1. INTRODUCTION

1.1 Project Background

The transport mechanisms and liberation of contaminants in platinum tailings storage facilities (TSFs) are poorly studied and rarely documented. Previously published studies have focussed mainly on gold-, copper-, zinc and lead tailings. This study highlights the importance of platinum TSFs as a contaminant producer due to mineral dissolution and oxidation. This is because these tailings materials may contain significant amounts of sulphide minerals, similar to gold tailings; appreciable amounts of copper derived from minerals such as chalcopyrite and bornite; and appreciable amounts of zinc derived from minerals such as sphallerite.

The mafic silicate mineral phases in platinum TSFs may also be large scale contributors of elevated major cations and -anions in groundwater, as these minerals are prone to breakdown and dissolution at earth surface conditions. This material also contains appreciable amounts of a spinel mineral which may liberate Cr^{3+}, which might potentially evolve under changing redox conditions to a more lethal form *viz.* Cr^{6+}. Therefore, platinum tailings storage facilities may provide material causing the combined contamination types of the waste rock generated by most other precious metal mining operations. The liberated contaminants may also travel in permeating fluids to aquifer level, reaching the underlying phreatic surface and subsequently allowing contaminant transport through hydrogeological pathways to receptors.

1.2 Objectives

The objectives of this study were:

- To identify the chemical and mineralogical composition of platinum tailings materials
- To investigate the dissolution potential of the mineral phases present in order to assess the contaminant contribution of each phase
- To identify the contaminants liberated by the mineral phases present
- To identify the saturated- and unsaturated hydraulic properties of the tailings material
- To identify the hydraulic properties of the underlying aquifer.

2 LITERATURE REVIEW

2.1 Redox Conditions

The uppermost layer of platinum TSFs, which varies in thickness between tailings, is the area where oxidation and subsequent destabilisation of minerals takes place. Minerals that most tailings have in common, including platinum tailings, are the sulphides of which the oxidation is described by Moncur *et al*. (2004) in a study at the Sherridon copper mine, Manitoba. After 70 years, the redox conditions in the upper 50 cm of the Sherridon tailings had become oxidising to the point of having a pH less than 1. Acidic conditions in the tailings due to sulphide mineral dissolution had caused Al-mineral depletion up to 1 m depth (Moncur *et al*., 2004). Many studies (Geelhoed, 2002; Moncur *et al*., 2009; Garrels & Christ, 1965; Piatak *et al.*, 2004; Koski *et al*., 2008; Lefebvre *et al*., 2001; Linklater *et al*., 2005; Molson *et al*., 2005; Yellishetty *et al.*, 2009) have found similar results. Acidic solutions that could potentially form from sulphide dissolution may also cause oxide minerals and silicates in TSFs, both products of platinum mining, to dissolve. The general redox conditions of mine waters permeating through TSFs are shown in *Figure 1*.

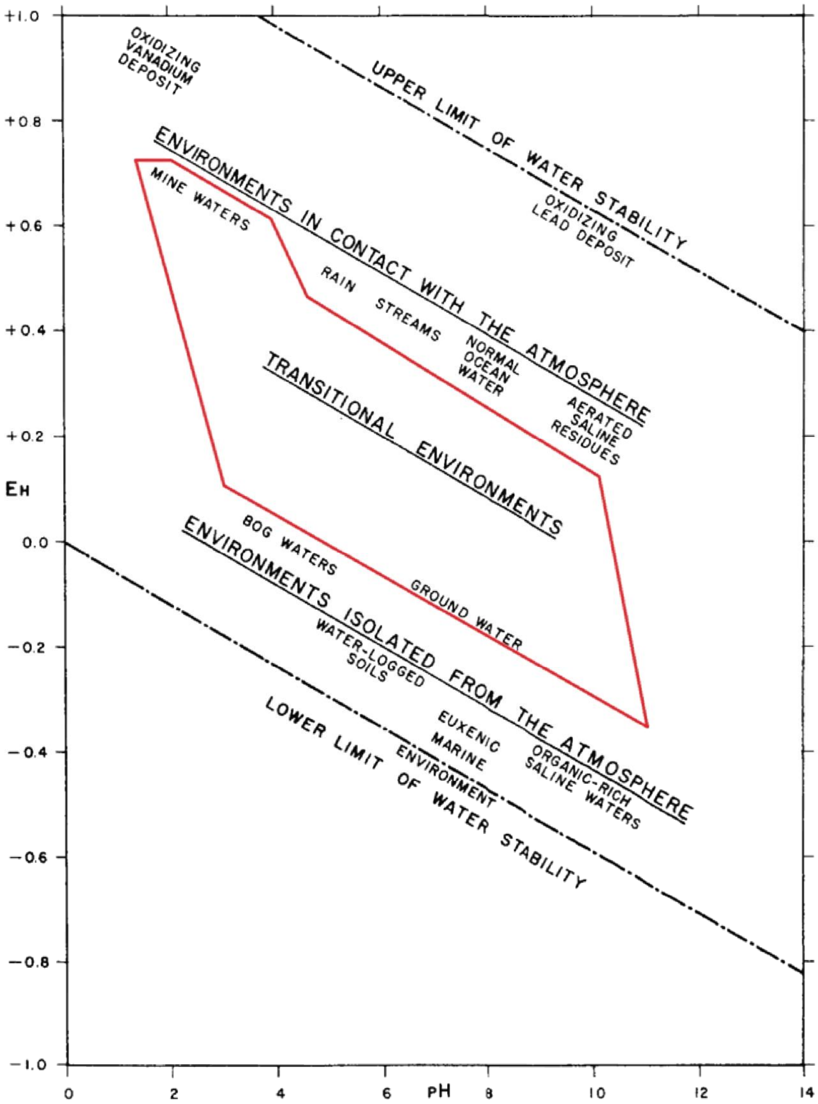

Figure 1: Redox conditions in different waters under 1 atmosphere total pressure and temperature of 25° C (Garrels and Christ, 1965).

Garrels and Christ (1965) illustrate with the use of this Eh-pH diagram, the general redox conditions in the uppermost part of tailings, a layer that is exposed to atmospheric gases and permeating fluids, rendering it oxidising. The general pH and Eh of mine tailings is assumed to be less than 5 and higher than 0.6 respectively, confining the stable minerals, species or ions present in the tailings to the prevailing redox conditions. This type of environment may be termed as oxic (Essington, 2004). However the limits of these redox conditions may vary with different temperatures, pressures, gas partial pressures as well as dissolved species (Garrels and Christ, 1965). This study will also accommodate changes in pressure-temperature conditions in the system to improve literature interpretation.

Redox conditions shift from oxidising to reducing from the top to the bottom of TSFs, as can be observed from the red stability field in *Figure 1*, and may result in the subsequent stabilisation and precipitation of different solid phases. However it is important to note that the original oxidised and dissolved reactant will very rarely be significantly re-precipitated, as many minerals require higher temperature and pressure conditions than those present, to form. An example would be the dissolution of Albite below.

$$2NaAlSi_30_8 + 2H^+ + 9H_2O \rightarrow 2Na^+ + 4H_4Si0_4 (aq) + Al_2Si_20_5 (OH_4) \qquad \textit{Equation 1}$$

Albite forms from silica rich magmas under temperatures ranging from 700–1000̊ C and is therefore thermodynamically unstable at surface conditions (Winter, 2004). Its re-precipitation will therefore be inhibited (Hem, 1985). Therefore neo-mineralisation may take place deeper in the TSF, inhibiting pollution. However, different species will also remain in solution. It is these species that may eventually reach groundwater and possibly cause contamination of the said environment. Redox conditions in groundwater are indicated by *Figure 1*. These conditions facilitate multiple Fe- sulphide species, SO_4^{2-}, various Cu species and precipitates, Cr^{6+} (Geelhoed *et al.*, 2004) and other heavy metal species in solution (Garrels and Christ, 1965).

2.2 Mineral Stability and Metal Liberation

Platinum mines in South Africa generally mine the Merensky platinum reef and the UG2 chromite reef. According to Vermaak and Hendriks (1976) the mineralogical composition of the pegmatoidal Merensky reef includes silicate- and oxide minerals such as:

- Orhopyroxene (Enstatite- $Mg_2Si_2O_6$; Ferrosillite- $Fe_2Si_2O_6$)
- Chromite- (Fe, Mg) Cr_2O_4
- Postcumulus feldspar (Anorthite- $CaAl_2Si_2O_8$)
- Postcumulus clinopyroxene (Diopside- $CaMgSi_2O_6$; Hedenbergite- $CaFeSi_2O_6$; Augite- (Ca, Na) (Mg, Fe, Al) Si_2O_6)
- Olivine and quartz-bearing facies also occur sporadically

The base metal sulphides present, according to Vermaak and Hendriks (1976) include:

- Pyrite (FeS_2)
- Pyrrhotite ($Fe_{1-x}S$)
- Chalcopyrite ($CuFeS_2$)
- Pentlandite ($(Fe, Ni)_9S_8$)

Precious minerals in the Merensky reef are generally associated with the base metal sulphides and the discreet phases present, according to Vermaak and Hendriks (1976) include:

- Braggite (Pt, Pd)S
- Cooperite PtS
- Laurite RuS
- Minor Sperrylite $PtAs_2$

According to the PHREEQC geochemical modelling databases (Appelo and Postma, 2010), each of these minerals has its own distinct reaction constant when dissolved in fluids indicating a product- or reagent favoured reaction. This takes place under different hydrogen ion concentrations i.e. pH conditions for each mineral, indicating its stability. Dissolution reactions and their subsequent reaction constants, of some of the mentioned minerals that may be found in platinum TSFs, are paraphrased from the PHREEQC databases in *Table 1* (Appelo and Postma, 2010).

Table 1: Fluid-mineral reaction constants of various minerals in mafic tailings material (Appelo and Postma, 2012).

Mineral Phase	Dissolution Reaction	Reaction Constant (log K)
Enstatite	$MgSiO_3 + 2H^+ = + 1H_2O + 1Mg^{2+} + 1SiO_2$	11.3269
Ferrosilite	$FeSiO_3 + 2\ H^+ = + 1\ Fe^{2+} + 1\ H_2O + 1\ SiO_2$	7.4471
Chromite	$FeCr_2O_4 + 8\ H^+ = + 1\ Fe^{2+} + 2\ Cr^{3+} + 4\ H_2O$	15.1685
Anorthite	$CaAl_2(SiO_4)_2 + 8\ H^+ = + 1\ Ca^{2+} + 2\ Al^{3+} + 2\ SiO_2 + 4\ H_2O$	26.5780
Diopside	$CaMgSi_2O_6 + 4\ H^+ = + 1\ Ca^{2+} + 1\ Mg^{2+} + 2\ H_2O + 2\ SiO_2$	20.9643
Hedenbergite	$CaFe(SiO_3)_2 + 4\ H^+ = + 1\ Ca^{2+} + 1\ Fe^{2+} + 2\ H_2O + 2\ SiO_2$	19.6060
Forsterite	$Mg_2SiO_4 + 4\ H^+ = + 1\ SiO_2 + 2\ H_2O + 2\ Mg^{2+}$	27.8626
Fayalite	$Fe_2SiO_4 + 4\ H^+ = + 1\ SiO_2 + 2\ Fe^{2+} + 2\ H_2O$	19.1113
Pyrite	$FeS_2 + 1\ H_2O = + 0.2500\ H^+ + 0.2500\ SO_4^{2-} + 1\ Fe^{2+} + 1.7500\ HS^-$	-24.6534
Chalcopyrite	$CuFeS_2 + 2\ H^+ = + 1\ Cu^{2+} + 1\ Fe^{2+} + 2\ HS^-$	-32.5638
Pyrrhotite	$FeS + 1\ H^+ = + 1\ Fe^{2+} + 1\ HS^-$	-3.7193

From these examples it can be seen that reaction constants are positive for silicate minerals, indicating a product favoured dissolution. Reaction constants for sulphide minerals are negative, indicating a reagent favoured dissolution. The chromite reaction constant is positive indicating product favoured dissolution. Reaction constants of these dissolution reactions may be fixed, but their reaction rates, however, are not. According to Yadav and Chakrapani (2006), pH conditions influence dissolution rates of minerals at high and low values, accelerating dissolution, whereas neutral pH conditions favour mineral stability and lowers solubility as illustrated by *Figure 2.*

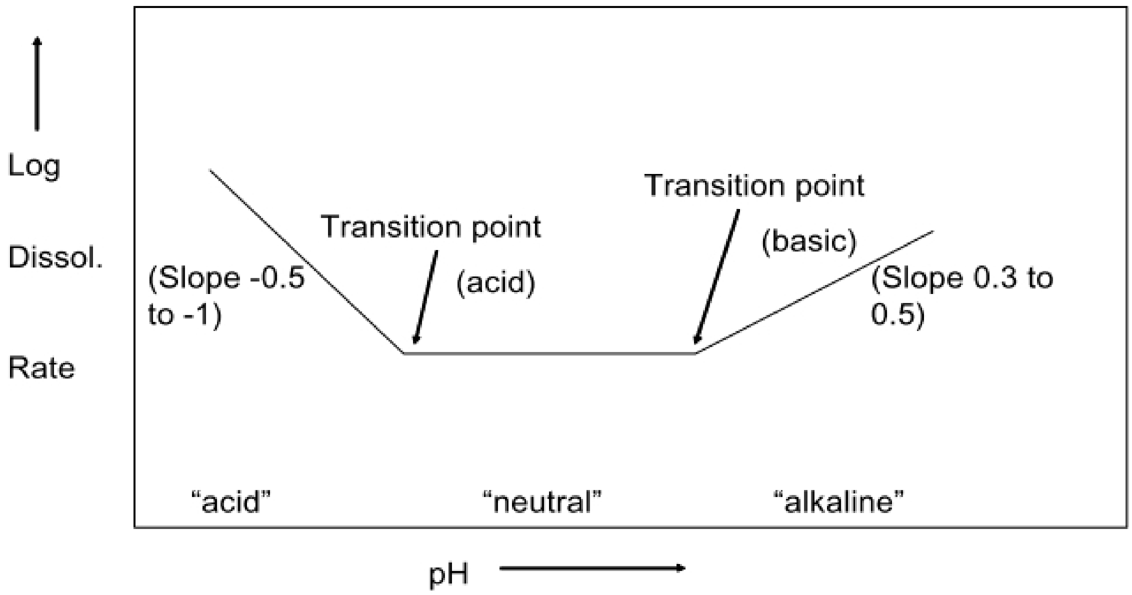

Figure 2: Logarithmic mineral dissolution rates at different pH levels (Yadav and Chakrapani, 2006)

This curve of dissolution is termed amphoteric and is constructed using the species in solution under different pH conditions, *viz.* the Cr^{6+} species is stable and abundant in solution, at a pH of 8 as illustrated by Geelhoed (2007) in *Figure 3*.

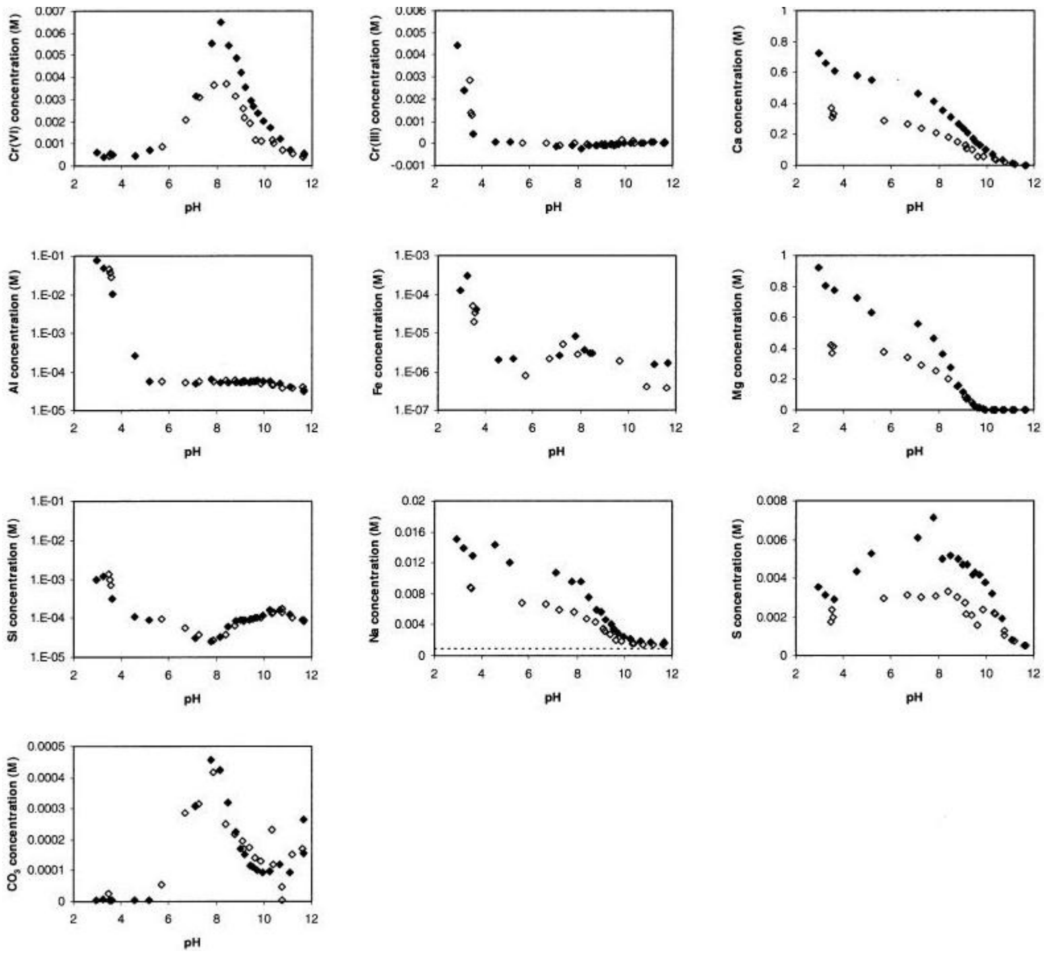

Figure 3: Concentrations of ions in solution under different pH conditions (Geelhoed, 2007)

Now that the mineral dissolution reaction constants are known, as well as the minerals found in platinum TSFs, an approximation can be made regarding the stability of these minerals under mine water redox conditions. Approximations and interpretations from Eh-pH diagrams can also be made to determine stable species and complexes under these conditions. Inferences from these stability diagrams can also be made about the precipitates that might form along the chemical evolution path of the permeating water, at different points in the TSF.

Some of the solid phases and species that are stable in platinum tailings are shown in and discussed below for each unique system.

2.2.1 Ferrous- and Ferric Hydroxides

Figure 4 indicates the stability of transitory, meta-stable iron species that may form in solution in a purely H_2O-Fe solution (Garrels and Christ, 1965). As mentioned, these species are of a transitory nature but remain stable in solution long enough to be noteworthy (Garrels and Christ, 1965). The most important species on this diagram with respect to platinum TSFs is $Fe(OH)_3$. Theoretically, if the tailings were kept at a temperature of 25° C and a pressure of 1 atmosphere from top to groundwater level, this species of iron would be found throughout the chemical stability field of the permeating fluid down to aquifer level. However, the chemistry of the tailings is not this simple and many more species are present. This diagram still gives an indication of which oxidation state of iron might be stable throughout the permeating fluid's path, *viz*. Fe^{3+} according to the inferred stability field.

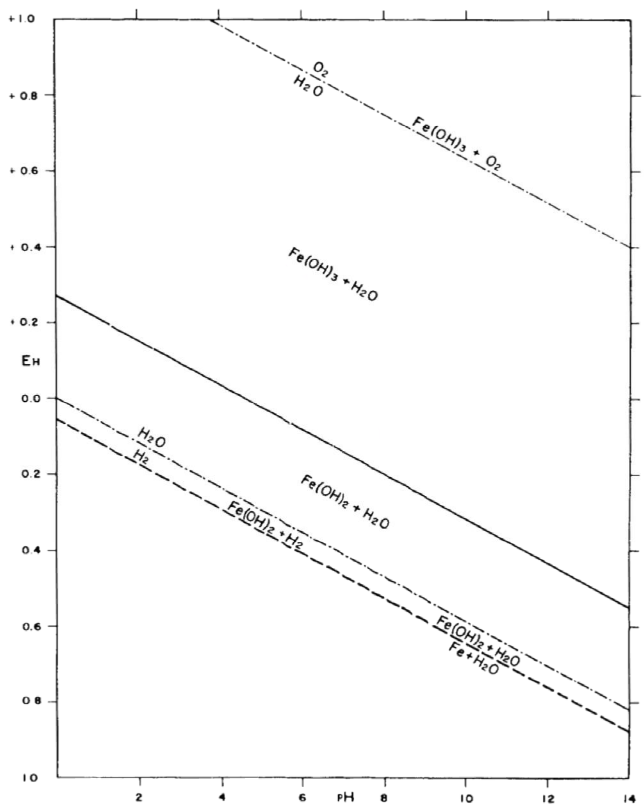

Figure 4: Eh-PH stability diagram of the Fe-O-H system 1 atmosphere total pressure and temperature of 25° C (Garrels and Christ, 1965)

2.2.2 Ferrous- and Ferric Oxides and- Sulphides

As mentioned, sulphur may be a significant component in platinum TSFs due to its presence, in varying oxidation states, in sulphide minerals which may be present in tailings. When sulphur is added to the system, iron speciation and the stability of these species and solid phases, changes somewhat from *Figure 4*. This change is evident in *Figure 5* (Garrels and Christ, 1965) where the stable form of iron occurs in the heamatite phase along with dissolved sulphate ions. This occurs under the assumption that temperature remains at 25˚ C and pressure at 1 atmosphere with 10^{-1} as the activity of dissolved sulphur. This phase is stable from the oxidative top of the tailings to groundwater level as indicated by the inferred stability field in red. This renders other solid phases such as pyrite, pyrrhotite and pure magnetite phases theoretically unstable anywhere in the tailings, making them prone to dissolution. *Figure 6* also illustrates this concept by indicating which solid phases of iron are present in the tailings under different Eh-pH conditions as well as which iron ion is present. Instability of the previously mentioned meta-stable solid phases may cause significant metal and sulphate contamination to groundwater. However, chemistry in the tailings is, more complex than a simple four-component system.

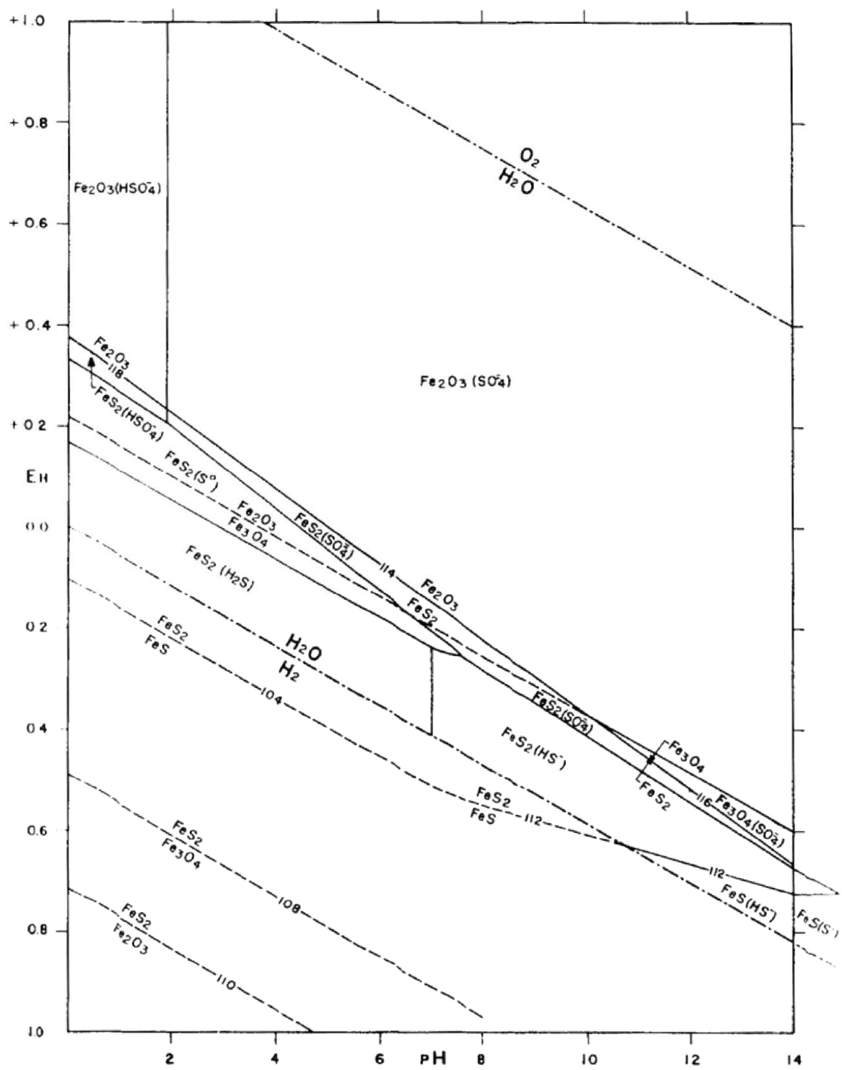

Figure 5: Eh-pH stability diagram of the Fe-S-O-H system at 1 atmosphere total pressure and temperature of 25˚ C (Garrels and Christ, 1965)

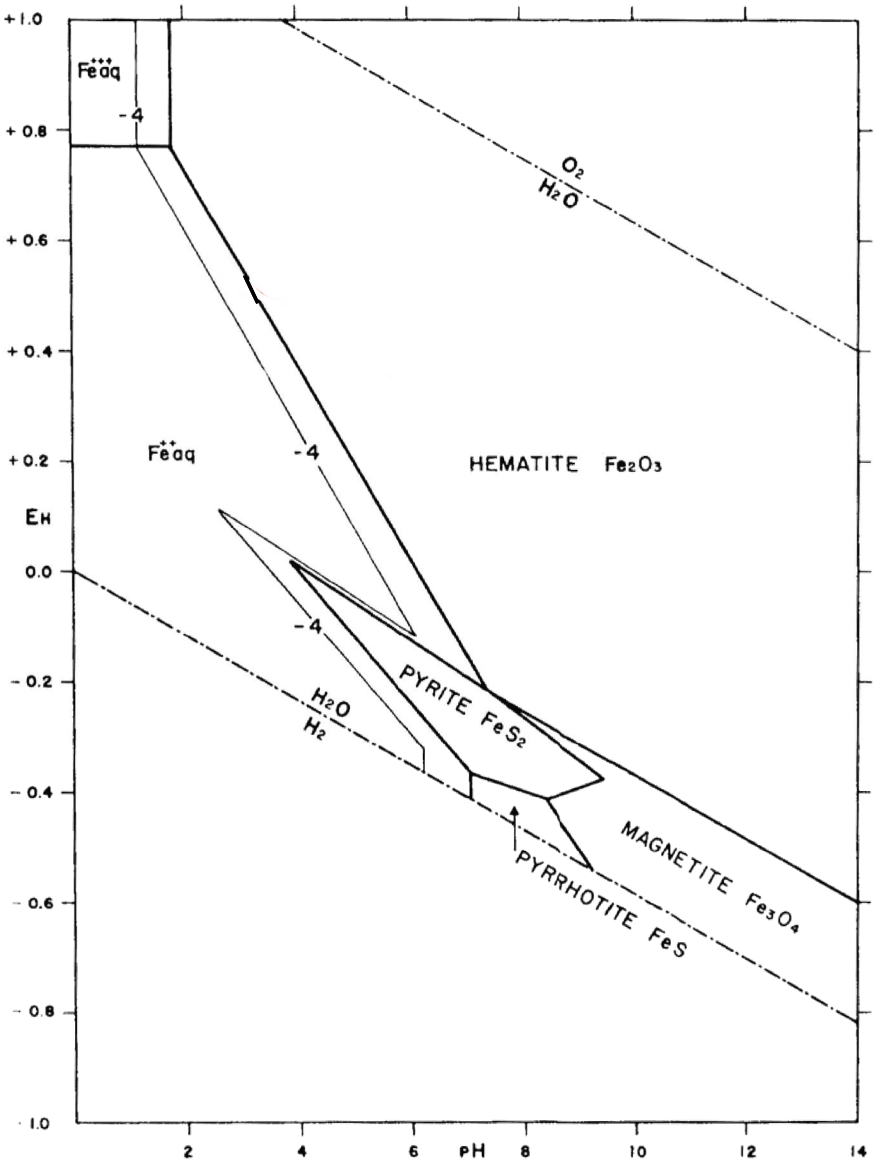

Figure 6: Eh-PH stability diagram of solid phases in the Fe-S-O-H system at 1 atmosphere total pressure and temperature of 25̊ C (Garrels and Christ, 1965)

2.2.3 Ferrous- and Ferric Oxides and – Silicates

*Figure **7*** illustrates a Fe-Si-O-H system. This diagram shows heamatite as the stable solid phase throughout the stability field of the permeating fluid from the oxidising upper zone of the TSF to groundwater level. Although Si is present in the system in the form of enstatite in this diagram, this solid phase remains unstable and will dissolve and speciate into the fluid. This in turn could also act as a control on the dissolution of other minerals (Essington, 2004). This diagram also illustrates pure magnetite as an unstable phase in tailings and at groundwater level.

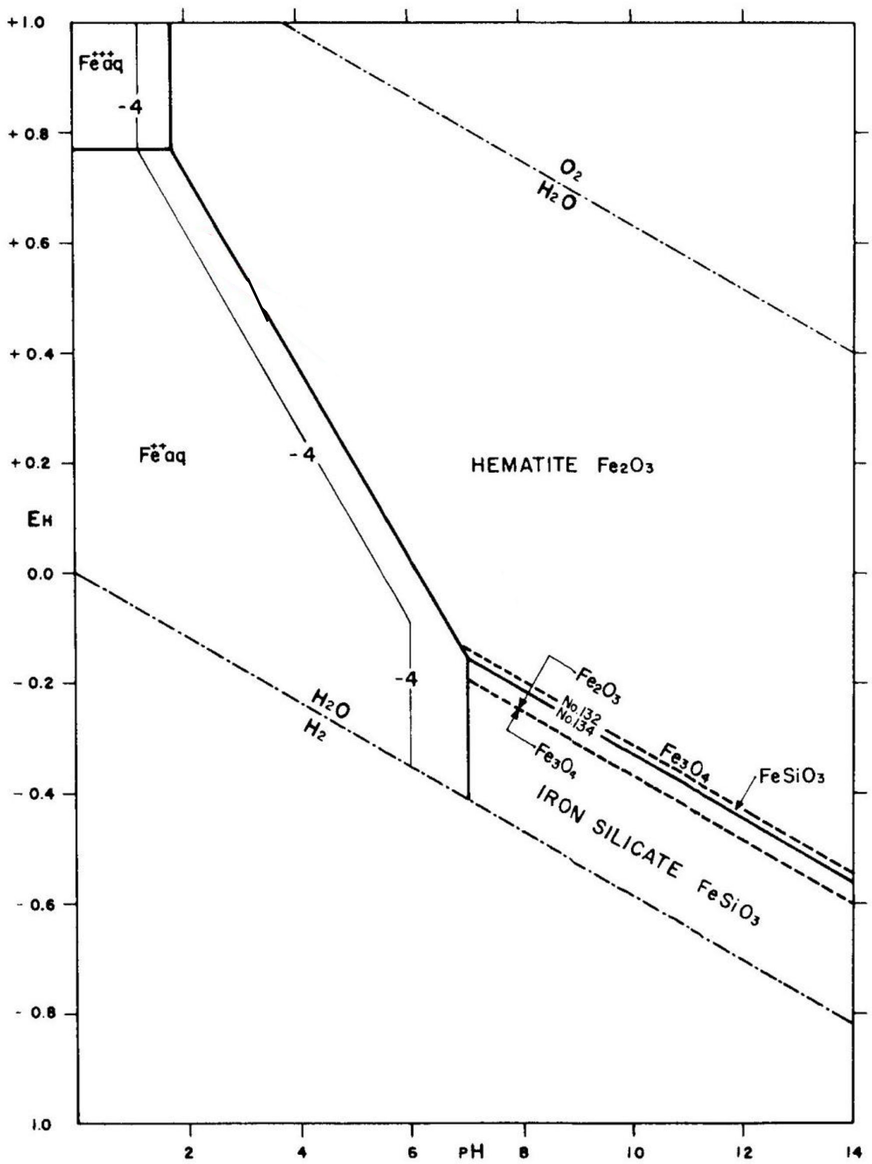

Figure 7: Eh-PH stability diagram of the Fe-Si-O-H system at 1 atmosphere total pressure and temperature of 25 C (Garrels and Christ, 1965)

2.2.4 The Cu-Fe-S-O-H system

This system is of special interest in the study of contamination from TSFs. This is because the principle contaminant and cause of acid mine drainage in tailings is conventionally accepted as sulphide minerals. *Figure 8* illustrates the thermodynamic conditions under which these minerals are stable relative to the stability field followed by permeating fluids through the tailings to groundwater level. Metals such as Fe^{2+} and Cu^{2+} are stable in solution in the upper tailings and as the solution migrates, heamatite once again becomes stable with Cu^{2+} remaining in solution as a stable species. Fe^{2+} activity therefore becomes lower while Cu^{2+} activity only lowers from 10^{-4} to 10^{-6} as the cuprite-heamatite stability field is approached. When these thermodynamic conditions are reached by the permeating fluid, cuprite and heamatite exist as distinct solid phases. These phases then destabilise to form native Cu and heamatite which evolve with the permeating fluid into solid phases of chalcocite and hematite in groundwater level thermodynamic conditions. An important point to note from this diagram is that pyrite, chalcopyrite and pyrrhotite are all unstable throughout the fluid's redox path, when compared to Figure 1, and may destabilise to liberate Fe, Cu and different sulphur species causing contamination to groundwater.

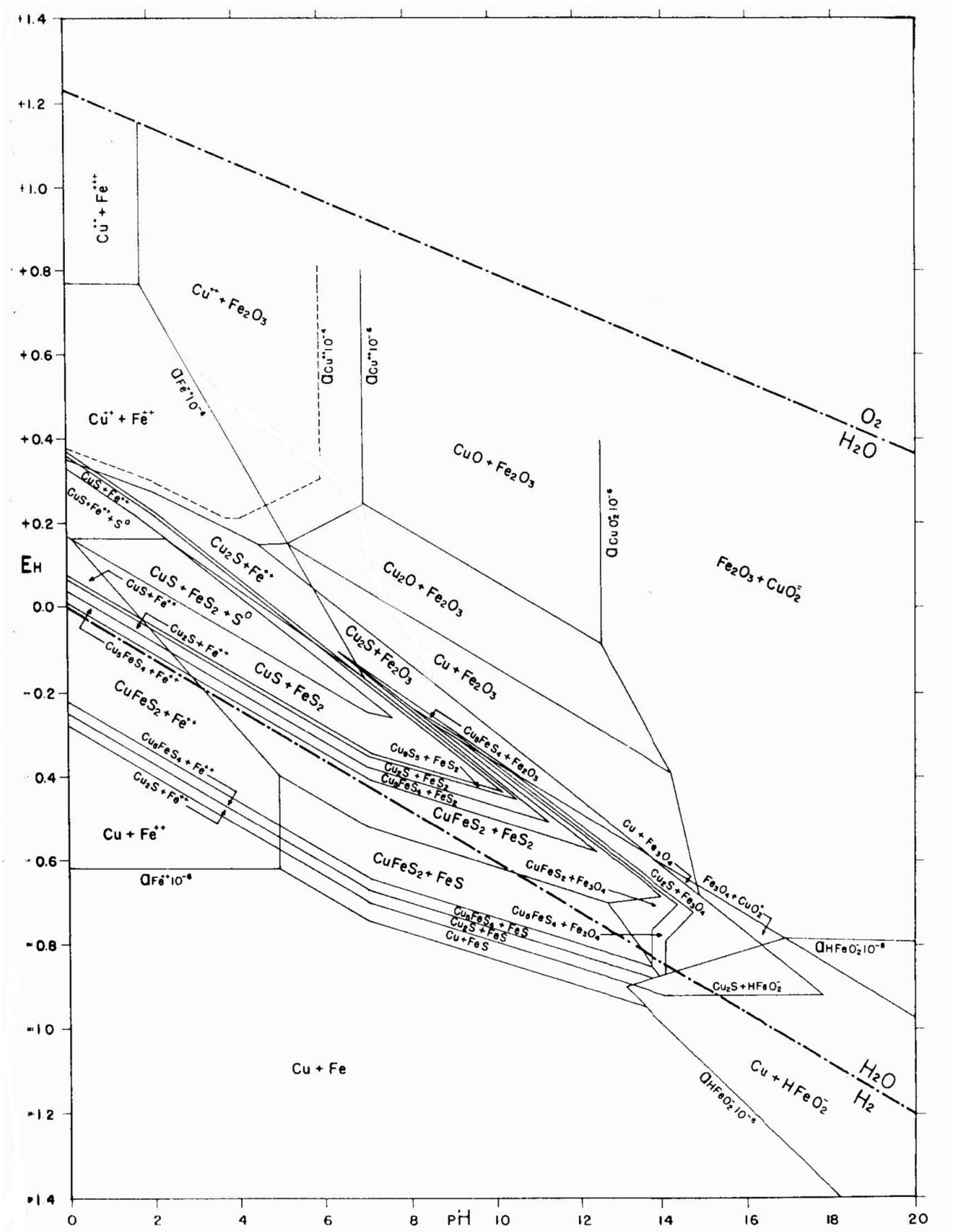

Figure 8: Eh-PH stability diagram of the Fe-Cu-S-O-H system at 1 atmosphere total pressure and temperature of 25̊ C (Garrels and Christ, 1965)

2.2.5 Sulphur Speciation

In *Figure 9* (Garrels and Christ, 1965), it is evident that the only stable sulphur species along the entire stability field, when compared to Figure 1, is SO_4^{2-} at an activity of 10^{-1}. Therefore other sulphur species will be significantly less abundant. The sulphur stability diagram is discussed individually for exactly this reason. SO_4^{2-} anion species are the main indicators of acid mine drainage, being the only stable form of dissolved phase sulphur in tailings and groundwater. These sulphates are free to mobilise and react with any mineral and fluid encountered along the indicated redox path, in Figure 1, and form sulphuric acid with water. Sulphuric acid is highly corrosive and is a major contaminant in surface water and groundwater. It also lowers pH significantly, accelerating the dissolution rates of the minerals present and causing unfavourable thermodynamic conditions for most solid phases, affecting their thermodynamic stability.

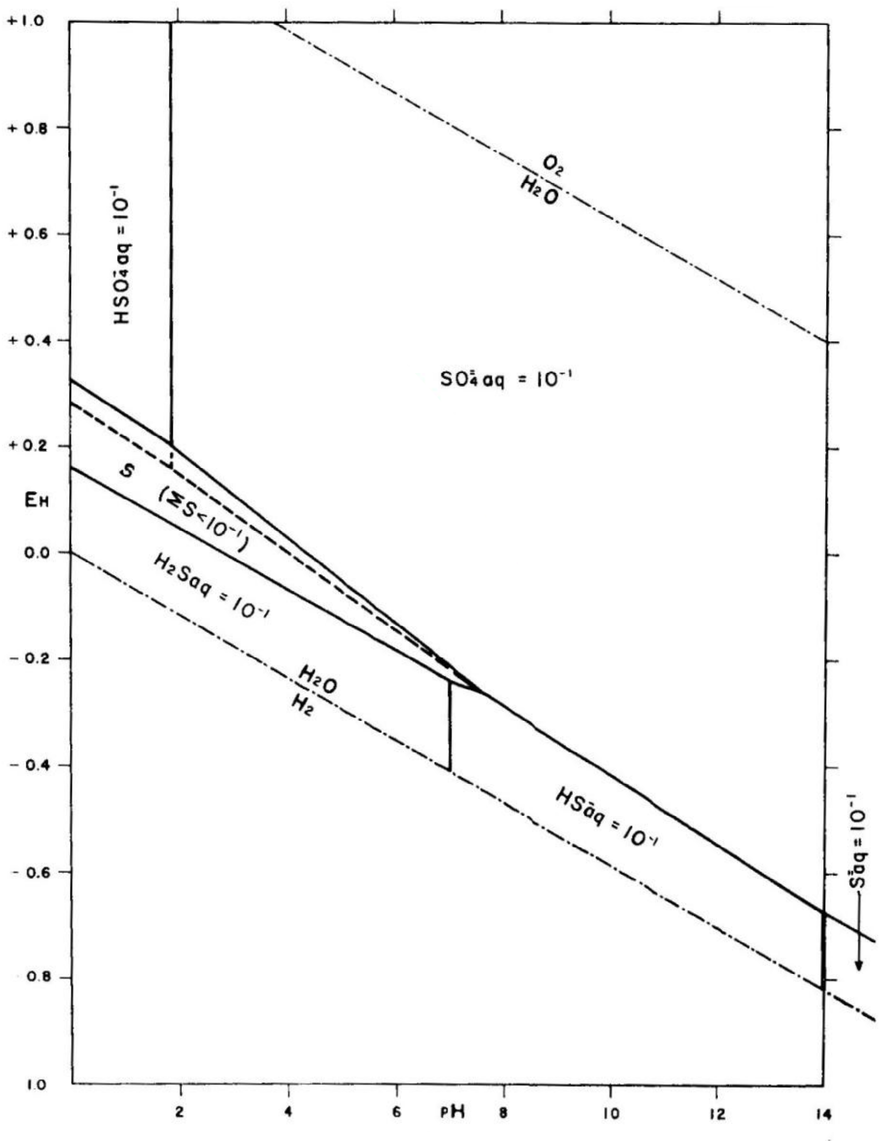

Figure 9: Eh-PH stability diagram for the S-O-H system at 1 atmosphere total pressure and temperature of 25̊ C (Garrels and Christ, 1965)

2.2.6 Chromite Dissolution and Chromium Speciation

As mentioned, chromite dissolves in water according to:

$FeCr_2O_4 + 8\ H^+ = 1\ Fe^{2+} + 2\ Cr^{3+} + 4\ H_2O$ *Equation 2*

This chemical reaction has a positive reaction constant which is indicative of a product favoured dissolution reaction with Fe and Cr being liberated, according to the PHREEQC databases. The ion of specific interest, liberated by this reaction is Cr^{3+}. This ion could be liberated throughout the entire stability field of acidic permeating fluids in tailings, even as an amorphous phase, as can be observed in *Figure 10*. The ion keeps its trivalent charge even in the redox conditions found in groundwater according to this figure. However, this ion might be oxidised in a higher Eh range, to its more lethal, hexavalent state (Geelhoed, 2002). Research conducted by Geelhoed (2002), indicates that high levels of Cr^{6+} may be present at a pH of 8 as indicated by *Figure 11*.

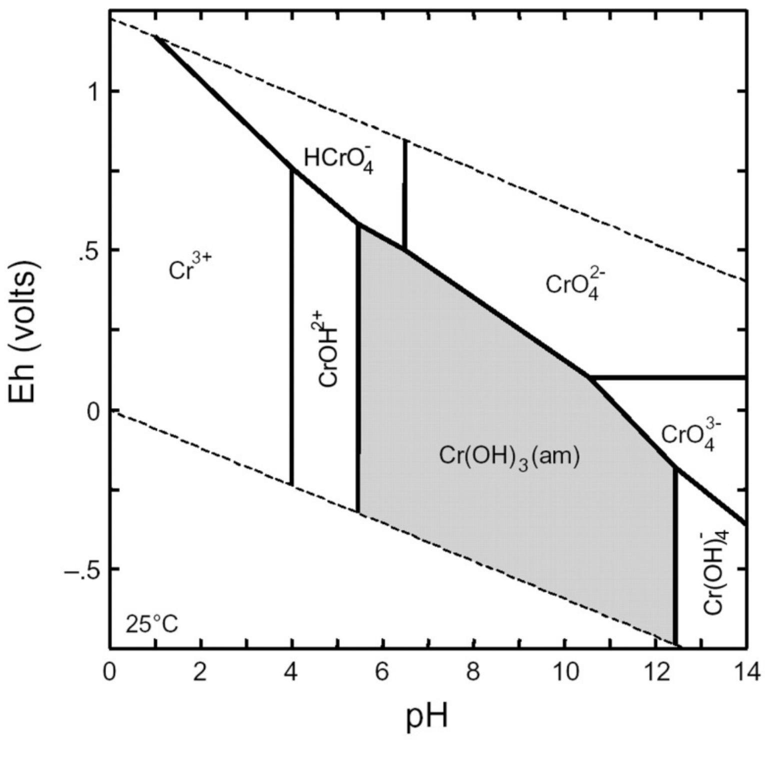

Figure 10: Eh-pH stability diagram of the Cr-O-H system at 1 atmosphere total pressure and temperature of 25̊ C (Indiana.edu, 2011)

Therefore, if the character of the tailings or groundwater changes to higher Eh or pH levels, or an oxidising agent such as Mn is released in significant concentrations, Cr^{6+} may become present in the system causing toxicity and environmental degradation. Eh can be considerably influenced and raised to up to +700 mV by increases in O_2 concentration (Radojevic and Bashkin, 2006). This is especially of concern in platinum TSFs as Cr is concentrated in this setting whereas its occurrence in natural systems is of trace abundance (Kotas and Stasicka, 1999).

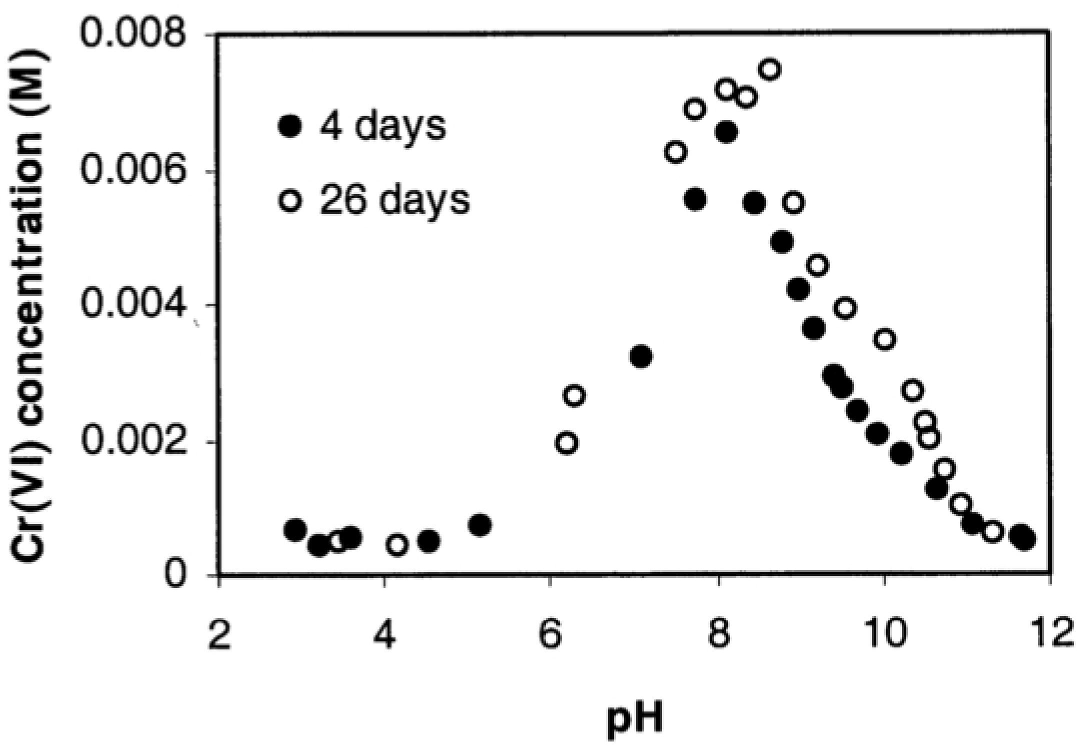

Figure 11: Scatter plot indicating Cr^{6+} concentration against pH value (Geelhoed,2002)

2.2.7 Silicate Weathering

Perhaps one of the major overlooked contaminators in platinum TSFs is the mafic silicate minerals. These minerals are abundant in the major platinum producing lithologies in South Africa, located in the Bushveld Igneous Complex (Vermaak and Hendriks, 1976). Silicate minerals such as olivine, pyroxene and calcic plagioclase species are found in many Bushveld tailings and contain cations such as Mg, Fe, Ca, K, Na and Cr. These ions may also be substituted in solid solutions by heavier metals such as Zn, Mn, Ti, Ni and others (Klein & Dutrow, 2008).

According to Wilson (2004) weathering of the primary silicate minerals is related to the inherent susceptibility of the mineral to weathering, which is in turn related to chemical composition, crystal structure and the distribution of defects. These defects may include dislocations and exsolutions which may contribute to the controls on the weathering reactions. All these defects are increased during the crushing and milling process. However, thermodynamic formation conditions may also play a role in mineral breakdown as phases formed at high pressures and high temperatures are more meta-stable at earth surface conditions. A lower energy state may subsequently be obtained from mineral breakdown in accordance with Ostwald's Step Rule (Bethke, 2011). This indicates that silicate phases in the Bushveld lithologies would be more prone to weathering than those found in felsic intrusions. This idea is supported by Wilson (2004) by indicating that the primary weathering sequence follows the reverse of the magmatic crystallisation series as proposed by Bowen (1928).

Most silicate minerals show an amphoteric dissolution curve when dissolution rates are plotted against pH as illustrated by Yadav and Chakrapani (2006). This indicates that higher dissolution rates are induced by high and low pH values respectively. Acid- or alkaline drainage is a common problem associated with mining activity and therefore may increase the concentrations of liberated cations from silicate minerals.

Platinum tailings material contains both mafic mineral phases and produce acid- or alkaline drainage. Therefore, increased cation release can be expected from the material. However, these cations may also act as buffers in solution, forming stable complexes with anions such as SO_4 which may inhibit acid formation (Essington, 2004). Complexes may also be adsorbed to secondary mineral surfaces, inhibiting rapid contaminant release.

2.3 Transport mechanisms

Contaminant transport following mineral dissolution, in natural systems as well as tailings material, occurs by diffusion, dispersion and advection. Each of these processes plays a governing role in the amount of contamination that may reach an aquifer.

2.3.1 Molecular Diffusion

The first and most important step in the determination of molecular diffusion close to dissolving mineral surfaces, is to calculate the ionic strength of the solution in which the mineral or aggregate is immersed (Essington, 2004). This will be discussed in more detail later in this section. Ionic strength is calculated using the equation below.

$$\boldsymbol{I} = \frac{1}{2}\sum \boldsymbol{C_i}.\left(\boldsymbol{Z_i^2}\right) \qquad \text{Equation 3}$$

Where:

I = Ionic strength of the solution which is defined by Essington as the amount of charges in solution

C_i = The concentration of the ion in solution (M)

Z_i = The charge of the ion.

The I-value obtained from this equation, is used to calculate an activity coefficient for the ion in question. This can be calculated by using the Debyë-Hückell equation, Extended Debyë-Hückell equation or the Davies equation. The Davies equation is the most robust of these three equations as it can be used for solutions with ionic strengths of 0 to 0.5. Therefore the Davies equation, given by the equation below, is most often used in these types of calculations.

$$\boldsymbol{log\gamma_i} = -\left[\boldsymbol{AZ_i^2}\left(\frac{\boldsymbol{I^{\frac{1}{2}}}}{\boldsymbol{1+I^{\frac{1}{2}}}} - \boldsymbol{0.3I}\right)\right] \qquad \text{Equation 4}$$

Where:

γ = The activity coefficient of the ion in question

i = The ion in question

A = An equation constant of 0.5

Z = The charge of the ion in question

I = The ionic strength of the solution.

The γ_i value calculated from the Davies equation is then used to calculate the activity of the free, unspeciated ion in solution by multiplying the concentration of the ion with its activity coefficient.

The diffusion of an ion into solution close to a dissolving mineral surface can now be calculated using Fick's first law. This law states that a substance put into solution will tend to diffuse towards constant concentration throughout the solution (Mondofacto, 1997) The equation for this calculation is given below, as defined by the University of Arizona's website (2007).

$$\boldsymbol{J} = -\boldsymbol{D}.\left(\frac{\Delta \boldsymbol{C}}{\Delta \boldsymbol{x}}\right)$$ *Equation 5*

Where:
J = The mass flux i.e. the movement of matter from one point to another per time unit
D = The diffusivity of a material. A constant that describes the material's diffusion speed
ΔC = The change in concentration of the ion in question
Δx = The change in distance that the material is diffusing.

An understanding of how an element diffuses from a dissolving mineral surface can now be obtained from Fick's law. This may influence dissolution kinetics and subsequently reaction kinetics and becomes another controlling factor, apart from thermodynamic conditions, on the amount of contaminant liberated and reaching groundwater from tailings material. Modern geochemical modelling software does not account for this mechanism and assumes instantaneous diffusion rather than a gradual process. However, diffusion may be such a negligible transport mechanism in moving fluids that other transport mechanisms may override it completely.

Diffusion will take place where a mineral is dissolving and subsequently reacting with a permeating fluid. The area where this is most likely to occur is the oxidising upper area of the TSF where metals and other contaminants are readily liberated. As the dissolved ion diffuses to lower parts of saturated tailings material, an inhibiting factor may come into play *viz*. adsorption. Mineral edges and surfaces may be altered, partially inducing a temporary or permanent negative charge. This causes diffusing ions in solution to be adsorbed onto mineral surfaces, lowering the activity of the specific ion in solution. This may, along with mineral precipitation, reduce contaminants reaching the underlying aquifer of the TSF.

2.3.2 Mechanical Dispersion

Mechanical dispersion of a solute in a fluid can be described as the pathway it follows through a matrix as illustrated in *Figure 12*. However, dispersion can be influenced by adsorption, diffusion speed, matrix type, fluid behaviour and other parameters. According to Kalmaz and Barbieri (1980), parameters controlling dispersion can be grouped into three categories:

- Media dependent such as intrinsic permeability
- Substance dependant such as decay constant
- Substance-environment dependence such as distribution coefficients in numerical models.

The most important parameters controlling dispersion in porous media are also paraphrased from Kalmaz and Barbieri (1980) as:

- Dispersion coefficient- a function of velocity and dispersivity
- Pore Velocity- a function of hydraulic gradient, permeability, effective porosity
- Equilibrium constant- a function of distribution coefficient, unit weight and porosity of the porous media
- Decay constant.

Therefore, when taking all these parameters into account, it can be concluded that the dispersion of solutes through the tailings material as well as aquifer media, is a physical process depending strongly on the properties of the media as well as the chemical characteristics of the solute.

However, lateral dispersion in the tailings material is minimal as fluids principally permeate due to gravity and the general movement vector is therefore vertical to sub-vertical. Lateral dispersion is therefore kept to a minimum in the tailings material. However, mechanical dispersion at aquifer level may cause pluming of dissolved contaminants as their movement occurs under the influence of hydraulic head and lateral- and vertical dispersion may now also take place.

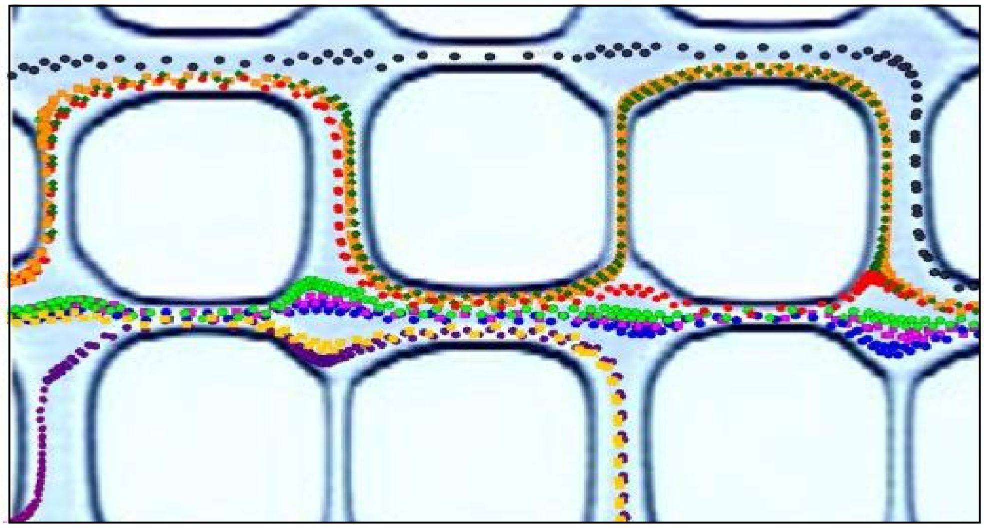

Figure 12: Schematic representation of mechanical contaminant dispersion through a matrix (Keller, 2004)

2.3.3 Hydrodynamic Dispersion

Bear and Bachmat (1967) defined hydrodynamic dispersion as a soluble substance, called a tracer, in a fluid flowing through a porous medium which spreads out, increasingly occupying a portion of the flow domain. Hydrodynamic dispersion is a function of three macroscopic transport parameters. These parameters are the permeability of a porous medium; the coefficient of mechanical dispersion of that medium; and the coefficient of molecular diffusion of that medium. Each of these parameters measures a different characteristic of the flow through the porous medium. Permeability measures the medium's ability to convey fluid movement; the coefficient of mechanical dispersion measures the temporal spreading of a solute in space; and the coefficient of molecular diffusion measures the spreading of a solute in a fluid when the fluid is stagnant (Bear and Bachmat, 1967). Therefore, hydrodynamic dispersion is a combination of mechanical and molecular spreading of a solute in a solvent during flow which is defined by a combination of diffusion and dispersion. This is of special concern at tailings level as fluid movement through the material is slow (Craig, 2004) and advection is unlikely to take place through preferred pathways as the media may be homogeneous and isotropic.

2.3.4 Advection

Advection is the transport of solutes via groundwater below the phreatic surface, under a hydraulic gradient, as illustrated by *Figure 13*. For a contaminant to rapidly progress away from its source, advection via groundwater along with dispersion is required.

This can only take place if groundwater is moving under a hydraulic gradient (Verral *et al*., 2008). If a positive hydraulic gradient is present, advection will take place in the flow direction of the hydraulic gradient and is of special concern below the tailings, as contaminants may reach a receptor much more rapidly due to elevated flow velocities relative to that of fluids at tailings level. However, advection, like dispersion, also depends on physical properties of the aquifer, as well as chemical properties of the contaminant.

Contaminants, such as metals, produced from tailings material will move via groundwater, if reached, in the form of advection. A smaller amount of dispersion may take place, depending on the aquifer properties, and even less diffusion depending on the contamination state of the water and the adsorptive properties of the aquifer material. Therefore, aquifers underlying TSFs, with a high hydraulic gradient, intrinsic permeability and porosity should be monitored much more closely for contaminant advection.

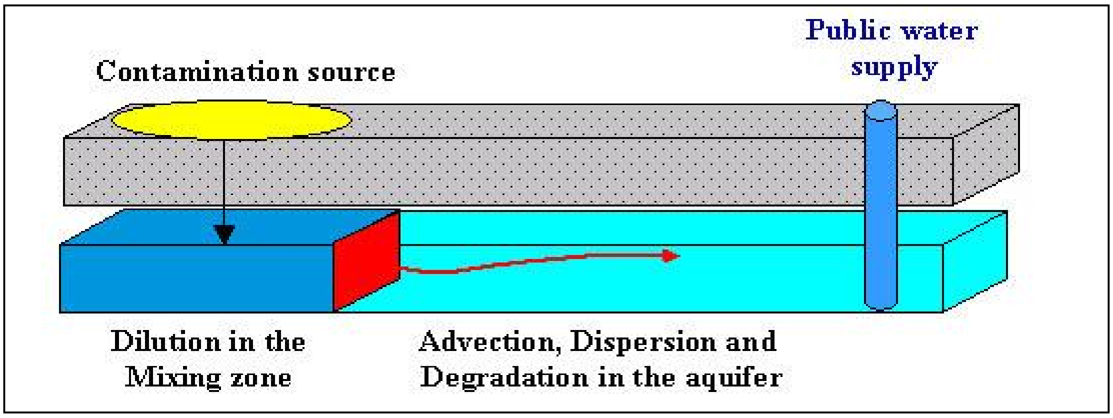

Figure 13: Conceptual model indicating contaminant transport by advection (Strassberg et al. 2011).

2.4 Analysis methods

To correctly characterise tailings material and the contaminants released from TSFs, different methods should be employed. Each method yields information about the tailings material's mineralogical and subsequent chemical composition; the leaching potential of the tailings material; the physical and hydraulic characteristics of the tailings material and underlying rock mass; the chemical composition of permeating fluids; the chemical composition of groundwater; and the potential contaminants present in or being liberated from the tailings material.

2.4.1 X-Ray Fluorescence Spectroscopy and X-Ray Diffraction

X-Ray Fluorescence Spectroscopy (XRF) is used to determine the chemical composition of the tailings material in terms of oxides. Each oxide then represents a weight percentage of the sample being analysed. From this analysis, it can be determined which contaminants are possibly concentrated in the tailings material as metals or other contaminants.

X-Ray Diffraction (XRD) on the other hand gives the composition of the tailings material sample in terms of the minerals present. This data can then be used in conjunction with thermodynamic data on the phases present to determine the possible dissolution of minerals, reaction kinetics, dissolution rates and mineral stability under a given set of conditions. It is important to note that XRD can only report the crystalline phases present above an abundance of 1 weight%.

2.4.2 Reflected Light Microscopy

Reflected light microscopy may be used to determine the presence of sulphide and oxide minerals in rock material. These minerals appear opaque in direct light microscopy which is performed by transmitting light through a thin section of rock. Reflected light microscopy is performed using mounted, polished sections, from which light is reflected, projecting an image of the opaque minerals such as sulphides and oxides, through the microscope oculars. By utilising direct observation and the optical properties of the minerals present, the relative amounts and compositions of these minerals can be determined and noted. This information is useful in determining the amount of contamination that may be released from these minerals, especially with respect to sulphides.

2.4.3 Acid-Base Accounting and Net Acid Generation

Acid-Base Accounting (ABA) is a static test which assesses the potential of a rock to produce or neutralise acid. This test is used as a first approximation of the acidity or alkalinity of leachate produced by the rock in the presence fluids. Components analysed in an ABA test are as follows:

- Acid Generating Potential (AGP) – this test determines the amount of acid that could potentially be generated by the rock material.
- Acid Neutralisation Potential (ANP) – this test determines the amount of acid that could potentially be consumed by the rock material. ANP is also expressed as kg of $CaCO_3$ per ton of rock to represent the amount of theoretical $CaCO_3$ available in the rock material, to neutralise acid.
- Net Acid Generation (NAG) Potential - This value is obtained by subtracting the ANP from the AGP. A positive value indicates potentially acid forming rock whereas a negative value indicates potentially non-acid forming rock. Vice versa to this is the Net Neutralising Potential (NNP) of the rock.

The potential of the rock to generate acid is classified according to a screening method utilising the NNP, percentage S as sulphide and the ANP:AGP ratio as follows:

- Rock material with an NNP less than zero kg $CaCO_3$ per ton will theoretically have a nett potential to produce acidic leachate. Rock material with an NNP higher than zero kg $CaCO_3$ per ton will theoretically have a net potential to neutralise acidic leachate. However, research shows that -20 kg $CaCO_3$ per ton to 20 kg $CaCO_3$ per ton is defined as an area of uncertainty in determining net acid generation or neutralisation potential. Therefore, rock material with an NNP above this value is considered to reduce acid. Rock material with an NNP below this range is considered to be likely to reduce acid.

- The ANP:AGP ratio can also be used to classify rock material as acid generating or –reducing with the method described by Price (1997) in *Table 2*.

Table 2: Screening method for classifying the acid generation potential of rock material (Price, 1997).

Potential for Acid Generation	NP:AP screening criteria	Comments
Rock Type I. Likely Acid Generating.	< 1:1	Likely acid generating.
Rock Type II. Possibly Acid Generating.	1:1 – 2:1	Possibly acid generating if ANP is insufficiently reactive or is depleted at a faster rate than sulphides.
Rock Type III. Low Potential for Acid Generation.	2:1 – 4:1	Not potentially acid generating unless significant preferential exposure of sulphides along fracture planes, or extremely reactive sulphides in combination with insufficient reactive ANP.
Rock Type IV. No Potential for Acid Generation.	>4:1	No further acid testing required unless materials are to be used as a source of alkalinity.

2.4.4 Inductively Coupled Plasma Analyses

Inductively coupled plasma optical emission spectrometry (ICP-OES) and -mass spectroscopy (ICP-MS) are used for analysing water samples for heavy metal and trace element concentrations, respectively. These analyses may be used to obtain concentrations of contaminants produced in acid leach tests as well as contaminants present in groundwater samples obtained from field work conducted around TSFs. Therefore the concentrations and subsequent activities of contaminants liberated from tailings material become evident and may be used in calculations pertaining to their transport and attenuation.

2.4.5 Permeameter Tests

Permeameter tests provide hydraulic conductivities and intrinsic permeabilities of the tailings material. This is a critical factor in determining flow velocities of contaminants produced by TSFs and how rapidly these contaminants may reach natural systems. Permeameter tests may be of falling- or constant head nature. The tests are performed by percolating a fluid, normally water, through a column of material and measuring the loss of head per unit time in falling head tests. In constant head tests, the amount of fluid added continuously to maintain a constant head per unit time is measured. However, for very fine, silt-sized particles such as tailings material, a falling head permeameter test is preferred (Craig, 2004).

2.4.6 Pumping Tests

Pumping tests are performed to estimate the hydraulic properties of an aquifer such as hydraulic conductivity, transmissivity and storativity. This is done by pumping a well that has been developed in the aquifer, which causes a subsequent stress by changing the hydraulic head in the said well.

This hydraulic head is measured by means of a dipmeter or data logger from the top of the well casing while pumping the well. This, subsequently, also gives the change in head over time which is termed the drawdown and is illustrated in *Figure 14* (Weight, 2008). A pumping test therefore has three phases, *viz*. planning, which includes a desk study and gathering of information with regards to previous test work, geology, pumping rates and any other information; data acquisition, which includes the actual pumping of the well and field measurements of waterlevels as mentioned; and data analysis, which entails the interpretation of the acquired data by using different analytical methods such as that of Theis (SANS, 2003).

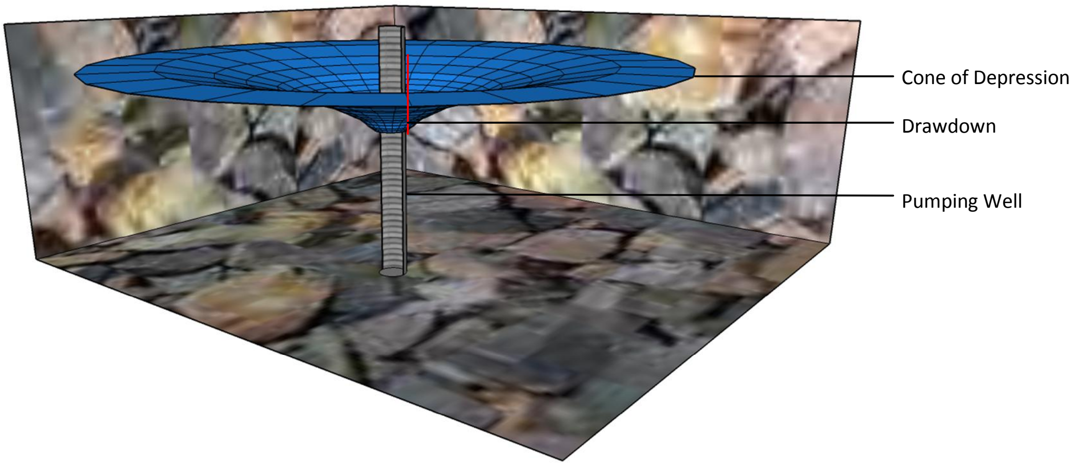

Figure 14: Schematic representation of a cone of depression and subsequent drawdown caused by a pumped well.

Different types of pumping tests exist *viz.* step-drawdown tests, which measure the performance of a well; and constant discharge tests, which measure the hydraulic properties of the aquifer (SANS, 2003). However, only constant discharge tests will be addressed in this study as the well tested is intended as a monitoring well and will be used to determine the hydraulic properties of the aquifer as well as boundary conditions to groundwater flow. These tests, performed over extended periods, yield information about the hydraulic conductivity and transmissivity of the aquifer by extending the cone of depression much further, which gives a long term estimate of the flow through the lithological unit/s (Dippenaar, 2008).

Interpretation of the acquired data can be done using several different methods. The earliest of these being developed by Theis in the 1930's (Weight, 2008). However, these methods must be applied with caution *viz.* the Theis method assumes the following as paraphrased from Weight (2008):

- No edge effects (aquifer is of infinite areal extent)
- Uniform thickness (pumping well fully penetrates and receives water from the full thickness of the aquifer)
- Constant heat source (constant pumping rate)
- Homogeneous and isotropic (aquifer is uniform in character and the hydraulic conductivity is the same in all directions)
- No sources or sinks (water is discharged instantaneously from storage and not from external sources by either adding or removing water).

Additional assumptions inherent to the Theis equations are:

- Pumping well is 100% efficient
- Laminar (Darcian) flow prevails throughout the well and aquifer.

These assumptions are almost never true in reality due to the complexity of geological features in nature with influences from rivers, streams, confining layers, discontinuities, fault- and shear zones, dykes, constructed barriers and the like (Weight, 2008).

These assumptions are used, almost universally, for different pumping test data analysis methods. However, these methods do provide an estimate of the hydraulic properties of an aquifer.

For fractured rock aquifers, such as the one that will be investigated in this study, a useful method is that of Moench developed and published in 1984. Moench developed a method which extends the normal transient block-to-fracture flow double porosity model by adding a fracture skin effect attributed to mineralisation in the said fracture. Moench (1984) found that if this mineralised fracture skin is of sufficient thickness, the flow from blocks to fractures becomes a pseudo steady-state process regulated by the hydraulic conductivity of the fracture skin and the applicability of the pseudo steady- state double porosity model becomes more plausible. An important finding by Moench (1984) is that at early time on a semi-logarithmic, time-drawdown plot, the early time curve indicates well bore storage with the flatter middle time section indicating fracture dewatering and a sharper gradient late time curve indicating matrix block dewatering. Van Tonder *et al*. (2002) found that changes in the slope of the semi-logarithmic curve might also indicate no-flow boundaries present by doubling (single no-flow boundary) or quadrupling (double no-flow boundary) of the slope.

3. STUDY AREA

The Tailings Storage Facility investigated in this study is located in the north of Mpumalanga Province, South Africa, on the Rustenburg Layered Suite of the Bushveld Igneous Complex, as illustrated in *Figure 15*.

The TSF is located at an undisclosed mine on the eastern limb of the BIC between Steelpoort and Mashishing (Lydenburg) in Mpumalanga.

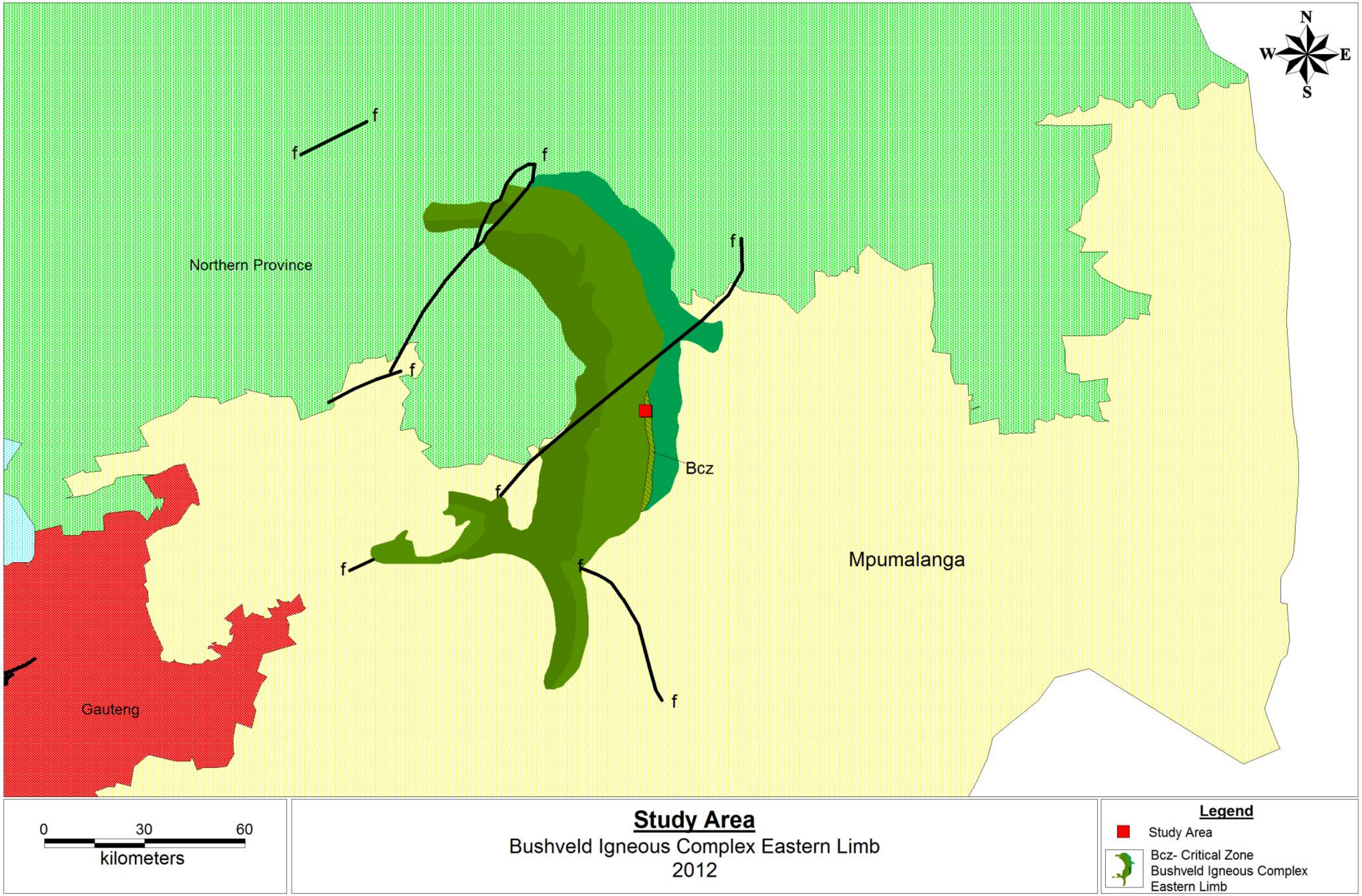

Figure 15: Study area located on critical zone lithologies of the eastern limb of the Bushveld Igneous Complex

3.1 Tailings Storage Facility

The Tailings Storage Facility under investigation is located in the north of Mpumalanga Province. UG2 and Merensky Reef lithologies from the eastern limb of the Bushveld Igneous Complex are generally mined in this area. The material present in the TSF is graded at -86 µm and is of a mafic to ultramafic nature. Therefore, metal content is high, specifically Fe and Mg, with salts precipitating on surface due to chemical reactions with acidic permeating fluids. This can be observed in *Figure 15*.

The mine where the investigated TSF is situated commenced full operation in 2008, three years from the initiation of the project phase. Currently, only the UG2 reef is being mined, producing the mafic minerals in the TSF. The Tailings Storage Facility is divided into 3 terraces. Sampling positions TAH01 and TAH03 are in the upper and lower terraces respectively, representing the second oldest and oldest cycles of tailings disposal. To ensure structural stability of the upper terrace, a second terrace was created in which sampling position TAH02 is situated, which represents the youngest cycle of tailings disposal. The TPH samples were collected from the upper terrace. It is assumed that all precious metals are removed from the processed ore.

3.2 Climate

As paraphrased from Stimmie *et al*. (2001), rainfall in the Steelpoort basin and subsequently in the Steelpoort area occurs predominantly in the summer months between October and March. January generally has the highest amount of rainfall. Average annual rainfall in the area is between 630 mm and 1000 mm, which is generally superseded by evapotranspiration figures. Thunderstorms are common in the Steelpoort basin with a low infiltration rate of soil in mountainous areas.

Rainfall data obtained from the South African Weather Service representing rainfall from the last decade partially supports these figures with annual rainfall reaching 643.2 mm and 663.6 mm in 2001 and 2010 respectively. This is illustrated by *Figure 17* and also supports the findings of Stimmie *et al*. (2001), indicating that rainfall predominantly occurs between October and April.

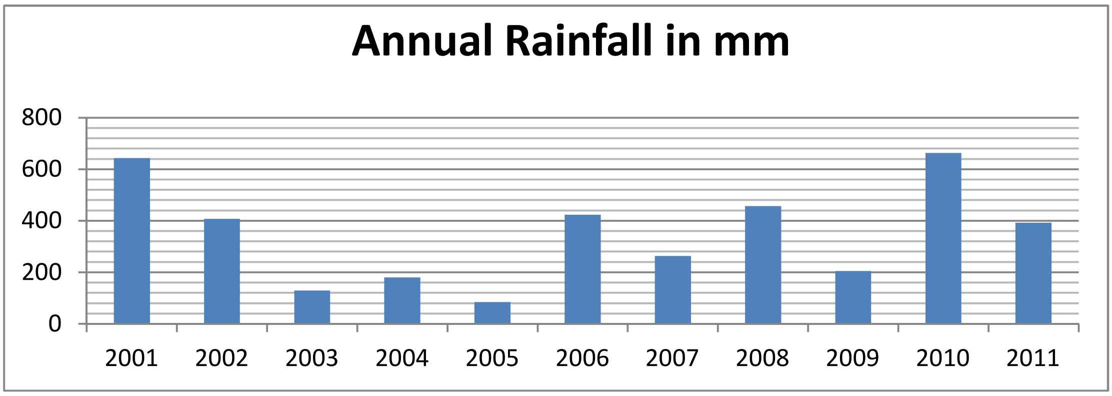

Figure 16: Annual rainfall in mm from 2001 to 2011, in the Steelpoort catchment, as measured by the SAWS weather station near Lydenburg

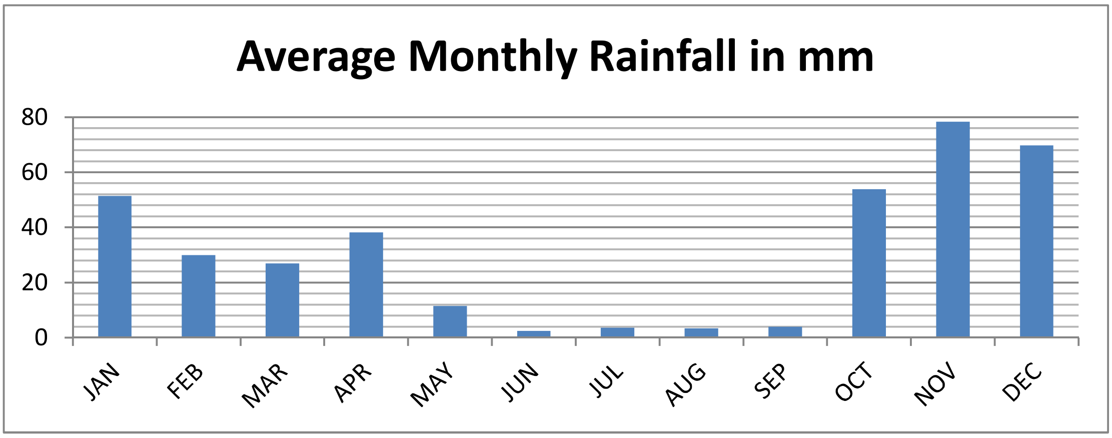

Figure 17: Average monthly rainfall in mm from 2001 to 2011 in the Steelpoort catchment, as measured by the SAWS weather station near Lydenburg

Stimmie et al. (2001) also found that average annual temperatures show little fluctuation. Temperatures range from 19°C to 22°C in summer while temperatures in winter range between 13°C and 19°C. Evaporation rates are also up to 80% higher in summer than in winter.

3.3 Regional Hydrology

As seen in *Figure 18* the topography around the mining area is mountainous with abundant valleys and regional surface flow following the topography towards the northeast via the Steelpoort river. The TSF is bound to by steep topography to the east and west with possible high runoff occurring during precipitation events. The Steelpoort river is the closest perennial surface water body to the tailings.

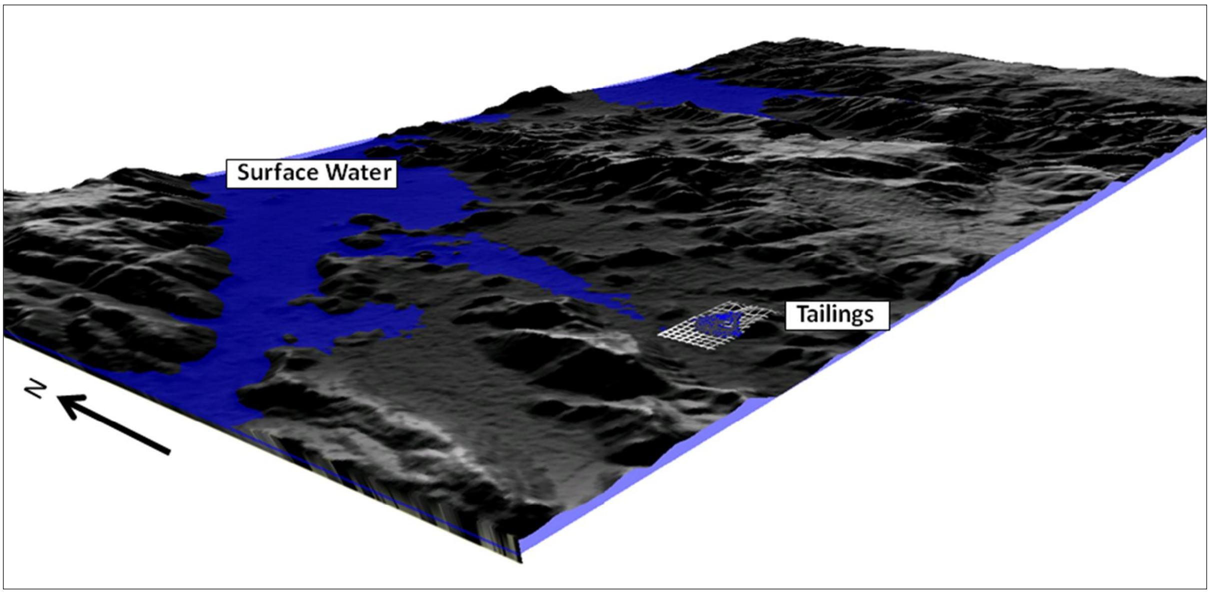

Figure 18: Simulated flooding indicating surface drainage to the northeast

Based on the data sourced from DWAF's GRDM3 database, the tailings facility falls within the B41G quaternary catchment within the Olifants Water Management Area. The catchments eco status category can be classified as A which is pristine. A summary of the relevant GRDM data is shown in *Table 3*.

Table 3: GRDM Data

GRDM Data	
Quaternary Catchment	B41G
Area	442.1 km^2
Mean Annual Precipitation	650mm/a
Mean Annual Run-Off	66mm/a
Base Flow	17mm/a
Population	0 Count
General Authorisation	$0m^3/ha/a$
Present Eco Status	A
Recharge	45.91mm/a
Current Usage	$1.66m^3/a$
Exploitation Potential	3 m^3/a
Average Depth to Groundwater	17.7mbgl

3.4 Regional Geology

The TSF under investigation is located on Critical Zone lithologies of the Bushveld Igneous Complex. According to Cawthorn et al. (2006), the Critical Zone consists of layered chromitite, pyroxenite, norite and anorthosite on scales of millimetres to tens of meters. The Critical Zone consists of 3 sub-zones as discussed below, from lower to upper:

3.4.1 Lower Critical Zone

The Lower Critical Zone consists of an 800 m thick sequence of pyroxenite cumulates with chromite disseminated throughout, almost ambiguously (Cawthorn et al., 2006). This sequence also contains an olivine interval as well as seven, distinct chromite seems of varying thickness.

3.4.2 Middle Critical Zone

The Middle Critical Zone marks the boundary between the Upper Critical Zone and Lower Critical Zone in the form of the MG2 chromitite layer where noritic-anorthositic cumulates first occur.

The base of this zone is marked by harzburgite- pyroxenite assemblages, while the upper part represents a different magmatic cyclic unit and includes anorthosite, subsequently changing the lithology (McCandless *et al*., 1999).

3.4.3 Upper Critical Zone

The Upper Critical Zone marks the transition to the famous Merensky Reef in the Main Zone of the Bushveld Igneous Complex. Here, cumulus anorthite is abundantly present along with the UG1 and UG2, as well as UG3 in the case of the eastern limb chromitite seams (Cawthorn *et al*., 2006).

3.4.4 Geological Structures

The TSF under investigation is bounded by the Dwarsriver- and Steelpoort thrust faults to the west and east respectively (South African Geological Map Series, 1986). The Dwarsriver fault is illustrated in *Figure 15* to the north of the study area. The Steelpoort fault, south-east of the study area, was probably active from Transvaal (2060 Ma) to post-Bushveld (2050 Ma) times (Hartzer, 1995). This fault is characterised by medium to high grade metamorphic assemblages, specifically andalusite and cordierite, indicating its compressive, thrust nature, as well as medium to high emplacement temperatures of the Lebowa Granite Suite (Hartzer, 1995). These faults are also preferred pathways for groundwater movement as the aquifer underlying the TSF is of secondary, fractured porosity. Therefore any contamination reaching the aquifer will potentially move by advection, along these secondary structures.

3.5 Conceptual Model

Based on the literature review performed and data obtained from the mine, a conceptual site model was developed to provide a conceptual understanding of the hydrogeological, geochemical and geological characteristics of the tailings-aquifer system (*Figure 19*).

The deposition of the tailings takes place using a jet method where finer tailings are deposited in the tailings dam with coarser tailings being deposited on the bank where the jet is located. Utilising this method, tailings banks are gradually generated over time from the coarser material. This method was used to generate three consecutive tailings terraces for stability of the pile. Keeping this in mind, sampling of the material was equally spaced between the three terraces to intercept the finer material. Samples of the coarser material were collected across the entire profile of the highest tailings bank to obtain representative samples of the entire tailings profile to soil level. This would also give a good indication of the moisture content distribution in the tailings to obtain data for the flow gradient and phreatic surface in the tailings.

Data on the groundwater monitoring system implemented by the mine was also provided. From this data, a generalised hydrogeological profile could be developed and was classified into two aquifer systems *viz.* a shallow, weathered aquifer system and a deeper, fractured rock aquifer system. The data also provided water levels in the monitoring boreholes, which were generally measured at depths within the weathered aquifer.

From the geological maps, it was evident that the Dwarsriver fault was present in a northeast-southwest orientation adjacent to the tailings and was therefore included as an important part of the conceptual model. The geological map also indicated the presence of alluvial sediments adjacent to the Steelpoort river and this was noted as a possible third aquifer system, but less relevant to the study in terms of the localised flow under the tailings facility.

The development of the conceptual model provided a clear conceptual understanding of possible redox conditions and flow directions in the system and aided in the planning of sample and data collection for the development of the geochemical and unsaturated flow models.

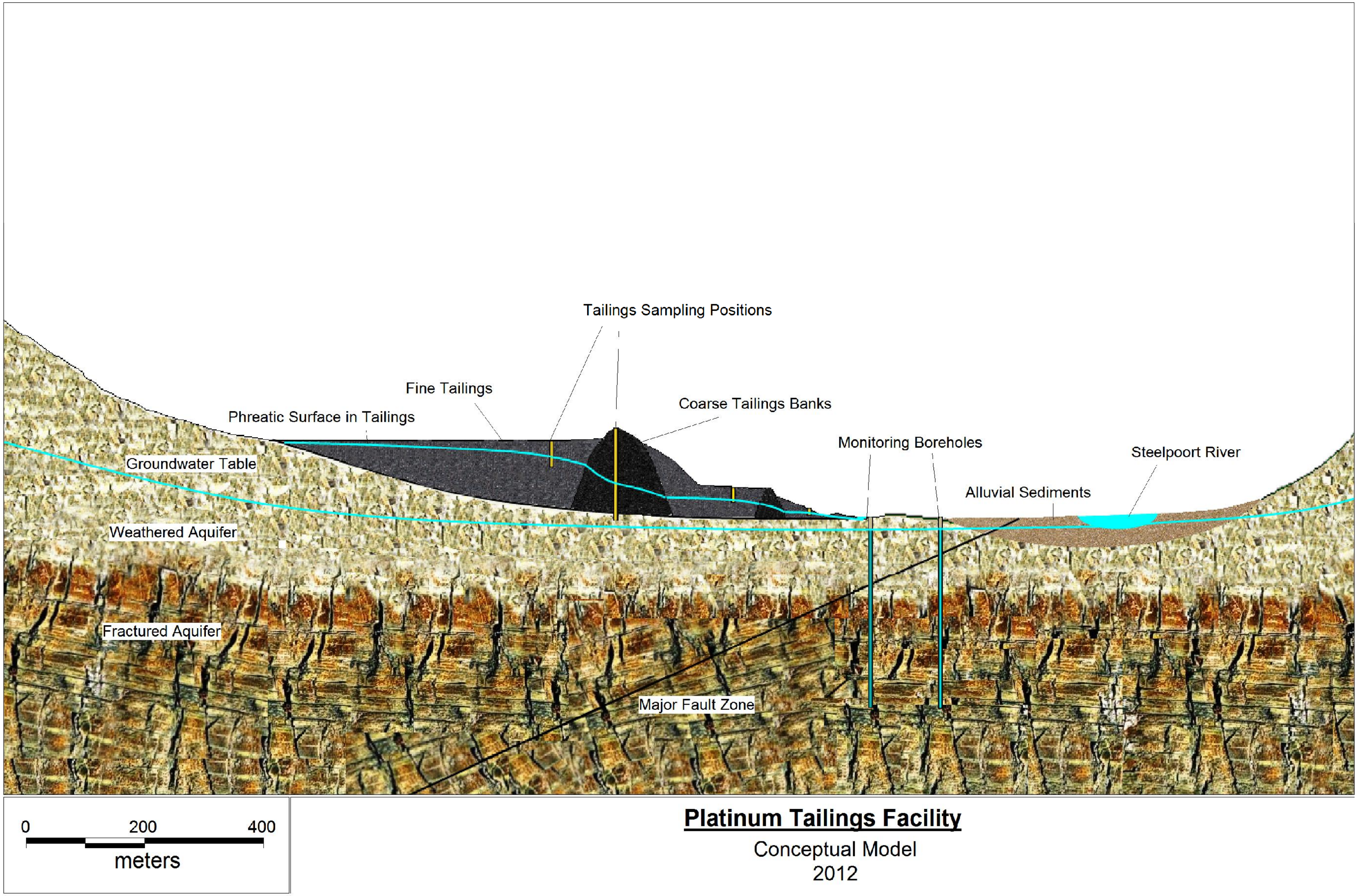

Figure 19: Conceptual Model of the Platinum Tailings Storage Facility