KINETIC DEVELOPMENT OF OXIDATION ZONES IN TAILINGS DAMS WITH SPECIFIC REFERENCE TO THE WITWATERSRAND GOLD MINE TAILINGS DAMS

Report to the
Water Research Commission

by

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DISCLAIMER

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> Study Of The Kinetic Development Of Oxidation Zones Of Tailings Dams With Specific Reference To The Witwatersrand Gold Mine Tailings Dams.

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The Reference Group responsible for this project consisted of the following persons:

Mr HM du Plessis	Water Research Commission (Chairman)
Dr J Burgess	Water Research Commission
Ms L Chauke	Chamber of Mines of SA
Mr N Swiegelaar	Dept. of Water Affairs and Forestry
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EXECUTIVE SUMMARY

MOTIVATION FOR THE PROJECT

The understanding of oxidation zones and phreatic water surfaces plays a very important role in the prediction of acid rock drainage (ARD). Frequently, assumptions on the development of oxidation zones and phreatic surfaces are made based on rule-of-thumb experience and extrapolations from other sites / experiences. 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.

Many gold mines from all the major gold mining regions within South Africa are currently engaged in active reclamation of gold tailings dams. This large-scale reclamation of dams provides a perfect opportunity to study tailings dam profiles and characterise their oxidation profiles. The major advantages are as follows:

- The gold tailings dams are exposed by the reclamation process; cross sections and full natural profiles can be observed and studied;
- Difficulties encountered during drilling of deep holes in tailings dams, such as collapsing and presence of groundwater are overcome; and
- Cost saving since no expensive drilling program will be necessary for the research.

The study of oxidation zones of tailings dams was initiated based on literature surveys conducted by PHD and personal communications, which showed that the reported values for the depth of the oxidation zones of gold mine tailing dams in the Witwatersrand Basin are inconsistent and have a considerable range from 20 cm to more than 7 m. The oxidation depth might be related to the age and other parameters of the tailings dams, but little study has been carried out in this regard. This research project attempted to solve a very practical and necessary issue which provides a key input in ARD prediction techniques related to tailings dams.

It is believed that the findings of this project have advanced our knowledge and ability to practically implement improved prediction capacity by being able to better understand the active oxidation zone within the tailings dams that needs to be described in a predictive model. It is generally accepted that only a portion of a tailings dam (the outer layers) actively participate in the oxidation processes and it is only this portion that is considered as reactive within predictive geochemical models.

The project has been sub divided into 5 major tasks in order to achieve the objectives and aims of the project, i.e. “understanding the development of oxidation zone in the tailings dams of the Witwatersrand basin”. All 5 tasks have been completed and a summary of the major findings from these tasks is presented below.

MAPPING OF THE OXIDATION ZONES IN TAILINGS DAMS

As oxidation processes are active in the unsaturated zone of the tailings dam, this is the zone which is the source of contaminants and low pH pore water. This implies that a reasonably accurate estimation of the oxidation depth will be critical in order to make a reliable quantification of both the acidic and the metal leaching aspect of the mine drainage assessment as the volume and quality of the ARD to be generated from a tailings dam is directly related to the volume of the oxidized/oxidizing tailings.

Five decommissioned dams were selected for the study and characterization of the selected dams. The following major objectives were met after the completion of Task 1:

a) The oxidation zones of the 5 tailings dams were established;
b) Sufficient samples were collected and analyzed for pore water quality data, mineralogy and slid chemistry of the tailings materials;
c) The data generated from b) has been interpreted and is covered in this report.

Cross sections and exposed profiles by the reclamation processes of the tailings dams have been used to map and characterize the intensity and variations of oxidation in the tailings dams. This together with logging of auger holes of up to 10 m depth resulted in the establishment of the oxidation zone depths and tracing of the un-oxidized parts of the tailings dams. Overall, 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 OZ and TZ constitute the total oxidizing zone. The depth of matured oxidation zone ranges from 150 cm (Stilfontein No. 2 dam) to 350 cm (CMR-3L1 and ERGO-5L29 dams). The combined depth of the active oxidizing zone (transition zone) and the mature oxidized zone varies from 450 cm (CMR-3L1) to 900 cm (ERGO-5L29 dam).

MINERALOGICAL AND GEOCHEMICAL EVOLUTION OF TAILINGS

Mineralogy

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, the oxidation evolution of the Wits basin tailings dams has been established and given. It has been shown that:

- Oxidation is intense and reached late stage in the mature oxidation zone of all the dams as evidenced by the mineral paragenesis, which shows complete consumption of sulphide minerals, and concomitant development of jarosite;
- The transitional zone of all the dams shows early advanced (Early-2) to mature oxidation stage evidenced by the presence of both pyrite and jarosite;
- Most of the unoxidised zones show varying degree of oxidation.
- The paragenesis of 5L29, 3L1, and 4L19 do not show oxidation progression beyond early (1) stage whereas dams 4L25 and Stilfontein are characterised by the presence of jarosite all the way up to their unoxidised zone suggestive of mature stage of oxidation.

Geochemistry

The XRF data of the samples from the unoxidised zones show high SiO_2 values for all the tailings dams, suggestive of the high quartz content of the mined ore. Enrichment of Al, Fe, Mg, Ca in the active oxidation zone and depletion at the mature oxidation zone is apparent. The percentage of Fe alone does not indicate the intensity of ARD-producing oxidation processes, due mainly to the fact that 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, as these metals are mainly leached out of sulphide minerals. Ni, Co, Zn in all the dams and Cu and Cr in two of the dams, 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.

The pore water chemistry was approximated from paste pH and AA analyses of water extracted from the samples and the data in general showed increase in pH and depletion of metals concentration with depth. 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 $(CO_3)_2$] (Morin et al., 1988; Blowes and Jambor, 1990; Blowes and Ptacek, 1994; Johnson et al., 2000; Jurjovec et al., 2002). In the early stage of oxidation, carbonate dissolution can maintain the pH of the pore water near neutrality. Sulphide oxidation results in the generation of abundant Fe^{+2}, which reacting with HCO_3^+ generated by the dissolution of calcite, forms secondary siderite ($FeCO_3$). In the case of the Wits basin tailings the contribution of calcite in keeping the pore water pH near neutral and generating secondary siderite is very limited due to the insignificant amount of calcite in the mineralogy of the tailings.

Kinetically limited dissolution of aluminosilicates provides Al to allow the precipitation of gibbsite [Al $(OH)_3$] or other Al-containing phases. The presence of gibbsite or other Al bearing secondary phases in tailings dams, including the Wits tailings, has not been reported. This may be due to the difficulty in identifying gibbsite or other Al-bearing precipitates (Blowes et al.,2003). The precipitation of Al-bearing phases is, however, supported by other indications. Two Al-bearing secondary phases have been observed in the Heath Steele tailings impoundments in Brunswick (Blowes et al., 1991). The breakdown of Al-bearing primary minerals in the tailings of the Wits 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 unoxidised tailings as compared to the oxidized zone tailings.

In most tailings, the oxidation of Fe^{2+} to Fe^{3+} causes the precipitation of ferric hydroxides, the most common of which is goethite [Fe $(OH)_3$].

The dissolution of the Al 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, Al 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; Jambor and Blowes, 1998).

The oxidation of sulphide minerals releases H^+ and SO_4^{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.

The overall 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.

As part of this study, pore water chemistry of the tailings dams has been analysed. The main geochemical characteristics of the tailings pore water is summarised in the Table below. 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.

Tailing Dams	**pH**	**SO_4 (mg/l)**	**EC (mS/m)**	**Redox (mV)**	**Fe (mg/l)**	**Ca (mg/l)**	**Al (mg/l)**	**∑Zn,Ni,Co (mg/l)**
ERGO 5L29	3.28-4.11	584-2934	115-314	215-255	30-157	193-265	2.4-233	10-22
Stilfon-2	2.5-6.2	1084-2347	190-483	324-618	<9-346	400-750	6-50	2-26
3L1	2.5-3.5	945-1234	204-269	452-522	2.3-119	15-340	12-73	6-18
4L19	3.3	887-2149	204-344	404-546	3.4-45	174-242	18-125	16-19
4L25	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 the Wits 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.

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.

The geochemical evolution of the tailings pore water provided useful information on the progress, depth and rate of oxidation processes. The geochemical evolution of the tailings pore water indicates that oxidation process in the studied tailings has reached an advanced stage as indicated by the pH of the pore water which has reached a range of 2.5-4.1. These low pH values mark the final stage of acid water generation (aluminosilicate break down stage) in all but the unsaturated zone of the Stilfontein No 2 dam (pH = 6.2) which suggests the latter is still at the earliest stage of oxidation (carbonate dissolution stage).

Qualitative assessment of the potential for tailings to oxidize and generate ARD shows that:

- The actual oxidation zone process as quantified by oxidation zone depths is ERGO 5L29=3L1>CMR- 4L25>CMR-4L19>>STILFON from the thickest to the thinnest oxidation zone
- With respect to $SO4^{=}$ release from the dams, from the highest to the lowest is: ERGO 5L29> STILFON >CMR4L19>CMR4L25>CMR3L1
- With respect to pH values the tailings are in the order:
  CMR3L1>CMR4L19>CMR4L25>ERGO5L29>STILFON.

Physical and hydraulic properties

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.

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 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 (Stilfontein No 2 dam) to 350 cm (Dam 3L1). The oxygen measurement on the other hand shows that oxygen diffusion ranges from about 200 cm (Stilfontein no 2 Dam) to 500 cm (Dam

3L1) with an average O_2 diffusion depth of about 400 cm (Figure 16). This comparison highlights the potential of O_2 concentration measurement to indicate the depth of active oxidation in tailings dams. The findings of the oxygen profiling can be summarised as follows:

1. A decrease of O_2 gas concentration within the pore spaces of the tailings with increasing depth is related to O_2 consumption in sulphide oxidation reactions.
2. Oxygen diffusion ranges from about 200 cm (Stilfontein no 2 Dam) to 500 cm (Dam 3L1) with an average O_2 diffusion depth of about 400 cm.
3. Mapped oxidation depth and depth of O_2 diffusion correlate well, thereby suggesting that measuring the O_2 diffusion (which can be accomplished cheaply and quickly) will give a good indication of active oxidation depth and hence the volume of oxidized tailings materials that needs to be considered in geochemical prediction exercises.

CONCLUSIONS AND RECOMMENDATIONS

While this research project did not involve the development or assessment of geochemical prediction techniques for ARD, useful data was collected from a number of tailings dams in the Wits basin that will have a positive impact on the accuracy of ARD predictions. Key conclusions and findings that have practical application are as follows:

1. The active oxidation zone wherein ARD formation occurs has been found to vary 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 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.

2. It has been demonstrated that measurement of oxygen diffusion into the dam correlates very well with the actual observed active oxidation zone and it is recommended that where a higher degree of confidence in the results of the prediction are required, that augering and oxygen measurement be undertaken to determine the depth of oxidation.

3. Tailings dam age did not appear to have a major impact on the ultimate depth of the active oxidation zone. While a recently decommissioned dam with an elevated phreatic surface will obviously have a very shallow oxidation zone, it is expected that with 10-20 years, most dams would have established the active oxidation zone of around 4 m thickness. Variations in this depth are more likely to be linked to physical properties such as particle size distributions and chemical properties such as levels of sulphides available than to facility age.

4. Oxidation does proceed deeper down into 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.

ABBREVIATIONS

AA	Atomic Absorption
ARD	Acid rock drainage
DO	Dissolved oxygen
DWAF	Department of Water Affairs & Forestry
EMPR	Environmental Management Programme Report
ERGO	East Rand Gold Mining Company Limited
LOI	Loss on ignition
MEND	Mine Environmental Neutral Drainage
ONC	Old North Complex
OZ	Oxidized zone (mature)
PGM	Platinum Group Metals
PHD	Pulles Howard & de Lange (Pty) Ltd
TZ	Transitional oxidized zone
UNIVEN	University of Venda for Science & Technology
UZ	Un-oxidized zone
WE-AA	Water extraction and AA analysis
WRC	Water Research Commission
XRD	X-ray diffraction
XRF	X-ray fluorescence

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CHAPTER 1
INTRODUCTION AND BACKGROUND

1.1 MOTIVATION FOR THE PROJECT

The understanding of oxidation zones and phreatic water surfaces plays a very important role in the prediction of acid rock drainage (ARD). Frequently, assumptions on the development of oxidation zones and phreatic surfaces are made based on rule-of-thumb experience and extrapolations from other sites / experiences. 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.

Many gold mines from all the major gold mining regions within South Africa are currently engaged in active reclamation of gold tailings dams. This large-scale reclamation of dams provides a perfect opportunity to study tailings dam profiles and characterise their oxidation profiles. The major advantages are as follows:

- The gold tailings dams are exposed by the reclamation process; cross sections and full natural profiles can be observed and studied;
- Difficulties encountered during drilling of deep holes in tailings dams, such as collapsing and presence of groundwater are overcome; and
- Cost saving since no expensive drilling program will be necessary for the research.

1.2 OBJECTIVES AND AIMS

The depth of oxidation zones in tailings is site specific (e.g. Nicholson et al. November 1997; MEND Project 4.6.5ac; Marsden, 1986; John Easton, 2002, personal communications) and is affected by many factors, e.g. 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 overall aims of the project can be summarised as follows:

1) Understand the development and characteristics of oxidation zones in gold tailings dams through field mapping, sampling, instrumental measurement, and laboratory tests of different sites; and
2) Identify the key parameters and characteristics of oxidation zones, which can be applied for ARD prediction, prevention and remediation.

The detailed aims are:

- Establish and characterise typical profiles of oxidation zones in terms of physical, geohydrological, mineralogical and geochemical properties in the Wits tailings dams.
- Identify and characterise phreatic surfaces in terms of positions, movements, and specifically retreating rates against their decommissioning ages.

- Identify indicator characteristics and parameters in the oxidation zones to better understand the hydrology and geochemical characteristics of tailings dams.
- Discussion of application of the findings to other similar deposits, e.g. Platinum Group Metals (PGM) and copper mine tailings.
- Development of procedures or guidelines for assessment of oxidation zones in tailings dams using the established typical oxidation profiles and other key findings of the project.

A unique opportunity to provide some answers to the uncertainty in the estimates of oxidation zones is presented in this project. Target groups include mines, regulators and consultants who are involved in commissioning, undertaking or reviewing assessments for mine waste residue deposits.

1.3 TASKS AND ACCOMPLISHMENTS

The project is subdivided into 5 tasks namely:

Task 1 - Select 5-8 tailings dams and characterise their oxidation.
Task 2 - Geochemical investigation of the selected dams with particular emphasis on oxidation zone development.
Task 3 - Establish typical oxidation zone profiles and phreatic surface features against age
Task 4 - Establish oxygen profiles
Task 5 - Application of the typical oxidation profiles

The following methodologies and experimental procedures were adopted for this study:

- Literature review
- Identify and select up to 5 tailings dams for study
- Detailed profile study of the selected tailings dams with the objective of sub-classifying the oxidation zones into geochemically meaningful zones
- Collect representative samples along profiles and from auger holes for laboratory analysis
- Geochemical and mineralogical characterisation of the samples
- Study the effect of variation in hydraulic properties (porosity, permeability, water content, preferential flow pathways such as cracks/fractures, mega-pores, etc) with depth on oxidation processes
- Oxygen flux measurement with depth

1.4 RESEARCH PRODUCTS

The five deliverables produced under this project are the following:

Task 1: Characterisation of oxidation zones for up to 5 to 8 selected tailings dam profiles.
Task 2: Characterisation of variations of geohydrological features including cracks, porosity, permeability, cracks with depth and all possible hydrologic path ways.
Task 3: Establishment of typical profiles for oxidation zones and for phreatic surface features against age.
Task 4: Establishment of oxygen flux (diffusion, convection) profiles for oxidation zones.
Task 5: Application of the established typical profiles to ARD prediction.

Task 6 is the final report, a concise report that details the research results on the study of oxidation zones in the tailings dams. As a result of the project, it is likely that certain recommendation will be made towards revisions of the DWAF Best Practice Guideline for the Prediction of Pollution from Mining Sites, and will be invaluable to mines, regulators and consultants.

1.5 TARGET GROUP

Target groups will include mines, regulators and consultants who are involved in commissioning, undertaking or reviewing assessments for mine waste residue deposits.

1.6 CAPACITY AND COMPETENCY DEVELOPMENT

University of Venda for Science and Technology (UNIVEN) is one of PHD’s major collaboration institutions for capacity building in South Africa. One student from UNIVEN used this opportunity to complete a Master degree through this project. Dr Bisrat Yibas and Professor Jason Ogola were the supervisors.

CHAPTER 2
OXIDATION ZONE PROFILING AND SAMPLING OF THE SELECTED TAILINGS DAMS

2.1 SITE SELECTION

The first task of the project was identifying and selecting up to 5 tailings dams for the study. Identification of potential tailings dams to be used for this project, were sourced by approaching several mining companies. Anglogold, Goldfields, ChemWaste and Crown Gold Recoveries agreed to make some of their facilities available (Table 2.1).

Table 2.1: Tailings dams identified as potential sites for the project

Site Name	Owner	Status	Location / Nearest town	Contact Person
ERGO 5l29 Dam	ERGO, Anglo Gold	Reclamation	ERGO	Fred Rautenbach
Chemwaste No. 2 dam, Stilfontein	Mine Waste Solutions / Chem Waste	Reclamation	Stilfontein	Melt Marais
CMR Dam	Crown Gold Recoveries	Reclamation	Near JHB	Louis Kleinhans
Rooikraal (Withok) Dam	Crown Gold Recoveries	Reclamation	Near JHB	Louis Kleinhans
Herriotdale Dam	Crown Gold Recoveries	Reclamation		Louis Kleinhans
Driefontein No. 3 Dam	Gold Field	Decommissioned	Carltonville	Andries Leuschner
Old North Complex	Anglo Gold-Ashanti	Decommissioned	West Wits Carltonville	Pieter Labuschagne
South Tailings dams / South Self Pay Dam	VRO Anglo Gold	Ready for reclamation	Vaal River operations, Klerksdorp	Pieter Swart
Gold Fields	Gold Field	Ready for Reclamation		Andries Leuschner
Blyvooruitzicht No. 2 dam, Carltonville	DRD	Reclamation	Carltonville	Mike Mariot
ERPM No. 2, & No. 4 Dams	East Rand	Decommissioned	East Rand	
Saaiplaas, No. 4	Harmony	Reclamation	Welkom	
Saaiplaas, No. 5	Harmony	Reclamation	Welkom	
Old president Steyn, No. 3	Harmony	Reclamation		
Old president Steyn, No. 5	Harmony	Reclamation		
President Brand Old Final Dams	Harmony	Reclamation		
A variety of old dams South of Johannesburg, Carltonville, Welkom /Virginia				

2.1.1 Site selection criteria and procedures

The following criteria were set out for the selection of study sites on the basis of the objectives of the project:

- The tailings dam should preferably be undergoing reclamation or going to be reclaimed in the immediate future
- The different tailing dams selected should represent different decommissioned ages for comparison of the development of their respective oxidation zones
- The dams to be selected should have historical data relevant to the project

- The sites should be safe for site investigation

Although the precise requirements for each site depend on the site characteristics, it was necessary to obtain information on the following parameters:

- Design and construction details for each site, including details for any under drainage systems that are installed.
- Construction history for each facility, including different deposition techniques that may have been applied during the life of the facility.
- Physical dimensions and volumes for each facility.
- Volume of seepage from under drains or seepage drains.
- Rainfall records at each facility.
- Historical water levels in and around each facility.

Preference was given to sites for which the mines have the required data or indicated where such data could be found.

The followings were additional pointers considered during site visits:

- Accessibility
- Exposure
- Suitability with respect to safety
- Extent and visibility of oxidation zone development
- Indicators of phreatic surface migration
- Suitability for instrumentation and monitoring

2.1.2 Site visits

A number of tailings dams were visited by the project team to identify the appropriate sites for the study. The prime objectives of the site visits were to evaluate the suitability of the various gold mine residue deposits and identify sites that meet the criteria as stipulated above. The site visits were also used to get an understanding of the area and the specific facility as well as to find out what data are available for each facility and its surrounding area.

The following issues were addressed for each site:

- Familiarise the project team with the sites and the mine personnel responsible for the sites
- Conduct a preliminary assessment of the sites with respect to:
    - the nature of the residue site
    - the depositional history
    - the physical characteristics of the facility (size, height, amount deposited per day)
- Identify data availability or gaps regarding:
    - the underlying soil and rock strata
    - the presence of clay layers underlying the tailings
    - water level data from boreholes surrounding the facility
    - the physical characteristics within the residue deposit (grain size distribution, porosity, moisture content)
    - the surface topography of the surrounding and beneath the deposit

- precipitation and evaporation
- infiltration, run off, leakage into deeper soil layers, seepage
- volume of water returned form the residue deposit
- hydrogeological features such as seepage points

Table 2. 2: Visited tailings dams

Mining company	Site Name	Status	Deposition Method	Dates of visit
Anglogold Ashanti	ERGO 5L29 Dam	Reclamation	Paddock	19/07/04, 27-30/07/04
	Vaal River Operations South Tailings dams / South Self Pay Dam	To be reclaimed soon	Paddock	19/07/04
	West Wits Old North Complex (ONC)	Decommissioned	Paddock	22-23/07/04
ChemWaste Solutions	No. 2 dam Stilfontein	Reclamation	Paddock	14-16/09/04
Crown Gold Recoveries (CMR)	CMR 3L1	Reclamation	Paddock	04-08/10/04
	CMR 4L19	Reclamation	Paddock	11-15/10/04
	CMR 4L25	Reclamation	Paddock	18-22/10/04
Goldfields	Driefontein No. 3 Dam	Soon to be reclaimed	Paddock	22-23/07/04

After consideration of all criteria and negotiations with the mining houses, which own or are responsible for the tailings dams, 7 tailings dams were selected as research sites for the project (all except the Vaal River Operations South tailings dams). Five of these were under reclamation whereas two were decommissioned dams (Table 2.2). Two of the tailings dams were investigated as part of a separate Water Research Commission Project (K5/1460) – AngloGold Ashanti West Wits Old North Complex and Goldfields Driefontein No 3 tailings dam.

2.2. MAPPING AND SAMPLING OF THE SELECTED TAILINGS DAMS

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. The mapping and sampling task included the following:

1. Detailed mapping and logging of the exposed profile of the tailings material from top to bottom (up to 10 m below surface),
2. Augering up to 10 m deep at selected sites on each tailings dam and logging and sampling of the tailings material,
3. Compiling the data from profile mapping into a detailed map on a scale depending on the available details.

A number of sections were exposed by the reclamation processes which allowed detailed characterisation, logging and sampling of the tailings materials. This was complemented by augering up to 10 m depth. Characterisation and sampling were performed for the two decommissioned dams, namely the ONC No. 3 and the Driefontein No 3 dams, by augering and excavation.

ONC and Driefontein dams are also study sites for another WRC research project (WRC Project No. K5/1460) by Pulles Howard and de Lange Inc. The information collected from that project was used to complement the research of this project.

2.2.1 ERGO-5L29 tailings dam

2.2.1.1 Mapping and sampling

ERGO 5L29 facility which was made available by AngloGold Ashanti Ltd is situated southwest of the town of Brakpan in the East Rand (Figure 2.1). ERGO-5L29 tailings dam is 50 years old with about 11 million tons of tailing deposits. It is situated on a local water divide and a large portion of the runoff from the facility flows easterly towards the Rietspruit (Figure 2.1). The height of the dam ranges from 10.5 to 22.5 m, with an average of 14 m. The depth of the oxidation zone is variable with an average of 5 m.

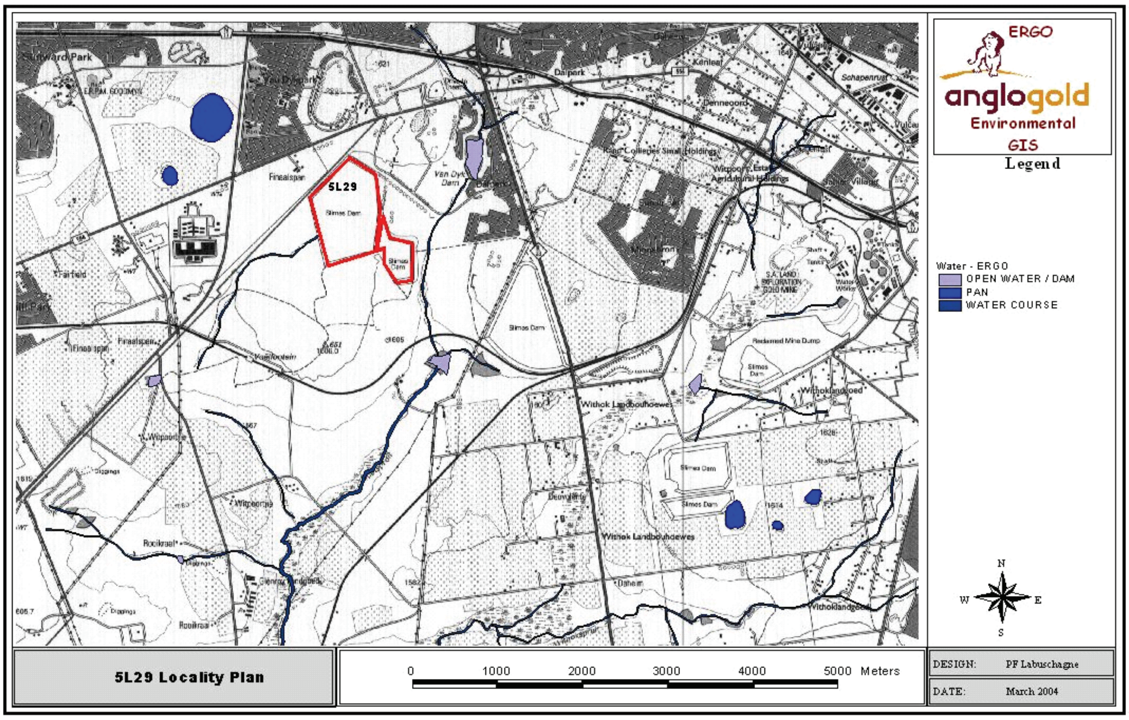
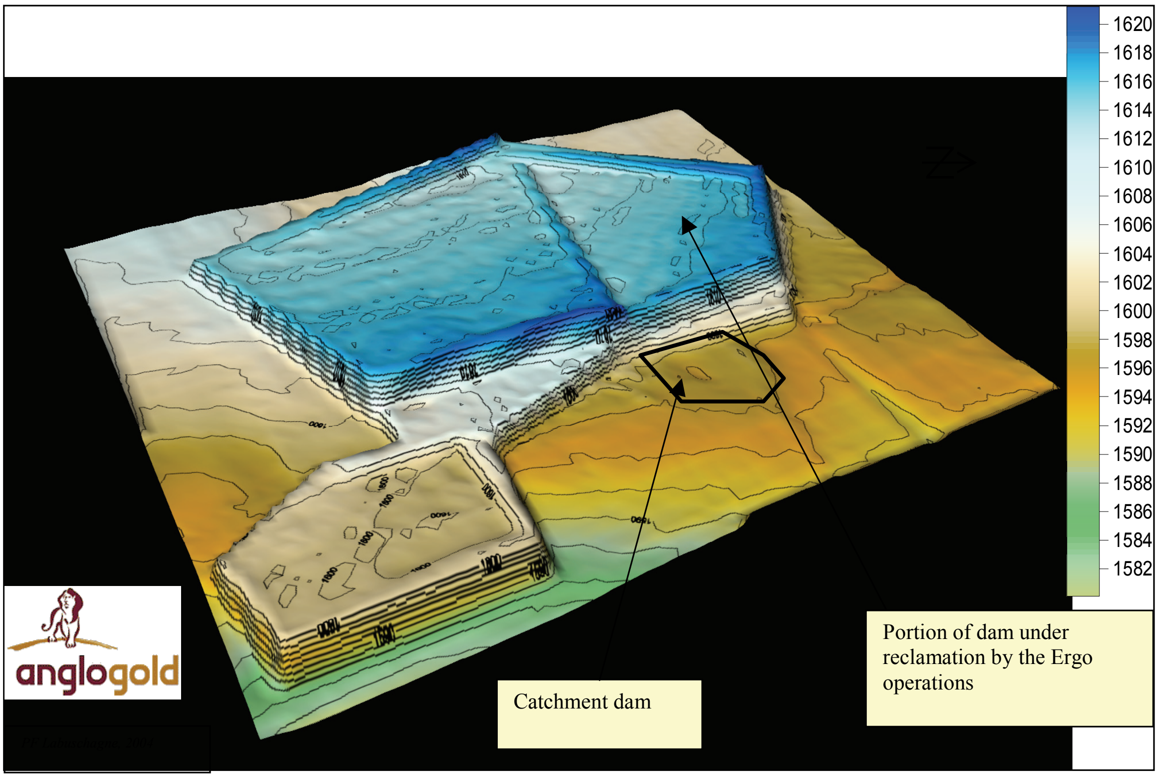


Figure 2.1: Local topography map for ERGO tailings facilities

The local surface geology constitutes sandstones, shale and siltstone formations of the Vryheid Group of the Karoo Supergroup. Seepages were visible in the surroundings of the dam and around the Rietspruit.

A number of sections exposed by the reclamation process were available. One of the exposed sections has about a 2.9 m deep oxidation zone (Figure 2.3). Four profile sections were studied in detail according to the methodology developed and 44 samples were collected from these profiles. These were complemented with six auger holes were dug with depths varying from 4.5 m to 10m from which 91 samples were collected at 50 cm intervals.



Portion of dam under reclamation by the Ergo operations

Catchment dam

Figure 2.2: 3D visualisation of the ERGO 5L29 dam.

2.2.1.2 Characterisation and classification of oxidation

Mapping of the exposed profiles as well as the auger sample logging showed oxidation variation both laterally and vertically. Based on this variation, the oxidation of the tailings material of the ERGO 5L29 dam could be classified into 3 zones as far as oxidation is concerned (Figure 2.4). These are:

1. Matured oxidized zone (OZ) - this is the zone where oxidation process is at maturity.
2. Transitional oxidation zone (TZ) - a zone where oxidation is aggressively active but not completed,
3. Un-oxidized zone (UZ) - there is little or no evidence of active oxidation taking place.

These zones can be further classified depending on the scale of mapping and details required.

Oxidized zone (OZ)

The mature oxidation zone (OZ) in 5L29 dam is 240 cm thick on average, which represents about 17% of the total height of the tailings dam. Although the OZ is characterised by a number of layers with different textural and structural characteristics, for the purpose of this study it can be sub-classified into the top leached zone (OZ-1) and the lower leached zone (OZ-2).

The OZ-1 is characterised by a buff to grey colour structureless mass with an average thickness of 75 cm, which is separated by a dark grey thin (mm-scale) layer from the underlying OZ-2. This zone is visible throughout the exposed sections of the tailings dam (Figure 2.3).

The OZ-2 is, on average, 165 cm thick and is dominantly brown in colour although thin mm-scale grey bands are also apparent. The OZ is gradationally followed by a transitional zone (TZ).

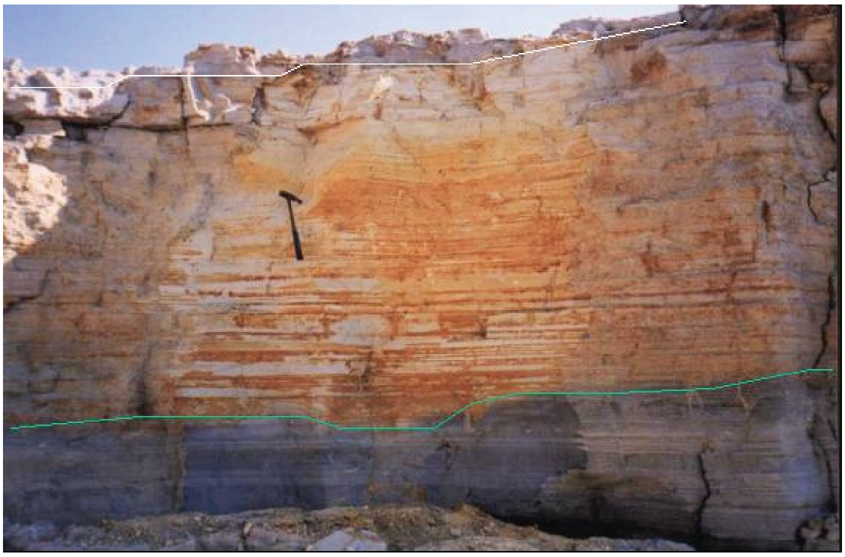


Figure 2.3: Typical oxidation zone profile (~4 m high) in ERGO 5L29 dam

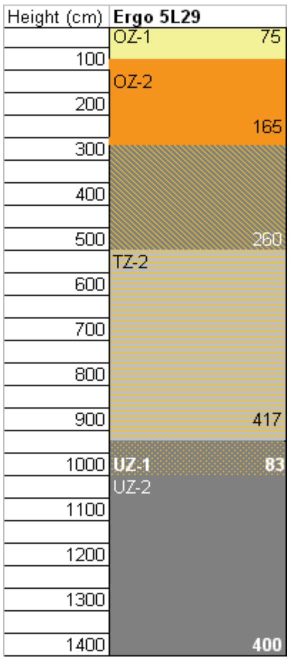


Figure 2.4: Oxidation zone development profile across the ERGO 5L29 dam

Transitional zone

This zone is characterised by a mixture of oxidized and un-oxidized materials in a complex manner, suggesting that the TZ is a zone where oxidation is active but not complete. The TZ of ERGO 5L29 dam is on average 417 cm thick and represents 30 % of the total height of the tailings deposit (Figure 2.4).

2.2.2 Stilfontein tailings dam

2.2.2.1 Mapping and sampling

Stilfontein No 2 Tailings dam is located in the northwest province east of Klerksdorp. According to Mr Melt Marais, Environmental Manager, of ChemWaste, the dam was decommissioned in 1973 and reclamation started in April 2003 by ChemWaste. The dam has an average height of 34 m.

Three sections exposed by the reclamation process were studied in detail and 36 samples were collected from these profiles. 8 auger holes were also dug with depths varying from 4 m to 10m from which 121 samples were collected at 50 cm intervals. All in all, the oxidation zones at 4 levels (benches) of the tailings dam were investigated.

Figure 2.5: Stilfontein No. 2 dam

Figure 2.6: Typical exposed section at Stilfontein No 2 dam

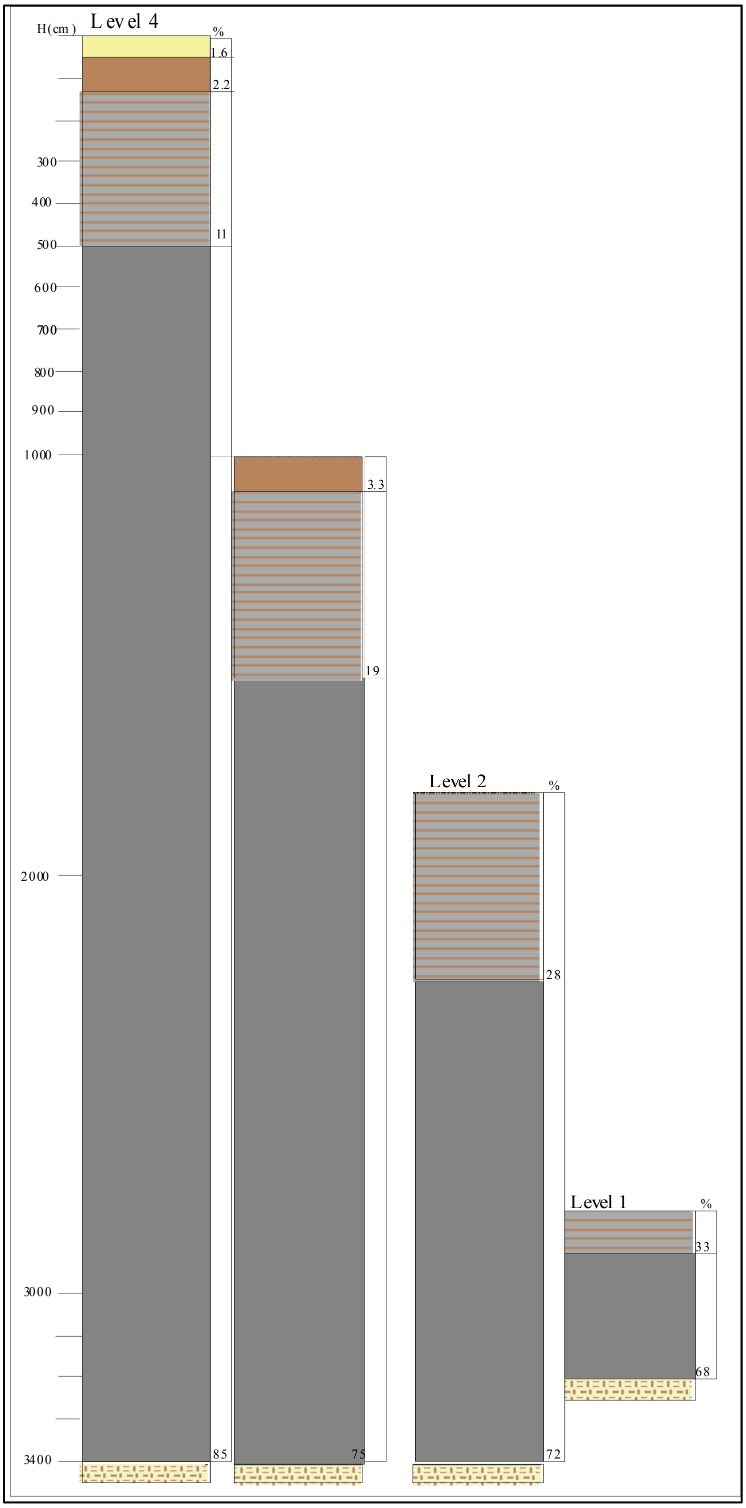


Figure 2.7: Oxidation zone development in Stilfontein No 2 dam

2.2.2.2. Characterisation and classification of oxidation

The profile and auger data show that oxidation processes in Stilfontein dam follows the original depositional patterns (bench type) in that the oxidation zone has also a stepwise pattern (Figure 2.6). The oxidation development progression in the Stilfontein tailings dam also shows the three zones (OZ, TZ and UZ) described for the ERGO 5L29 dam (Figures 2.5 and 2.6).

Mature oxidation zone (OZ)

OZ in the Stilfontein Tailings dam was observed in the auger holes of only one of the benches, namely the uppermost bench. The thickness of this zone ranges from 80 cm to 130 cm in the different auger holes. The OZ represents 3.3-3.8 % of the total height of the dam.

Transition zone

The Transitional zone (TZ) is widely developed in all the four levels and is characterised by partly oxidized and partly un-oxidized materials. This zone ranges in thickness from 430 cm to 530 cm and represents 11-19% of the bench heights of the tailings deposit.

2.2.3 CMR 3L1 tailings dam

2.2.3.1 Mapping and sampling

The CMR-3L1 Tailings dams were under reclamation by Crown Gold Recoveries Pty Ltd at the time of the study. It is one of the three tailings dams made available by Crown Gold Recoveries for the purpose of this project.

CMR-3L1 tailings dam has a total height of about 32 m. Two sections of 9.5 and 15 m deep that were exposed by the reclamation process were studied in detail from which 54 samples were collected. Six auger holes with a total depth of 49 m were dug and 98 samples were collected at 50 cm intervals. The depths of the auger holes range from 5.5 m to 9.5 m depending on the benches where the augers were located. Three levels (benches) of the tailings dam were investigated with a view to understanding the oxidation process and to classify the tailings material with respect to oxidation zones.

2.2.3.2. Characterisation and classification of oxidation

The exposed sections show the details, texture and structure of the tailings material in the OZ and TZ (Figure 2.8).

The oxidation zone development in CMR-3L1 dam follows the original depositional patterns (benching) in that the oxidation zone also has a step-wise pattern (Figure 2.9)

The profile and auger data has shown that the oxidation development in this material is also divided into OZ, TZ and UZ (Figure 2.9).

Oxidized zone (OZ)

Mature oxidation zone (OZ) was observed in all the 3 benches studied. The thickness of this zone ranges from 200 cm in the lower bench to 425 cm in the middle and upper benches representing 7% to 14% of the respective bench heights. The OZ can also be further classified into the top leached zone (OZ-1) and the lower leached zone (OZ-2).

Transitional zone (TZ)

The Transitional zone (TZ) is also observed in all the 3 benches. 50 cm, 200 cm and 75 cm thick transitional zones are observed in the upper, middle and lower benches respectively. This zone represents 2%, 7% and 3% of the height of the respective benches (Figure 2.9).

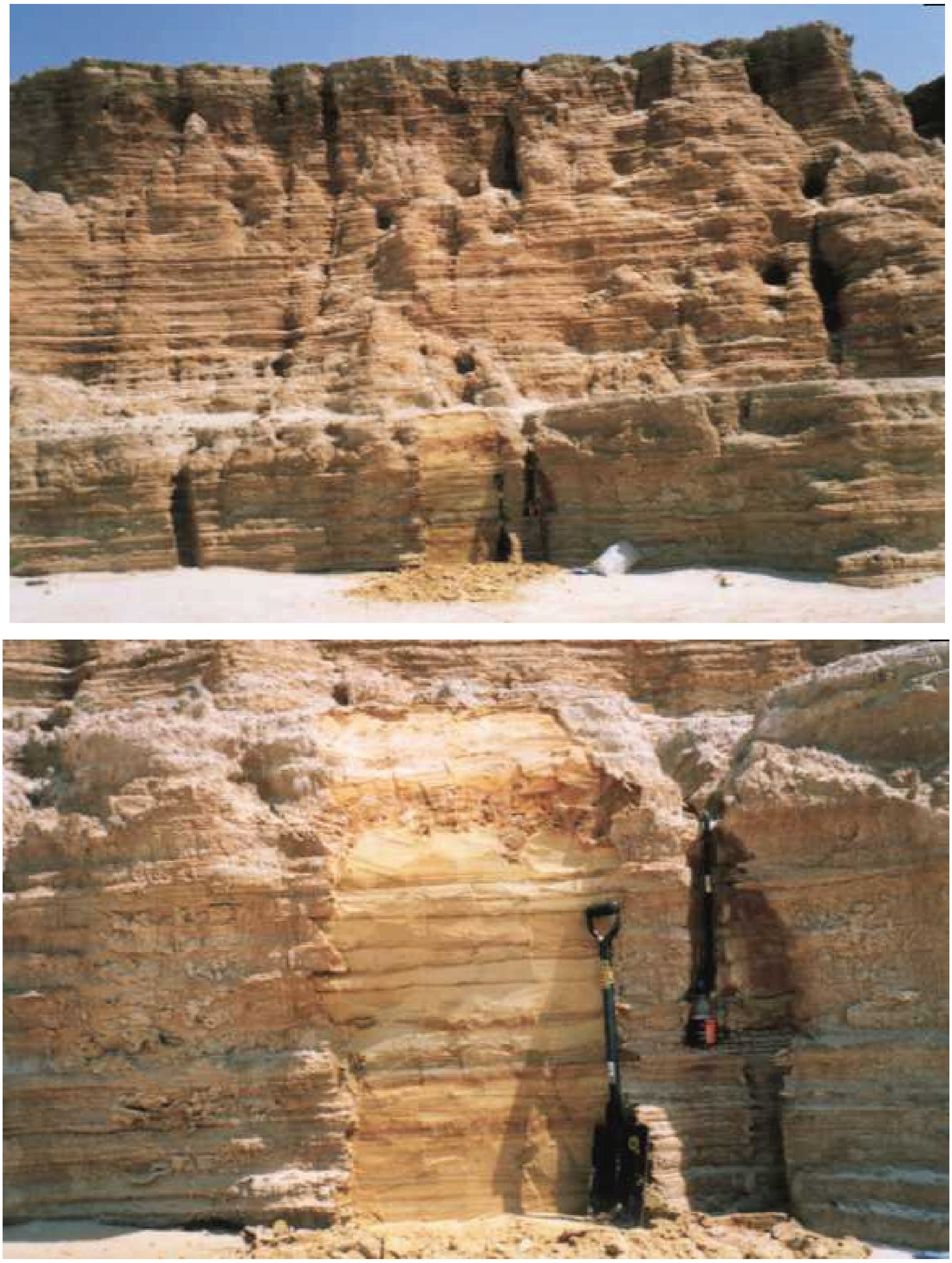


Figure 2.8: Exposed section in CMR-3L1 dam

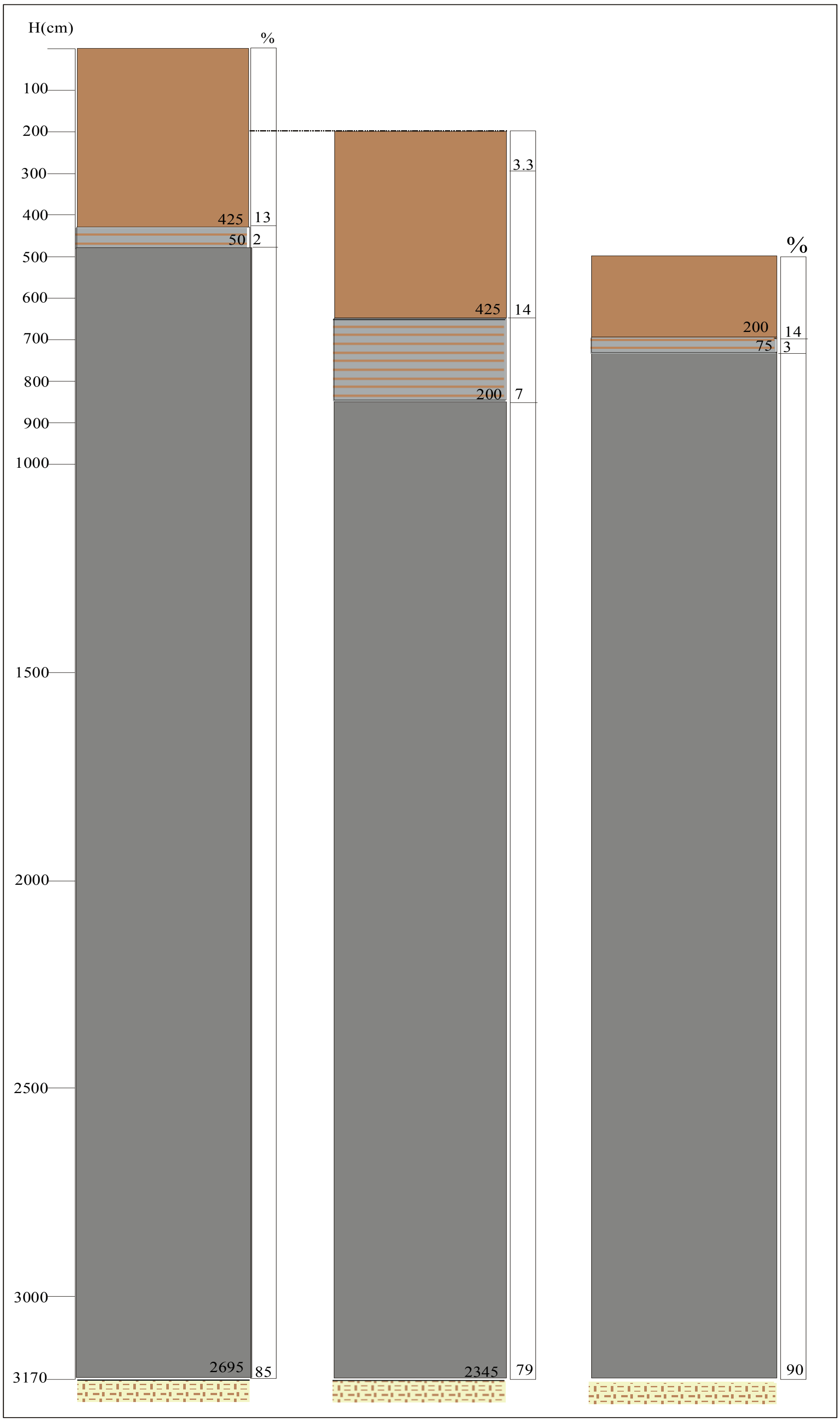


Figure 2.9: Representative oxidation zone profiles at different benches in CMR 3L1 dam

2.2.4 CMR 4L25 tailings dam

2.2.4.1 Mapping and sampling

The CMR 4L25 tailings dam was under reclamation by Crown Gold Recoveries Pty Ltd at the time of the investigation. The maximum height of the CMR 4L25 dam is about 25 m. Due to the inaccessibility and safety precautions only a 2.13 m deep exposed section was investigated from which 8 samples were collected.

Six auger holes with a total depth of 47 m were dug from which 94 samples were collected at 50 cm intervals. The depths of the auger holes range from 4.5 m to 9.5 m with an average depth of 7.8 m.

Figure 2.10: oxidation zones in exposed section of CMR 4L25 dam

2.2.4.2 Characterisation and classification of oxidation

The OZ and the TZ were both observed in all auger holes, although in the exposed section only the OZ. The thickness of the OZ ranges from 200 cm to 600 cm whereas the TZ ranges from 200 cm to 250 cm. This OZ represents 8% to 33% of the heights of the benches. The deep oxidation zone (6 m OZ and 2.5 m TZ) is developed on the easternmost part of the dam on a narrow bench, which is 9.5 m high (Figures 2.10 & 2.11).

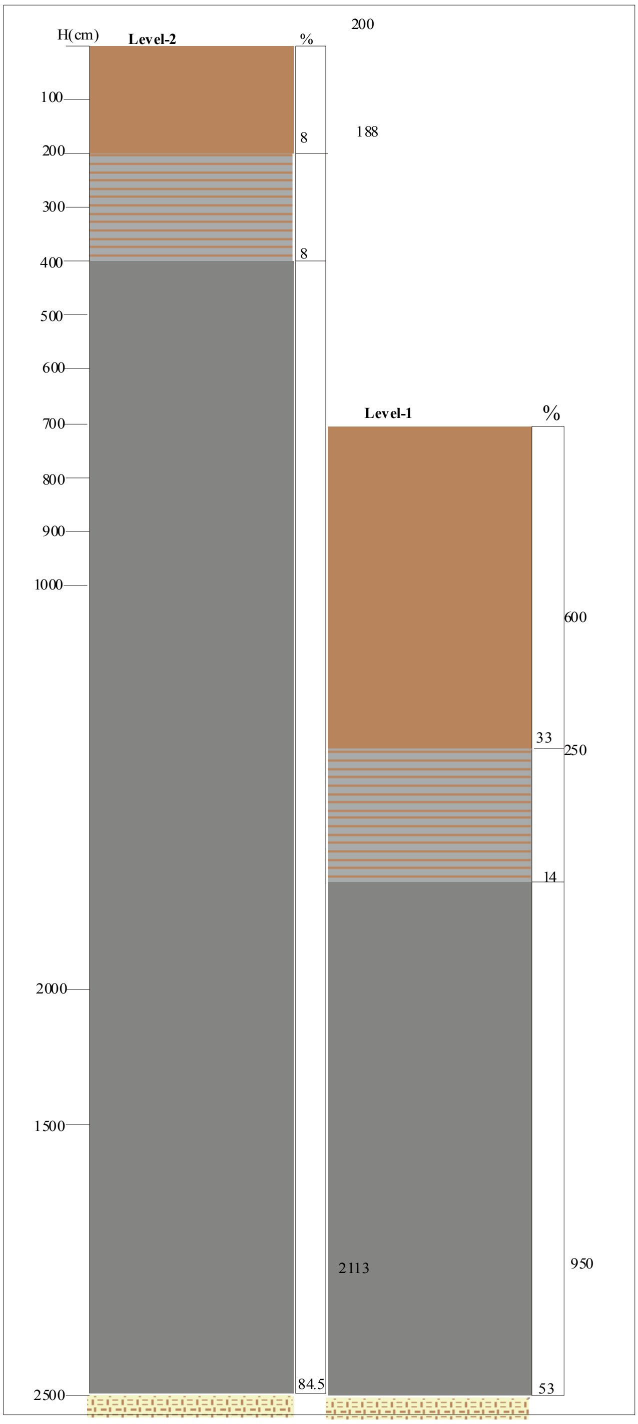


Figure 2.11: Representative oxidation profiles in CMR 4L25 dam

2.2.5 CMR 4L19 tailings dam

2.2.5.1 Mapping and sampling

The height of the CMR 4L19 Dam is about 19 m. One exposed section of 4 m high was studied in detail. The top 400 cm of the section is completely oxidised. Seven auger holes with a total depth of 50m were dug from which 91 samples were collected. The depths of the auger holes range from 4.5 m to 9 m with an average depth of 7.14 m. Although heterogeneity of oxidation in the TZ is characteristic in all the tailings, the presence of almost un-oxidized grey and wet layers which at places reaches 10 cm thick in the CMR 4L19 dam is enigmatic. The only oxidation observed in such layers is where there are fractures or cracks across these layers (Figure 2.12 bottom picture).

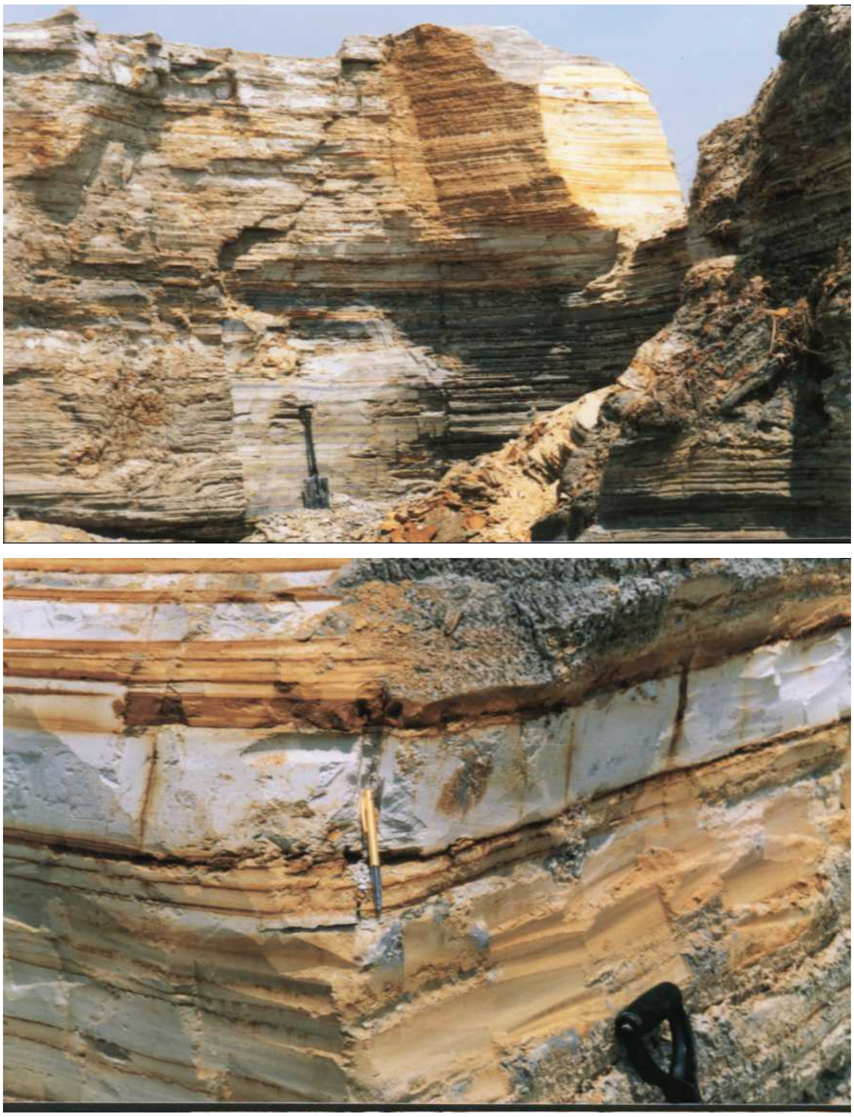


Figure 2.12: Exposed section in CMR 4L19 dam - top (overall view) and bottom (closer view)

2.2.5.2 Characterisation and classification of oxidation

Both well developed oxidized zone (OZ) and transitional zone (TZ) were observed in all auger holes, which were dug at 3 different benches. The thickness of the OZ ranges from 50 cm to 200 cm thick whereas the transitional zone (TZ) ranges from 150 cm to 300 cm representing 11-14 %, and 14 to 43% of the respective bench heights. The lowest bench which is only 3.5 m high shows 50 cm of the OZ and 150 cm TZ (Figures 2.12 & 2.13).

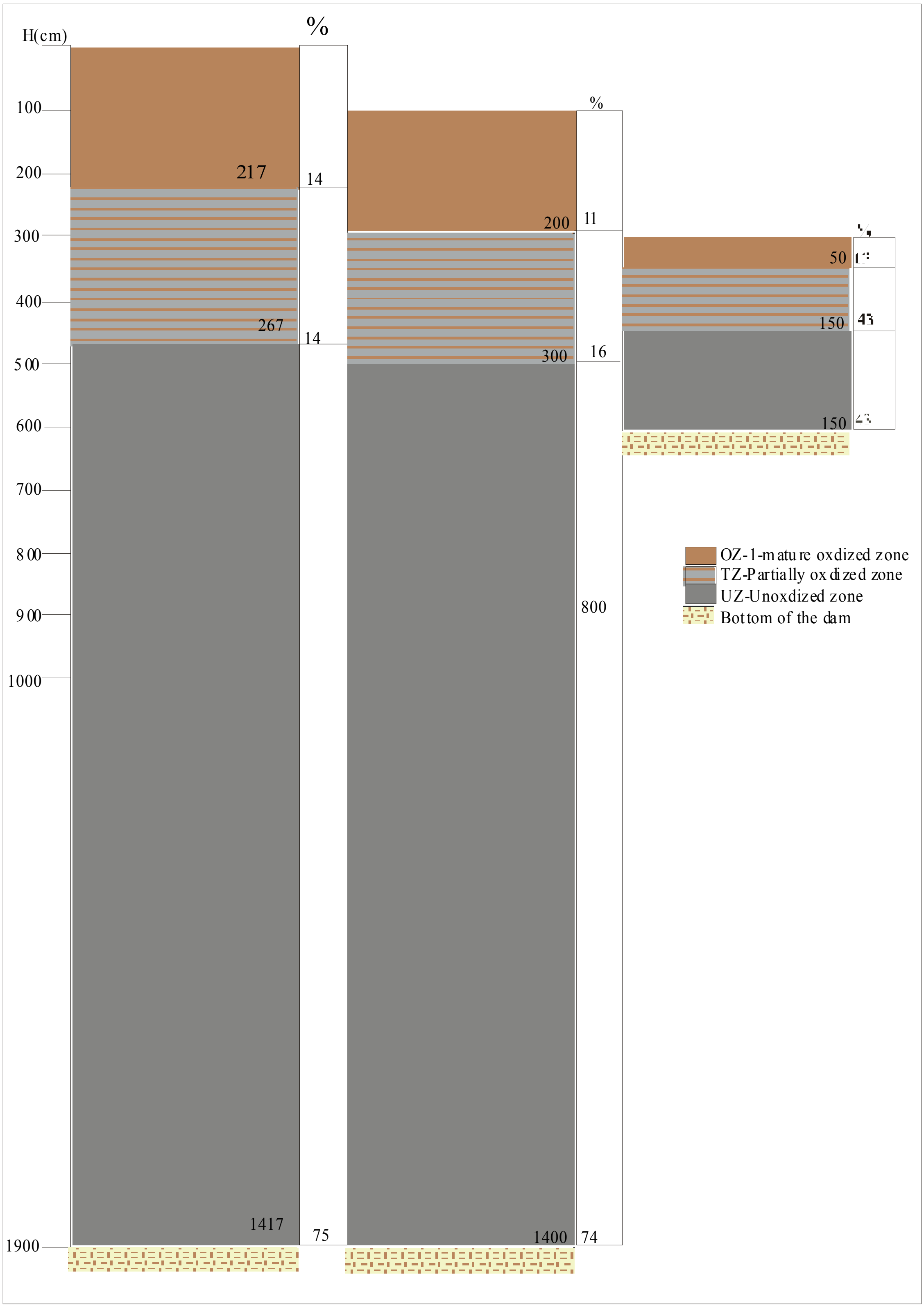


Figure 2.13: Oxidation zone profile of CMR 4L19 dam

2.3 SUMMARY

Cross-sections and exposed profiles resulting from the reclamation processes of the tailings dams have been used to map and characterize the intensity and variations of oxidation in the tailings dams. This together with logging of auger holes of up to 10 m depth resulted in the determination of the oxidation zone depths and tracing of the un-oxidized parts of the tailings dams. Overall, three zones of oxidation were recognized based on variation of oxidation intensities with depth. These zones are: a) mature oxidation zone (OZ), b) transitional zone (TZ) and c) primary or un-oxidized zone (UZ). The OZ and TZ constitute the total oxidation zone. Detailed field and laboratory investigation of the selected tailings dams for this study shows that the depth of OZ ranges between 150 cm (Stilfontein No. 2 dam) to 350 cm (CMR 3L1 and ERGO 5L29 dams). The combined depth of the OZ and TZ (transition zone) varies from 450 cm (CMR 3L1) to 900 cm (ERGO-5L29 dam).

CHAPTER 3
MINERALOGY, GEOCHEMISTRY AND HYDROGEOLOGY OF THE SELECTED TAILINGS DAMS

3.1 FACTORS CONTROLLING OXIDATION PROCESSES IN TAILINGS DAMS

The unsaturated zone of the tailings dam is the zone where oxidation processes are active, providing the source of contaminants and low pH pore water. This implies that a reasonably accurate estimation of the oxidation depth will be critical in order to make a reliable quantification of both the acidic and the metal leaching aspect of the mine drainage assessment as the volume and quality of the ARD to be generated from tailings dams is directly related to the volume of the oxidized tailings.

Oxidation processes in tailings dams are governed by interplay of many factors such as geochemical and mineralogical composition (specifically sulphides and buffer minerals, ferric iron), oxygen and water availability, catalysing bacteria, weathering of oxidation products by further reactions.

Mineralogy and chemistry, grain size, porosity, permeability, water retention capacity, water content, oxygen supply, climate (mainly rainfall and evaporation) and age of the tailings dam are identified as the most important criteria to determine the rate and intensity of oxidation.

Understanding the oxidation processes and oxidation depth is critical in the quantification of the geochemical evolution of the pore water both in terms of its acidity and metal loadings. The interplay of these factors in governing the rate and intensity of oxidation development in tailings dam is difficult to quantify. These key parameters are used herein to establish a scorecard method to rate tailings dams with respect to their favourability for oxidation processes.

The following most important factors for oxidation zone processes are used in the scorecard method:

1. Sulphide content (Py),
2. Trace metal abundance
3. Grain size
4. Porosity
5. Permeability (Ks)
6. O_2 concentration with depth
7. Residual water content (Wr)
8. Rainfall
9. Age of dams since decommissioned

3.2 GEOCHEMICAL AND MINERALOGICAL CHARACTERISATION

3.2.1 Sample selection and compositing

The samples collected during the characterisation and mapping of the tailings dams were composited to optimise the number of representative samples to be analysed from each tailings dams.

The following geochemical and mineralogical analyses were performed after compositing the samples:

- Paste pH
- WE-AA analyses (water extraction and AA analysis),
- Mineralogy (XRD), and
- XRF (Major and trace element analyses).

The paste pH and Water extraction and AA analyses is aimed at determining the chemistry of the pore water in the samples while the XRD and XRF analyses determined the mineralogical and chemical variations of the solid tailings with depth.

3.2.2 Pore water chemistry

3.2.2.1 ERGO-5L29 tailings dam

The interpretation of the pH and WE-AA results for the ERGO tailings dam are presented in Table 3.1 and Figure 3.1 and can be summarised as follows:

- Both paste pH and pH values range from about 3 to about 6.5 and increases with depth suggesting progressive decrease in acidity and hence less oxidation with depth.
- Ni, Zn, Co, and Cu are high in the OZ and in TZ when compared to the unoxidised zone (UZ) (i.e., they are depleted with depth consistent with depth of oxidation).
- Ca, Al, Mg and Fe also decrease with depth
- Na and K increase with depth
- SO_4, EC and Redox potentials progressively decrease with depth.

Table 3.1: Pore water quality data (in mg/l) for the ERGO-5L29 tailings dam samples

SAMPLE NAME	**5L29-OZ**	**5L29-TZ**	**5L29-UZ**
pH	3.28	3.9	4.1
Paste pH	3.62	4.1	6.4
Alkalinity ($CaCO_3$)	0.00	0	0
Conductivity (mS/m)	115	203.80	114.90
Redox Potential (mV)	217	235.00	217.00
SO_4	584	1215.35	584.09
Al	2	45.73	2.43
Ca	193	237.44	192.68
Cl	B.D.L	0.61	B.D.L
Co	2	3.66	2.45
Cu	0	0.42	0.05
Fl	0	0.81	0.12
Fe	30	49.39	29.59
Pb	0	0.25	0.25
Mg	24	60.15	23.81
Mn	5	5.84	4.87
Ni	5	9.81	5.32
K	7	3.63	6.79
Na	6	10.69	5.61
Zn	2	4.95	2.46

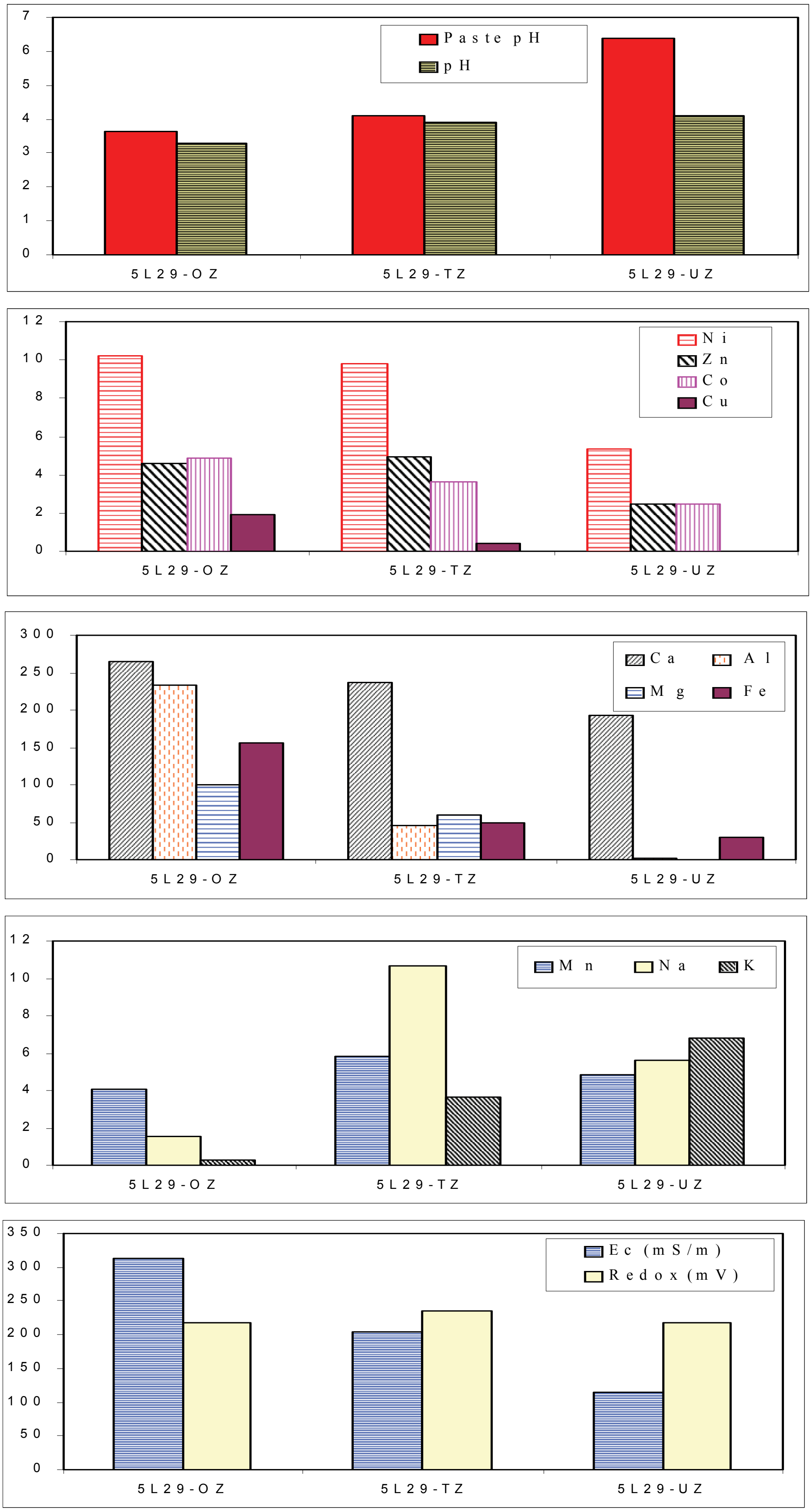


Figure 3.1: Pore water quality data for ERGO 5L29 dam

3.2.2.2 Stilfontein No. 2 tailings dam

The interpretation of the pH and WE-AA results are presented in Table 3.2 and Figure 3.2 and can be summarised as follows

- The pH and paste pH values are low (acidic) for the samples from the OZ and the TZ zones with progressive decrease in pH values from the OZ to the TZ and the topmost part of the UZ part. The UZ sample shows higher paste pH and pH values (6-7) consistent with the progression of oxidation.
- (Ni, Zn, Co, and Cu are high in the TZ and upper part of the UZ compared to those of the oxidized and unoxidised zones. SO_4, EC and Redox are also high in these zones.
- Fe, Al, Mg and Mn are enriched in the transition zone compared to the OZ and UZ. Ca however decreases systematically with depth whereas Na and K increase with depth.

This elemental variation in the pore water suggests that fluid migration beyond the transitional zone is minimal in the Stilfontein No. 2 Dam. However this needs further investigation using hydrological data.

Table 3.2: Pore water quality data (in mg/l) for the Stilfontein No. 2 tailings dam samples

SAMPLE NAME	**STA-OZ**	**STA-TZ**	**STA-UZ-A**	**STA-UZ-B**
PH	3.1	2.6	2.5	6.2
Paste pH	3.2	2.8	2.8	7.0
Conductivity (mS/m)	345	483	469	190
Redox Potential (mV)	456	606	618	324
SO_4	1791	2347	2280	1084
Al	25	50	43	6
Ca	750	643	571	400
Cl	8	28	27	11
Co	0	2.8	4.2	0.3
Cu	0.9	2.1	1.5	0.1
Fl	B.D.L	B.D.L	0.22	0.05
Fe	9.44	225.9	345.7	B.D.L
Pb	0.3	0.25	0.79	0.25
Mg	23.10	25.7	35.9	22.9
Mn	2.8	30.4	24.2	2.9
Ni	1.2	8.0	11.4	0.5
K	0.6	0.7	0.5	4.8
Na	2.6	2.9	6.7	15.3
Zn	0.8	10.7	11.1	0.1

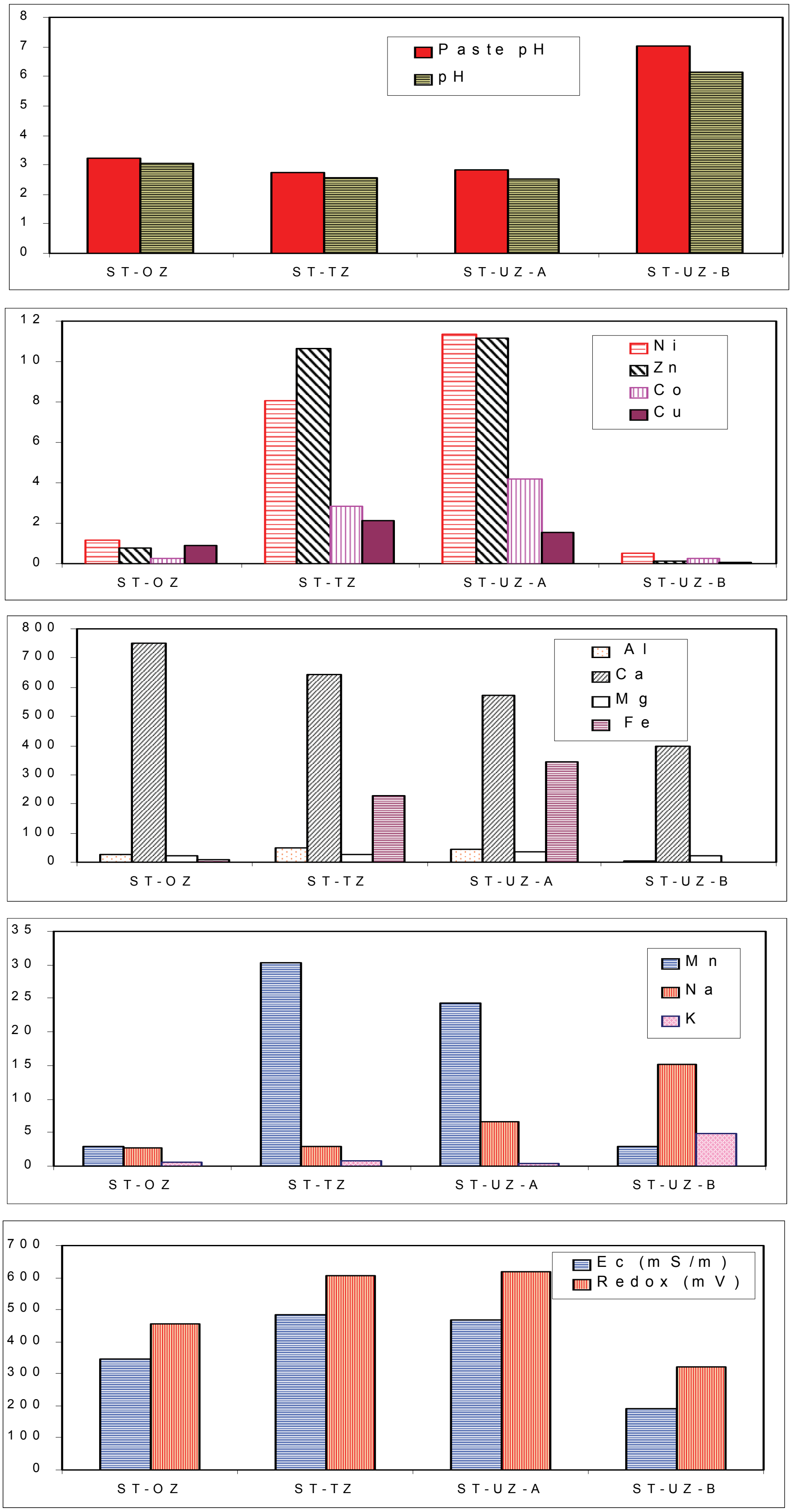


Figure 3.2: Pore water quality data for Stilfontein No. 2 dam

3.2.2.3 CMR-3L1 tailings dam

The interpretation of the pH and WE-AA results are presented in Table 3.3 and Figure 3.3 and can be summarised as follows:

- Both paste pH and pH values in the samples from the CMR 3L1 tailings decrease slightly from the OZ to the TZ and then increase at the UZ although the pH in the UZ is still acidic (Figure 3.3). This suggests fluid migration is probably unhindered at least up to the depth of sampling, or that oxidation is progressing below the depth of sampling.
- Ni, Zn and Co increase with depth from the OZ to the UZ zones, suggestive of unhindered fluid migration and progression of oxidation up to about 10 m.
- Ca, Al, Mg, Fe, Na, Mn and K increase with depth, although the concentration of these metals in the TZ is lower than that of the OZ (Figure 3.3).
- SO_4 is low in the TZ compared to the OZ and the UZ whereas EC and Redox shows slight enrichment in the TZ.

Table 3.3: Pore water quality data (in mg/l) for the CMR-3L1 tailings dam samples

SAMPLE NAME	**3L1-OZ**	**3L1-TZ**	**3L1-UZ**
pH	3.3	2.5	3.5
Paste pH	3.5	2.9	4.0
Conductivity (mS/m)	241	269	204
Redox Potential (mV)	505	522	452
SO_4	1234	945	1138
Al	73	50	12
Ca	239	15	340
Cl	20	19	6
Co	1.1	2.1	2.3
Cu	2.6	2.3	0.4
Fl	0.09	0.14	1.53
Fe	2.8	118.7	2.3
Pb	<0.50	<0.50	<0.50
Mg	46.5	2.9	33.1
Mn	1.8	2.0	5.7
Ni	3.8	5.6	8.2
K	1.3	0.8	2.5
Na	3.6	1.0	2.5
Zn	1.1	5.9	7.9

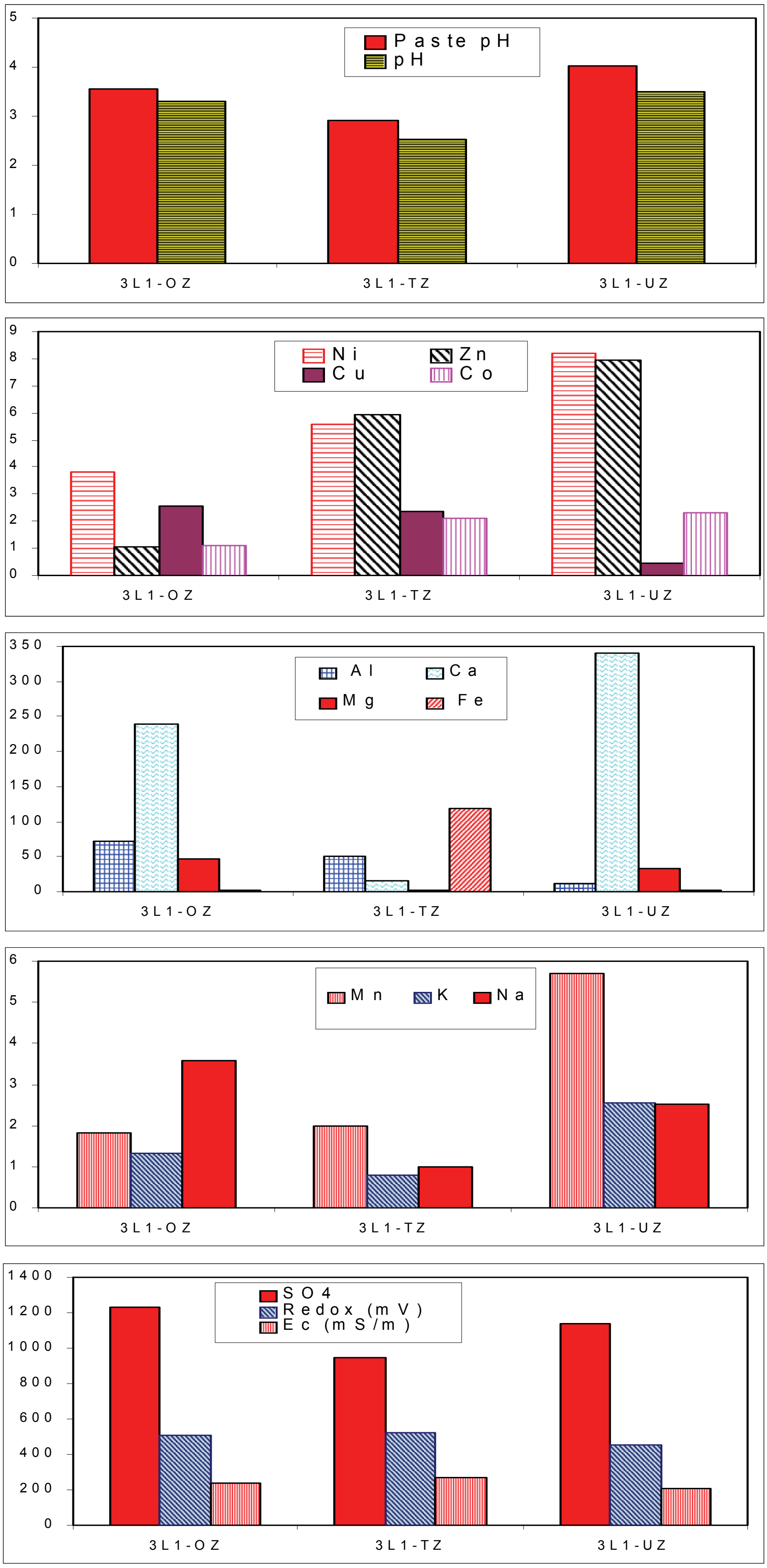


Figure 3.3: Pore water quality data for CMR-3L1 dam

3.2.2.4 CMR-4L19 tailings dam

The interpretation of the pH and WE-AA results are presented in Table 3.4 and Figure 3.4 and can be summarised as follows:

- Neither paste pH nor pH values show any distinct differences between the oxidized zones and the unoxidised zone although the pH for the UZ is slightly higher though still within acidic range. This suggests fluid migration is unhindered at least up to the depth of sampling.
- Almost all metals show slight enrichment at the TZ compared to the OZ (Figure 3.4).

Table 3.4: Pore water quality data (in mg/l) for the CMR-4L19 tailings dam samples

SAMPLE NAME	4L19-OZ	4L19-TZ	4L19-UZ
pH	3.31	3.3	3.3
Paste pH	3.55	3.6	3.8
Conductivity (mS/m)	323	344	204
Redox Potential (mV)	475	404	546
SO_4	1770	2149	887
Al	125	78	18
Ca	188	242	174
Cl	27	30	14
Co	3.2	4.3	2.3
Cu	3.3	2.4	1.2
Fl	0.04	<BDL	0.21
Fe	3.4	45.4	4.4
Pb	0.71	<0.50	<0.50
Mg	112.3	138.0	43.2
Mn	5.6	8.9	5.2
Ni	8.2	9.4	7.6
K	1.4	0.6	1.9
Na	2.3	2.2	6.0
Zn	4.4	5.7	7.7

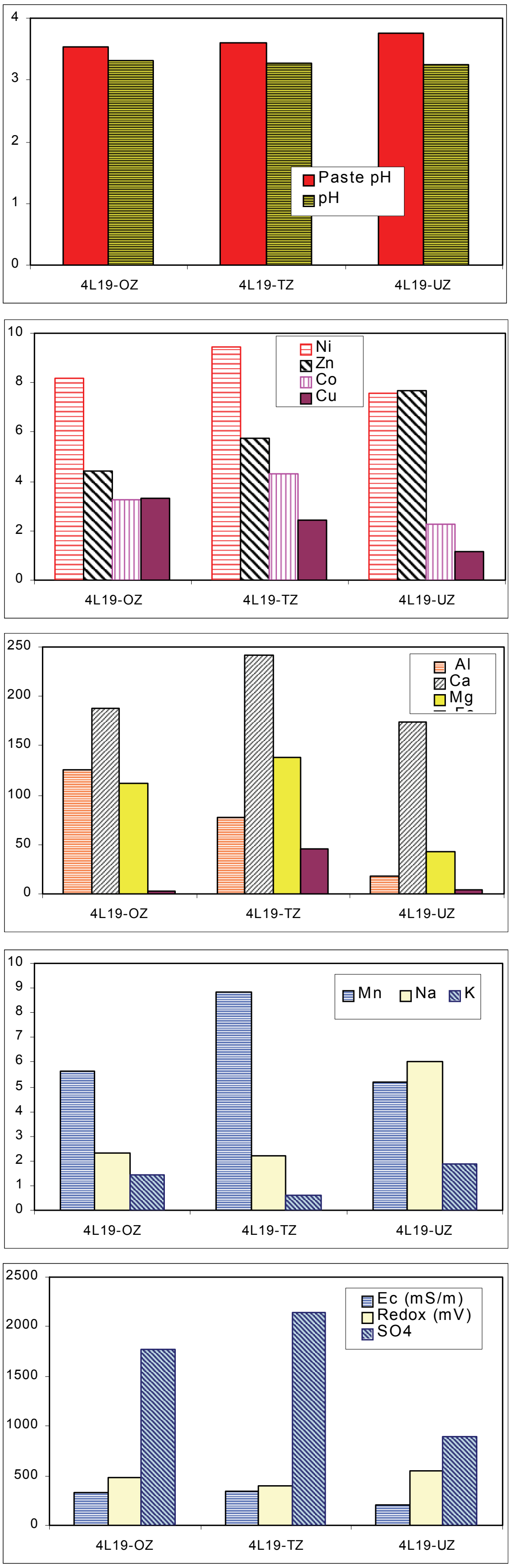


Figure 3.4: Pore water quality data for CMR-4L19 dam

3.2.2.5 CMR-4L25 tailings dam

The interpretation of the pH and WE-AA results are presented in Table 3.5 and Figure 3.5 and can be summarised as follows:

- Neither paste pH nor pH values show distinct differences between the oxidized zones and the unoxidised zone and all are acidic. This suggests fluid migration is unhindered at least up to the depth of sampling.
- Ni, Zn, Co, and Cu show enrichment in the transitional zone at the expense of the OZ.
- Ca, Al and Mg also show similar patterns in that they are also enriched at the transitional zone. While Ca is the most highly enriched, Na and K do not show this trend but rather are higher in the OZ than in the TZ and UZ. Mn shows a clear systematic increase with depth.
- SO_4, redox and EC are high in the TZ.

Table 3.5: Pore water quality data (in mg/l) for the CMR-4L25 tailings dam samples

SAMPLE NAME	CMR-4L25-OZ	CMR-4L25-TZ	CMR-4L25-UZ
Paste pH	3.56	4.1	4.0
pH	3.41	3.2	3.3
Conductivity mS/m	315	405	237
Redox Potential (mV)	454	531	529
SO_4	1576	2114	1213
Al	81	101	19
Ca	401	564	364
Cl	20	23	10
Co	1.70	4	2
Cu	2.00	2	1
Fl	0.12	0	0
Fe	2.30	4	2
Pb	<0.50	<0.50	<0.50
Mg	85	71	52
Mn	3.8	7	8
Ni	5.3	28	8
K	2.5	1	2
Na	2.9	2	2
Zn	2.2	11	7

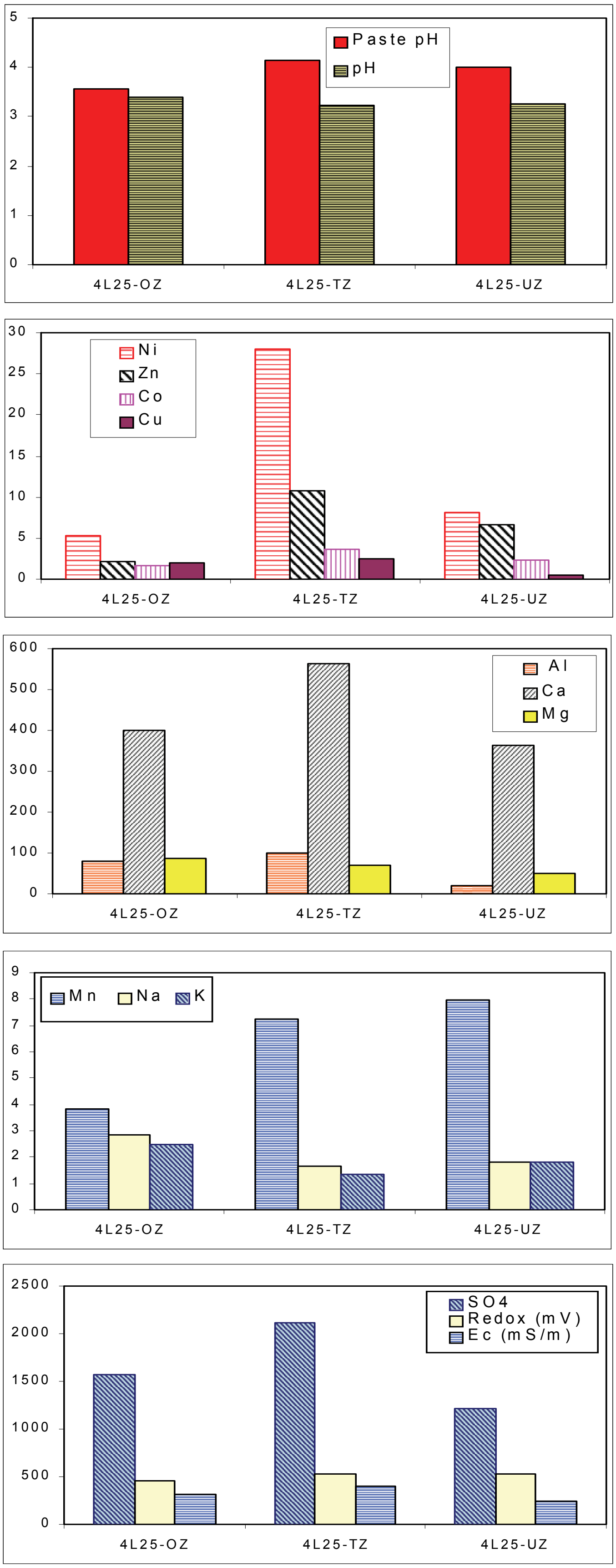


Figure 3.5: Pore water quality variation with for CMR-4L25 dam

3.2.3 Tailings solid geochemistry (XRF)

3.2.3.1 ERGO-5L29 tailings dam

There is a general trend of enrichment in major elements at the Transitional zone. The major oxides show less concentration in the unoxidised zone and tend to show higher concentration in the transitional zone (Table 3.6, Figure 3.6). The relationship amongst the major elements and with the oxidation zone in response to the oxidation processes is not apparent and requires further investigation.

Table 3.6a: Major element chemistry (wt %) for ERGO-5L29 tailings dam

Sample ID	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	LOI	TOTAL
5L29-OZ	80.4	0.53	7.83	3.61	0.02	0.71	0.3	0.17	1.8	0.05	4.1	99.48
5L29-TZ	82.6	0.53	7.26	3.05	0.02	0.51	0.2	0.2	1.8	0.04	2.9	99.14
5L29-UZB	82.1	0.52	7.51	3.1	0.02	0.56	0.2	0.19	1.8	0.04	3	99.06
5L29-UZBC	82.0	0.54	7.49	3.32	0.01	0.51	0.2	0.23	1.8	0.05	2.5	98.71

The following observations can be made with respect to the trace metals distribution

- Cr, V and Cu show systematic decrease with depth and are positively correlated
- Zn, Ni, Co, show enrichment at the upper part of UZ

Table 3.6b: Trace element chemistry (ppm) for ERGO-5L29 tailings dam

Sample ID	Rb	Sr	Y	Zr	Nb	Co	Ni	Cu	Zn	V	Cr	Ba
5L29-OZ	59	21	19	174	10	97	318	68	116	92	570	210
5L29-TZ	62	23	18	191	10	95	337	65	123	82	452	172
5L29-UZB	60	24	18	181	10	142	443	58	134	76	456	171
5L29-UZBC	61	23	17	191	10	66	217	52	89	75	449	175

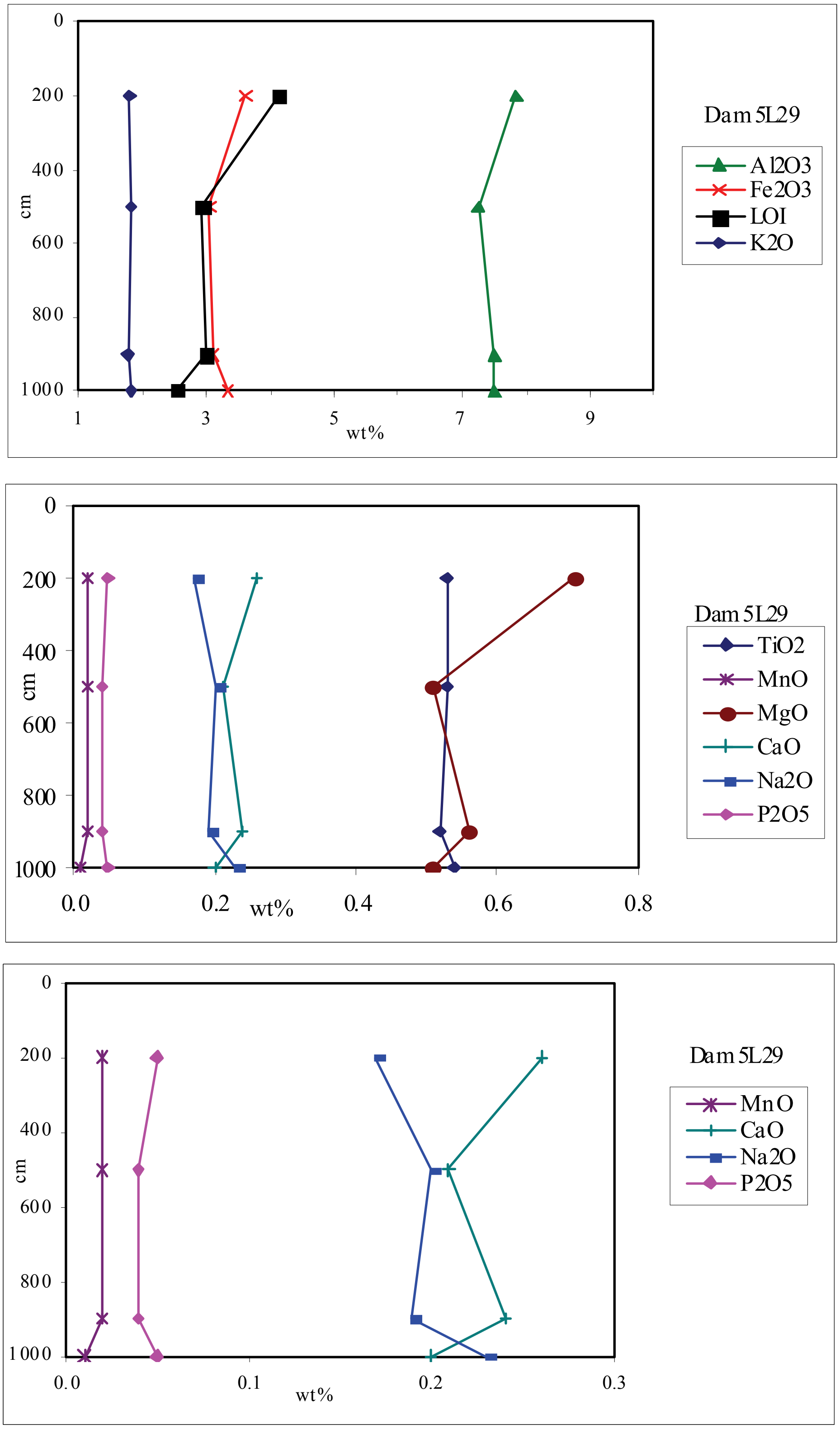


Figure 3.6: Major element patterns with depth in dam 5L29

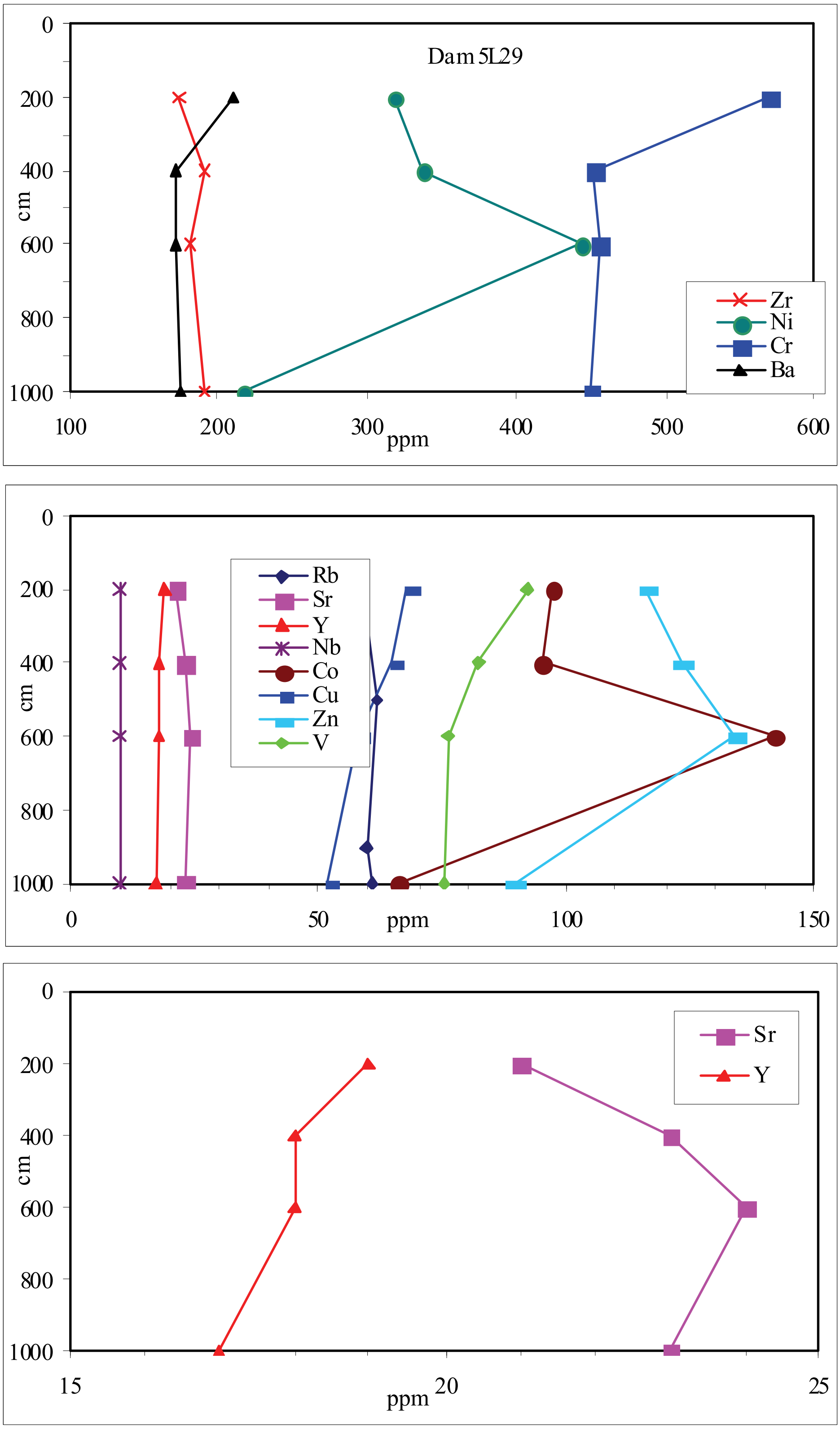


Figure 3.7: Trace element variation in 5L29 dam

3.2.3.2 Stilfontein No. 2 tailings dam

SiO_2 concentration is slightly high in the solid samples from the TZ and upper part of the UZ compared to the OZ and the lower part of the UZ samples. With the exception of Fe and Al, most of the major oxides show depletion at the transitional zone and upper part of UZ. K_2O and Al_2O_3 depict this pattern most distinctly. Exception to this pattern is shown by Fe, which shows slight enrichment at the TZ as compared to the OZ and UZ (Table 3.7a, Figure 3.8)

Table 3.7a: Major element chemistry (wt%) for Stilfontein No 2 tailings dam

Sample ID	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	LOI	TOTAL
STA-OZ	82	0.33	10	2.05	0.01	0	0.5	0.26	1.1	0.07	3	99.62
STA-TZ	83	0.31	8.2	2.57	0.05	0	0.6	0.2	0.7	0.06	3.7	99.23
STA-UZ (1)	84	0.31	8.9	3.2	0.05	0	0.4	0.17	0.6	0.05	3.3	99.46
STA-UZ (2)	82	0.32	10.4	2.3	0.03	0.14	0.5	0.3	1.3	0.09	2.6	99.99

The trace elements concentration in the Stilfontein dam No. 2 is presented in Table 3.7 b and in Figure 3.8. The following major points can be deduced from the preliminary interpretation of the data:

- Co, Ni, Cu and Zn are depleted in the OZ and enriched in the TZ and upper part of UZ. Furthermore, the concentrations of these metals in the OZ are less than that in the UZ.
- Ba and Rb show slight depletion at the TZ and upper part of UZ.
- Pb and Zr show enrichment at the OZ with a general depletion pattern with depth although this pattern seems to be disturbed in the TZ and in the upper part of UZ.

In general the patterns depicted by the trace elements clearly show signatures of oxidation although further study is required to ascertain these relationships.

Table 3.7b: Trace element chemistry (ppm) for Stilfontein No 2 tailings dam

Sample ID	Rb	Sr	Y	Zr	Nb	Co	Ni	Cu	Zn	V	Cr	Ba	Pb
STA-OZ	44	51	23	223	11	13	35	24	48	49	202	309	135
STA-TZ	35	46	29	227	11	39	124	44	253	45	201	270	124
STA-UZ (1)	33	43	32	233	11	47	150	45	284	51	232	196	134
STA-UZ (2)	54	51	25	192	9	23	79	35	151	52	185	296	97

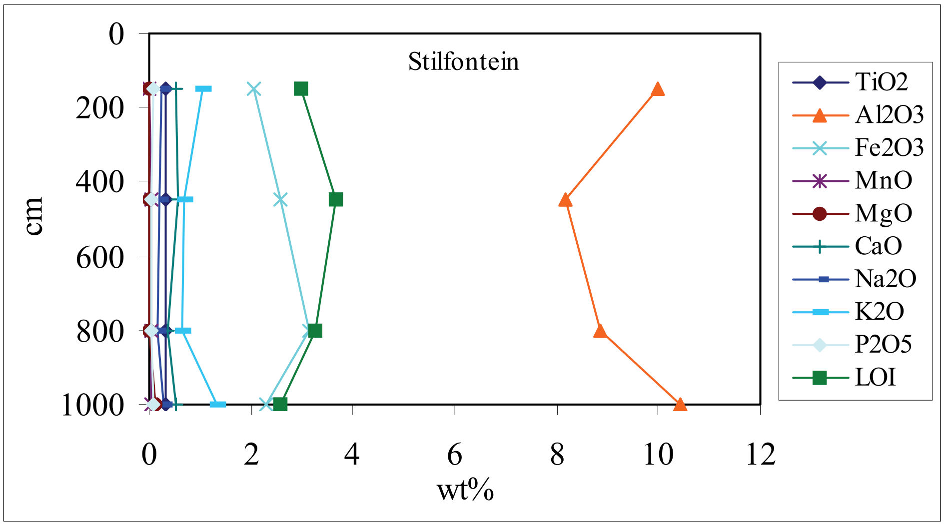
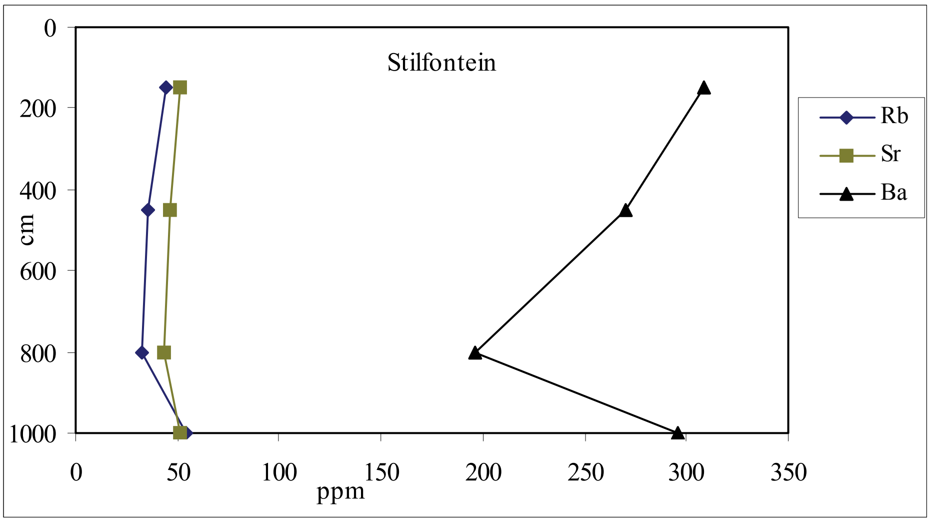


Figure 3.8: Major element distribution with depth in the Stilfontein No 2 dam



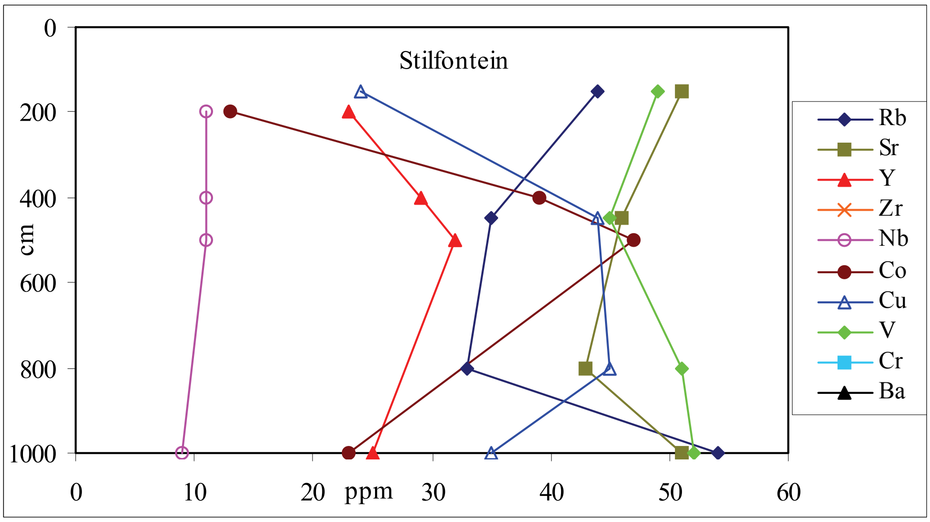


Figure 3.9: Trace element distribution with depth in Stilfontein No 2 dam

3.2.3.3 CMR-3L1 tailings dam

The following major deductions can be drawn from the major element data, which is presented in Table 3.8a and Figure 3.10:

- Fe_2O_3 and MnO show systematic increase in concentration with depth.
- Al_2O_3, MgO, and to some extent Na_2O and TiO_2 are slightly depleted at the intermediate depth
- P_2O_5 is the only element, which shows systematic though slight decrease in abundance with depth.
- With the exception of Si, Ti, Ca and P_2O_5 the other oxides show depletion with depth up to the TZ then increase at the UZ (Figure 3.10). This pattern could be attributed to oxidation processes.
- Si, Ti, and P do not show any definite pattern. These metals are relatively immobile in oxidation processes.
- Whether or not the patterns depicted by the major elements can be interpreted as a function of oxidation requires more detailed investigation.

Table 3.8a: Major element chemistry (wt%) for CMR-3L1 tailings dam

Sample ID	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	LOI	TOTAL
3L1-OZ (1)	84	0.29	8.13	2.78	0.03	0.35	0.19	0.33	0.82	0.10	2.40	99.53
3L1-OZ(2)	85	0.28	7.43	3.04	0.03	0.27	0.22	0.31	0.77	0.05	2.83	100.1
3L1-TZ	87	0.28	6.45	3.28	0.03	0.21	0.09	0.25	0.64	0.08	2.13	100.02
3L1-UZ	82	0.3	8.98	3.73	0.04	0.39	0.23	0.34	0.95	0.05	2.29	99.48

Trace elements:

- While Co, Ni, Zn and Cr show high concentrations in the UZ, a general depletion pattern for the zones where oxidation is active (OZ and TZ) is observed. Co, Ni and Zn show a systematic decrease with depth if the average of the OZ data is considered. This pattern could be a function of the decrease in oxidation intensity with depth
- Ba and Rb show a clear enrichment with depth, which, considering their high mobility should be attributed to oxidation (Figure 3.11).

Further study is required to understand more on the relationship of the trace element with oxidation processes.

Table 3.8b: Trace element chemistry (ppm) for CMR-3L1 tailings dam

Sample ID	Rb	Sr	Y	Zr	Nb	Co	Ni	Cu	Zn	V	Cr	Ba	Pb
3L1-OZ (1)	34	40	18	127	5	15	69	41	58	60	210	235	43
3L1-OZ(2)	32	40	17	121	5	11	39	22	47	57	213	234	42
3L1-TZ	26	33	19	137	5	24	86	36	80	48	204	208	26
3L1-UZ	33	41	22	133	5	31	141	25	194	55	219	242	43

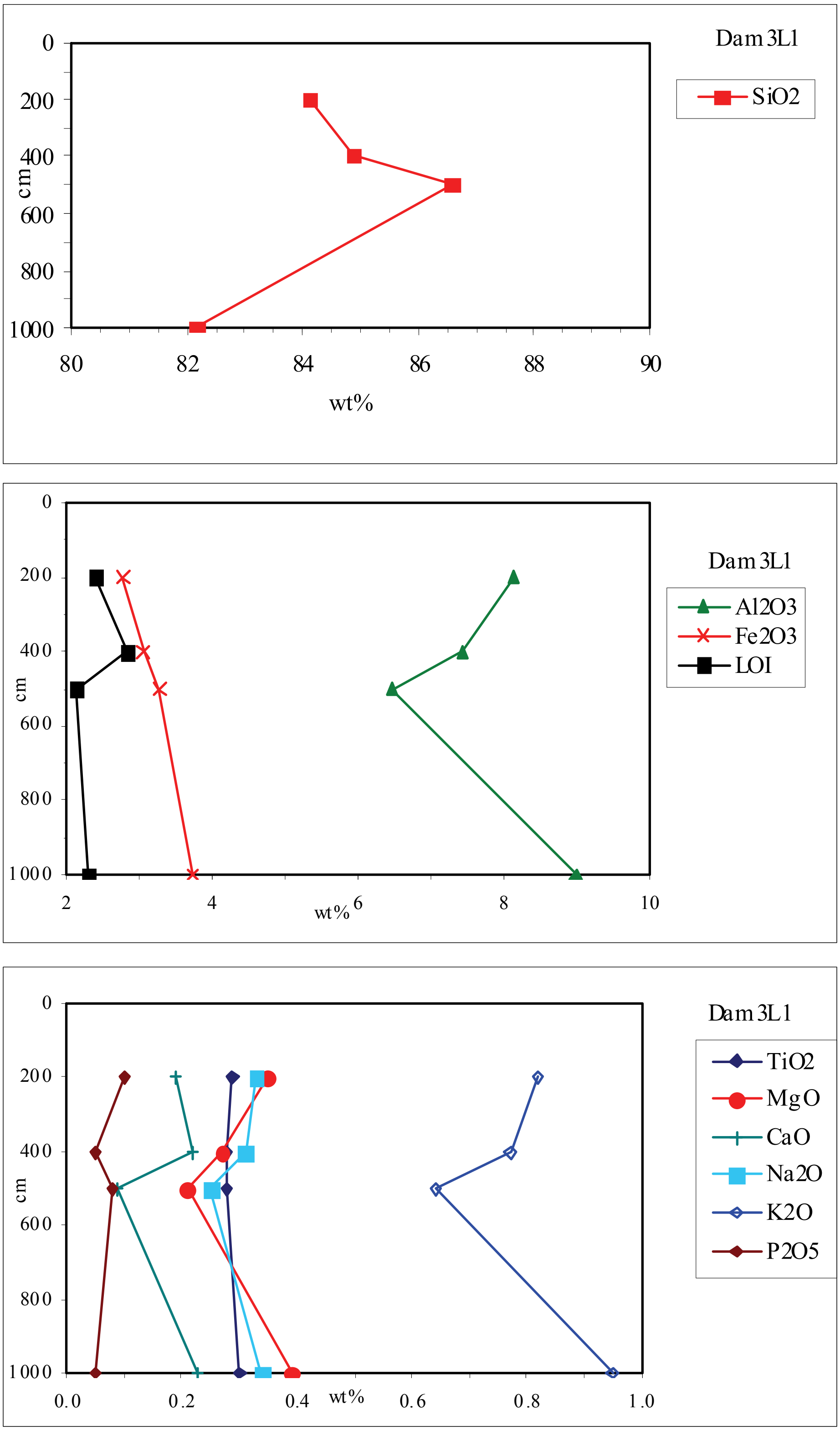
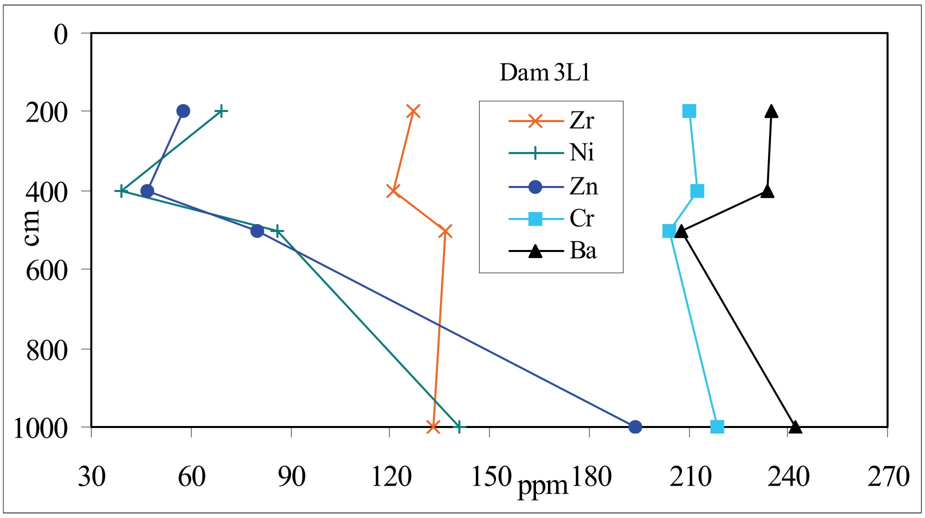


Figure 3.10: Major element distribution with depth in the 3L1 tailings dam



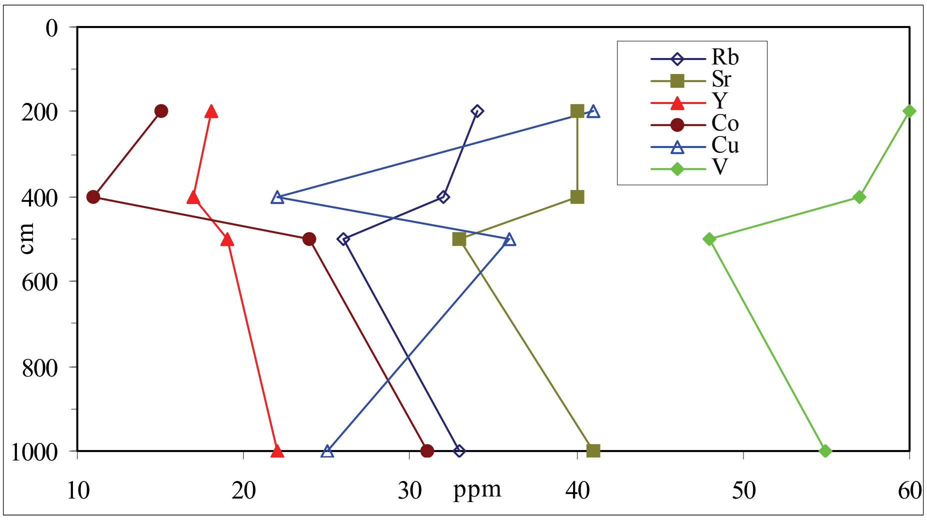


Figure 3.11: Trace element distribution with depth in the 3L1 tailings dam

3.2.3.4 CMR-4L19 tailings dam

Major elements:

- SiO_2, TiO_2, Na_2O and P_2O_5 have low concentrations in the TZ when compared to the OZ and the UZ
- Fe_2O_3 and MnO show systematic enrichment with depth probably attributed to oxidation
- The average MgO and CaO concentrations in the OZ samples show relative depletion compared to the TZ and the UZ.

The patterns depicted by the major elements are not clearly systematic and cannot be related to oxidation processes. This lack of correlation could be attributed to original geochemical differences rather than oxidation processes.

Table 3.9a: Major element chemistry (wt%) for CMR-4L19 tailings dam

Sample ID	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	LOI	TOTAL
4L19-OZ (1)	80.2	0.32	8.81	3.28	0.03	0.34	0.1	0.41	1.5	0.06	3.9	98.97
4L19-OZ(2)	78.7	0.33	9.74	3.66	0.04	0.42	0.2	0.38	1.6	0.04	3.9	99.06
4L19-TZ	78	0.31	9.51	3.52	0.04	0.49	0.5	0.38	1.5	0.04	4.2	98.56
4L19-UZ	81.1	0.32	9.36	3.78	0.04	0.42	0.2	0.39	1.6	0.07	3.1	100.4

The trace element distribution data for the samples form CMR-4L19 tailings are presented in Table 3.9b and Figure 3.12. The following preliminary and general observations can be made form the data:

- Co, Ni, Zn and (Pb and Sr to some extent) systematically increase with depth suggesting a relationship with oxidation processes considering the lowest or average concentration of these metals are found in the OZ zone.
- Cu shows a gentle but systematic decrease with depth.
- Ba, Cr, V and Rb show high concentration at the TZ, which could be due to pore water migration into the TZ.

In general the transitional and base metals show systematic variation that can be related to oxidation processes.

Table 3.9b: Trace element chemistry (ppm) for CMR-4L19 tailings dam

Sample ID	Rb	Sr	Y	Zr	Nb	Co	Ni	Cu	Zn	V	Cr	Ba	Pb
4L19-OZ (1)	54	57	20	118	5	20	72	51	70	58	215	421	27
4L19-OZ(2)	56	52	23	119	5	32	116	47	107	65	233	416	31
OZ-Average	**55**	**55**	**22**	**119**	**5**	**26**	**94**	**49**	**89**	**62**	**224**	**419**	**29**
4L19-TZ	60	52	21	119	5	28	104	44	104	72	240	444	30
4L19-UZ	55	56	23	120	5	33	116	43	157	61	218	412	31

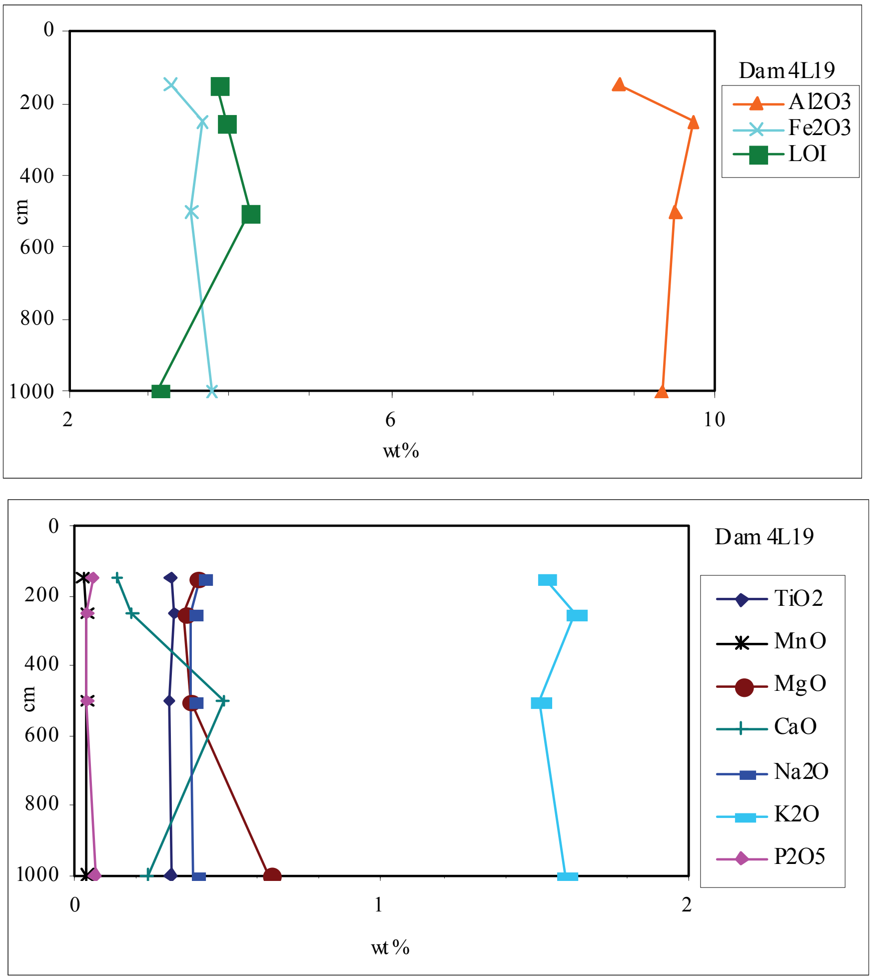


Figure 3.12: Major element distribution patterns in 4L19 tailings dam

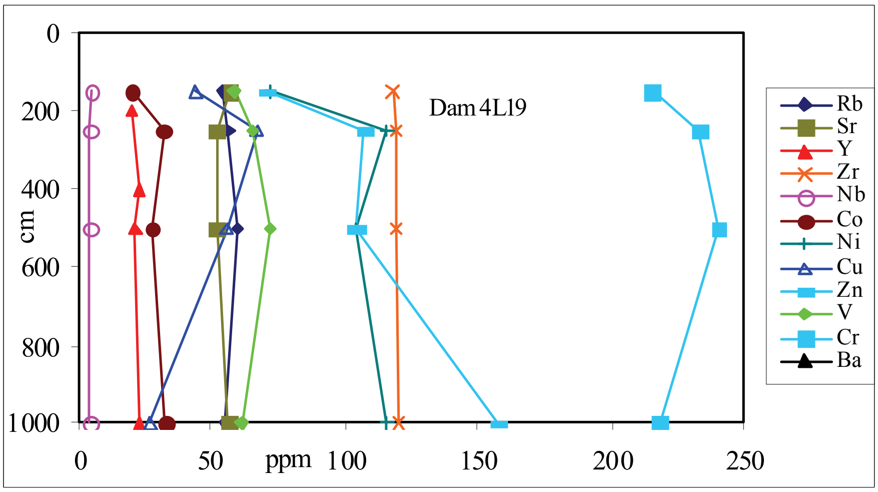


Figure 3.13: Trace elements distribution with depth in the 4L19 tailings dam

3.2.3.5 CMR-4L25 tailings dam

The major element distribution data are given in Table 3.10a and are plotted in Figure 3.14. The following points can be deduced from the preliminary assessment of the data:

- Fe_2O_3, MnO, and Na_2O increase consistently with depth
- SiO_2, MgO, CaO and Na_2O decrease with depth.

The patterns of the two groups of oxides above could be related to oxidation.

Table 3.10a: Major element chemistry (wt%) for CMR-4L25 tailings dam

Sample ID	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	LOI	TOTAL
4L25-OZ	83	0.35	7.02	3.32	0.03	0.38	0.7	0.33	1.05	0.08	3.31	99.19
4L25-TZ	82	0.33	7.54	3.39	0.04	0.6	0.4	0.35	1	0.09	3.2	98.72
4L25-UZ	82	0.36	7.47	3.97	0.04	0.5	0.3	0.36	1	0.05	2.8	98.98

Trace elements:

- Co, Ni, Cu and Zn show elevated concentrations in the UZ. These metals, with the exception of Cu, show their highest concentration in the UZ.
- Pb is high in the TZ and low in the OZ.
- Rb, Sr, Y and Zr do not show any significant variation with depth

The patterns of the trace elements and their relationship to oxidation processes need further investigation.

Table 3.10b: Trace element chemistry (ppm) for CMR-4L25 tailings dam

Sample ID	Rb	Sr	Y	Zr	Nb	Co	Ni	Cu	Zn	V	Cr	Ba	Pb
4L25-OZ	41	39	20	138	5	30	132	56	127	59	249	300	34
4L25-TZ	39	41	21	137	4	14	57	27	55	61	246	287	47
4L25-UZ	41	40	22	143	5	37	166	39	217	67	260	297	44

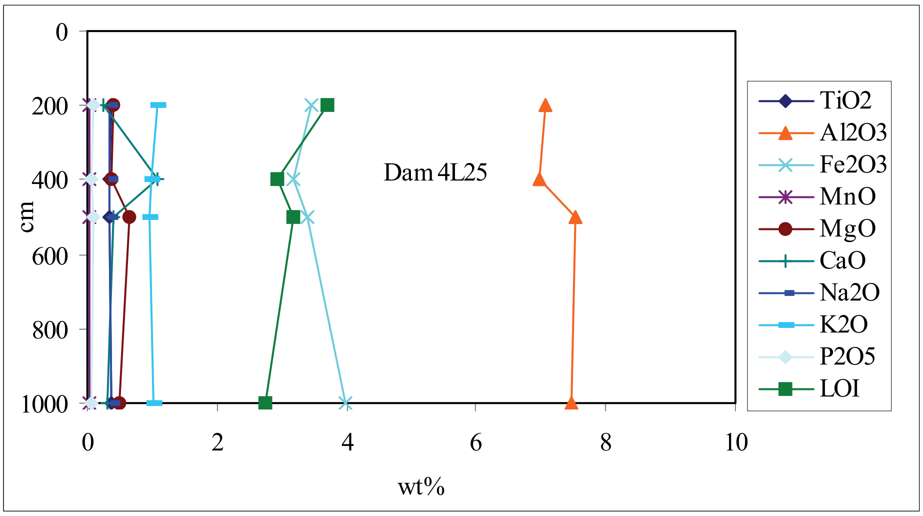


Figure3.14: Major element distribution with depth in the 4L25 tailings dam

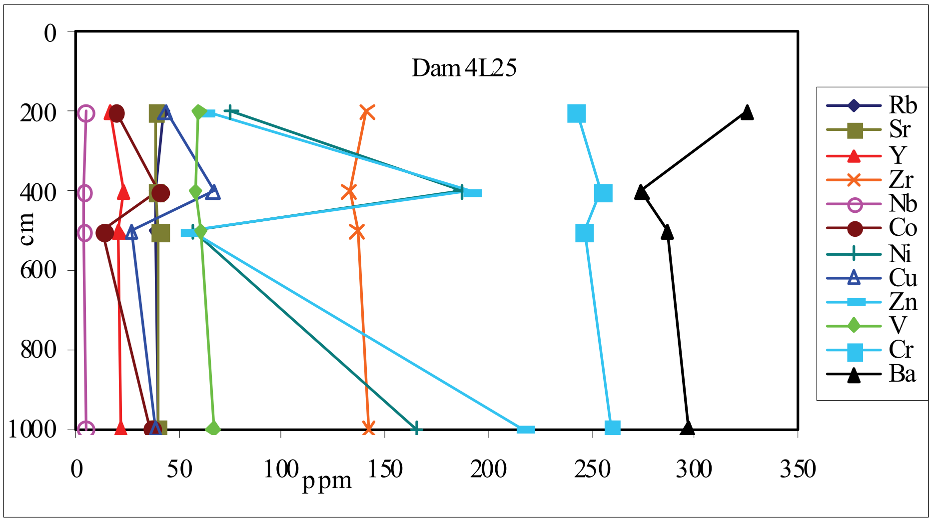


Figure 3.15: Trace element distribution in the 4L25 tailings dam

3.2.4 Mineralogy

3.2.4.1 ERGO-5L29 tailings dam

The 3 most important (major) minerals that constitute the ERGO 5L29 tailings are quartz, mica and chlorite. Quartz constitutes over 80% of all the samples (Table 3.11, Figure 3.16). Mica and chlorite are both < 10 % each. 1% of pyrite is reported in the transitional zone and upper part of the UZ whereas only traces (<1%) of pyrite are reported in the un-oxidized zone. Secondary minerals, mainly jarosite and gypsum are, as expected, reported in the upper part of the oxidation zone.

Table 3.11: XRD mineralogical data for ERGO-5L29 tailings dam

	Jarosite	Pyrite	K-feldspar	Quartz	Mica	Chlorite	Gypsum	Clay
5L29-OZ	2	<1	-	80	8	8	1	1
5L29-TZ1	1	1	1	82	9	7	-	-
5L29-TZ2	1	1	1	80	10	7	-	-
5L29-UZ	-	<1	1	80	11	7	-	-

3.2.4.2 Stilfontein No. 2 tailings dam

The 3 most important (major) minerals that constitute the Stilfontein No. 2 tailings dam are quartz, pyrophyllite and mica. Quartz, which forms between 64 and 76% of the mineralogical composition in the tailings samples, increases progressively with depth. Pyrophyllite and mica decrease with depth (Figure 3.17). The concentration of pyrite and jarosite are in agreement with the progress of the oxidation zone with depth in that jarosite decreases in concentration with depth whereas pyrite increases.

Table 3.12: XRD mineralogical data for Stilfontein No 2 tailings dam

Sample ID	Pyrite	Jarosite	Chloritoid	Quartz	Mica	Chlorite	Pyrophyllite
STA-OZ	-	2	2	64	8	3	22
STA-TZ	1	2	3	66	5	3	20
STA-UZ	2	1	2	76	3	3	14
STA-UZ	-	1	2	78	6	3	10

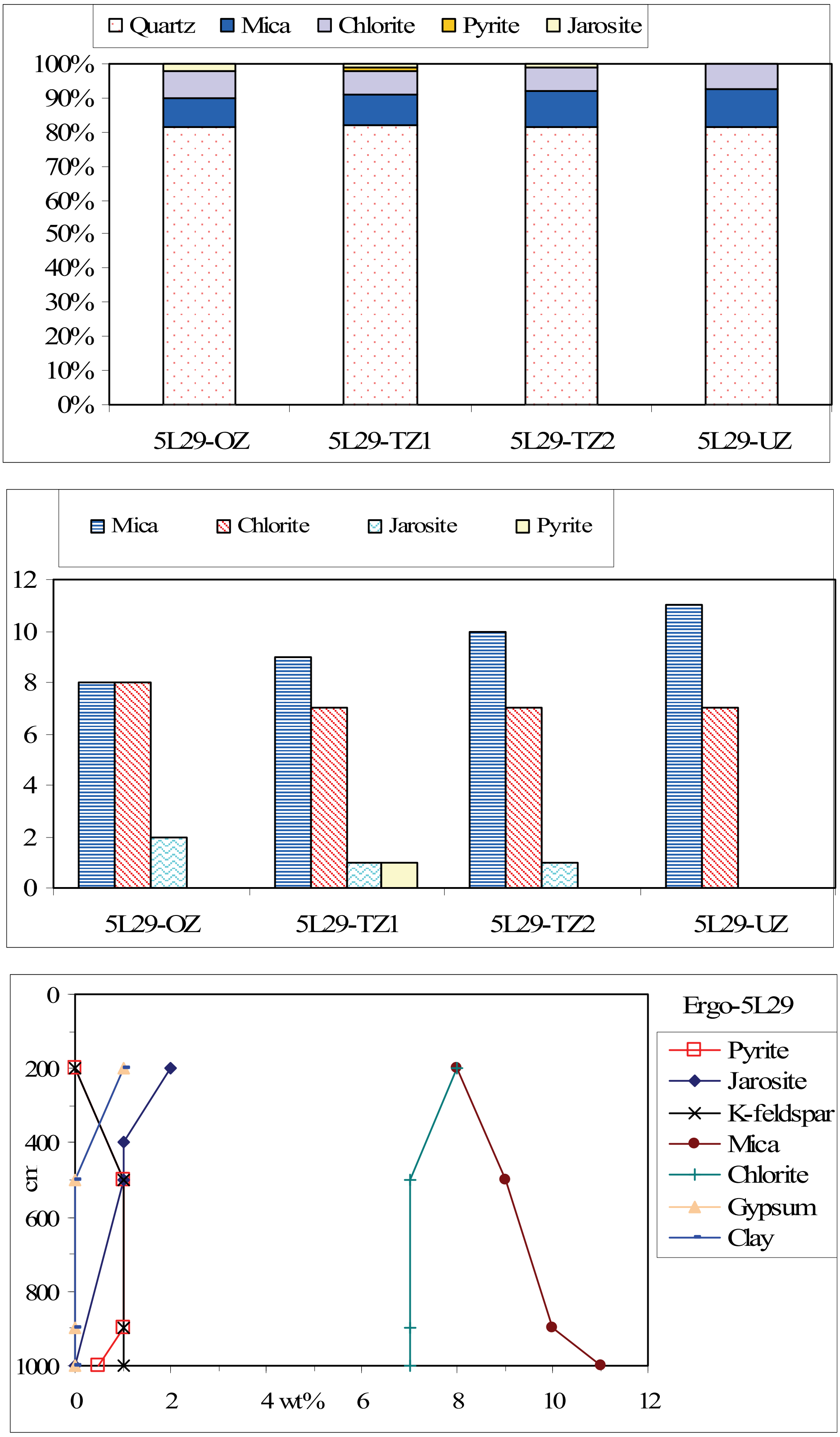


Figure 3.16: Mineralogical distribution data for 5L29 tailings dam

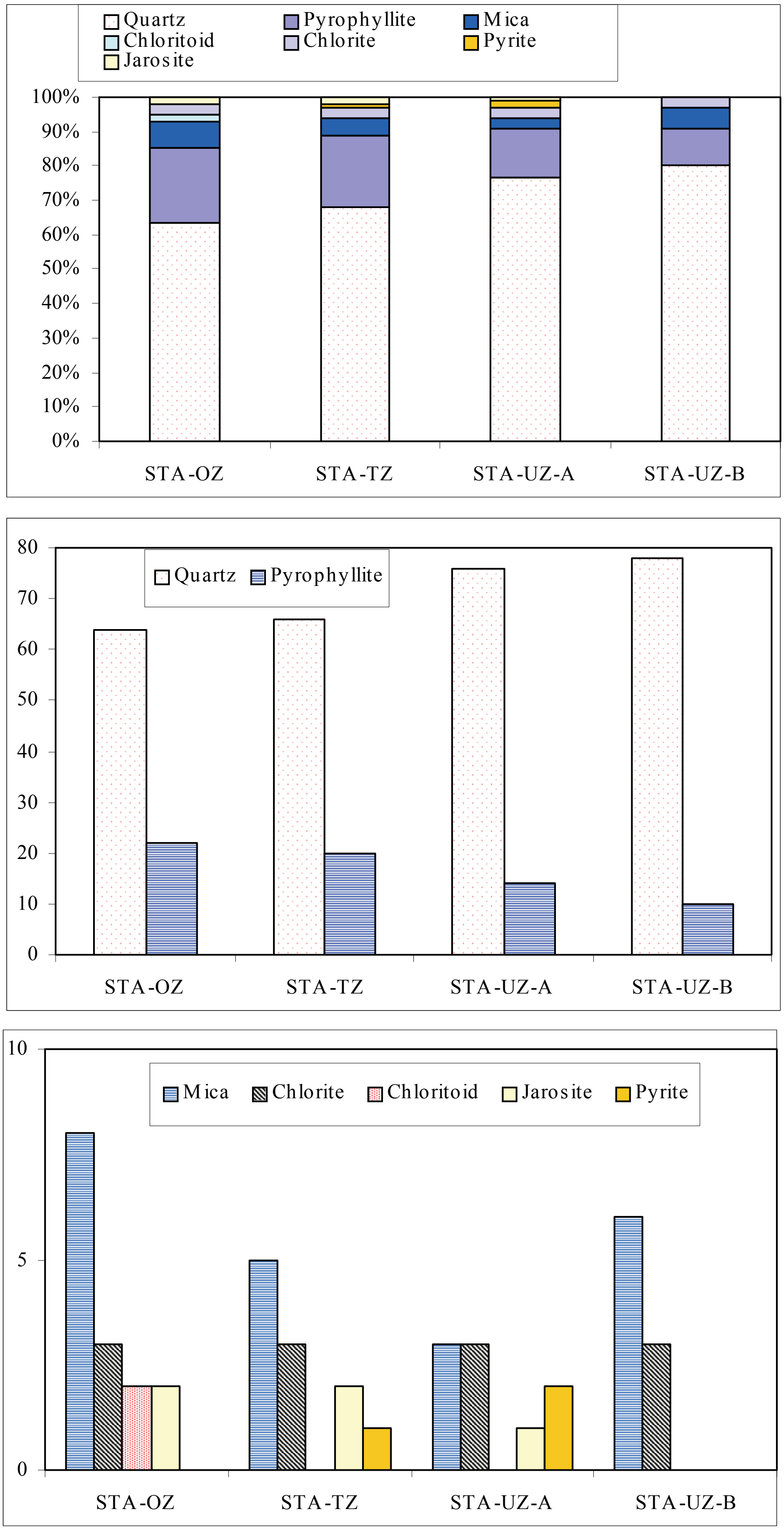


Figure 3.17: Mineralogical distribution data for Stilfontein No 2 tailings dam

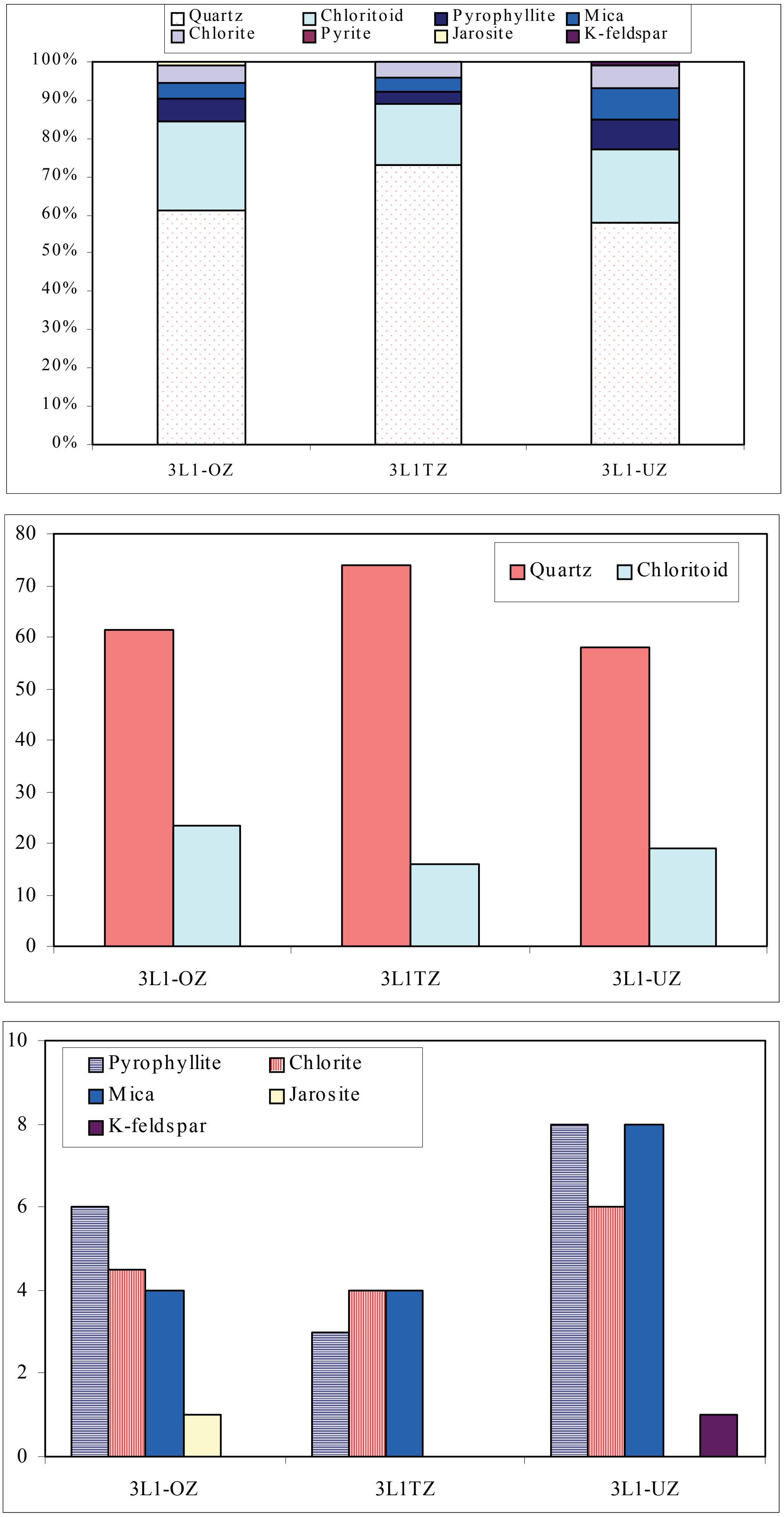


Figure 3.18: Mineralogical distribution data for 3L1 tailings dam

3.2.4.3 CMR-3L1 tailings dam

The mineralogical data is given in Table 3.13 and plotted in Figure 3.18. Pyrite and jarosite are essentially absent. Quartz is elevated in the transition zone while chloritoid is depleted.

Table 3.13: XRD mineralogical data for CMR-3L1 tailings dam

Sample ID	Pyrite	Jarosite	Chloritoid	K-feldspar	Quartz	Mica	Chlorite	Pyrophyllite
3L1-OZ	-	1	22	<1	61	4	4	6
3L1-TZ	-	-	15	<1	74	4	4	3
3L1-UZ	-	-	20	1	59	8	6	8

3.2.4.4 CMR-4L25 tailings dam

The mineralogical data is given in Table 3.14 and plotted in Figure 3.19. Quartz decreases with depth whereas the mafic minerals increase. However, the jarosite and pyrite negative correlation is suggestive of the effect of oxidation on the mineral distribution patterns.

Table 3.14: XRD mineralogical data for CMR-4L25 tailings dam

Sample ID	Pyrite	Jarosite	Chloritoid	K-feldspar	Quartz	Mica	Chlorite	Clay
4L25-OZ	-	1	13	1	72	6	6	1
4L25-TZ	1	-	10	<1	75	6	6	-
4L25-UZ	-	1	22	<1	61	7	8	-

3.2.4.5 CMR-4L19 tailings dam

The mineralogical data is given in Table 3.15 and plotted in Figure 3.20. The relative concentration of pyrite and jarosite is consistent with oxidation patterns.

Table 3.15: XRD mineralogical data for CMR-4L19 tailings dam

CMR-4L19 Samples	Pyrite	Jarosite	Chloritoid	K-feldspar	Quartz	Mica	Chlorite
4L19-OZ (1)	-	1	12	-	69	9	8
4L19-OZ (2)	-	2	7	1	74	10	6
4L19-TZ	1	1	10	1	67	10	10
4L19-UZ	1	-	9	-	71	10	9

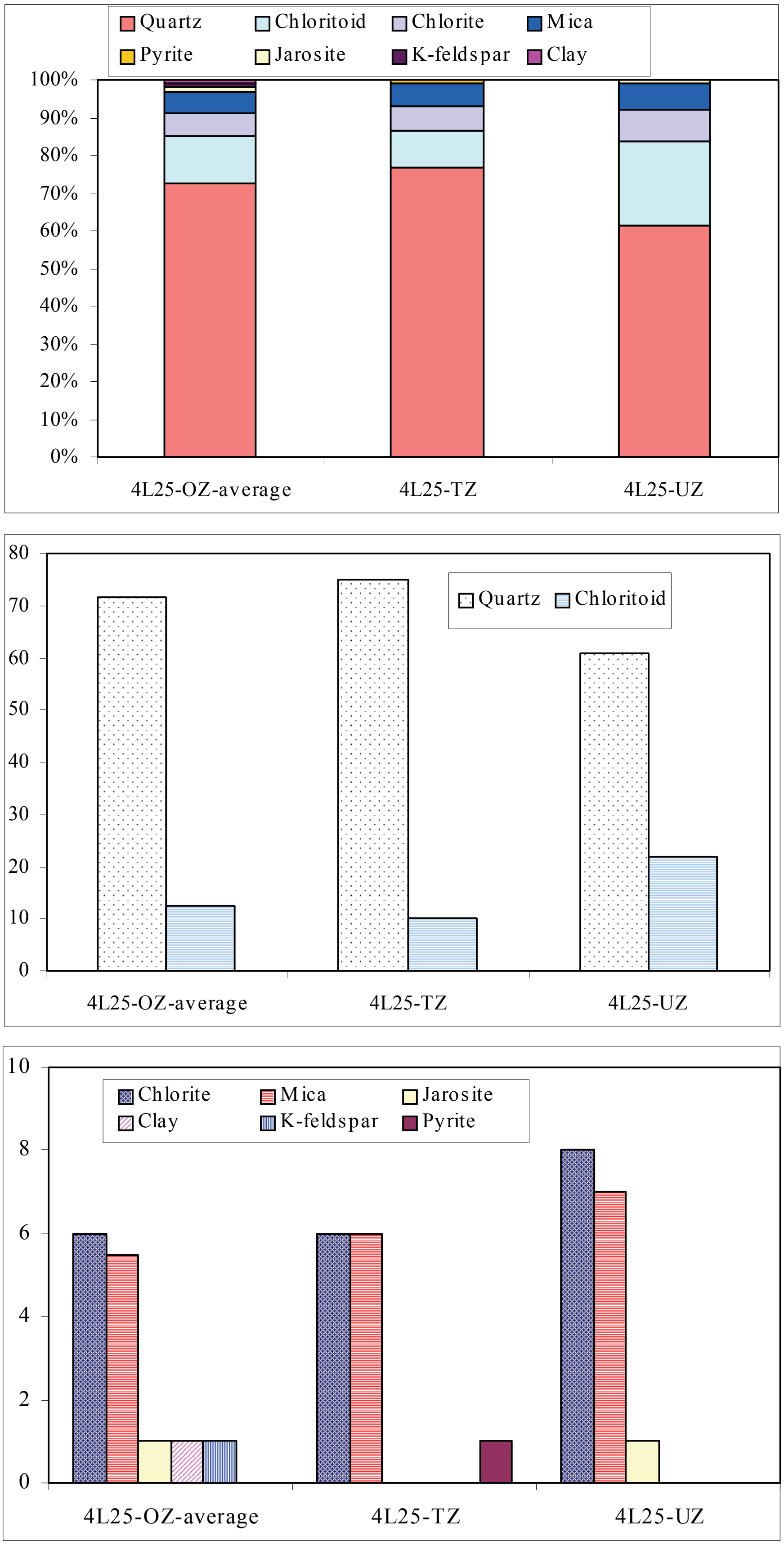


Figure 3.19: Mineralogical distribution data for 4L25 tailings dam

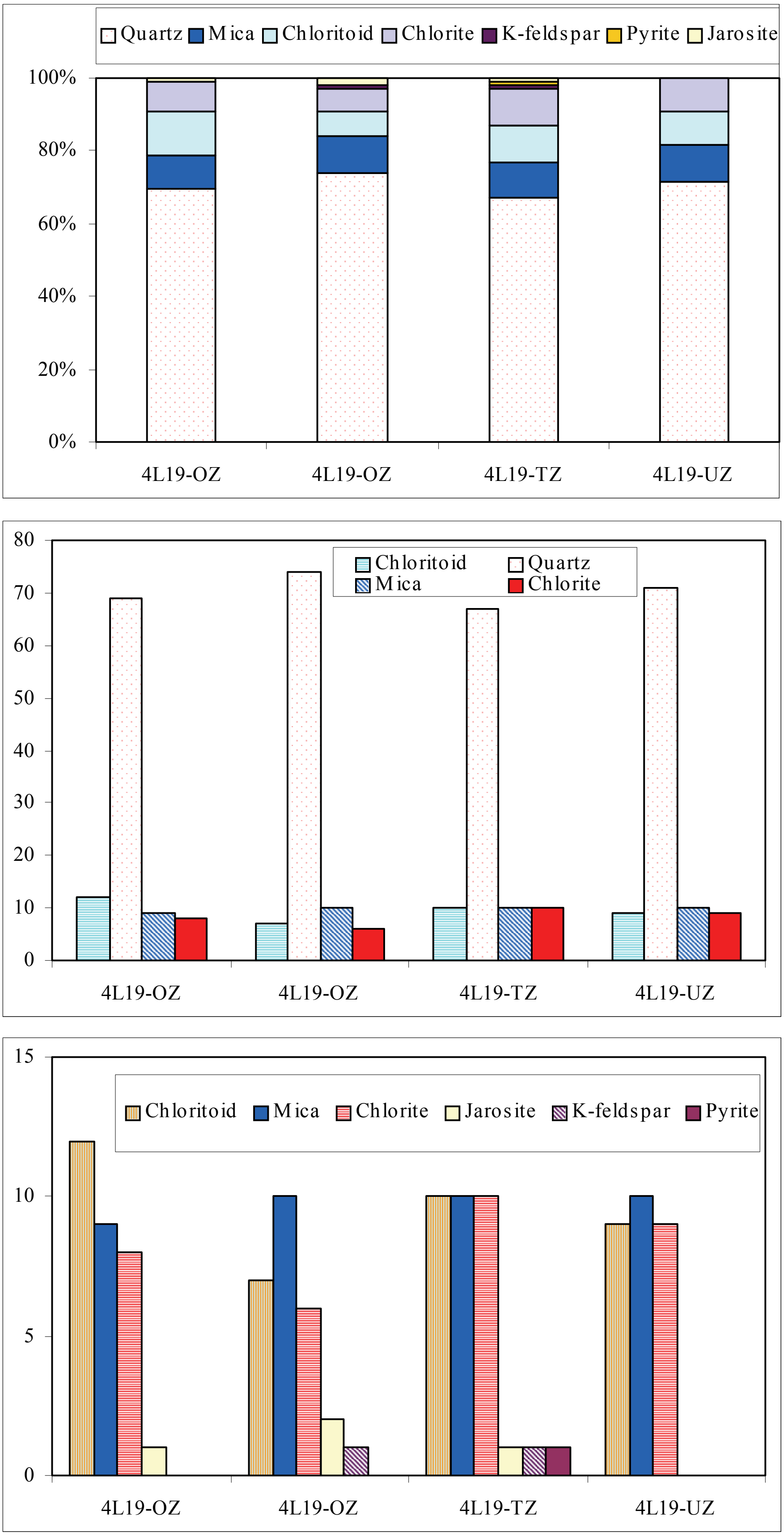


Figure 3.20: Mineralogical distribution data for 4L19 tailings dam

3.2.5. Geochemical and mineralogical evolution of tailings during oxidation

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 decreases with depth with concomitant appearance of jarosite.

Based on the paragenetic relationships (sequence in which minerals have formed) observed in sulphide-bearing mine wastes, Jambor (2003) classified the geochemical evolution of mine wastes into early maturing and late stage of oxidation (Table 3.16a).

Table 3.16a: Schematic representation of the progressive oxidation of a mine waste containing sulphides - pyrite (py) and pyrrhotites (po) (after Jambor (2003)

Early (1)	**(Early(2)**	**Maturing**	**Late**
Oxidation of Fe sulphides	Acceleration	Slowing	Consumed
Native Sulphur	-	-	-
Marcasite	-	-	-
Fe oxyhydroxides	Fe oxyhydroxides	Goethite	Goethite
Fe sulfates	Fe^{2+} sulfates to Fe^{2+}, Fe^{3+}	Fe^{3+} sulfates	-
	Jarosite	Jarosite	Jarosite
Po +Py	Py>Po	Py	-

Table 3.16b: Summary of the mineralogy and classification of progressive oxidation of selected tailings dams from the Wits Basin

Zone	**Pyrite**	**Jarosite**	**Gypsum**	**Chloritoid**	**K-feldspar**	**Quartz**	**Mica**	**Chlorite**	**Pyrophyllite**	**Oxidation Stage**
5L29-OZ	0.00	2	1		0	80	8	8		Late
5L29-TZ	1.00	1	0		1	82	9	7		Early (2)
5L29-UZ	1.00	0	0		1	80	11	7		Early (1)
3L1-OZ	0.00	1		22	0	65	4	3	5	Late
3L1TZ	0.25	0		16	0	74	4	4	3	Early (1)
3L1-UZ	0.00	0		19	1	58	8	6	8	Early (1)
4L25-OZ	0.00	1		13	1	72	6	6	-	Late
4L25-TZ	1.00	0		10	Trace	75	6	6	-	Early (1)
4L25-UZ	0.00	1		22	Trace	61	7	8	-	Early (2) –Mature
4L19-OZ	-	2		7	1	74	10	6	-	Late
4L19-TZ	1.00	1		10	1	67	10	10	-	Early (2)-Mature
4L19-UZ	1.00	-		9	-	71	10	9	-	Early (1)
STILF-OZ	-	2		2	-	64	8	3	22	Late
STILF-TZ	1.00	2		3	-	66	5	3	20	Mature
STILF-UZ-A	2.00	1		2	-	76	3	3	14	Mature
STILF-UZ-B	-	1		2	-	78	6	3	10	Early (2)-Mature

As can be seen from Table 3.16b, oxidation is intense and reached late stage in the OZ of all the dams as evidenced by the mineral paragenesis, which shows complete consumption of sulphide minerals, and concomitant development of jarosite. The TZ of all the dams shows early advanced (Early-2) to mature oxidation stage evidenced by the presence of both pyrite and jarosite. Most of the UZ zones show varying degrees of oxidation. The paragenesis of 5L29, 3L1, and 4L19 do not show oxidation progression beyond early (1) stage whereas dams 4L25 and Stilfontein are characterised by the presence of jarosite all the way up to their UZ suggestive of mature stage of oxidation.

The XRF data of the samples from the UZ zones shows high SiO_2 values for all the tailings dams suggestive of the high quartz content of the mined ore. Enrichment of Al, Fe, Mg, Ca in the active oxidation zone and depletion at the mature oxidation zone is apparent. The percentage of Fe alone does not indicate the intensity of ARD producing oxidation processes due mainly to the fact that 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 as these metals are primarily leached out of sulphide minerals. Ni, Co, Zn in all the dams and Cu and Cr in two of the dams show enrichment in the active oxidation zone at the expense of depletion in the mature oxidation zone. However these patterns are not always straightforward due to interplay of factors such as relative positions of the mm-scale hard pans, upward capillary/ osmotic actions, variations in permeability, and original geochemical variation of the tailings. The pore water chemistry was approximated from paste pH and AA analyses of water extracted from the samples and in general, showed an increase in pH and depletion of metals concentration with depth. The metal concentrations in TZ are higher than that of the mature oxidation zone suggestive of pore water migration with soluble secondary minerals into the TZ.

3.3 HYDROGEOLOGY OF GOLD TAILINGS DAMS

3.3.1 Review

Tailings dams are 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 residue deposits for operational and non-operational tailings dams are conceptually different and as such should be studied differently. The geohydrology of tailings dams has the following general characteristics:

- Tailings dams are in most cases variably saturated with respect to moisture;
- The saturated zone water balance components are relatively well understood and can be estimated or calculated with relative ease whereas the estimation or calculation of the surface flux components above the unsaturated zone is not well understood;
- Measurement of these surface flux components above the unsaturated zone is expensive and time consuming;
- The unsaturated zone varies in thickness from the edge to the centre of the dam,
- There will be spatial variation of the water balance components from the edge of the pool to the centre of the dam. This is due to the availability of moisture in the profile which in turn is related to the presence and depth of the phreatic surface (Rykaart and Wilson, 2003);
- The position and shape of the phreatic surface are governed by the tailings properties,
- Numerical modelling is the only option available to determine the components of the unsaturated zone water balance (Rykaart and Wilson, 2003 for example);
- The existence of spatial distribution of the surface fluxes (infiltration and evaporation) along tailings dam profiles 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 modelling (Rykaart and Wilson, 2003).

In decommissioned tailings dams, as in the operational 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 is at a maximum at the edge of the pool and at a minimum at the centre of the pool whereas evaporation is at a maximum at the centre of the pool and at a minimum at the edge of the pool (Figure 3.21).

Decommissioned tailings dams, which are the subject of this project, have the following main characteristics:

- Have spatially varying unsaturated zones which makes simple physical water balance calculation inappropriate;
- Unlike the operational dam where saturated zone is near the surface, the entire exposed surface of the non-operational dams is variably unsaturated;
- The depth of the phreatic surface and rate of drop of this surface is difficult to estimate accurately.

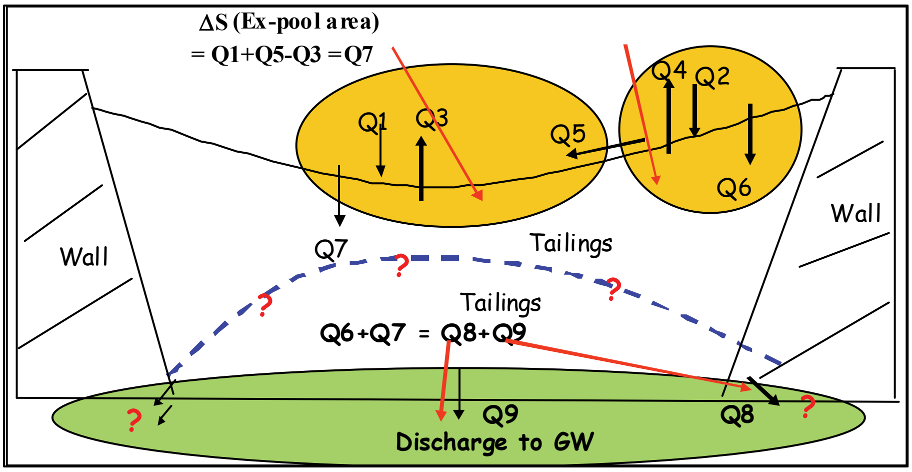


Figure 3.21: Schematic of water balance components for decommissioned tailings dams

3.3.2 Methodology and experimental procedures

Whereas the water balance of the saturated (phreatic) zone could be estimated or calculated with relative ease, no clear methodology is available to accurately estimate the water balance of the unsaturated zone component of a tailings dam.

The methodology adopted for this study was prepared taking into account the acute knowledge gap in the unsaturated zone hydrology of tailings dams. However, Pulles Howard and De Lange Inc. is simultaneously undertaking a project on the water balance of gold mine residue deposits of South Africa (WRC Project No. K5/1460). The information gathered from that project is being used to complement the hydrogeological data generated from this project for the assessment and understanding of the water flow process within the tailings dams with an emphasis on the understanding of processes of oxidation in tailings deposits.

The following tasks were envisaged for the investigation of the water flow processes of the tailings dam under study:

- Field investigation of fractures and macroscopic features which may act as preferential pathways as well as in-situ hydraulic permeability tests with depth.

- Laboratory investigation of the geohydrological properties of the tailings materials,
- Estimation of phreatic surface retreat with age,
- Studying the effect of variation in hydraulic properties (porosity, permeability, water content, preferential flow pathways such as cracks/fractures, mega-pores, etc) with depth on oxidation processes,
- Literature review.

3.3.3 Field Investigation of geohydrological features

Unsaturated flow processes dominate the hydrogeology of decommissioned tailings dams as in all other unsaturated media where pore water flow is mainly vertical and governed by complex physical parameters of the tailings. Hydraulic conductivity in unsaturated porous media is a complex function of volumetric water content, which varies with depth and is controlled by hydraulic pressure head. Other factors that complicate unsaturated flow processes in porous media are particle size distribution, mineralogy and preferential flow paths such as fractures/cracks and partings on bedding planes.

The field investigation focused on documenting all observable features such as preferential flow paths, in order to gain a better understanding of the flow processes in tailings materials.

3.3.3.1 Fractures and cracks

Evidence of preferential flow paths due to fractures or cracks, intersections of fractures and bedding planes has been observed during the field investigation. A closer investigation of the oxidation zones shows that oxidation was not uniformly developed even within the mature zone of oxidation. Heterogeneity of the oxidation process reflects non-uniform movement of oxygen and water within the tailings. Intense oxidation development around preferential flow paths such as fractures, voids and along impartations of bedding planes is evident (Figures 3.22, 3.23 and 3.24). Note the grey irregular parts of the material representing less oxidised parts of the tailings within the mature oxidation zone.

Figure 3.22: Heterogeneity of oxidation zone development in ERGO 5L29 dam

Figure 3.23: Intense oxidation developed around preferential flow paths. Blue lines = bedding planes, red solid lines = pre/syn oxidation processes, broken red lines = post oxidation cracks

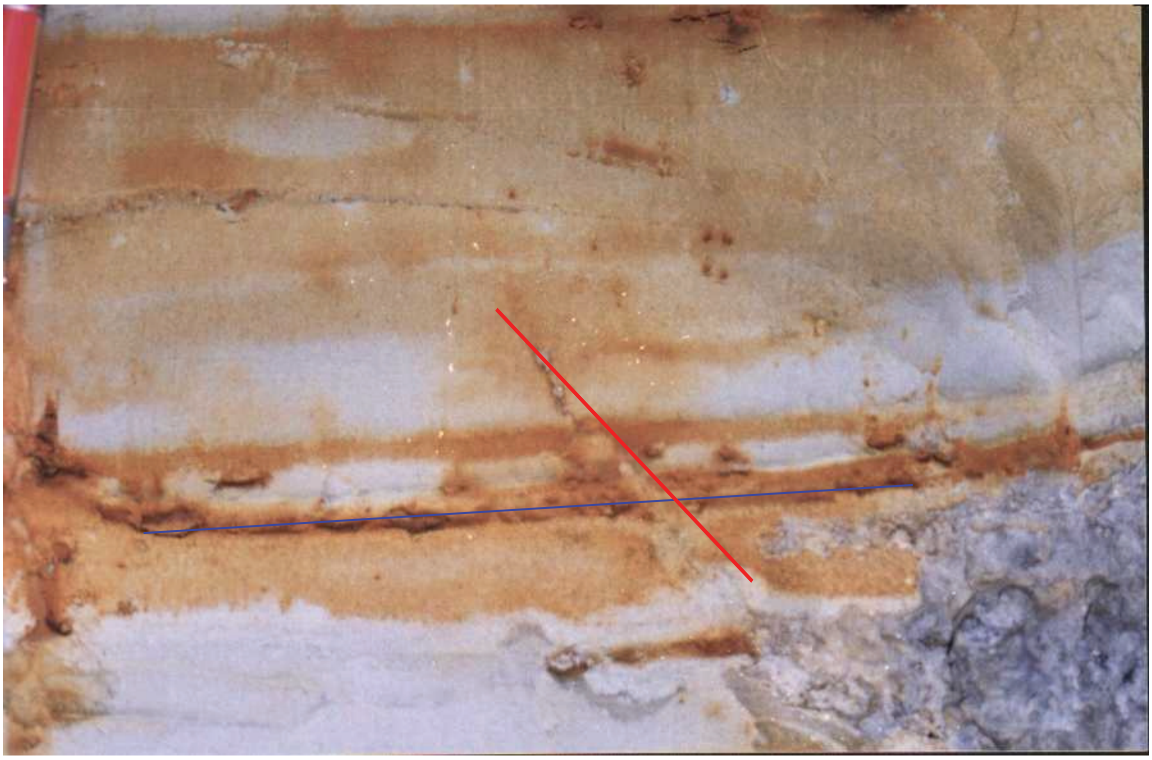


Figure 3.24: Bedding parallel oxidation. Note the bedding/fracture intersection

3.3.3.2 Vegetation

The effect of vegetation in creating preferential flow paths is minimal in most tailings dams as they are not the best growth medium due to the dominant proportion of quartz in their mineralogy and low pH. However, the relatively old decommissioned dams such as the dams under study in this project have significant vegetation density with a mixture of grass and tree populations (Figure 3.25a and 3.25b) or only grass growth. The effect of vegetation in creating preferential flow paths in these tailings dams could be significant and variable (Figures 3.25). For example development of thick up to 20 cm organic rich dark grey soil with grass roots penetrating as deep as 15 cm are observed in most of the dams (Figure 3.25a) and root induced cracks as evidenced in CMR-5L1 dam (3.25b) complicates the understanding of flow processes in the tailings dams.

Figure 3.25a: Vegetation on ERGO-5L29 dam (top) and CMR-4L19 dam (bottom)

Figure 3.25b: Root-induced fractures in CMR-3L1 tailings dam

3.3.4 Laboratory investigations

In a porous unsaturated medium the water flow paths and moisture content is governed by a number of factors such as grain size distribution, compaction and mineralogy. Analyses have been performed on the tailings samples at the SoilLab in Pretoria to estimate the variation of the following hydraulic properties with depth:

- Particle size distribution
- Moisture content and bulk density
- Permeability/hydraulic conductivity and
- Water retention characteristics at 4 pressures

3.3.4.1 Particle size distribution

Sieve and hydrometer analyses were performed on four samples from each dam to assess the grain size distribution with depth. The grain size distribution of the tailings for this study is dominantly sandy silt with the exception of the Stilfontein No. 2 Dam tailings, which is silty sand (Figure 3.26).

The tailings from the Stilfontein No. 2 and CMR 4L19 dams decrease in grain size with depth (Figures 3.26a and 3.26b). The Tailings at the 400-500 cm depth (transitional zone) of CMR 3L1 dam are coarser than the oxidized zone tailings, which in turn are coarser than the tailings representing the unoxidised zone. The CMR 4L25 tailings on the other hand do not reveal any clear patterns of grain size distribution patterns with depth.

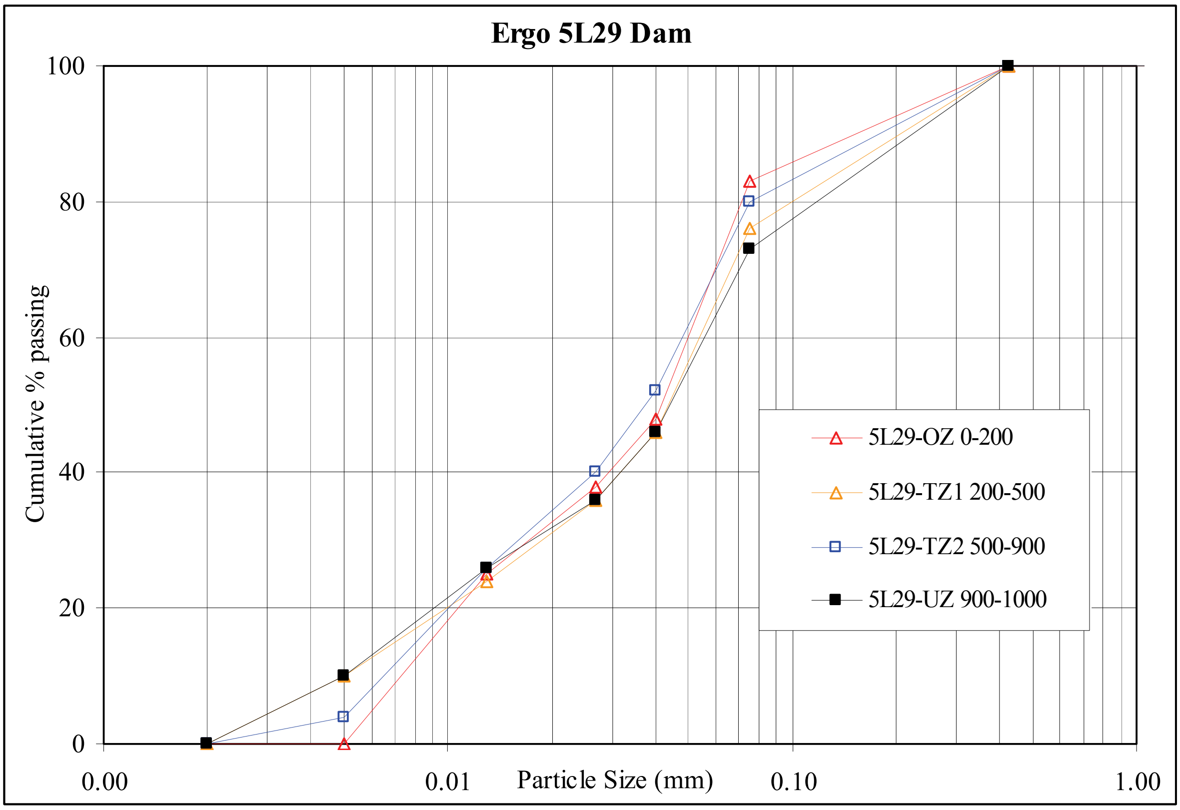
The grain size distribution of the materials from ONC No 2 Dam (Figure 3.27) shows a clear dominance of the fine grain size proportions with depth. This data further shows a break in grain size distribution pattern at 600 cm depth particularly with the finer than 0.1 mm portions of the materials.

Comparison of the grain size distribution of the relatively less oxidized tailings of the ONC dam with the other dams with mature oxidation zones suggests that the grain size distribution of the latter has been reworked by oxidation and weathering processes.

Anglo American (1995) recognized four types of tailings with respect to their grain size distribution namely, FC/FF, CC/CF, FC/FF and CC/FF, with C representing coarse and F representing fine. The authors described the Witwatersrand gold tailings as FC/CF type and relatively uniformly graded.

Table 3.17: Summary of the particle size distribution data

Dam 5L29				
Zone	5L29-OZ	5L29-TZ1	5L29-TZ2	5L29-UZ
Depth (cm)	0-200	200-500	500-900	900-1000
% 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
Stilfontein Dam No. 2				
Zone	STI-OZ	STI-TZ	STI-UZ-A	ST-UZ-B
Depth (cm)	0-150	150-450	450-800	800-1000
% 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
Dam CMR-3L1				
Zone	3L1-OZ1	3L1-OZ2	3L1-TZ	3L1-UZ
Depth (cm)	0-200	200-400	400-500	500-1000
% 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
Dam CMR-4L25				
Zone	4L25-OZ1	4L25-OZ2	4L25-TZ	4L25-UZ
Depth (cm)	0-200	200-400	400-500	850-1000
% 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
Dam CMR-4L19				
Zone	4L19-OZ2	4L19-OZ1	4L19-TZ	4L19-UZ
Depth (cm)	150-250	0-150	250-500	500-800
% 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



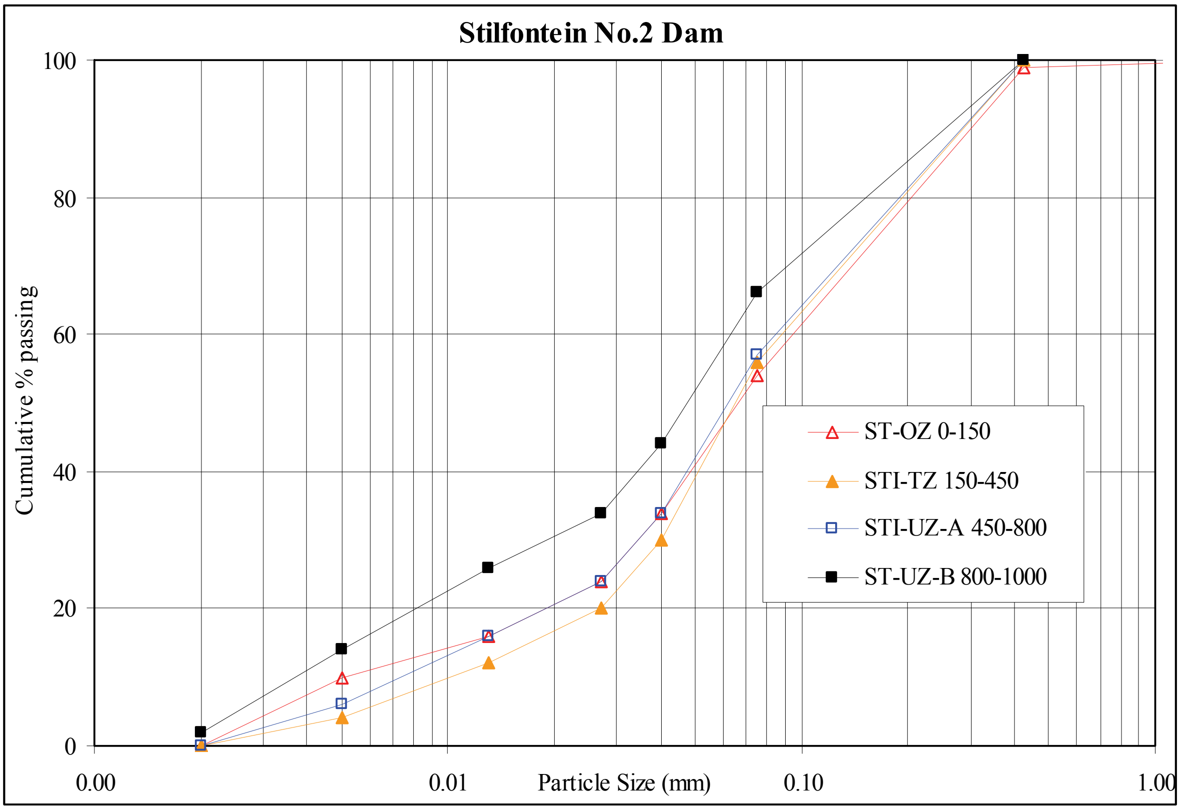
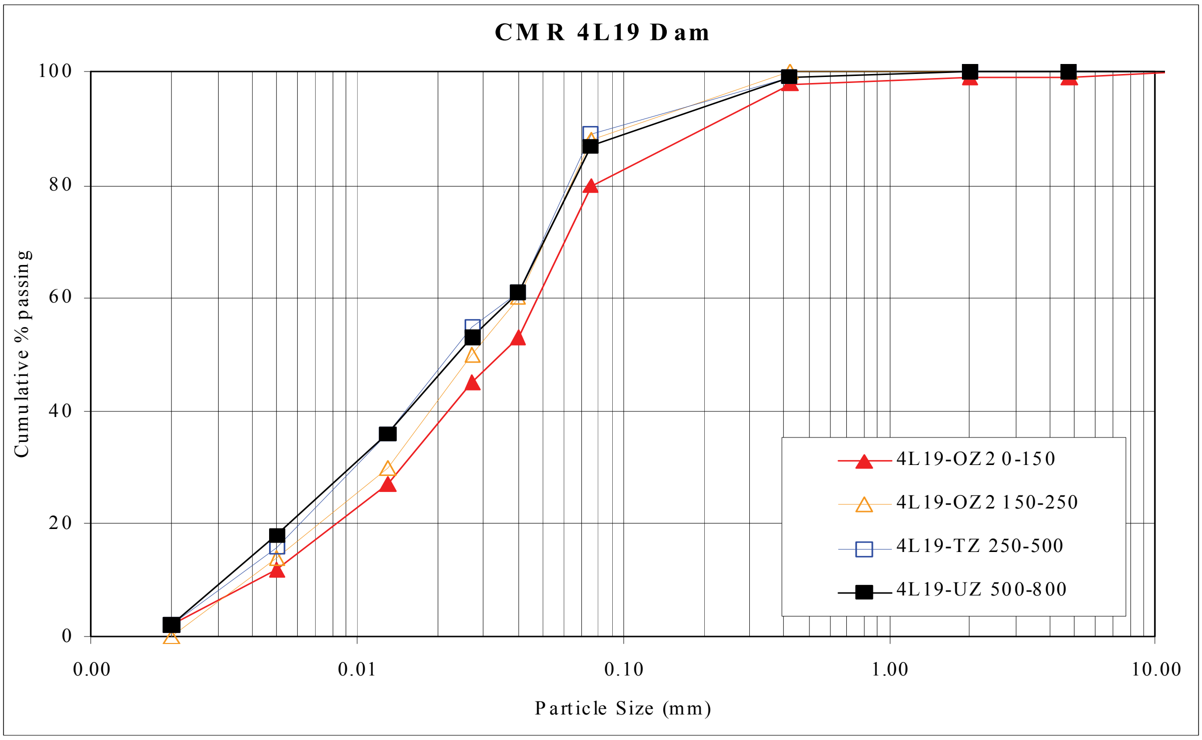


Figure 3.26a: Particle size distribution with depth for ERGO-5L29 and Stilfontein tailings dams



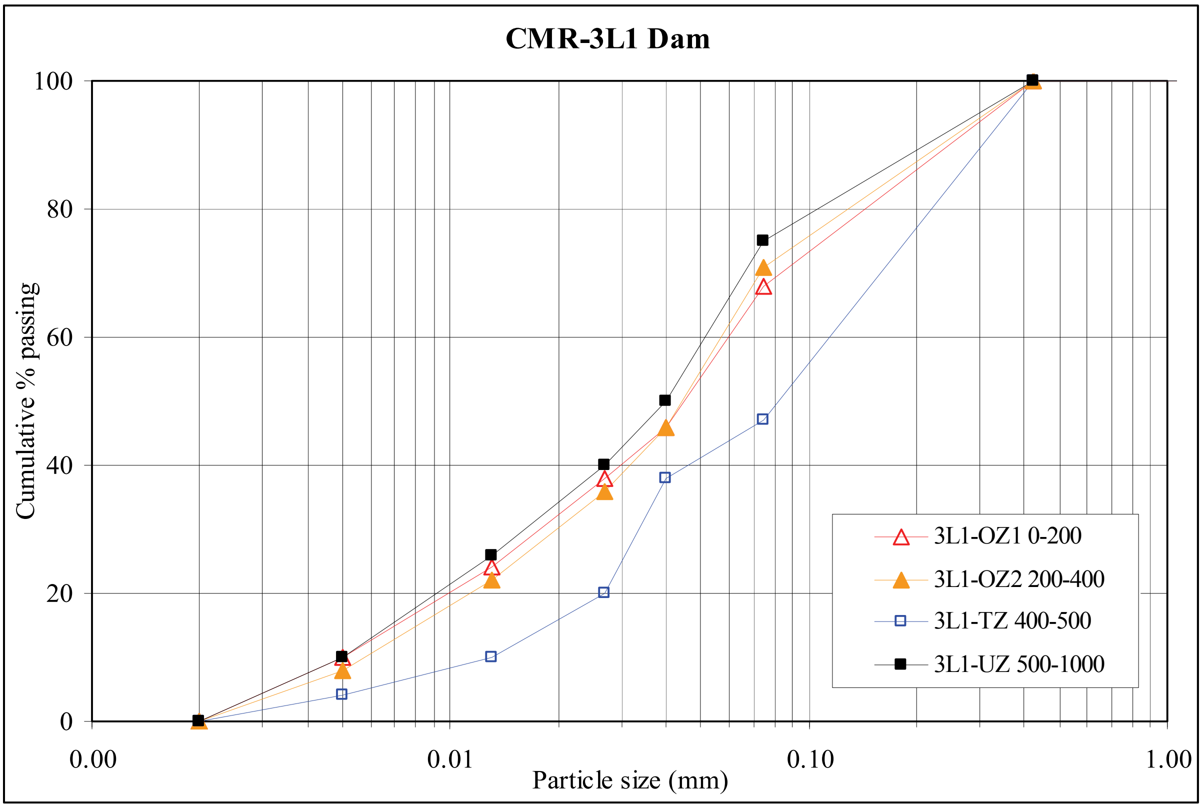


Figure 3.26b: Particle size distribution with depth for CMR-4L25 and -3L1 tailings dams

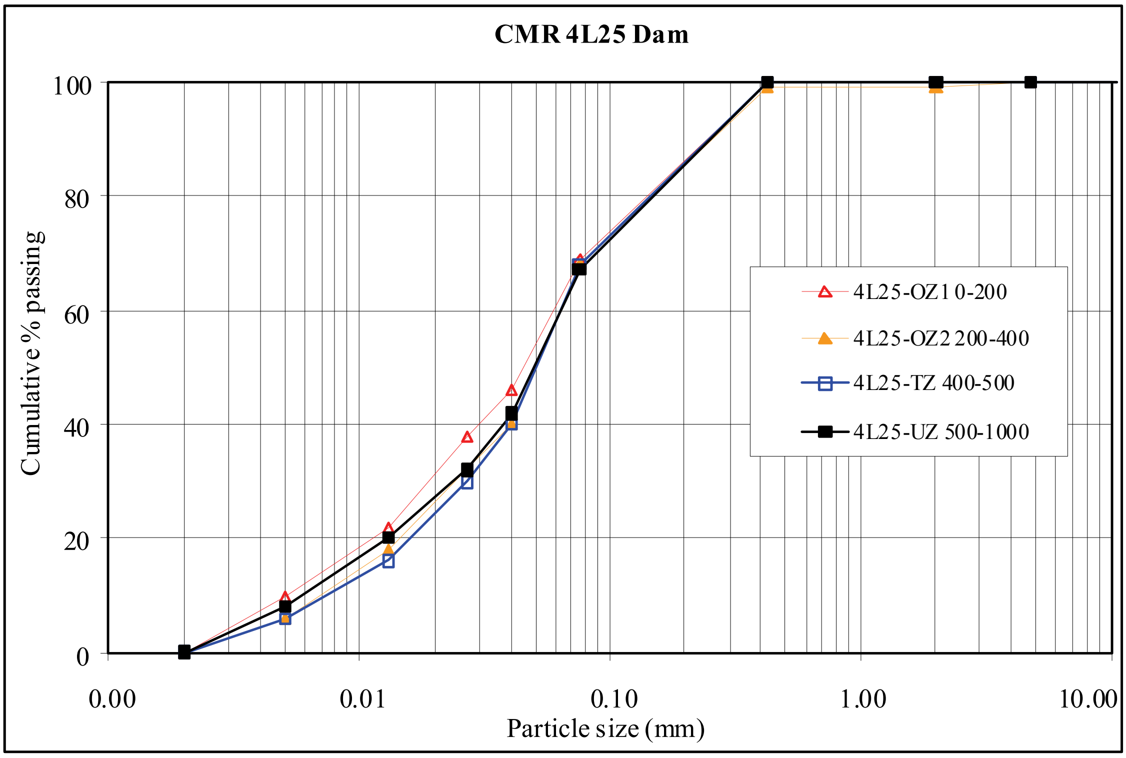


Figure 3.26c: Particle size distribution with depth for CMR-4L19 tailings dam

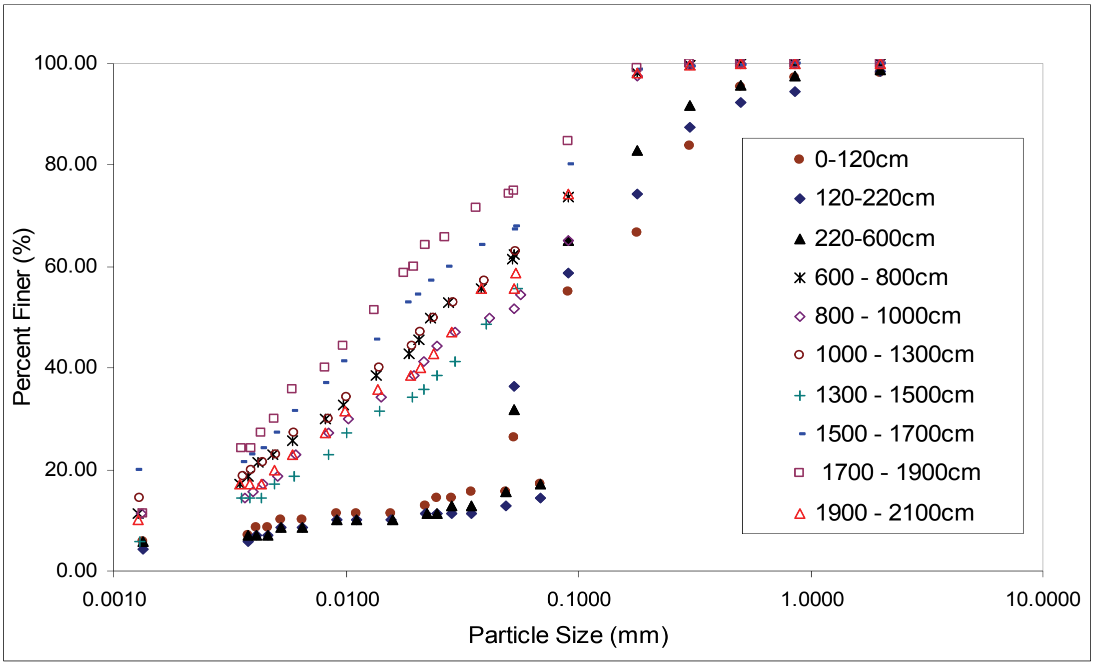


Figure 3.27: Particle size distribution with depth for ONC No. 3 tailings dam

3.3.4.2 Hydraulic conductivity

Due to the relatively uniformly graded nature of the particles of the Witwatersrand tailings no significant variability is expected in the saturated conductivity values (Anglo American, 1995). The well-graded tailings tend to form a relatively flat beach and hence relatively uniform permeability.

Particle size distribution variation from the edges (wall) to the beach/pool is expected with fine grain size portions dominating towards the pool which further complicates the hydraulic permeability variations both laterally and vertically. Field observation showed alternations of fine and coarse beds. Such depositional variations create capillary breaks, which complicates flow of water in tailings materials.

In-situ and laboratory measurements of hydraulic conductivities have been obtained to get a better understanding of water flow processes with depth in tailings. The laboratory measured hydraulic values for the samples from the 5 dams ranges from 7.1 x 10^{-5} to 1.2 x 10^{-2} cm/s.

The in situ hydraulic conductivity values of the Driefontein tailings (Figure 3.28) show relatively flat patterns indicating a large pore size distribution. In general the data shows a higher K value for 2000mm depth than that for the surface. The K values for the intermediate depths show intermediate although the K values for 500mm depth are higher than that of the 250 and 1000mm depths. What is apparent from the current data set is a general trend of increasing K values with depth, which is consistent with increasing grain size with depth. The inconsistency in this relationship may be due to wide variation and heterogeneity of pore size distribution with depth.

Table 3.18: Laboratory hydraulic characteristics data

Dam ID	Depth (cm)	Initial Moisture (wt %)	Bulk density (kg/m3)	Porosity	Coefficient of permeability (K) (cm/s)
Dam CL1	0-200	7	1158	0.56	
	200-400	8	1163	0.56	
	400-500	13	1424	0.46	3.356 X 10-4
	500-1000	11	1235	0.53	7.102 X 10-5
Dam 4L25	0-200	11	1222	0.54	1.848 X10-4
	200-400	8	1256	0.53	
	400-500	14	1294	0.51	
	500-1000	15	1363	0.49	1.891 X 10-4
Dam 4L19	0 -150	19	1283	0.52	
	150-250	16	1200	0.55	1.039 X 10-3
	250-500	20	1354	0.49	1.204 X 10-2
	500-1000	28	1840	0.31	
Stilfontein No.2	0 -150	14	1339	0.49	3.176 X 10-5
	150 - 450	19	1540	0.42	
	450 - 800	16	1531	0.42	
	800 -1000	19	1439	0.46	1.245 X 10-4
ONC 1	0-120	9	1378	0.48	
	120-200	13	1425	0.46	
	220-600	11	1531	0.42	
Dam 5L29	0-200	15	628	0.76	7.6 X 10-4
	200-500	17	772	0.71	
	500-900	14	612	0.77	
	900-1000	20	1219	0.54	7.967 X10-4

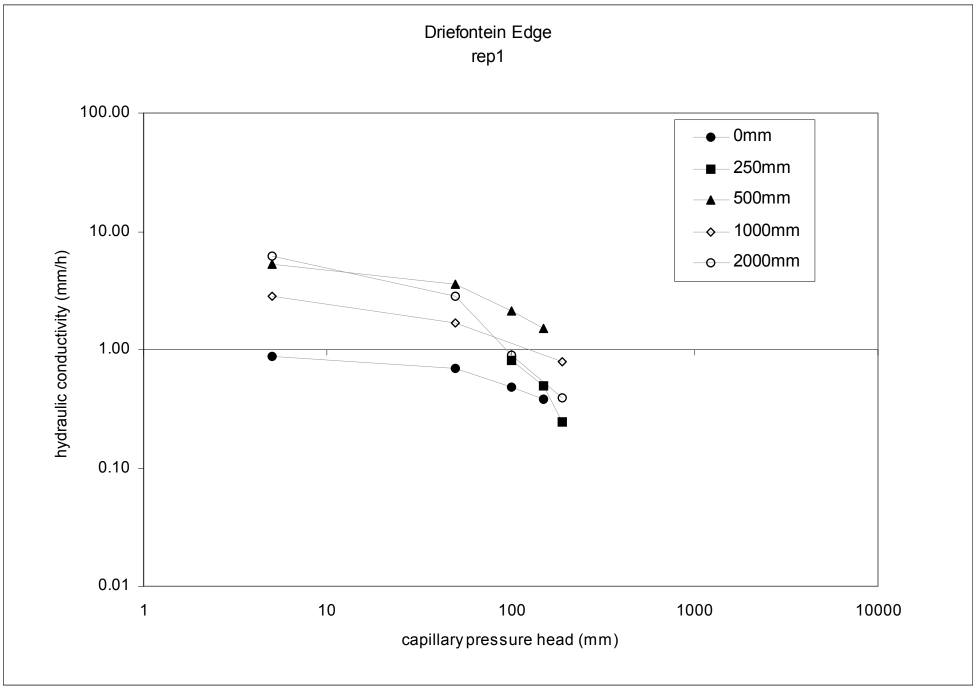


Figure 3.28: Unsaturated hydraulic conductivity of the 0-2000mm profile at the Driefontein tailings dam at the edge site conducted in duplicate

3.3.4.3 Moisture content

The moisture content of tailings material is variable and is governed by various factors such as climatic variation (rainfall, temperature and evaporation rate) as well as mineralogy, geochemistry of the tailings material and age of the dams after closure and decommissioning. Previous data on moisture contents of tailings from decommissioned dams range between 20 and 40 % by volume (Pulles, Howard and de Lange, 2002).

The result of initial moisture contents measured from the tailings of the dams used for this study is given in Table 3.18. The data shows an overall increase of moisture content with depth. It ranges from 7 to 20 wt % for all the dams. The lowest water content is recorded for the CMR-CL1 tailings dam, which ranges from 7 to 13wt% whereas the highest moisture content is recorded for Dam4L19 which ranges form 19-28 wt%.

3.3.4.4 Bulk density and porosity

Bulk densities were determined for samples extracted with thin walled tubing from ONC tailings dam (Table 3.18). The bulk densities increase with depth to 600mm. The density of a single surface sample from the Driefontein edge station is comparable to the densities obtained at the edge site of the ONC tailings dam. Additional bulk densities have been determined for the samples for which water retention characteristics have been analysed. The data fall within the range of the bulk densities determined for the ONC tailings (Table 3.18). Porosities have been estimated from the bulk densities, using a value for particle density of 2.65 kg/m^3, Table 3.18).

3.3.4.5 Water retention characteristics

Water retention at four pressures was measured for samples from each tailings dam. The residual water contents of this material ranges from 5.5 to 10.5 (Table 3.18 and Figure 3.29) decreasing with depth for the tailings of 5L29, Stilfontein and 4L19 Dams. The residual water content for the ERGO 5L29 and CMR 4L19 tailings are relatively high when compared to the other three dams. The residual water contents of the tailings dams for the samples from the ONC and Driefontein dams are high ranging from 10% to 20 % (after Pulles Howard and de Lange, in progress).

Table 3.19: Water retention characteristics of tailings materials with depth

		Water Retention at pressure (in kPa)			
Zone	**Depth (cm)**	**33**	**80**	**500**	**1500**
5L29-OZ	0-200	21.61	18.74	15.82	10.50
5L29-TZ	200-500	20.46	13.96	12.94	9.19
5L29-UZ	500-1000	21.88	18.98	16.05	9.11
STA-OZ	0-150	19.42	11.64	7.77	5.68
STA-TZ	150-450	19.65	11.82	7.32	5.47
STA-UZ	450-1000	16.23	10.42	6.44	4.92
3L1-0Z	0-200	16.93	10.89	9.72	4.41
3L1-UZ	500-1000	18.88	11.60	11.22	5.05
4L25-OZ	0-400	15.88	11.88	10.33	4.73
4L25-TZ	400-500	15.47	10.90	9.54	4.75
4L25-UZ	500-1000	18.84	14.80	10.51	5.54
4L19-OZ	0-250	25.98	19.46	18.23	8.90
4L19-TZ	250-500	29.84	17.15	10.03	7.16
4L19-UZ	500- 1000	34.91	22.15	9.76	6.05

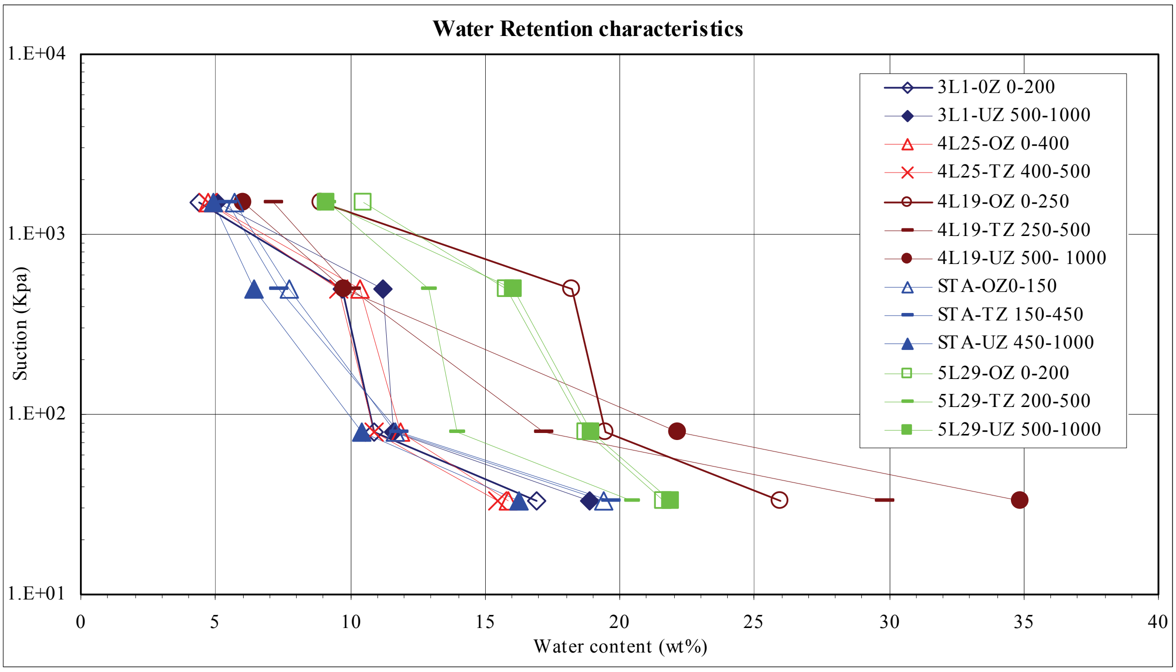


Figure3.29: Water retention characteristics as measured at 4 pressures

3.3.5 Summary

Field investigations focusing on developing an understanding of the relationship of preferential flow paths and oxidation in conjunction with the laboratory investigation of the hydraulic properties of the tailings with depth has provided useful information to understand the relationship between hydraulic properties and oxidation processes.

The following are the main findings with regard to the hydraulic properties:

- Grain size variation with depth is observed. While there are some anomalies, generally particle sizes get smaller with depth. On occasions, a sudden change of grain size from coarse to fine with depth is evident as is the case for the ONC tailings that showed this change at a depth of 600 cm.
- An order of magnitude of variation in hydraulic conductivity values with depth is observed for most tailings, with higher K values recorded for the materials from the deeper part. This is consistent with initial moisture content data, which also increases with depth.
- Water retention characteristic data shows that residual water content increases with depth for most tailings.

CHAPTER 4
OXYGEN PROFILES AND OXIDATION OF TAILINGS DEPOSITS

4.1 WATER INFILTRATION AND OXYGEN DIFFUSION

The geochemically significant reactions for the generation of low quality water are variable and depend on many factors such as the prevalent weather and climate conditions. Whereas intensive work has been done on oxidation of pyrite in aqueous solution, much remains to be done on oxidation of pyrites in mine waste residues stockpiled above ground level, occurring in aerial/sub-aerial conditions. If pyrite oxidation rates and mechanisms can be better understood, ways of reducing ARD generation at its source could be devised, thereby reducing the downstream impacts from the mine residue deposits.

Oxidation in tailings dams can occur in an aqueous/sub-aqueous system where water content and oxygen flux will govern the rate of oxidation of minerals - mainly pyrite. As the phreatic surface migrates, the system will change into sub-aerial/aerial system whereby partial pressure of oxygen and vapour pressure are the main factors controlling oxidation processes. Mine waste residue deposits are mostly not submerged and therefore pyrite oxidation occurs in aerial conditions rather than aqueous conditions (see for example Jerz and Rimstidt, 2000).

The development of oxidation zones in tailings dam is mainly a function of oxygen and water availability, which are required for the continual oxidation of sulphide minerals, mainly pyrite.

Pyrite when exposed to atmosphere oxidises to create acidic solutions by the complex, multi path reaction that can be expressed as follows:

$$FeS_2+7/2O_2+H_2O \rightarrow Fe^{2+}+2SO_4+2H^+$$

The key factors governing the progress and complexity of the reaction paths of pyrite oxidation and, therefore the development of oxidation zone in tailings deposits are relative humidity and partial pressure of oxygen (PO_2).

Oxidation increases with increase of relative humidity (RH). While the vapour phase in the uppermost part of the waste deposits controls the relative humidity by exchanging with the atmosphere, it is the activity of water in solution in the pore spaces that plays a role in the lower portion of the waste beneath the surface. A study of the effect of the relative humidity on the oxidation rate of pyrite is required to better constrain the kinetics of pyrite oxidation. Relative humidity is proportional to the activity of water (aH_2O), which in turn is inversely proportional with the ionic strength of the pore space solution. The pore space solutions in the mine waste deposits are usually very concentrated.

PO_2 in pore spaces decreases with depth in the waste deposit due to the consumption of oxygen as a result of oxidation of pyrite and other minerals.

Therefore the rate of sub-aerial pyrite oxidation should be investigated as a function of relative humidity and partial pressure of oxygen (Jerz and Rimstidt, 2000). The relative humidity and partial pressure of oxygen is dependent on site-specific factors such as geochemistry, mineralogy, texture and structure of the mine waste deposit and chemistry of the pore space solution.

4.2 DIFFUSION OF OXYGEN IN PYRITE PARTICLES

Particles that undergo oxidation are assumed to have a homogeneous distribution of pyrite within them. All oxidation reactions are assumed to occur in the aqueous phase in contact with or near a reacting solid. Oxygen in the pore space partitions from the gas phase to the aqueous phase of the immobile water film. According to Henry's law the oxygen diffuses from the particle surface through the porous oxidized coating toward the unoxidised core of the particle, where the oxidation of pyrite occurs. The diffusion of oxygen into the particles is driven by the oxygen concentration gradient between the surface and the core of the particles (Figure 4.1).

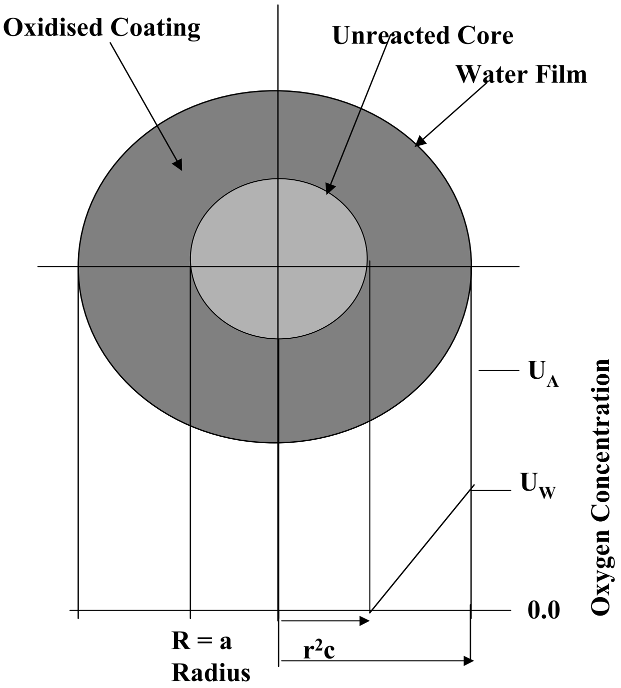


Figure 4.1: Partially oxidized pyrite grain. Oxygen concentration gradient between surface of particle and unreacted core causes oxygen to diffuse into particle (Wenderly et al., 1996)

As the reaction between oxygen and sulfide minerals within the particles progresses, the radius of the unreacted core will decrease, while the thickness of the oxidized shell increases. The rate at which the unreacted core shrinks is about 1,000 times slower than the flow rate of oxygen within the particle; about the same as the density difference between gas and solid (Levenspiel, 1972). It can be assumed therefore that the reaction front is stationary with respect to the oxygen concentration gradient between the outside of the particle and the reaction front. Thus the concentration of oxygen within the oxidized coating of the particles decreases linearly from the outside of the particle surface to the unreacted core boundary (steady state within one time step) (Wenderly et al., 1996).

After the onset of the first pyrite oxidation reaction, the role of oxygen continues, without direct involvement of water in the production of ferric iron, which is another oxidant of sulphide minerals.

Several variables control the development of oxygen profiles such as the availability of oxygen, the quantity of pyrite and other sulphides, the rate of pyrite oxidation, the age of the dam, the buffer capacity of the dam rock, and the location of the profile on the dam (Ritchie, 1994).

4.3 OXYGEN PROFILES IN TAILINGS MATERIALS

Oxygen can be transported into the tailings deposit by 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 tailings material (Werner, 2000). The last mechanism is the dominant mechanism for transporting the atmospheric oxygen from the surface of the tailings to the depth where the oxidation takes place (Jaynes et al., 1984; Nicholson et al., 1989; Pantelis and Ritchie, 1991; Yanful, 1993).

Oxygen concentration inside the tailings dam varies depending on the degree of water-saturation, temperature, the rate of water infiltration and the rate of oxygen consumption. Elberling et al. (1993) conducted field studies on uncovered unsaturated tailings deposits in Canada. They reported that the pore gas oxygen concentration decreased from atmospheric concentrations (20.9 vol-%) to less than 5 vol-percent within the upper 60 cm of the impoundments. This showed that oxygen gradients exist in unsaturated tailings. At water-saturated conditions, i.e. below the groundwater table, the oxygen concentration is limited to the solubility of oxygen in water, or 258 μM at 25^{o}C (i.e. 20.9 vol-%). In general, however, the dissolved oxygen (DO) levels are very low in saturated tailings deposits.

In many cases the diffusion of oxygen into mine tailings impoundments can be considered a one-dimensional problem. This assumption is reasonable because mine tailings are commonly spread laterally over hundreds or thousands of square meters, whereas the depth over which oxidation occurs is commonly only a few meters. At the impoundment surface the concentration of oxygen is constant and equal to the atmospheric concentration of oxygen. The oxygen diffusion rate in the unsaturated zone is high, relative to the saturated zone, since the oxygen diffusion rate is 10 000 times faster in air than in water. Therefore, in the unsaturated zone, the sulphide oxidation rate may be relatively rapid, since the potential availability of both water and oxygen is large. Below the groundwater table, oxygen diffusion is heavily reduced, and the oxygen content will be limited to its solubility in water, which means that sulphide oxidation should occur slowly below the groundwater table (Yanful, 1993). The water table constitutes a zero concentration gradient boundary condition (Wenderly et al., 1996).

The partial pressure of oxygen, PO_2, in the impoundment is a result of the balance between the rate of transport into pore spaces, by diffusion and advection, and the rate of oxygen consumption. If the rate of transport is relatively fast, the overall reaction rate is controlled by the surface reaction, and the PO_2 will be equal to the atmospheric PO_2 (0.2 atm). If the rate of transport is of a similar order of magnitude as the rate of consumption, or slower, the overall reaction rate will be mixed kinetic or transport controlled, and PO_2 will decrease.

4.4 OXYGEN MEASUREMENT WITH DEPTH IN THE TAILINGS DAMS OF THE WITS BASIN

The shape of an oxygen profile is controlled by the rate and manner in which oxygen diffuses or advects into the dam and the rate at which it is consumed within the dam. The consumption of oxygen results in the development of oxygen profiles that evolve over time as the oxidation process progresses (Ritchie, 1994). Measurement of oxygen concentration in tailings dams and establishment of oxygen profiles has become part of mine waste characterisation studies. Previous studies of tailings dams have demonstrated that the consumption of pore-gas O_2 through in-situ reactions results in decreasing O_2 concentrations with depth when transport is controlled by vertical diffusion of O_2 to the atmosphere (Shaw, 2004).

Oxygen measurement has been initiated for 6 of the selected tailings dams of the project, with the view to establish oxygen profiles of the tailings dams and understand oxidation processes in the tailings deposits. The 6 tailings dams are CMR 4L25, CMR 3L1, ERGO 5L29, Stilfontein No. 2, Driefontein No. 3 and ONC No. 3 Dams.

The objectives of determining oxygen profile with depth are:

- Oxygen flux measurement with depth in the study sites (tailings dams).
- Establish oxygen profiles in the tailings dams
- Interpretation of the oxygen profiles in light of the other available data

4.4.1 Methodology

A multilevel oxygen measurement methodology used by Shaw (2004) has been adopted and constructed for the purpose of this study (Figure 4.2). It was constructed using different length 6 mm diameter polyethelene sample tubes installed into 10m deep and 8 cm diameter auger holes. The construction allows pore gas sampling from 9 sampling points spaced at 1 m depth interval. The inlets of the sample tubes were placed within 20 cm of 13 mm gravel stones, i.e. 10 cm below and 10 cm above the port to prevent particulate uptake and prevent clogging of the sample tubes. The well screen at the bottom of the centre stock extended to a depth of 10m with a 90 cm bentonite layer between the 9th and 10th meter level to minimise vertical airflow from the bottom of the tailings dam. Fine-grained sand (0.2-0.3 mm) was placed in between each sampling port for 60 cm to minimise the vertical movement of pore gas. Coarse-grained sand (0.8-1.0 mm) was placed immediately above the 20 cm of gravel for a width of 30 cm to promote horizontal flow of the pore-gas. At the tailings surface the annular space in the drill hole was sealed to 0.9 m depth with bentonite (Figure 4.1).

The tube outlets at the top of the tailings protruded for 30 cm and were securely sealed with rubber stoppers from Rochelle Chemicals. The 30 cm above ground protrusion is to allow easier measurement of oxygen using the Gas Alert Max Probe (from BW Technologies Ltd., Canada), which is equipped with a plug-in motorised sampling pump to suck out all the gas that is in the sample tubes. The reading is displayed on the monitor and recorded manually.

This instrument pumps oxygen samples at a rate of 250 ml/min (minimum). Its detection range for oxygen is 0-30% in 0.1 increments and uses a plug-in electrochemical cell sensor type.

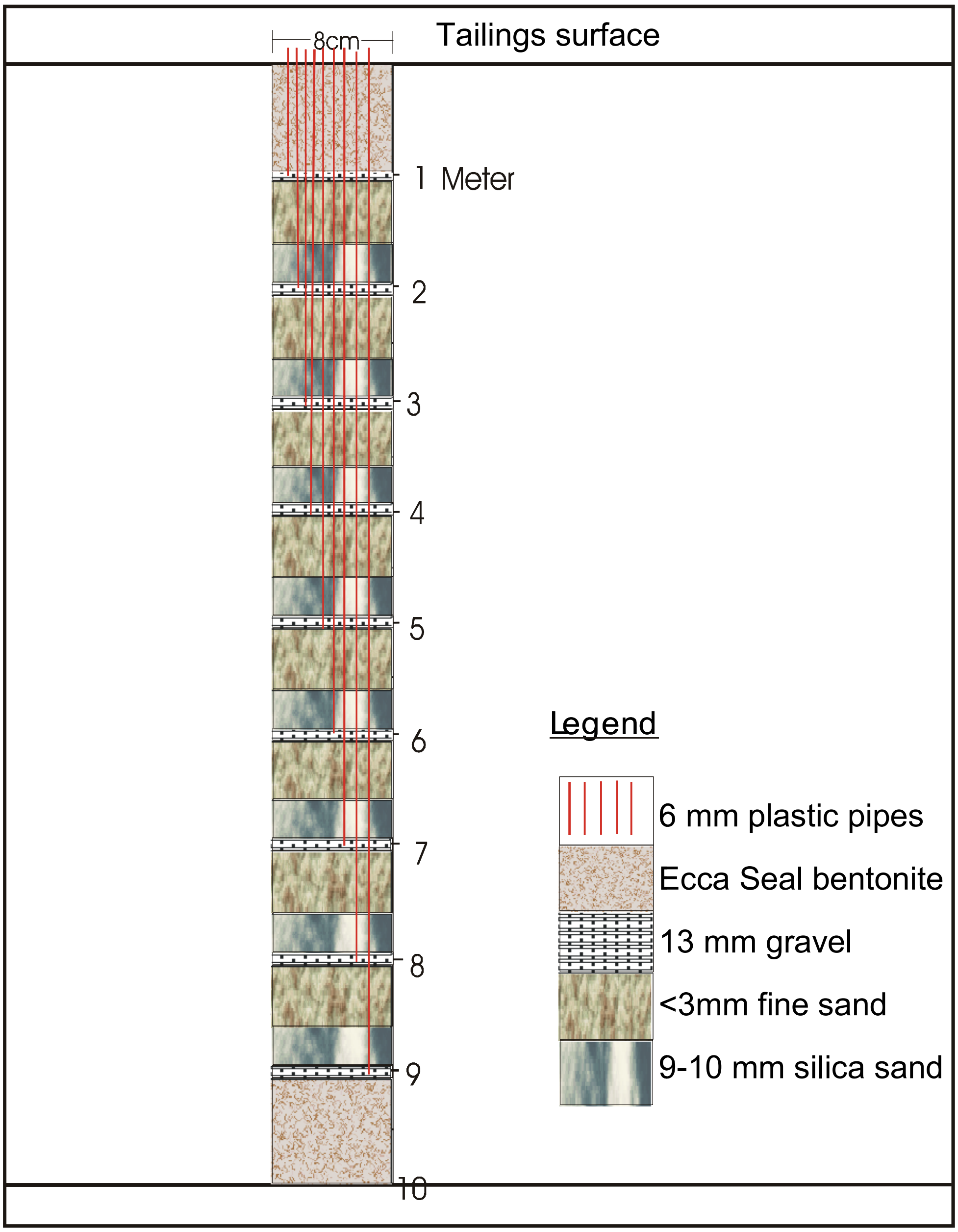


Figure 4.2: Schematic diagram (not to scale) of the Multi Level Gas Sampler (MLGS) used to measure pore oxygen in tailings deposits (adopted from Shaw, 2004).

4.4.2 Oxygen measurement data

Five sets of measurements have been collected from each dam at different depths (9 sampling points per dam) and the average results for each study site are given in Table 4.1.

Table 4.1: Average O_2 gas concentration (vol-%) with depth in the tailings dams

Depth (m)	5L29	4L25	3L1	Stilfontein No 2	Driefontein	ONC	Average
1	10.76	17.2	13.3	5.42	7.38	9.67	10.62
2	3.88	10.68	10.42	1.62	2.64	7.73	6.16
3	1.2	3.36	8.04	1.14	0.84	0.87	2.57
4	0.56	0.58	3.78	1.00	0.6	0.63	1.19
5	0.42	0.4	0.68	0.90	0.38	0.60	0.56
6	0.38	0.44	0.42	0.74	0.42	0.53	0.49
7	0.52	0.42	0.42	0.50	0.46	0.47	0.46
8	0.44	0.48	0.38	0.48	0.4	0.37	0.42
9	0.5	0.4	0.4	0.40	0.38	0.40	0.41
10	ND	ND	ND	ND	ND	0.43	0.43

4.4.3 Data interpretation and discussion

The following main observations can be made from the oxygen measurements in the 6 tailings dams (Table 4.1 and Figure 4.3):

- O_2 concentration in the tailings dams at 1 m depth ranges from 15% to 3.45 % and the tailings dams are rated with respect to their O_2 concentration as 4L25>3L1>ONC>5L29>DRF>STILF.
- At 2 m depth O_2 concentration ranges from 9 to 0.55% and the dams are rated as 3L1>ONC>4L25>5L29> DRF>STILF
- At 3 m depth the oxygen concentration is significantly depleted to less than 1% with the exception of that of 3L1 (6.8%) and the dams are rated as 3L1>>>ONC>>STILF>DRF=5L29>4L25.
- At 4 m depths O_2 decreases to $\leq$ 0.5% for all the dams except 3L1, which recorded 3.3 % of O_2.
- Overall the oxygen concentration ratings is 3L1>4L25>ONC> 5L29> DRF>STILF
- The variation in O_2 concentration from 4 m to 9 m depths is not significant
- No significant difference in oxygen diffusion can be established between the youngest and least oxidized tailings dam (Driefontein and ONC No. 3 dams) and the older dams.
- The average oxygen diffusion in the tailings dams shows that there is significant diffusion up to about 3 m, below which O_2 diffusion decreases significantly.
- The data is similar to all previous O_2 gas concentration data for tailings deposits undertaken elsewhere in the world in that O_2 gas within the pore spaces of the tailings decreases with depth.
- The relationship between O_2 concentration and the other factors such as porosity, permeability, particle size distribution, moisture content and vegetation density depicts a complex interplay of the various factors. O_2 concentrations in all the dams show negative correlation with porosity, permeability, and percentage of sand size grains and moisture content and positive correlation with increase of the percentage of silt size grains. Good positive correlation is observed between O_2 concentration and vegetation density. The apparent negative correlation with porosity, permeability and moisture content can be interpreted to suggest that the dominant diffusion mechanism in the upper 3-4 m of these tailings deposits is not diffusion in gaseous and aqueous phases through pores but rather by free or forced air convection through the top layer of the deposit. This interpretation is corroborated by the positive correlation observed between oxygen concentration and vegetation density and also by the relative fracture densities observed in the various dams (see Chapter 3).

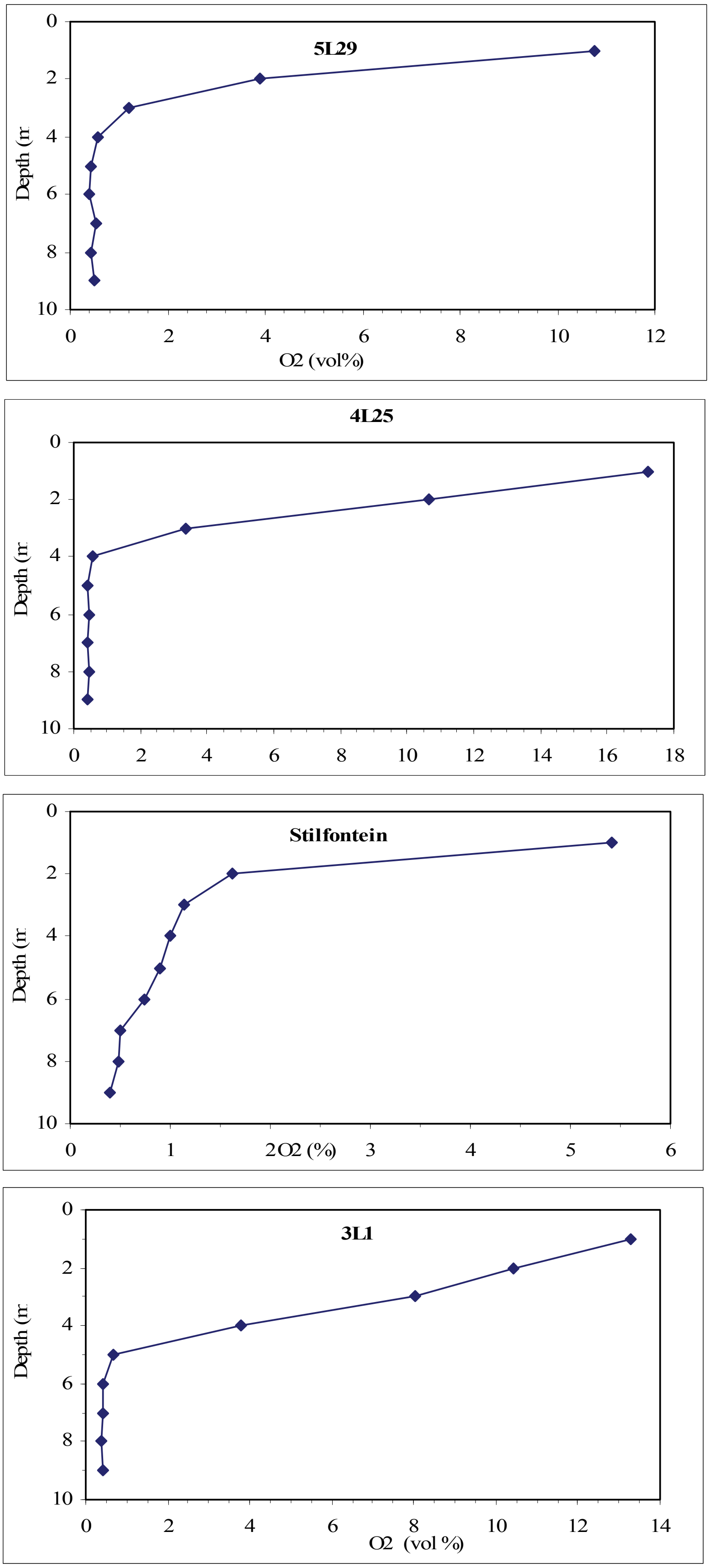


Figure 4.3: O_2 gas concentration profile in the tailings deposits

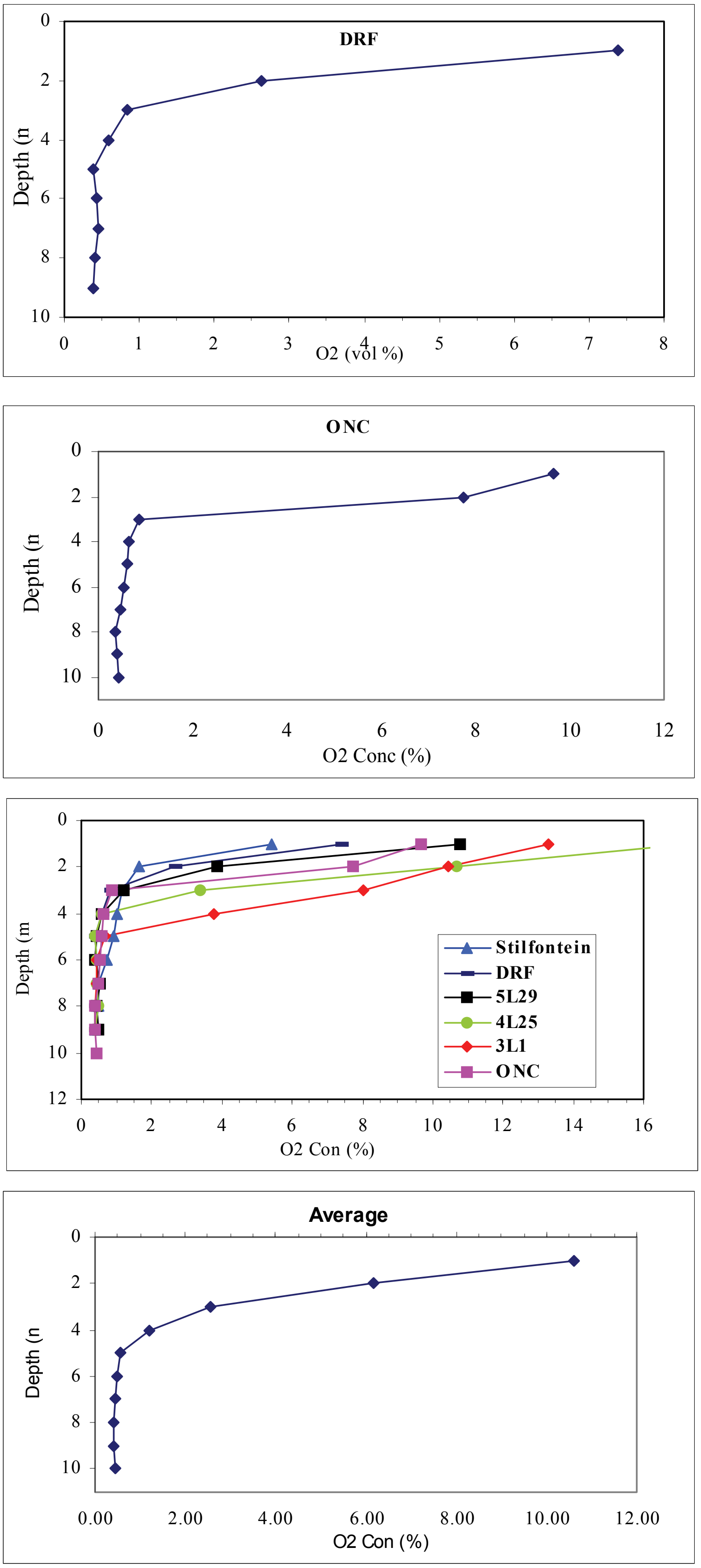


Figure 4.3: Continued.

4.5 SUMMARY

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 is adopted for this study from 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 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 studied tailings dams herein showing a positive strong correlation between depth of mature oxidation zone and O_2 gas concentration with depth (Figure 4.3). Accordingly the depth of active oxidation zones as measured from the field observation ranges from about 150 cm (Stilfontein No 2 dam) to 350 cm (Dam 3L1). The oxygen measurement on the other hand shows that oxygen diffusion ranges from about 200 cm (Stilfontein no 2 Dam) to 500 cm (Dam 3L1) with an average O_2 diffusion depth of about 400 cm (Figure 4.3). This comparison highlights the potential of O_2 concentration measurement with depth to decipher the depth of active oxidation in tailings dams.

CHAPTER 5
ASSESSMENT OF ACID ROCK DRAINAGE IN TAILINGS DAMS

5.1 OXIDATION PROCESSES AND ACID ROCK DRAINAGE

The objective of a geochemical prediction for ARD is to generate information that enables regulators, mines and other stakeholders to make appropriate management and technical decisions towards preventing, mitigating or managing the impacts of ARD generation (or the absence thereof) from mining sites. The information required by regulators, the mines or the other stakeholders, therefore, varies. Mines may require information regarding ARD for mine planning, EMPR studies (e.g. risk management, long-term lifecycle assessment, liability protection; and financial provision for wastewater treatment. Regulators may on the other hand require information regarding ARD to assess risk management issues associated with the commissioning, operations and closure of a mine and the scale of post-closure ARD risks.

In order to prescribe an appropriate prediction technique to a particular ARD question, an understanding of the questions to be answered and the required level of confidence in the answers generated from the technique need to be clearly identified.

Prediction of acid rock drainage from the tailings dams is not the objective of this study. However, the application of the knowledge and information generated from this study of oxidation processes within the tailings dams does have direct implications for the assessment and prediction of ARD.

The signature (quality) of acid rock drainage that will be generated from a tailings dam depends at which stage of mineralogical and geochemical evolution (i.e., early maturing, or late stage of oxidation) the tailings dam is.

As can be seen in the preceding chapters, oxidation processes are very active and have reached late stage in the OZ in all the dams that were studied. This was evidenced by the mineral paragenesis, which shows complete consumption of sulphide minerals and concomitant development of jarosite in the OZ. The presence of both pyrite and jarosite in the TZ of all the dams shows that oxidation at the TZ is at an early advanced (Early-2) to mature oxidation stage. Most of the UZ zones show varying degrees of oxidation, primarily along hydraulically active zones and cracks. The paragenesis of 5L29, 3L1, and 4L19 do not show oxidation progression beyond early (1) stage whereas dams 4L25 and Stilfontein are characterised by the presence of jarosite all the way up to their UZ, suggestive of a mature stage of oxidation.

The XRF data of the samples from the UZ zones shows high SiO_2 values for all the tailings dams indicative of the high quartz content of the mined ore. Enrichment of Al, Fe, Mg, Ca in the active oxidation zone and depletion in the mature oxidation zone is apparent. The percentage of Fe alone does not indicate the intensity of ARD producing oxidation processes due mainly to the fact that 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 as these metals are leached mainly out of sulphide minerals. Ni, Co, Zn in all the dams and Cu and Cr in two of the dams show enrichment in the active oxidation zone at the expense of depletion in the mature oxidation zone. However these patterns are not always straightforward due to interplay of factors such as relative positions of the mm-scale hard pans, upward capillary/ osmotic actions, variations in permeability, and original geochemical variation of the tailings. The pore water chemistry was approximated from paste pH and AA analyses of water extracted from the samples and which in general showed increase in pH and depletion of metals concentration with depth. The metal concentrations in TZ are higher than that in the mature oxidation zone (OZ) suggestive of pore water migration with soluble secondary minerals into the TZ.

5.2 ACID NEUTRALISATION

A conceptual model to describe acid neutralisation in mine wastes was proposed by Morin et al. (1988) and later refined by others (Blowes and Jamborm, 1990; Blowes and Ptacek, 1994; Johnson et al., 2000; Jurjovec et al., 2002). According to this model a sequence of equilibrium and kinetically limited precipitation-dissolution reaction controls the pH of the pore water (Dubrovsky et al., 1985; Morin et al., 1988; Blowes and Jambor, 1990; Blowes and Ptacek, 1994; Coggans et al., 1999; Johnson et al., 2000; Jurjovek et al., 2002; Blowes et al., 2003) (Table 5.1).

Table 5.1: Summary of the sequence of reactions taking place in oxidation processes of tailings materials

Reaction type	Involved minerals	Sequence (stage)	Effect- Maintain pH	Rate relative to ground water velocity
Dissolution	Carbonates	Early stage	Above 5-5.5, 4.8-6.3	Rapid
Precipitation & kinetically limited dissolution	oxyhydroxides	Intermediate stage	4-4.3, 2.5<3.5	Moderate
Dissolution	Aluminosilicates	Late stage	<3	Slow

These acid neutralising reactions begin with dissolution of carbonate minerals (calcites [$CaCO_3$], siderite [$FeCO_3$], ankerite [Ca (Fe, Mg) $(CO_3)_2$, and dolomite [$CaMg(CO_3)_2$]). In the early stage of oxidation, carbonate dissolution can maintain the pH of the pore water near neutral. Sulphide oxidation results in the generation of abundant Fe^{+2}, which reacting with HCO_3^+ generated by the dissolution of calcite, forms secondary siderite ($FeCO_3$). In the case of the Wits basin tailings, the contribution of calcite in keeping the pore water pH near neutral and generation of secondary siderite is very limited due to the insignificant amount of calcite in the mineralogy of the tailings.

Kinetically limited dissolution of aluminosilicates provides Al to allow the precipitation of gibbsite [Al $(OH)_3$] or other Al-containing phases. The presence of gibbsite or other Al-bearing secondary phases in tailings dams, including the Wits tailings, has not been reported. This may be due to the difficulty in identifying gibbsite or other Al-bearing precipitates (Blowes et al., 2003). The precipitation of Al-bearing phases is, however, supported by other indications. Two Al-bearing secondary phases have been observed in the Heath Steele tailings impoundments in Brunswick (Blowes et al., 1991). The breakdown of Al-bearing primary minerals in the tailings of the Wits 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 un-oxidized tailings as compared to the oxidized zone tailings.

In most tailings the oxidation of Fe^{2+} to Fe^{3+} causes the precipitation of ferric hydroxides, the most common of which is goethite [Fe $(OH)_3$].

The dissolution of the aluminium hydroxides and ferric hydroxides will be the primary buffers maintaining near constant pore water pH values after the dissolution of all available carbonates. After the consumption of the carbonates, aluminium hydroxides and ferric hydroxides, the dissolution of aluminosilicate minerals becomes the principal process in releasing Al and Si and buffering the pH of the pore water. The dissolution of aluminosilicates varies but is generally slow relative to the rate of groundwater flow, hence it is kinetically limited under the condition that prevails in tailings dams (Blowes et al., 2003; Jambor and Blowes, 1998).

5.3 EVOLUTION OF PORE WATER GEOCHEMISTRY

The oxidation of sulphide minerals releases H^+ and SO_4^{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.

The overall geochemical evolution of the tailings pore water is governed by the combination of physical and geochemical processes as a result of the products of the pH-buffering reactions combining with products of sulphide oxidation reactions.

As part of this study, pore water chemistry of the tailings dams has been analysed and the details are reported in Chapter 3. The main geochemical characteristics of the tailings pore water are summarised in Table 5.2. The overall geochemical pattern of the tailings pore water shows progressively lower pH values and high metal loading upwards.

Table 5.2: Summary of tailings pore water quality data with depth

Tailings Dam	pH	SO_4 (mg/l)	EC (mS/m)	Redox (mV)	Fe (mg/l)	Ca (mg/l)	Al (mg/l)	∑ Zn,Ni,Co (mg/l)
ERGO 5L29	3.28-4.11	584-2934	115-314	215-255	30-157	193-265	2.4-233	10-22
Stilfontein	2.5-6.2	1084-2347	190-483	324-618	<9-346	400-750	6-50	2-26
3L1	2.5-3.5	945-1234	204-269	452-522	2.3-119	15-340	12-73	6-18
4L19	3.3	887-2149	204-344	404-546	3.4-45	174-242	18-125	16-19
4L25	3.2-4.1	1213-2114	237-405	454-531	2-4	364-564	19-101	9-43

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

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 remain immobile until the pH decreases to 4.0. This sequence has also been established for Wits tailings from this study (Tables 5.1 & 5.2).

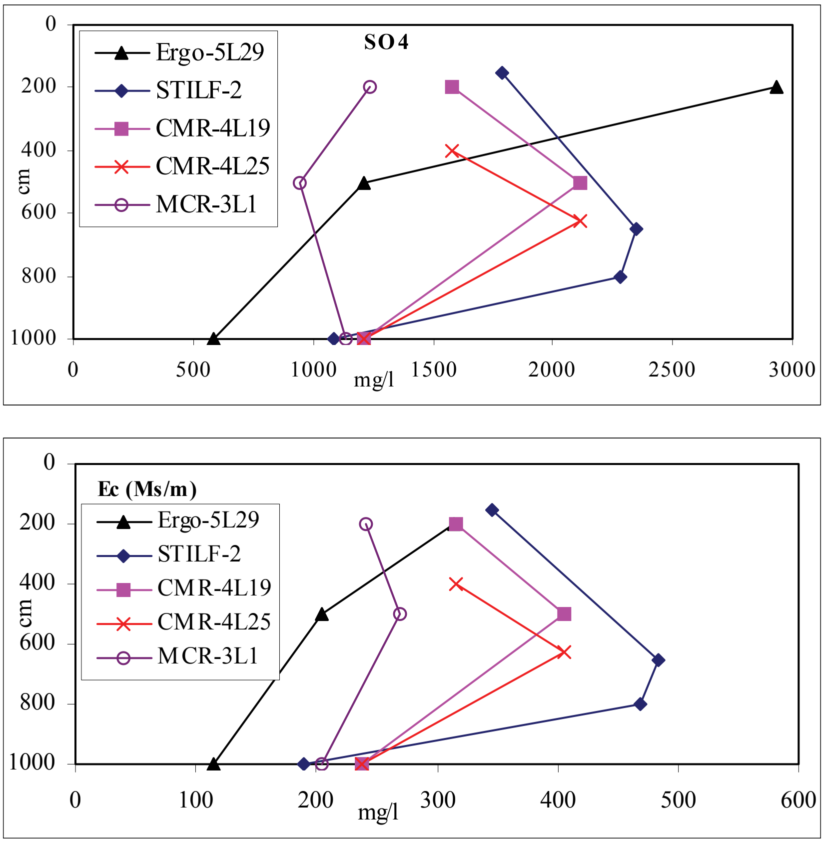


Figure 5.1: Tailings pore water SO_4 and conductivity variation with depth

5.4 RELATIONSHIP BETWEEN THE FACTORS CONTROLLING OXIDATION PROCESSES AND QUALITY OF ARD

The source of contaminants and low pH pore water is within the unsaturated zone of the tailings dam as oxidation processes are active in this zone. A reasonably accurate estimation of the oxidation depth will be critical in order to make a reliable quantification of both the acidic and the metal leaching aspect of the mine drainage assessment. As shown in the preceding chapters, the depth of active oxidation (thickness of the oxidized zone) has been determined for the studied tailings dams by way of field mapping and by monitoring the O_2 concentration with depth. The volume of the oxidation zone can be calculated using the oxidation depth and the area of the dam. This volume then can be used to calculate or model (kinetic and equilibrium geochemical modelling) the total metal load and the evolution of the pore water geochemistry with time. A comparative rating of the potential to generate ARD has been given to the studied tailings dams as follows:

- With respect to the actual oxidation zone depths as follows:
  ERGO5L29 = 3L1 > CMR- 4L25 > CMR-4L19 >> STILF.

- With respect to the maximum $SO4^{=}$ release as follows:
  ERGO 5L29 > STILFON > CMR4L19 > CMR4L25 > CMR3L1

- With respect to pH values:
  CMR3L1 > CMR4L19 > CMR4L25 > ERGO5L29 > STILFON.

CHAPTER 6
SUMMARY AND DISCUSSION

The study of oxidation zones of tailings dams was initiated based on literature surveys conducted by PHD and personal communications, which showed that the reported values for the depth of the oxidation zones of gold mine tailing dams in the Witwatersrand Basin are inconsistent and have a considerable range from 20 cm to more than 7 m. The oxidation depth might be related to the age and other parameters of the tailings dams, but little study has been carried out in this regard. This research project attempted to solve a very practical and necessary issue which provides a key input in ARD prediction techniques related to tailings dams.

It is believed that the findings of this project have advanced our knowledge and ability to practically implement improved prediction capacity by being able to better understand the active oxidation zone within the tailings dams that needs to be described in a predictive model. It is generally accepted that only a portion of a tailings dam (the outer layers) actively participate in the oxidation processes and it is only this portion that is considered as reactive within predictive geochemical models.

The project has been sub divided into 5 major tasks in order to achieve the objectives and aims of the project, i.e. "understanding the development of oxidation zone in the tailings dams of the Witwatersrand basin". All 5 tasks have been completed and a summary of the major findings from theses tasks is presented below.

6.1 MAPPING OF THE OXIDATION ZONES IN TAILINGS DAMS

Because oxidation processes are active in the unsaturated zone of the tailings dam, this is the zone which is the source of contaminants and low pH pore water. This implies that a reasonably accurate estimation of the oxidation depth will be critical in order to make a reliable quantification of both the acidic and the metal leaching aspect of the mine drainage assessment as the volume and quality of the ARD to be generated from a tailings dam is directly related to the volume of the oxidized/oxidizing tailings.

Five decommissioned dams were selected for the study and characterization of the selected dams. The following major objectives were met after the completion of Task 1:

a) the oxidation zones of the 5 tailings dams were established;
b) sufficient samples were collected and analyzed for pore water quality data, mineralogy and slid chemistry of the tailings materials;
c) the data generated from b) has been interpreted and is covered in this report.

Cross sections and exposed profiles by the reclamation processes of the tailings dams have been used to map and characterize the intensity and variations of oxidation in the tailings dams. This together with logging of auger holes of up to 10 m depth resulted in the establishment of the oxidation zone depths and tracing of the un-oxidized parts of the tailings dams. Overall, 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 OZ and TZ constitute the total oxidizing zone. The depth of matured oxidation zone ranges from 150 cm (Stilfontein No. 2 dam) to 350 cm (CMR-3L1 and ERGO-5L29 dams). The combined depth of the active oxidizing zone (transition zone) and the mature oxidized zone varies from 450 cm (CMR-3L1) to 900 cm (ERGO-5L29 dam).

6.2 MINERALOGICAL AND GEOCHEMICAL EVOLUTION OF TAILINGS

6.2.1 Mineralogy

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, the oxidation evolution of the Wits basin tailings dams has been established and given. It has been shown that:

- Oxidation is intense and reached late stage in the mature oxidation zone of all the dams as evidenced by the mineral paragenesis, which shows complete consumption of sulphide minerals, and concomitant development of jarosite;
- The transitional zone of all the dams shows early advanced (Early-2) to mature oxidation stage evidenced by the presence of both pyrite and jarosite;
- Most of the unoxidised zones show varying degree of oxidation.
- The paragenesis of 5L29, 3L1, and 4L19 do not show oxidation progression beyond early (1) stage whereas dams 4L25 and Stilfontein are characterised by the presence of jarosite all the way up to their unoxidised zone suggestive of mature stage of oxidation.

6.2.2 Geochemistry

The XRF data of the samples from the unoxidised zones show high SiO_2 values for all the tailings dams, suggestive of the high quartz content of the mined ore. Enrichment of Al, Fe, Mg, Ca in the active oxidation zone and depletion at the mature oxidation zone is apparent. The percentage of Fe alone does not indicate the intensity of ARD-producing oxidation processes, due mainly to the fact that 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, as these metals are mainly leached out of sulphide minerals. Ni, Co, Zn in all the dams and Cu and Cr in two of the dams, 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.

The pore water chemistry was approximated from paste pH and AA analyses of water extracted from the samples and the data in general showed increase in pH and depletion of metals concentration with

depth. 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 $(CO_3)_2$] (Morin et al., 1988; Blowes and Jambor, 1990; Blowes and Ptacek, 1994; Johnson et al., 2000; Jurjovec et al., 2002). In the early stage of oxidation, carbonate dissolution can maintain the pH of the pore water near neutrality. Sulphide oxidation results in the generation of abundant Fe^{+2}, which reacting with HCO_3^+ generated by the dissolution of calcite, forms secondary siderite ($FeCO_3$). In the case of the Wits basin tailings the contribution of calcite in keeping the pore water pH near neutral and generating secondary siderite is very limited due to the insignificant amount of calcite in the mineralogy of the tailings.

Kinetically limited dissolution of aluminosilicates provides Al to allow the precipitation of gibbsite [Al $(OH)_3$] or other Al-containing phases. The presence of gibbsite or other Al bearing secondary phases in tailings dams, including the Wits tailings, has not been reported. This may be due to the difficulty in identifying gibbsite or other Al-bearing precipitates (Blowes et al., 2003). The precipitation of Al-bearing phases is, however, supported by other indications. Two Al-bearing secondary phases have been observed in the Heath Steele tailings impoundments in Brunswick (Blowes et al., 1991). The breakdown of Al-bearing primary minerals in the tailings of the Wits 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 unoxidised tailings as compared to the oxidized zone tailings.

In most tailings, the oxidation of Fe^{2+} to Fe^{3+} causes the precipitation of ferric hydroxides, the most common of which is goethite [Fe $(OH)_3$].

The dissolution of the Al 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, Al 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; Jambor and Blowes, 1998).

The oxidation of sulphide minerals releases H^+ and SO_4^{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.

The overall 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.

As part of this study, pore water chemistry of the tailings dams has been analysed. The main geochemical characteristics of the tailings pore water is summarised in the Table below. 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.

Tailing Dams	pH	SO_4 (mg/l)	EC (mS/m)	Redox (mV)	Fe (mg/l)	Ca (mg/l)	Al (mg/l)	∑Zn,Ni,Co (mg/l)
ERGO 5L29	3.28-4.11	584-2934	115-314	215-255	30-157	193-265	2.4-233	10-22
Stilfon-2	2.5-6.2	1084-2347	190-483	324-618	<9-346	400-750	6-50	2-26
3L1	2.5-3.5	945-1234	204-269	452-522	2.3-119	15-340	12-73	6-18
4L19	3.3	887-2149	204-344	404-546	3.4-45	174-242	18-125	16-19
4L25	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 the Wits 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.

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.

The geochemical evolution of the tailings pore water provided useful information on the progress, depth and rate of oxidation processes. The geochemical evolution of the tailings pore water indicates that oxidation process in the studied tailings has reached an advanced stage as indicated by the pH of the pore water which has reached a range of 2.5-4.1. These low pH values mark the final stage of acid water generation (aluminosilicate break down stage) in all but the unsaturated zone of the Stilfontein No 2 dam (pH = 6.2) which suggests the latter is still at the earliest stage of oxidation (carbonate dissolution stage).

Qualitative assessment of the potential for tailings to oxidize and generate ARD shows that:

- The actual oxidation zone process as quantified by oxidation zone depths is ERGO 5L29=3L1>CMR- 4L25>CMR-4L19>>STILFON from the thickest to the thinnest oxidation zone
- With respect to $SO4^{=}$ release from the dams, from the highest to the lowest is: ERGO 5L29> STILFON >CMR4L19>CMR4L25>CMR3L1
- With respect to pH values the tailings are in the order: CMR3L1>CMR4L19>CMR4L25>ERGO5L29>STILFON.

6.2.3 Physical and hydraulic properties

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.

6.2.4 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 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 (Stilfontein No 2 dam) to 350 cm (Dam 3L1). The oxygen measurement on the other hand shows that oxygen diffusion ranges from about 200 cm (Stilfontein no 2 Dam) to 500 cm (Dam 3L1) with an average O_2 diffusion depth of about 400 cm (Figure 16). This comparison highlights the potential of O_2 concentration measurement to indicate the depth of active oxidation in tailings dams.

The findings of the oxygen profiling can be summarised as follows:

1. A decrease of O_2 gas concentration within the pore spaces of the tailings with increasing depth is related to O_2 consumption in sulphide oxidation reactions
2. Oxygen diffusion ranges from about 200 cm (Stilfontein no 2 Dam) to 500 cm (Dam 3L1) with an average O_2 diffusion depth of about 400 cm.
3. Mapped oxidation depth and depth of O_2 diffusion correlate well, thereby suggesting that measuring the O_2 diffusion (which can be accomplished cheaply and quickly) will give a good indication of active oxidation depth and hence the volume of oxidized tailings materials that needs to be considered in geochemical prediction exercises.

6.2.5 Application of research results to ARD prediction

While this research project did not involve the development or assessment of geochemical prediction techniques for ARD, useful data was collected from a number of tailings dams in the Wits basin that will have a positive impact on the accuracy of ARD predictions. Key conclusions and findings that have practical application are as follows:

1. The active oxidation zone wherein ARD formation occurs has been found to vary 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 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.

2. It has been demonstrated that measurement of oxygen diffusion into the dam correlates very well with the actual observed active oxidation zone and it is recommended that where a higher degree of confidence in the results of the prediction are required, that augering and oxygen measurement be undertaken to determine the depth of oxidation.

3. Tailings dam age did not appear to have a major impact on the ultimate depth of the active oxidation zone. While a recently decommissioned dam with an elevated phreatic surface will obviously have a very shallow oxidation zone, it is expected that with 10-20 years, most dams would have established the active oxidation zone of around 4 m thickness. Variations in this depth are more likely to be linked to physical properties such as particle size distributions and chemical properties such as levels of sulphides available than to facility age.

4. Oxidation does proceed deeper down into 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.

CHAPTER 7
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