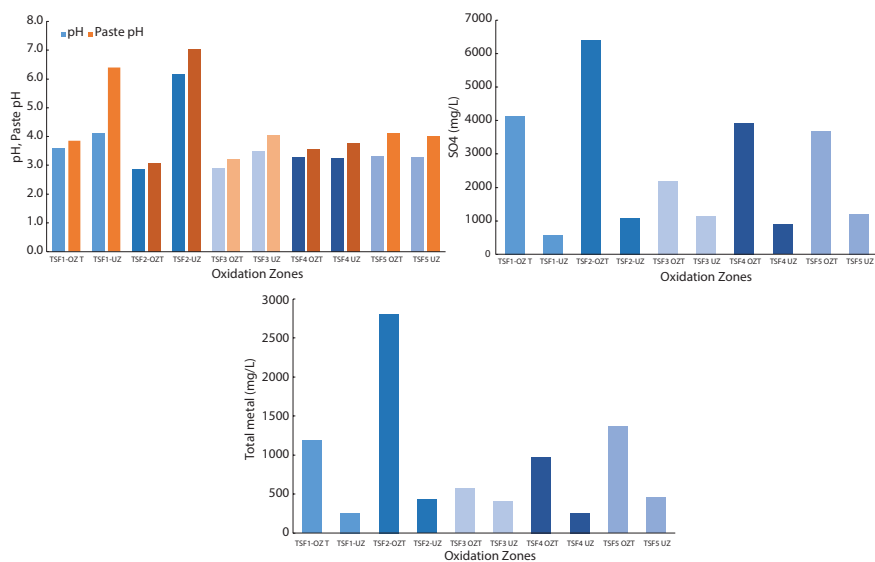

Figure 4.11 Comparison of pore water quality in the total oxidation zone (MOZ and TZ) and UZ.

4.5   Discussion, Conclusion, and Recommendations

4.5.1   Discussion

4.5.1.1   *Mapping of the Oxidation Zones in Tailings Dams*

Detailed site investigation and mapping of tailings profiles exposed by reclamation operations, logging of several auger-holes each up to 10-m deep in selected Witwatersrand TSFs provided classification of the TSFs into: MOZ, TZ, and UZ. The OZ and TZ constitute the

total oxidizing zone and are separated from the UZ by the active oxidation front. The volume of oxidized mine residue deposits depends on the combined thickness of the MOZ and active oxidizing zone (transition zone), which ranges from 4.5 to 9 m.

4.5.1.2   Hydrogeological Situation

Tailings storage facilities are a variably unsaturated porous medium with an unsaturated upper part and a saturated lower part with phreatic surface marking the boundary between the two. The proportion of the saturated zone shrinks with time in non-operational and decommissioned TSFs. Therefore, unsaturated flow processes dominate in such TSFs where pore water flow is mainly vertical and governed by the interplay of hydraulic properties of the tailings. Hydraulic conductivity with depth in unsaturated upper part of a TSF is dependent on the volumetric water content of the tailings which varies with depth. Other factors that complicate unsaturated flow processes in TSFs are grain size, porosity, bulk densities, and mineralogy.

Laboratory and *in situ* investigations of the hydraulic properties provided insight on the relationship between hydraulic properties and oxidation processes. Although the tailings were dominantly uniformly graded sandy silt when deposited, detailed field observation and hydrometer analyses showed alternations of fine and coarse layers. This was attributed to the lateral grading of the tailings from coarse grained to fine grained from the edges to the center of the TSFs during deposition. Such depositional variations create capillary breaks, which complicates the flow of water in the tailings materials [3]. Tailings samples from the different oxidation zones show slight change in grain size distribution in that the TZ materials are coarser than those of the MOZ. The UZ materials are all sandy silt and finer than the overlying TZ and MOZ materials and reflects the original depositional particle size distribution. The consistent coarser grain size at TZ compared to the MOZ indicates reworking of the vertical grain size distribution due to oxidation and weathering.

The slimes and slurries of gold mines during deposition commonly have moisture contents approximately 1:1 [23], which after deposition naturally decrease in time and space due to various factors such as climatic variation (rainfall, temperature, and evaporation rate) as well as mineralogy, geochemistry, and time after closure and decommissioning. Measured moisture content ranges from 7 to 28 wt. **%** with an overall increase with depth. Water retention capacities and residual water content decreases with depth consistent with the general particle size distribution pattern, increasing bulk densities, and decreasing porosities with depth. An order of magnitude of variation in hydraulic conductivity values with depth is observed for most tailings, with higher K values recorded for the deeper parts. This is consistent with initial moisture content data, which also increases with depth.

The formation of fractures, cracks, desiccation cracks, and bedding planes provide preferential flow for water and oxygen movement for oxidation to occur in the deeper part of the UZ beyond the active oxidation front [2]. However, this oxidation process is probably not relevant compared to the normal oxidation processes.

4.5.1.3   Oxygen Diffusion With Depth

The TSFs exhibit variable oxygen concentrations with depth ranging from 10.62 vol. % at 1-m depth and decreasing substantially to an average concentration of 0.49 vol. % at 6-m

depth and drops to 0.41 vol. % at 9-m depth. The optimum oxygen diffusion depth in the TSFs for oxidation to proceed varies from 2 to 5 m with an average depth of about 4 m, correlating well with the observed depth of active oxidation front.

4.5.1.4 Mineralogical and Geochemical Evolution of Tailings

Quartz, mica, and chlorite or chloritoid are the major minerals with rare pyrophyllite and K-feldspar presence as trace minerals. Pyrite is the major primary disulfide mineral with jarosite as the prevalent secondary sulfide mineral ranging from 2 wt. % to <0.5 wt. % in abundance. Pyrite generally increases and jarosite decreases with depth, consistent with oxidation progression. The oxidation evolution in the TSFs was established based on the mineral paragenetic relationships as follows:

- the MOZ in all TSFs shows complete consumption of sulfide minerals, and presence of jarosite indicating that the zone has reached "Late Stage" oxidation;
- the TZ shows the concomitant presence of pyrite and jarosite in all the TSFs supporting "Early advanced (Early-2)" to "Mature oxidation" stages;
- most of the UZ zones show varying degrees of oxidation ranging from "Early-1" to "Maturing Stage" of oxidation and none of the UZ show "Late Stage" oxidation wherein complete consumption of sulfides is expected.

There are evidences of geochemical reworking of the tailings due to the oxidation and leaching processes. Although the tailings are high in SiO_2 due to the high quartz content of the mined ore which is also reflected in the high SiO_2 content of the UZ, there is a slight increase in the proportion of SiO_2 in the MOZ compared to the TZ. Al, Fe, Mg, and Ca are enriched in the TZ and depleted in the MOZ. Ni, Co, Zn or Cu, and Cr are enriched in the TZ and are depleted in the MOZ.

4.5.1.5 Evolution of Pore Water Chemistry

The pore water chemistry in general shows a pH-increase with depth. SO_4, electrical conductivity and total metal concentrations are all consistently high in the TZ and low in UZ with intermediate values recorded in the MOZ. Due to the migration of secondary minerals in pore water from the MOZ into the TZ, there is a general increase of total metal concentrations with depth. Because the total oxidation zone is the summation of the MOZ and the TZ, the total sulfate and metal concentrations in the pore water indicate the potential drainage quality if discharged from these TSFs.

4.5.1.6 Oxidation Processes and Drainage Formation

The mineralogical and geochemical evolution of the tailings presented in the preceding sections show that oxidation has reached "Late-stage" and is active at "Maturing" and "Advanced (Early-2)" stages of oxidation. The presence and absence and the amount of sulfides and acid neutralizing minerals could be estimated indirectly by the pH of tailings material.

The pore water pH which is confined between 3 and 4 in the total oxidized zone (MOZ + TZ) supports the mineralogical evidence that the oxidation processes reached "Late-stage" and attained the aluminosilicates buffering stage as shown by the Al^{3+} and Si^{4+} concentrations in the pore water. When the pore water pH is below 6, the mobility of Zn, Ni, and Co increases, whereas Al, Cr, V, and Pb become mobile only after the pH decreases to 4. Such mobility patterns are associated with pH plateaus and related to periods of predominance of certain buffer reactions.

The leachate generated from a TSF which is represented herein by the pore water quality reflects the stage of oxidation that governs the acid generating and acid neutralizing reactions. The oxidation of sulfide minerals releases protons, SO_4^{2-}, Fe^{2+}, and metals. The amount of metals released is a function of the tailings mineralogy, sulfide mineral oxidation rates, and formation of secondary minerals by the removal of metals from the pore water.

In regard to neutralization reactions in the Witwatersrand tailings the contribution of carbonate minerals is very limited due to the minor concentration of carbonates in the original mineralogy of the tailings. No gibbsite or other Al bearing secondary phase were evident. This may be due to the difficulty in identifying gibbsite or other Al bearing precipitates [4]. The precipitation of Al bearing phases is, however, supported by other indications. The breakdown of Al bearing primary minerals in the tailings of the Witwatersrand basin is evidenced by the presence of Al^{3+} in the tailings pore water and by the relatively high Al_2O_3 in the bulk samples of the unoxidized tailings as compared to the oxidized zone tailings. The oxidation of Fe^{2+} to Fe^{3+} causes in most tailings the precipitation of ferric hydroxides, the most common of which is goethite [$Fe(OH)_3$]. In the absence of carbonates, the near constant pore water pH should only be attained due to the primary buffering capacity of Al and ferric hydroxides by releasing Al and Si into the pore water system. Blowes *et al.* [20] and Jambor and Blowes [24] argued that the dissolution kinetics of aluminosilicates varies but is generally slow compared to the groundwater flow rate.

4.5.2   Conclusions

All factors governing oxidation processes and drainage formation from the Witwatersrand TSFs have been investigated. The data collected from the TSFs have improved our understanding of mine drainage formation processes and the accuracy of drainage predictions for TSFs.

Oxidation processes and its variation with depth as well as the total oxidation thickness and the position of the active oxidation front are established. Modification of the grain size distribution takes place during oxidation and leaching processes. Although the principal mechanism of oxygen diffusion and moisture inflow into the tailings is progression of oxidation processes, the interplay of primary and secondary hydraulic properties (geological structures as preferred potential follow paths) improves our understanding of oxygen and water infiltration mechanisms and oxidation processes at the active oxidation front and deeper below the front. The measured rate of oxygen diffusion has shown to vary in the different TSFs from about 2 to 5 m in depth with an average of 4 m, consistent with the observed and measured oxidation fronts.

The mineralogical and geochemical evolution of the tailings' materials and the pore water chemistry has been established and is well understood. The effect of oxidation in the mineralogy of the tailings is evidenced by the appearance of jarosite as a secondary mineral

and its increase as oxidation process is intensified whereas pyrite decreases and disappears in the AOZ but reappears in the UZ. Oxidation process reached "Late-stage" in in all the TSFs as evidenced by the mineral paragenesis (absence of sulfide and presence of jarosite) while still active at "Early advanced (Early-2)" to "Maturing" oxidation stages as evidenced by the concomitant presence of pyrite and jarosite.

The low pH values the pore water (2.5–4.1) and the total metal concentrations of the pore water mark the final stage of acid generation (aluminosilicate buffering). The various pH buffer plateaus (6, 4, and 2.5–3) of the pore water indicate the times when specific acid-neutralization reactions predominate which in turn determine the leaching sequence of metals. Zn, Ni, and Co leach into the pore water when the pH of the pore water decreases to below 6, whereas the decrease of pH to 4 starts leaching of Al, Cr, V, and Pb.

The extent of the acidity and the metal concentrations reflected in the pore water chemistry are by far lower than what would be expected if all the products of the oxidation and leaching processes remained in the TSFs as pore water.

4.5.3   Recommendations

Key findings that have practical application are as follows:

1) The depth of active oxidation zone varies between 1.5 and 5 m in depth with an average value of around 4 m. This suggests that, in the absence of more site-specific data, geochemical prediction assessments for tailings dams should consider the active oxidizing layer to be around 4-m thick. A further approximately 4 m of depth marks the active oxidation front;

2) Oxygen diffusion depth correlates very well with the actual observed active oxidation front and it is recommended that where a higher degree of confidence in the results of the prediction are required, oxygen diffusion measurement be undertaken to determine the depth of oxidation front;

3) It is expected that in 10–20 years, most TSF would have established an active oxidation zone of around 4m thickness. Variations in this depth are more likely to be linked to physical properties such as particle size distributions and chemical composition (e.g., available sulfides) than to TSF age after decommissioning.

Acknowledgements

References

1. Rosner, T., Boer, R., Reyneke, R., Aucamp, P., Vermaak, J., A preliminary assessment of pollution contained in the unsaturated and saturated zone beneath reclaimed gold mine residue deposits. *WRC Rep.*, 2001. *No* 797/1/01, p314.

2. Yibas, B., Pulles, W., Nengovhela, C., Kinetic Development of Oxidation Zones In Tailings Dams With Specific Reference To The Witwatersrand Gold Mine Tailings Dams. *Water Res. Commission Rep.*, 2010. No. 1554/1/10, p105.

3. Yibas, B., Pulles, W., Lorentz, S., Maiyana, B., Development of water balances for operational and post-closure situations for gold mine residue deposits to be used as input to pollution prediction studies for such facilities. *Water Res. Commission Rep.*, 2011. No. 1460/1/11, p104.

4. Nengovhela, A.C., Yibas, B., Ogola, J.S., An investigation into the availability of oxygen in gold tailings dams of the Witwatersrand basin with reference to their acid mine drainage potential. *Water SA*, 33, 2, 271–274, 2007.

5. Nengovhela, A.C., Yibas, B., Ogola, J.S., Characterisation of gold tailings dams of the Witwatersrand Basin with reference to their acid mine drainage potential, Johannesburg, South Africa. *Water SA*, 32, 4, 409–506, 2006.

6. Sibanda, L.K. and Broadhurst, J.L., Exploring an alternative approach to mine waste management in the South African gold sector, in: *11th ICARD/IMWA conference proceedings*, Wolkersdorfer, Ch., Sartz, L., Weber, A., Burgess, J., Tremblay, G. (Eds.), pp. 1130–1135, 2018.

7. Nicholson, R.V., Gillham, R.W., John, A.C., Reardon, E.J., Reduction of acid generation in mine tailings through the use of moisture-retaining cover layers as oxygen. *Can. Geotech. J.*, 26, 1, 1–8, 1989. https://doi.org/10.1139/t89-001.

8. Wilson, G.W., Williams, D.J., Rykaart, E.M., The Integrity of Cover Systems – An Update, in: *Proceedings of the 6th International Conference for Acid Rock Drainage,* T. Farrell and G Taylor (Eds), pp. 445–451, Australian Institute of Mining & Metallurgy, Queensland, Australia, 2003.

9. Yibas, B., Pulles, W., Lorentz, S., Maiyana, B., Nengovhela, C., Oxidation process and hydrology of tailings dams: Implication for acid mine drainage from TSFs management – The Witwatersrand experience, South Africa, in: *Proc. Intern. Mine Water Assoc. Annual Conf.*, McCullough, C.D., Lund, M.A., Wyse, L. (Eds.), pp. 245–255, 2012.

10. Werner, K., Soil-cover remediation of mill tailings deposits: Effects on oxygen transport and hydrological conditions, in: *Licentiate Thesis*, p. 111, Royal Institute of Technology, Stockholm, 2000.

11. Jaynes, D.B., Pionke, H.B., Rogowski, A.S., Acid mine drainage from reclaimed coal strip mines, 2. Simulation results of model. *Water Resour. Res.*, 20, 243–250, 1984.

12. Pantelis, G. and Ritchie, A.I.M., Macroscopic transport mechanisms as a rate-limiting factor in dump leaching of pyretic ores. *Appl. Mathem. Model.*, 15, 3, 136–143, 1991.

13. Yanful, E.K., Oxygen diffusion through soil covers on sulphidic mine tailings. *J. Geotech. Eng.*, 119, 1207–1228, 1993.

14. Ritchie, A.I.K., Sulfide oxidation mechanism-Control and rates of oxygen transport, in: *The Environmental Geochemistry of sulfide Mine-Wastes*, vol. 22, J.L. Jambor and D.W. Blowes (Eds.), pp. 210–245, Mineral. Assoc. Canada, Short Course Ser, Quebec, Qc, Canada, 1994.

15. Elberling, B., Nicholson, R.V., David, D.J., Field evaluation of sulphide oxidation rates. *Nordic Hydrol.*, 24, 323–338, 1993.

16. Shaw, S.A., Determining the long-term persistence of mercury releases to the environment from cyanide-rich gold mine tailings, in: *Unpublished MSc thesis*, The University of New Brunswick, Canada, 2004.

17. Smyth, D.J.A., Hydrogeological and geochemical studies above the water table in an inactive uranium tailings impoundment near Elliot Lake, Ontario, in: *MSc thesis*, University of Waterloo, Waterloo, 1981.

18. Blowes, D.W. and Jambor, J.L., The pore water geochemistry and mineralogy of the vadose zone of sulphide tailings, Waite Amulet, Quebec, Canada. *Appl. Geochem*, 5, 327–346, 1990.

19. Blowes, D.W., Reardon, E.J., Jambor, J.L., Cherry, J.A., The formation and potential importance of cemented layers in inactive sulphide mine tailings. *Geochim. Cosmochim. Acta*, 55, 965–978, 1991.

20. Blowes, D.W., Ptacek, C.J., Jurovec, J., Mill Tailings: Hydrogeology and geochemistry, in: *Environmental Aspects of Mine Wastes*, vol. 31, J.L. Jambor, D.W. Blowes, A.I.M. Ritchie (Eds.), pp. 95–116, Mineral. Assoc. Can. Short Course Ser, Ottawa, Ontario, Canada, 2003.

21. Jambor, J.L., Mine waste mineralogy and mineralogical perspective of Acid-Base Accounting, in: *The Environmental Geochemistry of Sulphide Mine-Wastes*, vol. 31, J.L. Jambor and D.W. Blowes (Eds.), pp. 117–147, Mineral. Assoc. Can. Short Course Ser, Ontario, Canada, 2003.

22. Jurjovec, J., Ptacek, C.J., Blowes, D.W., Acid neutralisation mechanisms and metal release in mine tailings: A laboratory column experiment. *Geochim. Cosmochim. Acta*, 66, 1511–1523, 2002.

23. Rosner, T. and van Schalkwyk, A., The environmental impact of gold mine tailings footprints in the Johannesburg region, South Africa. *Bull Eng. Env.*, 59, 137–148, 2000.

24. Jambor, J.L. and Blowes, D.W., Theory and applications of mineralogy in environmental studies of sulphide-bearing mine tailings, in: *Modern Approaches to Ore and Environmental Mineralogy*, vol. 27, L.J. L.J Cabri and D.J. Vaughan (Eds.), pp. 367–401, Mineral Assoc. Can. Short Course Ser, Ottawa, Canada, 1998.