6. Oxidation-reduction potential (ORP) of New Machavie

6.1 Introduction

Oxidation and reduction reactions are the driving force of the environment. Although TDFs are man-made they rely on these same chemical reactions. They determine the type of reactions that will occur as well as the tempo of reaction. All elements in nature have oxidation ranges that either mobilize them or produce chemical species that are insoluble and will be retained.

6.2 Objectives and motivation

Since the mobility of U is influenced by the oxidation state of the environment, it is important to investigate the oxidation state as it will influence the concentration and subsequently the ore grade of U as a resource within a gold TDF.

This section aims to quantify the oxidation-reduction potential in a gold TDF and to relate the oxidation state to U and Th content.

6.3 Oxidation zones in gold TDFs

Both Bezuidenhout & Rousseau (2005) and Yibas *et al*. (2010) have identified distinctive zones within a TDF based on oxidation profiles and hydraulic properties of Witwatersrand gold tailings. Figure 6.1 is a basic representation of these zones. These authors describe the characteristics of these zones as follows:

The saturated zone is the region of the TDF that is saturated with water. During active deposition, the top of this zone forms a pool which is surrounded by the "beach". The unsaturated zone is the region where oxygen penetration may occur and thus the region most likely to form acid mine drainage. As deposition stops, the saturated zone tends to move lower since no water is added into the system, increasing the depth to which the unsaturated zone extends. The oxidized zone is characterised by a depletion of pyrite relative to chlorite, low pH and high electrical conductivity (EC) conditions, mobilisation and leaching of trace metals. The oxidizing front has enrichment of metals relative to pyrite and extremely low pH. This is typically the zone where pyrite oxidation is currently occurring. The un-oxidized zone has higher levels of pyrite and a neutral to high pH, and little to no mobilisation of metals occurs in this zone. Photo 6.1 indicates the visual diverence between oxidized and un-oxidized tailings. (Bezuidenhout *et al*. 2005., Yibas *et al*. 2010).

The chemical speciation of U in the oxidized zone will be dominated by the complexation of the uranyl (UO_2^{2+}) ion to form U sulphates (UO_2SO_4 and $UO_2(SO_4)^{2-}$). Both these U sulphate species are mobile and leachable. In the un-oxidized zone and the saturated zone, U will be in the U^{4+} state and will be relatively immobile although colloidal movement may occur. (Vandenhove *et al.* 2009., Pulford, 2010., Alloway, 2012)

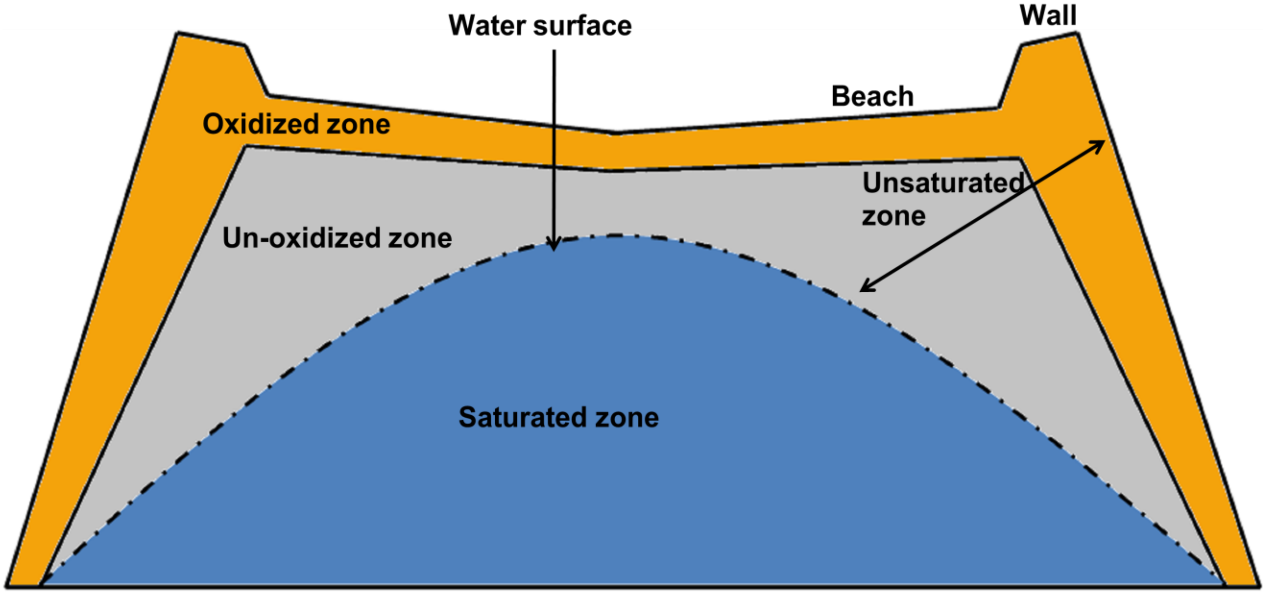

Figure 6.1: Oxidation Zones within a TDF (Bezuidenhout *et al*. 2005., Yibas *et al*. 2010)

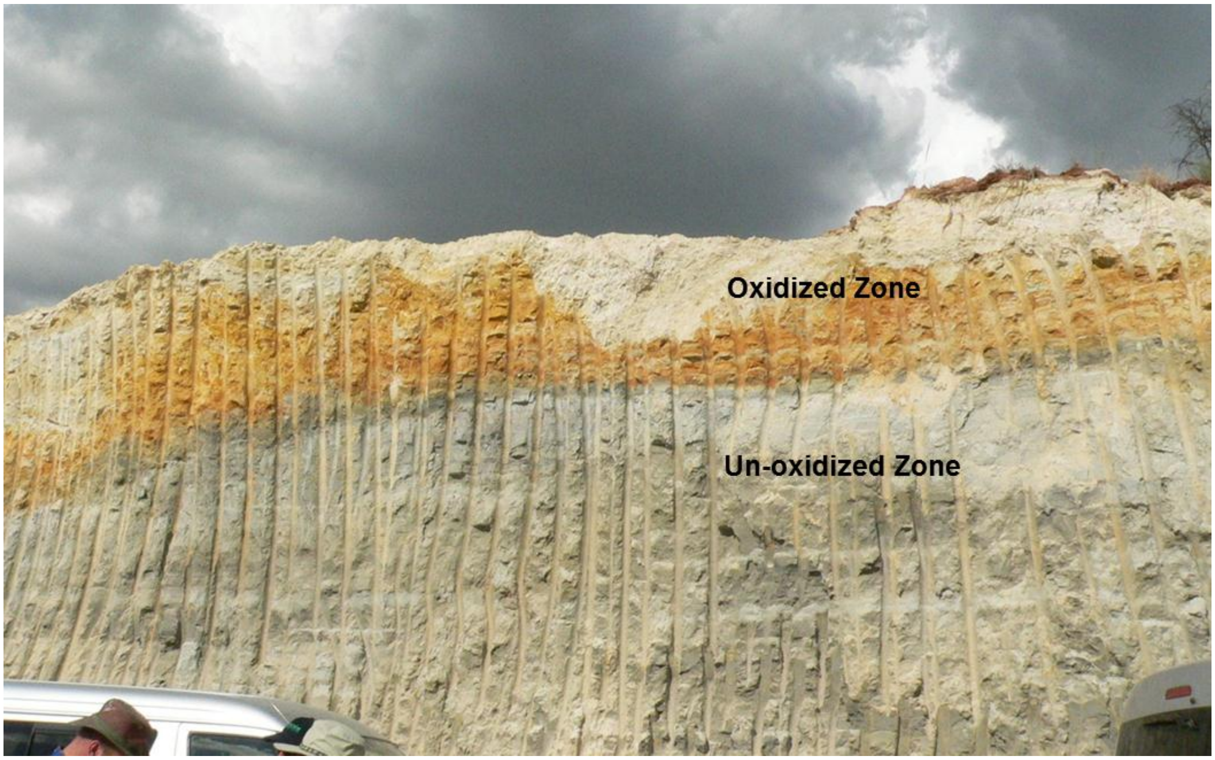

Photo 6.1: Oxidation zones in a gold TDF (Photo by P.W. van Deventer)

6.4 Methodology

In order to identify the oxidized and un-oxidized zones, the oxidation-reduction potential (ORP) of samples were tested using a platinum electrode ORP metre (Eutech instruments). ORP meters measure the ability of a medium to accept or release electrons through chemical reactions in millivolts (mV) (Bier, 2013). The ORP meter was calibrated to Standard Hydrogen Electrode potentials using a 240mV reference solution. Measurements were taken in the field as soon as samples were extracted. Samples were taken at 20 cm depth intervals using a core sampling bit on a hydraulic auger. Exposure to the atmosphere initiates oxidation reactions and may produce erroneous measurements. A saturated paste was made using deionised water with an ORP of 170 mV in tightly sealed containers. Samples were left for 10 min for the deionised water to fully penetrate the tailings and to mobilize any mobile salts. The samples were then tested and resealed. These samples were left for 24 h at 30^{o}C, and retested to determine the degree of change after the introduction of air and water.

A new hole was drilled 5 m away from a previously drilled hole (hole Z4, Figure 4.2) that was sampled and logged in order to compare U and Th content with ORP.

6.5 Results and discussion

The ORP profile of New Machavie is presented in Figure 6.2. Four distinct features can be discerned from this profile, namely the oxidized zone, oxidizing front, un-oxidized zone and saturated zone.

6.5.1. Oxidized zone

The oxidized zone has a high positive oxidation potential as pyrite has been oxidised in this zone and oxygen penetrates readily into this zone, fuelling a range of oxidation reactions. The result of pyrite oxidation creates an environment with a fairly low pH. Due to the low pH and highly oxidised conditions, elemental mobility is increased together with transportability.

When comparing the down-hole U results of borehole Z4 (Figure 6.3) with the ORP profile, one sees that the U content of the oxidized zone (0 – 250 cm) is slightly lower than the zones below. The element Th does not show significant signs of being leached which can be attributed to the stability of Th under oxidizing conditions.

6.5.2. Oxidizing front

The oxidizing front is characterized by a sharp increase in oxidation potential at a depth of 280 cm and then a major drop in oxidation potential to a depth of 320 cm. The sharp increase indicates where pyrite is actively being oxidized and in this case the oxidizing front falls in a range of approximately 20 cm, followed by 20 cm where oxidation is currently being initiated.

No definitive features can be seen in this zone regarding U and Th content. U shows an increase whilst Th shows a decrease, which can rather be attributed to depositional concentrations than secondary alterations.

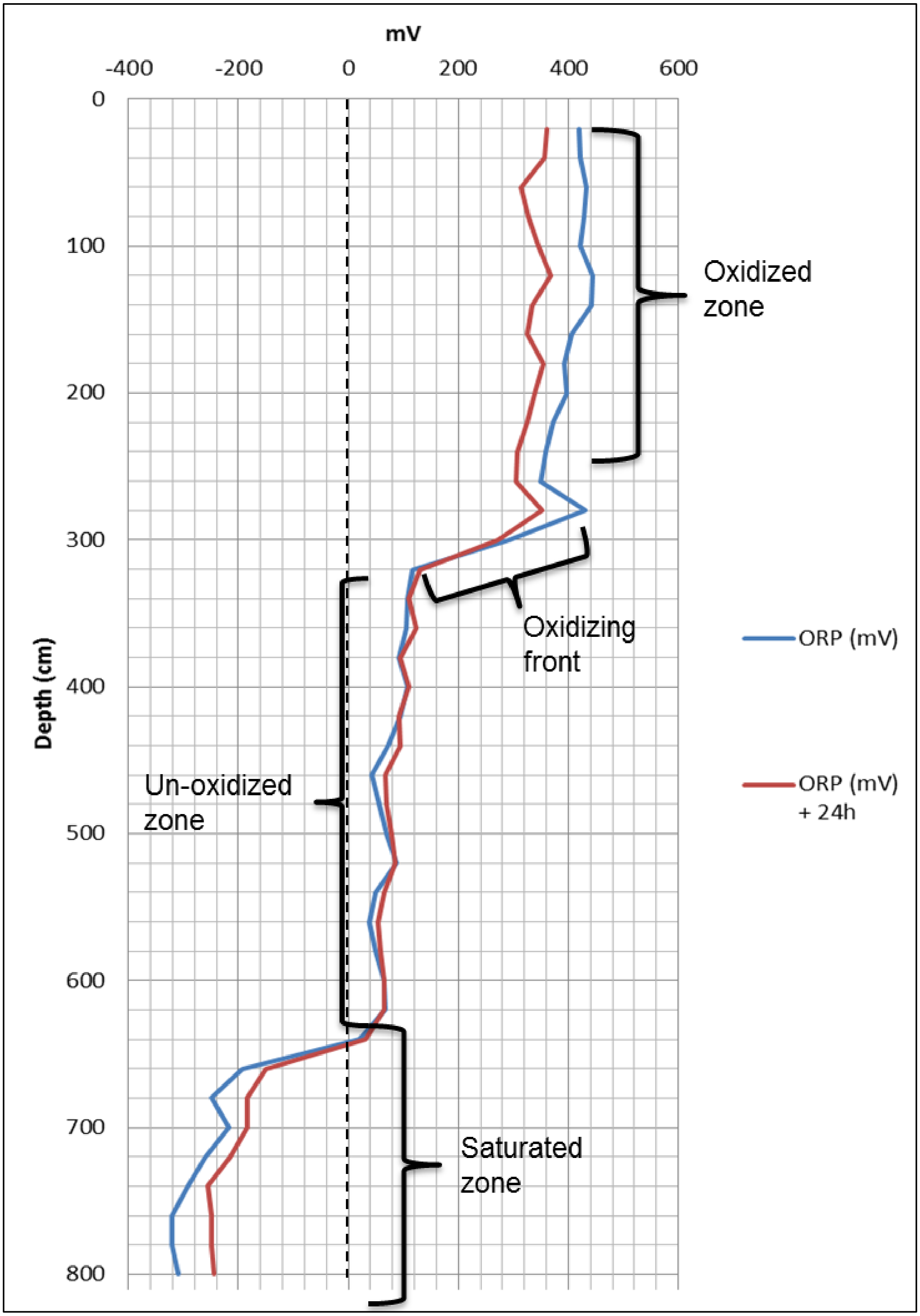

Figure 6.2: ORP profile of New Machavie (5 m from hole Z4)

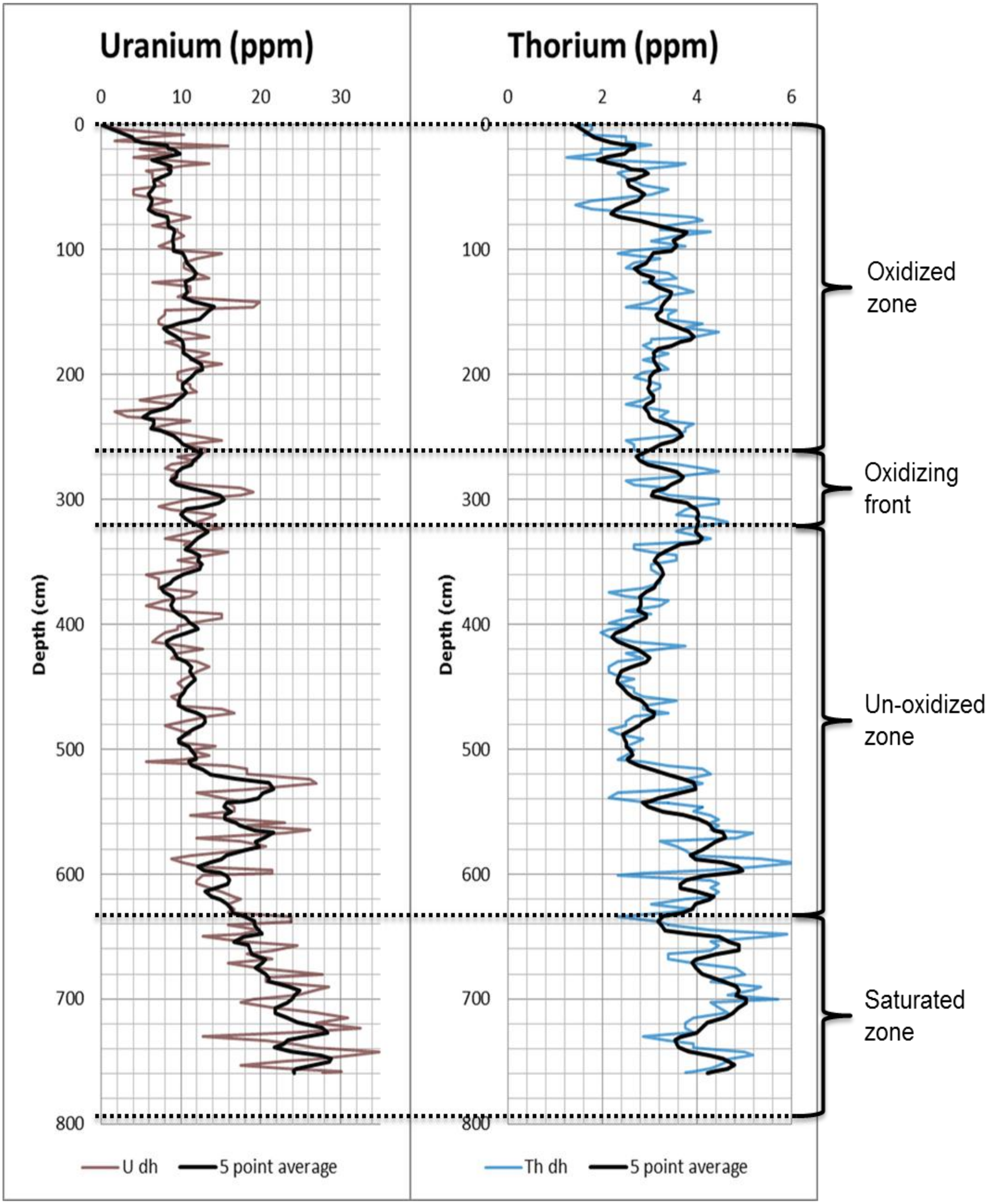

Figure 6.3: Down-hole (dh) probing results of hole Z4

6.5.3. Un-oxidized zone

The un-oxidized zone follows the oxidizing front from a depth of approximately 320 cm to 640 cm. The character of this zone is defined by fairly low oxidation potentials which are still positive. As oxygen penetration decreases with depth and the oxidizing front utilizes most of the oxygen as seen in reactions *(1)* and *(2)* (Section 2.6), this zone is depleted of oxygen as an oxidizing agent and uses other oxidisers like Fe^{3+}, which is the reason that this zone has a positive ORP. The un-oxidized zone may also periodically and partially be saturated with water depending on the amount of rainfall and the level of groundwater below the TDF. This rainfall effect may alter the level of the saturated zone by assimilating lower parts of the un-oxidized zone until the water level decreases again.

Uranium in this zone has a slightly higher average content than the oxidized zone although not as significant compared to the saturated zone. Surprisingly, Th shows lower concentrations in this zone than in the oxidized zone, for unknown reasons.

6.5.4. Saturated zone

The saturated zone is permanently saturated with water and has no oxygen to act as an oxidizing agent. Thus, negative ORP readings indicating a reducing environment define this zone. New Machavie has been a derelict mine for decades, meaning that no water (except rain) has been added for over 60 years. This has allowed the hydraulic properties to fully adapt and conform to the surrounding environment. The natural relief of the study area is the highest in the north-west and the lowest in the south-east. Whilst drilling, only the south-eastern quarter of the New Machavie TDF had enough pore-fluid to qualify as a saturated zone. This means that the natural flow direction is mimicked within the TDF to some extent; however, further study is needed to quantify the extent of the saturated zone. The ORP testing was done in late winter after the TDF had not received rain for a number of months.

The reduced form of U (U^{6+}) is insoluble and can only be transported in fluids as colloidal particles. The saturated zone will immobilize U and prevent transportation of U away from the TDF. Comparing the U content to the saturated zone’s profile, one sees that there is a significant increase in the U content. The same applies for Th but it is less pronounced (average increase of ±1 ppm vs±10 ppm for U). One can speculate that mobilized U and Th accumulate in the saturated zone as these elements are reduced and immobilized. Further investigation is needed to verify if accumulation has occurred.

ORP tests done after 24 hours showed a decrease in oxidation potential in the oxidized zone. The samples in the oxidized zone were taken relatively dry when deionized water was added to create a saturated paste. The addition of water in combination with the time spent in a sealed container allowed a reducing environment to form. The result is a decrease in oxidation potential in the highly oxidized samples.

The un-oxidized samples remained relatively stable but tended to oxidize slightly. In this case the formation of a slightly reducing environment slowed the oxidation reactions; however, since the samples were exposed to oxygen after they were extracted, they were still able to oxidize.

Samples taken from the saturated zone tend to oxidize more readily with depth. The samples were saturated upon extraction and very little water was needed to create a saturated paste. The exposure to oxygen was enough to start the pyrite oxidation reaction and being sealed did not slow the reaction, although the reactions do slow and eventually stop once trapped oxygen in the containers has been depleted. The samples that oxidized more readily with depth can be attributed to their location relative to a fluctuating water level. Higher samples in the saturated zone may form part of the un-oxidized zone when the level of the saturated zone lowers, whilst samples that have remained saturated since their deposition oxidized more readily.

6.6 Conclusion

New Machavie, an old mine upon which tailings deposition has not occurred for decades has developed a very low saturated zone that follows the natural relief. Uranium and Th are affected by the oxidation and reducing conditions within the TDF since the oxidised, un-oxidized and saturated zones all show different levels and trends regarding these elements. The un-oxidized zone has ORP measurements that falls under the oxidization range although considerably lower than the oxidized zone. In both cases where one zone changes to another, a sharp transition occurs within 20 to 40 cm, and since the sampling interval was 20 cm, these transitions may be even sharper than indicated. The transition between the oxidized and un-oxidized zone is where pyrite is actively being oxidized. This zone has a definitive pattern in the ORP profile namely a sharp increase in ORP followed by a sharp decrease. The sharp decrease below the oxidation front is caused by the relative depletion of oxygen in the oxidation front. Not enough oxygen is left to drive the oxidation reactions, thus other elements that are less reactive fulfil the role of oxidant in the un-oxidized zone (producing lower oxidized measurements).

Uranium has a stronger relation to the ORP than Th. Uranium content increases with a decrease in ORP. Some results need further investigation including:

- Decreased Th in the un-oxidized zone relative to the oxidized and saturated zones;
- Accumulation or depositional U content in the saturated zone as the cause of higher U content measurements;
- ORP measurements should be taken as soon as samples are exposed to the atmosphere. The addition of water may reduce the oxidation potential whilst the exposure to oxygen will increase the oxidation potential of un-oxidised samples.
- pH measurements must be included for more accurate geochemical assessments

Further study should include a profile on New Machavie and other gold TDFs where toxic metal solubility can be related to ORP.