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CYANIDE AND CYANIDE COMPLEXES IN THE GOLD-MINE POLLUTED LAND IN THE EAST AND CENTRAL RAND GOLDFIELDS, SOUTH AFRICA.

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CHAPTER ONE – INTRODUCTION

1.1 The history of mining on the Witwatersrand Basin

The metropolis of Johannesburg, South Africa's largest city and financial centre, owes its origin to the gold-bearing rocks of the Witwatersrand Basin (Figure 1.1). The basin-roughly oval in shape, approximately 350 km north east to south west direction and stretching over 150 km across-host seven major goldfields.

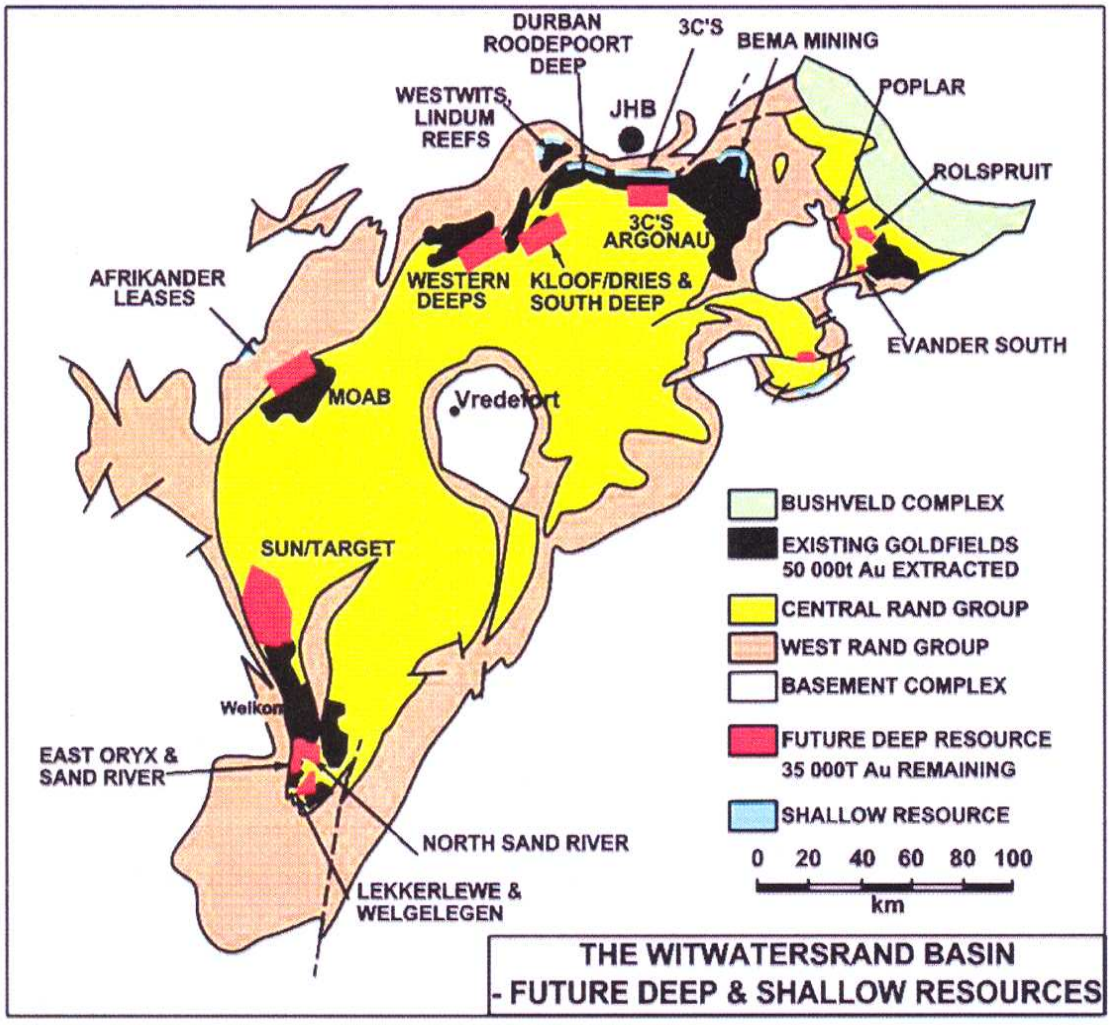


Figure 1.1 The Witwatersrand basin (Viljoen and Reimold, 1999)

The gold-bearing conglomerate mined in the Witwatersrand Basin has a typical mineralogical composition of (Feather and Koen, 1975):

- Quartz (70-90%);
- Phyllosilicates (10-30%), consisting mainly of sericite, $KAl_2(AlSi_3O_{10})(OH)_2$;
- Accessory and minor minerals (1-5%).

Some 70 different ore minerals have been identified in the conglomerates, the most abundant of which, after pyrite, are uranite (UO_2), brannerite (UTi_2O_6), arsenopyrite (FeAsS), cobaltite (CoAsS), galena (PbS), pyrrhotite (FeS), gerdofite (NiAsS) and chromite ($FeCr_2O_4$).

Amalgamation

Amalgamation was the principal gold recovery method used in South African gold mines at the start of mining in 1886. Crude amalgamation is still practiced by some artisanal gold miners in South Africa, mainly in the Mpumalanga Province. Unfortunately the method is in widespread use in some African countries (Sudan, Tanzania, D.R. Congo, Zimbabwe), with devastating consequences for human health and the environment as mercury is released into rivers during processing (Global mercury Project, 2007).

In large-scale commercial applications of amalgamation, ore was crushed and ground in stamp mills, and later in tube mills which represented a significant technological improvement. The crushed ore, as fine as talcum powder, was hydrated to form a viscous pulp that was passed over copper plates (4.57 meters long by 1.52 meters wide, 18% slope) coated on their upper surface with mercury. By virtue of its high relative density, the gold sank through the pulp to contact with the mercury and converted into amalgam. This amalgam (a solution of gold in mercury that took the form of a thick paste) was scraped off the plates, and retorted to yield a gold sponge.

Despite regular scraping, hard layers of gold amalgam accumulated on the plates. These were periodically removed, and the mercury-gold amalgam scraped off and distilled to recover the gold. The tailings were transported to dumps near the extraction plant, producing the sand dumps (Crown Gold Recovery, 2003).

However, the introduction of the tube mill forced a move away from amalgamation since the slurry was coarser and less suitable to such treatment. Amalgamation was still retained after the introduction of cyanidation in 1915 in SA because it allowed for the recovery of as much gold as possible at an early stage in processing.

With mining operations becoming deeper and more pyrite being encountered, the mercury amalgamation method became less efficient (mercury reacts with sulphur, making it less selective for gold). Cyanidation became an extraction method of choice.

Cyanidation

Two methods are currently employed for preparation of tailings for the recovery of gold:

Front-end loading for sand dumps and monitoring spray or water jet spray for slimes dams.

The Front-end loader dumps the sand tailings onto a conveyer belt from where the sand is passed over a vibrating panel screen where water is added. The screen's undersize pulp is pumped to the pulp receiver tank to blend with slime. Slimes are reclaimed by means of a monitoring or hydraulically with the slurry flowing from the dump into a launder. The launder discharges the slime into a sump where it is pumped out by a vertical spindle pump and discharged onto a panel screen. The panel screen's undersize pulp is pumped to the pulp receiver tank to blend with the sand pulp. At the treatment plant, lime is added to the pulp to keep the pH above 10.

The pulp is then treated with a diluted solution (about 0.01 - 0.03%) of KCN or NaCN, plus air to oxidize the mixture. Currently, CaCN (about 170 ppm) has been most widely used since it is cheaper (Crown Gold recovery, 2003). The MacArthur-Forrest process or cyanidation, is a metallurgical method used to separate gold and other metals from its ore. This process required finer milling and the tailings are piped to disposal sites called slimes dams (see process in Figure 1.2). The gold is dissolved according to the Elsner reaction:

$$2Au_{(s)} + 4CN^- + O_{2(g)} + 2H_2O_{(l)} \rightarrow 2Au(CN)_{2(aq)} + 4OH^- \quad \text{(Reaction 1.1)}$$

Today, cyanidation is the most used technique in the world for the processing of gold, but due to cyanide's highly toxic nature the process is very controversial (UNEP/OCHA Environment Unit, March 2000).

The two methods of cyanidation used are Vat Leaching and Heap Leaching. Vat Leaching is used when twenty grams or more of gold are present within a ton of the ore; the ore and solvent are put in large tanks for hours to dissolve the gold. Heap Leaching is employed by the mining company for the low-grade ores, solution of sodium (potassium) cyanide are sprayed to dissolve the gold. Once the ore has been mined, it is finely ground in a large-revolving cylinder containing large steel balls. If the ore contains impurities, it can either be roasted or sent through a flotation process, which will concentrate the ore even further. If the gold particles are too large, the dissolution of the gold would take too long, and as such the larger gold particles are taken out through the flotation process. Once the mineral has been sent through either of these processes, lime (calcium hydroxide) or soda (sodium hydroxide) is added to ensure that the pH is over 10.5 during cyanidation.

At low pH, the toxic HCN gas is formed (Clesceri et al., 1989; Encyclopedia cyanide):

$$CN^- + H^+ \rightarrow HCN \quad \text{(Reaction 1.2)}$$

Although the kinetics of the reaction is slowed by raising the pH, the production of toxic hydrogen cyanide gas is curtailed.

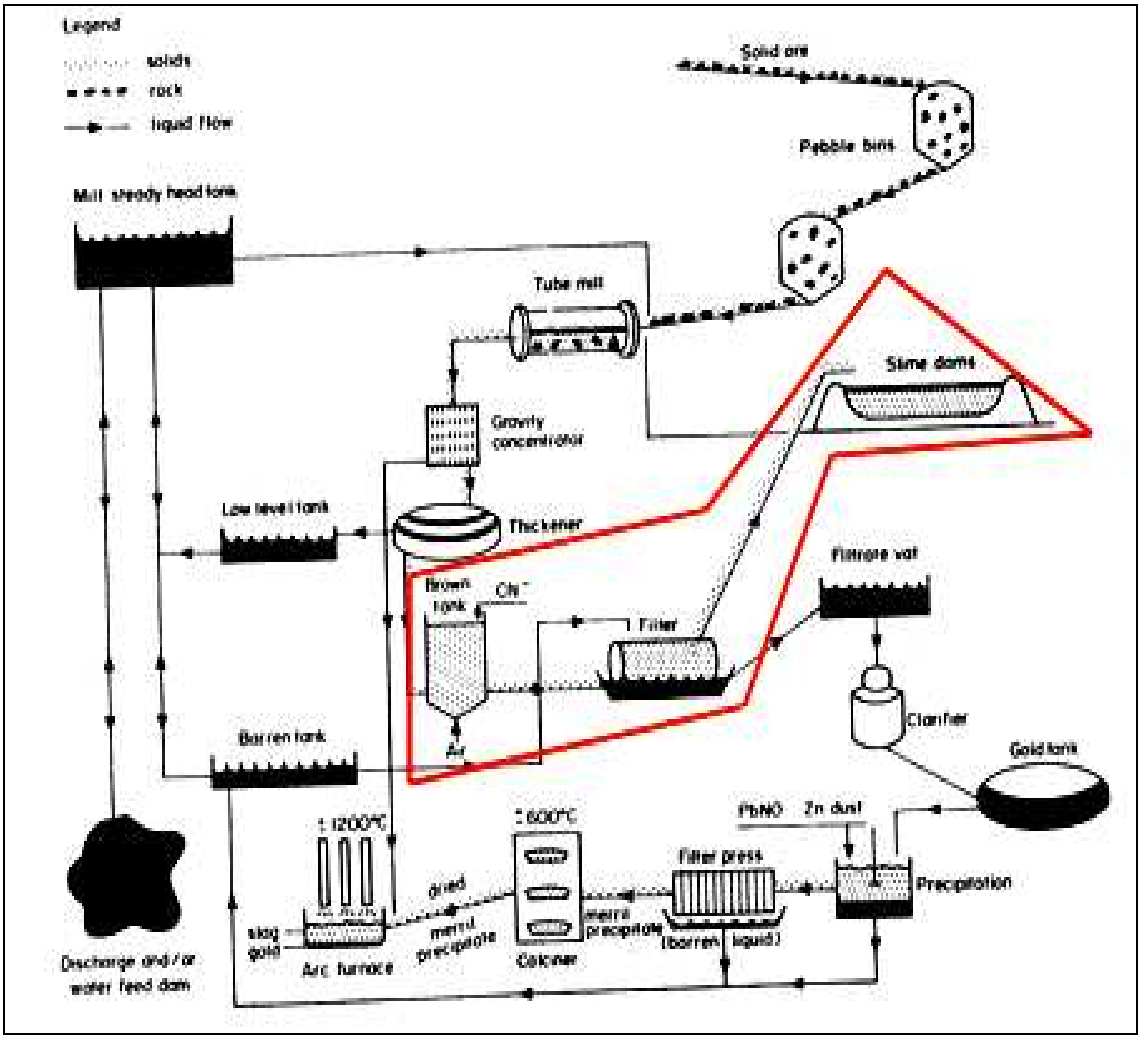


Figure 1.2 Schematic diagram showing gold extraction

The ore is then combined with either sodium cyanide or calcium cyanide. Oxygen must be bubbled up through the pulp for the dissolution of the gold to occur. The cyanide anions release the gold's cations, oxidizing the gold and making a soluble aurocyanide metallic complex, $\underline{NaAu}(CN)_2$.

The resulting gold cyanide complex is very stable (pK=. 56). The solution is allowed to percolate through the heaps. The leach slurry trickles to the bottom, collecting on an impermeable membrane, where it is channelled to reservoirs (International Cyanide Code, 2005; Habashi, 2005; Recent advances in gold metallurgy) The gold in the solution can be recovered by zinc cementation (using the Merrill-Crowe Process, Carbon in Pulp (CIP), Electrowinning, or the Resin in Pulp process). The most widely-used process is the CIP Process because of its cost-effectiveness. The activated carbon is introduced into the solution, where it traps the gold on it. The carbon adsorbs the gold relatively quickly (8-24 hours) (International Cyanide Code, 2005). Elution is the method by which the gold is then recovered from the activated carbon, usually with a hot aqueous caustic cyanide solution. Afterwards, zinc cementation or electrowinning is employed to retrieve all the gold. If the gold contains too many base metals it is taken directly into smelting to be purified to either 99.99% or 99.999% (International Cyanide Code, 2005). Gold absorbed onto charcoal is recovered by elution and submitted to the same hydrometallurgical process. More recently, the carbon-in-pulp process has become an important method to win gold (Stanley, 1988; Lang, 1986; Adamson, 1972).

Activated carbon (Carbon-in-pulp)

The application of activated carbons to gold recovery has its origins in the patented use of wood charcoal for the recovery of gold from chlorination leach liquors in 1880.

The carbon-in pulp (CIP) process, which was developed to its present form in South Africa during the 1970s, is considered to be the most significant advance in gold recovery technology in recent years. By 1995, there were 42 CIP circuits installed in South Africa (Mpephu, 2004).

CIP makes use of the tremendous physical affinity 'activated' carbon has for gold (it can attract 7% of its weight in gold) which it readily attracts to its surface in cyanide solution. The finely ground ore (typically about 75 μm particle size), and the slurry of fine ore and water (the 'pulp') are treated with cyanide in large tanks that are stirred mechanically or by air-agitation.

Activated carbon is used to adsorb the gold directly from the cyanide pulp which flows continually from the first vessel to the last in the series, and the carbon is transferred intermittently by pumping in the opposite (counter current) direction. The gold value of the pulp decreases downstream, and the gold loading on the carbon increases upstream, with the highest value in the first tank.

The CIP process consists of three essential stages: (i) adsorption in which the dissolved gold in the pulp is loaded onto aerated carbon;(ii) elution, in which the gold is removed from the carbon into an alkaline cyanide solution; and (iii) electro-winning, in which the gold is removed by an electrical process from the alkaline cyanide solution and deposited on steel wool electrodes. The carbon is then treated with sulfurique acid to remove contaminants, after which the acid itself is treated. Both are then recirculated into the adsorption-elution circuit. When the leach and absorption circuits are combined, the process is described as carbon-in leach (Figure 1.3).

1.2 Statement of the problem

The use of sodium, potassium or calcium cyanide in the gold mining industry poses a potential environmental threat. Cyanide is a very poisonous substance which may infiltrate water sources or escape into the air. Thus it may be inhaled by human beings, drunk if it gets into the potable water system, or may enter the food chain unobtrusively.

The important environmental problem is the discharge of solid waste at the disposal units that receive wastes from cyanidation operations.

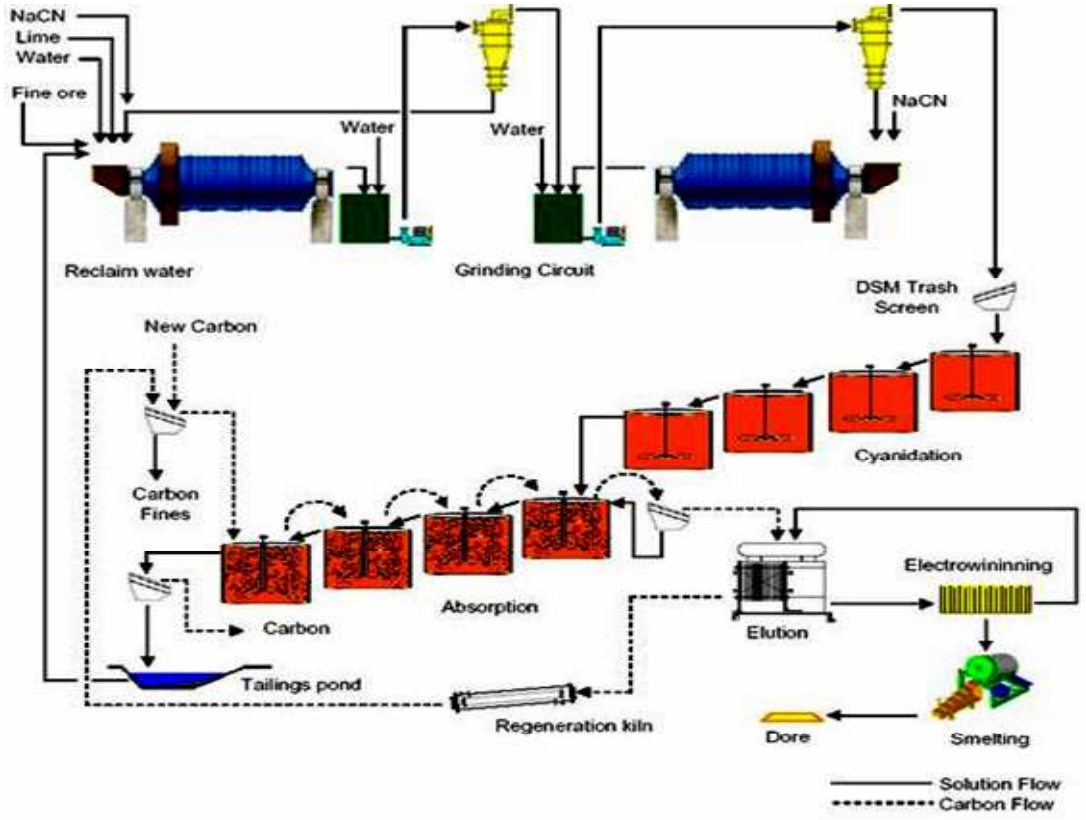


Figure 1.3 Schematic diagram of grinding and Carbon in pulp circuit (http://www.e- goldprospecting.com, 2007).

The existence of cyanide species in effluent is of interest to the environment. If the effluent ponds and dams are not managed properly this could be a recipe for disaster as these species are highly toxic. There is need to ascertain the possible dangers that could be posed by the effluent if it is no treated to reduce the levels of these species available in the waste. It is important to know if there is any degradation or accumulation of various cyanide species with time. In recent years, there has been a growing concern among members of the gold mining industry with regards to cyanide management. The stability of the cyanide present in large volumes in tailing storage facilities, as well as cyanide emissions across leaching operations, are issues of concern with respect to environment impacts, health and

safety issues, respectively. Tailings containing residual amounts of cyanide are generated as wastes. These wastes are typically treated to neutralize or destroy cyanide before disposal in the tailings impoundments because tailings impoundments typically operate as zero discharge units under the clean water act (cyanide heap leach closure, 1993).

Several states are debating between metal-cyanide weak acid dissociable (CN_{WAD}) and cyanide free (CN_{free}) or cyanide total (CN_T), thus, the cyanide species levels in spent ore must be rinsed until effluent reaches 0.2 mg/l CN_{WAD}, 0.2 mg/l CN_{free} and pH 6 – 9. Many states use these levels as guidelines and may issue site-specific variances if a facility is unable to meet these levels. Prior to disposal or abandonment of the spent ore, process contaminated water drained from leached ore must be stabilized at a pH of 6.5 to 9.0, or CN_{WAD} levels are to be reduced to 0.2 mg l^{-1} (E.U. 2006). In South Africa, any effluent solution (including storm water) exiting the Metallurgical Treatment Facility boundary should conform to the limit of Weak acid dissociable cyanide = 0.50 mg l^{-1} (0.0005%) except where the solution is returned to the metallurgical process (Lotz et al., 2000).

Scaling and wash water should not be allowed to accumulate in the area and should be returned to the process as soon as possible at a point where the pH is in excess of 10.5 after proper complexing has occurred (South Africa guideline on cyanide management, 2001). The gold mining in SA doesn't treat tailings prior to discharge (Thrip, personal communication, August, 2008), with the assumption that cyanide will decompose within a relatively short period of time. In treatment process, either chemical (INCO, Acidification-Volatilization-Recovery, Hydrogen peroxide) or biological treatment are utilised to convert cyanide into less toxic compounds (SCN^-, CNO^-, NH_4^+). In many cases, treatment has not effectively lowered cyanide to the required levels. It should also be noted that the effluent limitation guideline was developed for mills that use cyanide and predates the widespread use of heap leaching to recover gold, however, the zero discharge standards have been universally applied to heap leach operations.

Another significant concern is the generation of acid drainage, often caused by the presence of sulphides that break down to form sulphuric acid. Pyrite is often an important element of the matrix of the conglomerate and hosts most of the gold in very fine state. It is discharged as a constituent of the tailings during mining and metallurgical processes of extracting gold. On the surface of the tailings dams, oxidation processes of the residual sulphide minerals, especially pyrite, result in the generation of acid mine drainage (AMD) and the subsequent release of heavy metals and metalloids. The oxidation of pyrite in the tailings can be described by the reaction (Singer and Stumm, 1970):

$$FeS_{2(s)} + 7/2O_2 + H_2O \rightarrow 2SO_4^{2-} + Fe^{2+} + 2H^+ \qquad \text{(Reaction 1.3)}$$

The buffering capacity of the tailings is usually insufficient to neutralize the acid, and acidification occurs. Oxidation reactions involving other minor minerals release dissolved uranium, arsenic, copper, nickel, lead, cobalt and zinc. The products of these reactions are transported downwards by percolating acidified water into the underlying aquifers (Blowes *et al*., 1998). Upon discharge to nearby surface water bodies, ferrous iron is oxidised to ferric iron (Reaction 1.4). The stability of ferric iron depends on the pH.

At pH lower than 3.5, the ferric iron continues in solution and acts as another oxidising agent of pyrite (Reaction 1.5).

However, at pH greater than 3.5, the ferric iron precipitates as a ferric hydroxide (Reaction.1.6) (Singer and Stumm, 1970; Stumm and Morgan, 1996):

$$Fe^{2+} + 1/4O_2 + H^+ \rightarrow Fe^{3+} + 1/2H_2O \qquad \text{(Reaction 1.4)}$$

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \qquad \text{(Reaction 1.5)}$$

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+ \qquad \text{(Reaction 1.6)}$$

The precipitation of $Fe(OH)_3$ is acid generating and buffers the pH (between 2.5 and 3.5) of the AMD (Espana et al., 2005). This process has a two opposing consequences: (1) the acidity increases the mobility and toxicity of metals, and (2) the ferric hydroxide precipitation produces co-precipitation and adsorption of metals in solution. The latter is considered the more prevalent process (Webster et al., 1994; McGregor et al., 1998).

Through mine drainage, this above mentioned pollutants (including free and complexes cyanides) can leach and therefore cause contamination of the land, surface and groundwater. An improperly designed tailings impoundment could result in dam failure or a breach in the liner. The release of cyanide solution and mill tailings from a tailings impoundment may occur during heavy storms unless the impoundments are designed to hold the additional volume. Further, these constituents may degrade surface and groundwater, soil, and/or air quality during and after the cyanide leaching process. Birds and other animals that come into contact with the tailings impoundment and holding ponds may be also exposed to the risk. The major contamination threat during and after cyanide leaching is the release of cyanide and/or soluble metal bearing solution into the surface and groundwater.

Air pollution

The advent of AMD means that free cyanide can reset according to Reaction 1.2. ($CN^- + H^+ \rightarrow HCN$) to form the volatile and toxic HCN. The low pH regimes tend to destabilise metal-cyanide complexes thus liberating more free CN^- and consequently HCN.

Laboratory data indicate that free CN^- is liberated upon photodegradation of dissolved complex cyanide (Meussen et al., 1992). During daytime photodegradation might occur at the surface of waterlogged or moist, soils and in puddles with stagnant water.

1.3 Study area and distribution of mining-related pollution in the Witwatersrand Goldfields

The geology of the Central Rand has been well documented (Mellor, 1917; Pretorius, 1964). Over the century of active mining, some 1.3 billion tonnes of ore were extracted (Handley, 2004), and the tailings deposited in dumps along the outcrop zone (Figure 1.4).

The climate of the region is temperate, with a short mild winter and a warm to hot summer. The rainfall occurs predominantly in summer (October to March) as intense thunderstorms accounting for most of the rainfall. Annual precipitation ranges from 600 to 732 mm. The average annual temperature is about 16^{o}C. Annual potential evaporation is about 1700 mm (Weather Bureau, 1998).

The area is characterised by a well defined drainage system including streams and wetlands which form the tributaries of the upper Klip River, in turn a tributary of the Vaal River, from which Johannesburg obtains the bulk of its water supply. The streams include the Klipspruit, Natalspruit and Russel streams. Many lakes such as the New Canada Dam, Wemmer Pan and Rosherville Dam were constructed in the early years of mining to supply water to the mines (Figure 1.4). Extensive wetlands are developed along the course of the Klip River, especially where it flows on dolomite of the Transvaal Supergroup. Smaller wetlands are also developed along tributaries of the Klip River. The streams in the study area are of importance since they drain the reef outcrop, areas of tailings dumps, light industrial areas and old mine workings, which serve as sources of pollution.

Previous studies (Tutu, 2005) develop a conceptual model of the generation and dispersal of mining-related pollution in the study region. The overall model is summarised in Figure 1.5, and involves several sub-components (dumps, streams, wetlands and lakes) that will be discussed separately.

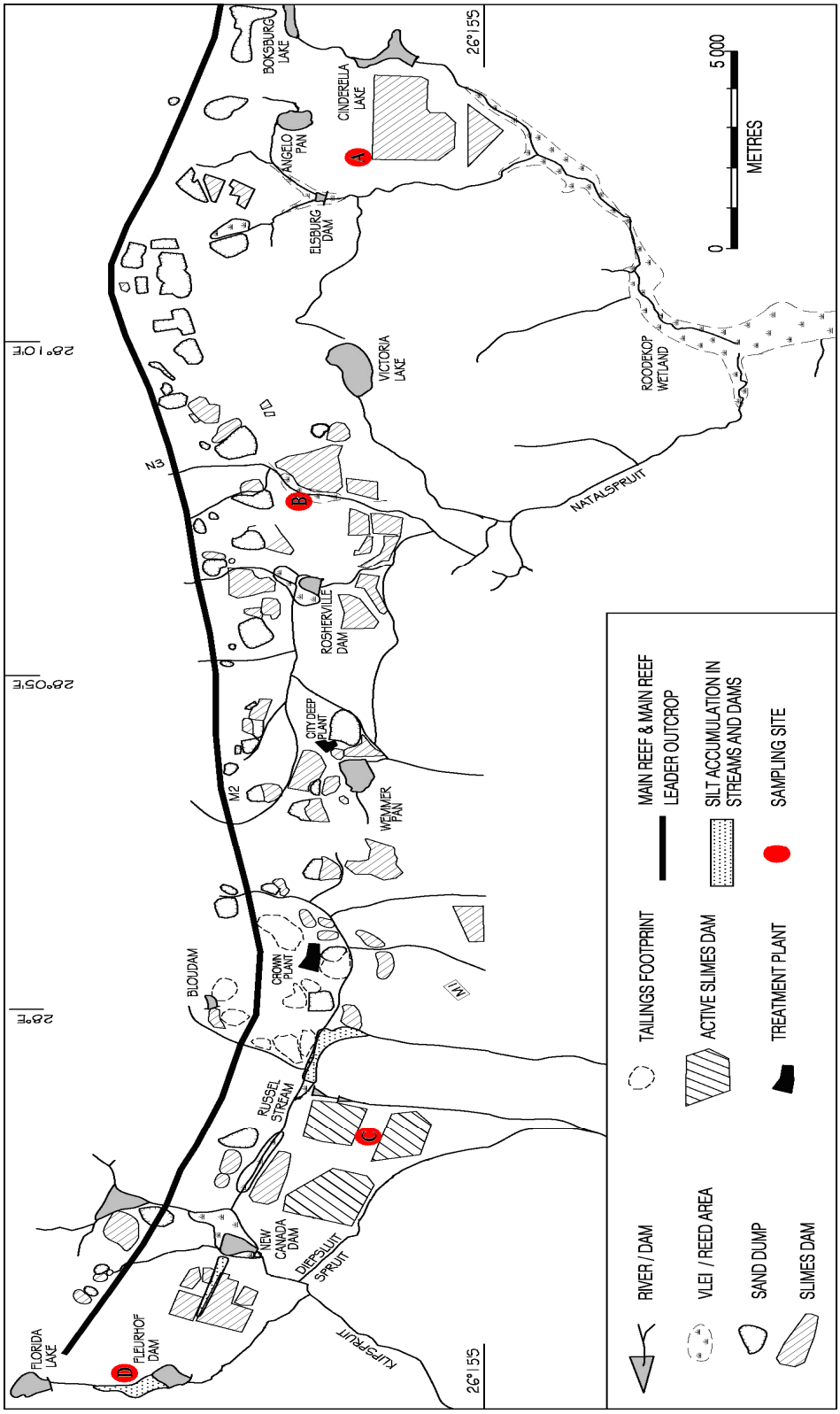


Figure 1.4 Map of tailings dumps and drainage system in the Central Rand

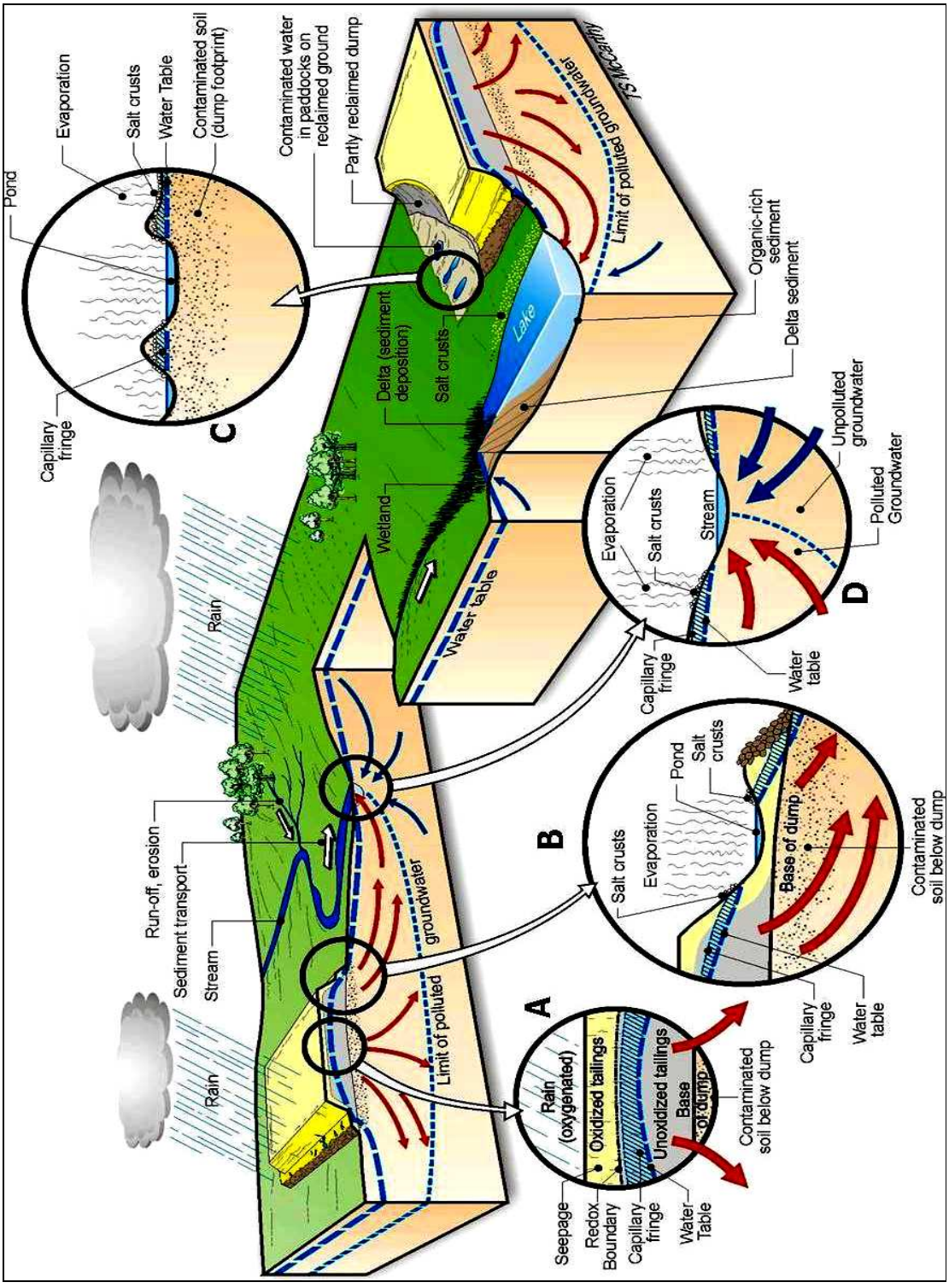


Figure 1.5 Generic model for water pollution and distribution pathways (Courtesy of T.S.M. McCarthy, 2005)

a) Dumps

In the areas surrounding the Witwatersrand Goldfields, tailings dumps are the main source of pollution since they are generally composed of elevated proportions of pyrite and other minor metallic sulphides. Oxygenated water percolating down the dump produces a visible oxidation front (Figure 1.6, inset A; Figure 1.7a).



Figure 1.6 Picture of a profile through tailings dump (Tutu, 2005)



Figure 1.7a Efflorescence along a capillary fringe at Brakpan dump (Photograph by Tutu, 2007)

The elevated water table within the dump or its associated capillary fringe may impinge on the sides or surface of the dump, where evaporation takes place forming efflorescent crusts of metal sulphates (Figure 1.7b).



Figure 1.7b Efflorescence along a solution trench at Crown Mines (Nasrec dump) (Photograph by Tutu, 2005)

The colour of these crusts varies and depends on the composition of the dissolved salt load in the groundwater. White crusts, dominated by gypsum (derived from partial neutralisation of AMD by lime), are the most common, but colours ranging from pale pink (Co, Mn) to various shades of green (Ni, Fe), and even yellow (U) have been observed (Tutu, 2005; Mphephu, 2004; Winde et al., 2004).

Paddocks and solution frenches are usually constructed around the base of dumps to control erosion (Figure 1.7b).

Dumps have or are presently being removed for retreatment, and during this process, the underlying soil is limed to reduce the acidity of the footprint and immobilise heavy metals. Paddocks are usually constructed on the cleared site to minimize run-off of rainwater.

b) Streams

Many of the streams passing through the mining areas of the Witwatersrand are perennial and derive their base flow from groundwater seepage. The stream samples include streams flowing through tailings footprints and reprocessing areas, distributaries and natural streams near or distal to pollution sources. In the vicinity of dumps, polluted groundwater emerges at surface and contributes to stream flow (Jones *et al*., 1988; Naicker *et al*., 2003; Winde and Sandham, 2004; Figure 1.4, inset D). The capillary fringe above the water table impinges on the land surface on the stream banks and evaporation of the groundwater results in efflorescent crusts (Naicker *et al*., 2003; Figure 1.7c).



Figure 1.7c Efflorescence along a capillary fringe at the Natalspruit stream (red arrow showing crusts) (Photograph by Tutu, 2005)

c) Wetlands

Wetlands are areas that have soils that are saturated or nearly saturated with water and have high organic content. They generally have perennial surface water but

may also be seasonal (Mitsch and Gossenlink, 1986). Wetlands are common along the streams and rivers in the mining areas, and are vegetated mainly by *Phragmites* and *Typha* spp. reeds. Some have thick (<4 m) deposits of peat consisting of partly decomposed plant material.



Figure 1.7d An expanse of a wetland vegetated by *Phragmites* ssp. Reeds at Fleurhof Dam (Photograph by Tutu, 2005)

d) Lakes

The mining areas contain several lakes, most of which were constructed during the early years of mining to trap summer rainfall for use on the mines during the dry winter months. Several of these lakes are used for recreational purposes. The lakes trap sediment (including tailings) eroded from the upstream catchments, and several of the oldest lakes have been silted. It has recently been discovered that the lake sediments often contain elevated gold concentrations, and some have been mined (personal communication Kleynhans, Crown Recoveries; Ndasi, 2004). Most lakes in the mining areas have extensive wetlands around the mouths of inlet streams, and inflowing water is exposed to a wetland environment prior to discharge into lakes.

The study was conducted at the Sites shown in Figure 1.4. Site A is a representative tailing dam undergoing rehabilitation; Site B is a stream near a tailings reprocessing site; Site C is a representative active slimes dam and Site D is a representative wetland and dam.
The details and further description of these sites are made in Chapter 6.

CHAPTER TWO – LITERATURE REVIEW

As mentioned in chapter 1, one of the pollutants of concern emanating from tailings dumps in the study area is cyanide. The species of cyanide determine its environmental fate, transport and toxicity. Its behaviour in soils and groundwater is governed by many interacting chemical and microbial processes. The following sections provide an overview of the physical-chemical properties and behaviour of cyanide in the environment. The environmental legislation concerning cyanide is discussed and the important aspects concerning its speciation and toxicity are addressed.

2.1 Cyanide

The Swedish chemist Carl Wilhelm Scheele (1782) discovered a flammable, water-soluble acidic gas, later identified as HCN, when he heated the cyanide-bearing Solid Prussian Blue in aqueous sulphuric acid solution (Young, 2001; Bunce et al., 2004). The name given to the evolved gas was Prussian Blue Acid, also referred to as prussic acid or blue acid (Young, 2001). This same gas caused Scheele's death four years later (Scheele, 1786).
For many, the word cyanide evokes emotions of death. In the 20th century, HCN gas was used in the gas chambers in the World War II holocaust, in prison for execution of criminals with death sentences, and also as a chemical warfare agent.

In 1811, Gay Lussac determined the composition of the gas consisting of one molecule each of carbon, hydrogen and nitrogen (Bunce et al., 2004).
In 1953, Stanley Miller demonstrated that HCN and certain organic compounds including aldehydes and amino acids can be formed from the constituents of the prebiotic earth atmosphere, that is, methane, hydrogen and water (Miller and Orgel, 1953).

2.2 Sources of cyanide

Cyanide is produced naturally in the environment by various bacteria, algae, fungi and numerous species of plants including beans, fruits, vegetables and roots.
Today, cyanogenic compounds can be found in more than 3000 species of plants, animals, microbes and fungi (Ward and Lebeau, 1962; Stevens and Strobel, 1968).
Cyanide is produced by plants as a defence against herbivores. All plants produce cyanides, however in most cases, cyanide is present in extremely small quantities. A level of 10 mg HCN per kg of plant is the minimum amount for a plant to be considered cyanogenic. Cyanogens are glycosides of a sugar and a cyanide containing aglycone. Cyanogenic glycosides can be hydrolyzed by enzymatic action with the release of hydrogen cyanide (HCN). When plant tissues are damaged, due to herbivores, trampling, intense heat or frost, the following reaction takes place (Cheeke, 1998; Salkowski and Penny, 1994):

Cyanogenic glycosides --------> sugar + aglycone (enzyme: glycosidase)
Aglycone -------> HCN + aldehyde or ketone (enzyme: hydroxylnitrile lyase)

The natural distribution of cyanide occurring in the environment is (Dzombak, 2006):

Soy protein products:	0.07 – 0.3 $\mu g\ g^{-1}$
Cereal grain:	0.001 – 0.45 $\mu g\ g^{-1}$
Apricot:	0.0 – 4.0 $\mu g\ g^{-1}$

Cherry pits: 0.0 – 4.0 μg g^{-1}

Sorghum leaves: 192 – 1250 μg g^{-1}

Cassava roots: 86 – 1458 μg g^{-1}

Incomplete combustion during forest fires is believed to be a major environmental source of cyanide, and incomplete combustion of substances containing nylon produce cyanide through depolymerization (Li et al., 2000). Cyanide is also produced incidentally in significant quantities in a number of industrial processes, including coal coking and gasification, iron, aluminium and steel manufacturing as well as petroleum refining. The principal human made cyanide forms are HCN, NaCN and KCN. However, anthropogenic inputs of cyanide into the environment are greater in amount than natural inputs.

2.3 Uses of cyanide

About three million tons of hydrogen cyanide are produced annually worldwide, of which about 8 % is converted into sodium cyanide and used in the metals industries (mining and metal plating). The remaining 94% of the hydrogen cyanide is used in the production of a wide range of industrial and consumer items. The use of hydrogen cyanide worldwide is shown in Figure 2.1.

Currently, there are about 875 gold and silver operations in the world, of which about 460 utilize cyanide (Dzombak, 2006).

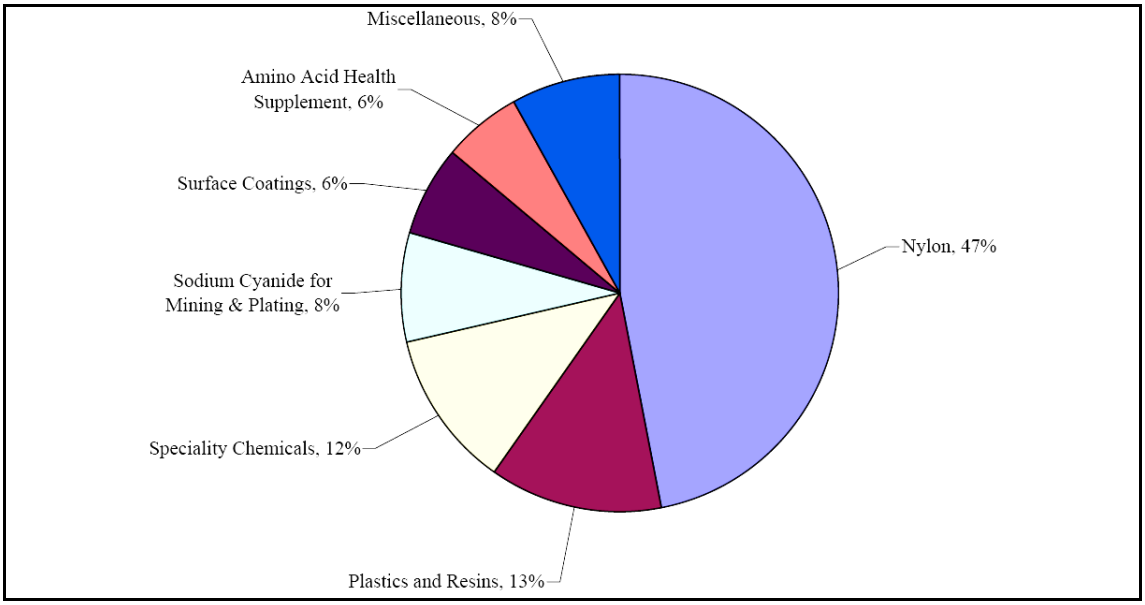


Figure 2.1 Use of hydrogen cyanide (www.cyantists.com, 2008)

2.4 Chemistry of cyanide

Cyanides refer to chemical compounds which contain the cyano group CN, consisting of one carbon atom and one nitrogen atom joined with a triple bond ($C \equiv N$). The most toxic form is the free cyanide anion (CN^-) and hydrogen cyanide $HCN_{(g)}$. HCN is a colourless, volatile, extremely poisonous chemical compound whose vapours have a bitter almond odour. It melts at -14°C and boils at 26°C, it is miscible in all proportions with water and ethanol. Its water solution is a weak acid and its solubility in water is high and it decreases with increased temperature and under highly saline conditions.

2.4.1 Physical and chemical forms of cyanide

Cyanide occurs in many different forms in water and soil system. The specific form of cyanide determines the environmental fate and transport of cyanide. The various forms of cyanide are quite different in their reactivity and their toxicity.

Gaseous forms

Three gaseous forms of cyanide are of interest in water and soil system: hydrogen cyanide (HCN), cyanogen chloride (CNCl), and cyanogen bromide (CNBr) (Xie and Hwang, 2000). The cyanogen halides CNCl and CNBr are also colourless gases with high vapour pressures (1230 mmHg and 121 mmHg at 25°C for CNCl and CNBr, respectively). Like hydrogen cyanide gas, CNCl and CNBr are highly toxic to humans if inhaled or absorbed. These are soluble in water, but degrade by hydrolysis very rapidly at high pH. The hydrolysis degradation product is the cyanate ion (CNO^-), which can subsequently hydrolyze to CO_2 and NH_3 at alkaline pH conditions (CDC, 2005; IPCS/INCHEM, 2005).

Aqueous forms

Common aqueous forms of cyanide can be broadly divided into four major classes:

Free cyanide: HCN, CN^-

HCN (aq) is a weak acid and can dissociate into cyanide ion according to the following dissociation reaction (Sharpe, 1976; Smith and Mudder, 1991):

$$HCN\ (aq) \leftrightarrow H^+ + CN^- \quad pKa = 9.24 \text{ at } 25°C \qquad \text{(Reaction 2.1)}$$

Figure 2.2 shows the distribution of HCN and CN^- species as a function of pH for a simple aqueous solution at 25°C.

At pH 9.2; CN^- and HCN are in equilibrium; equal amount of each present.

At pH 11; over 99% of the cyanide remains in solution as CN^-.

At pH 7; over 99% of the cyanide exists as HCN.

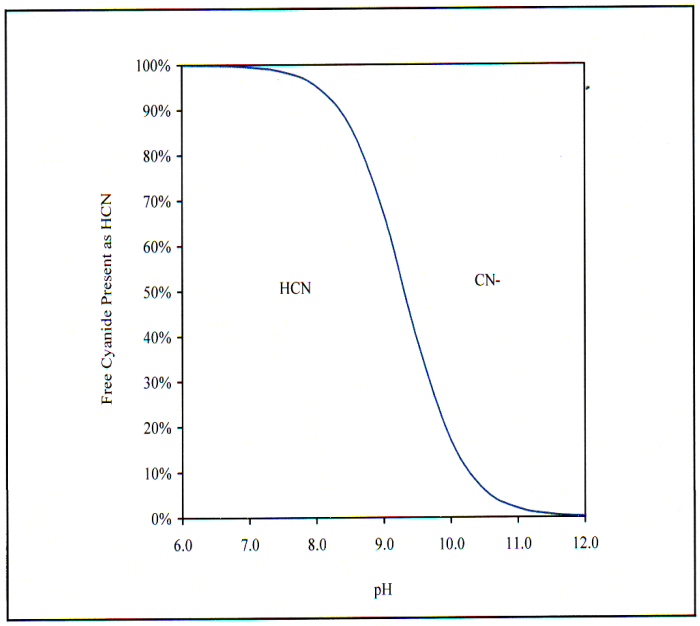


Figure 2.2 Relationship between the cyanide anion (CN^-) and molecular hydrogen cyanide (HCN) as function of pH (25°C) (www.cyantists.com, 2007)

Metal-cyanide complexes: M (CN) $_x^{n-}$

The cyanide anion is a versatile ligand that reacts with many metal cations to form metal-cyanide complexes. These species, which are typically anionic, have a general formula $M(CN)_x^{n-}$, for example $Fe(CN)_6^{4-}$. The stability of metal-cyanide complexes is variable and requires moderate to highly acidic pH conditions in order to dissociate. Metal-cyanide complexes are classified into two categories:

- Weak metal-cyanide complexes ($Cu(CN)_3^{2-}$, $Zn(CN)_4^{2-}$, $Ni(CN)_4^{2-}$, $Hg(CN)_2$, $Cd(CN)_4^{2-}$) dissociate under mildly acidic conditions (pH 4 to 6).
- Strong metal-cyanide complexes include $Pt(CN)_4^{2-}$, $Fe(CN)_6^{4-}$, $Fe(CN)_6^{3-}$, $Au(CN)_2^-$, $Co(CN)_6^{3-}$ which require strong acidic conditions pH < 2 to dissociate.

Cyanate and Thiocyanate (CNO^-, SCN^-).

Free cyanide can be oxidized to form cyanate (CNO^-) or, depending on the pH, its protonated form HOCN (pKa=3.45 at 25°C) (Bard et al., 1985).

$$CN^- + H_2O \rightarrow CNO^- + 2H^+ + 2e^- \quad \text{(Reaction 2.2)}$$

$$HCN + H_2O \rightarrow HCNO + 2H^+ + 2e^- \quad \text{(Reaction 2.3)}$$

Cyanate hydrolyzes fairly rapidly under acidic conditions to carbon dioxide and ammonia (FMC, 2005):

$$CNO^- + 2H_2O \rightarrow CO_2 + NH_3 + OH^- \quad \text{(Reaction 2.4)}$$

Free cyanide can react with various forms of sulphur (S_xS^{2-}, $S_2O_3^{2-}$) to form thiocyanate, which is relatively less toxic than free cyanide.
The reactions of polysulfide and thiosulfate with the cyanide ion are as follows (Luthy and Bruce, 1979; Smith and Mudder, 1991; Zagury et al., 2004):

$$S_xS^{2-} + CN^- \rightarrow S_{x-1}S^{2-} + SCN^- \quad \text{(Reaction 2.5)}$$

$$S_2O_3^{2-} + CN^- \rightarrow SO_2^{3-} + SCN^- \quad \text{(Reaction 2.6)}$$

Organocyanide complexes

Organic cyanide compounds contain functional group that is attached to a carbon atom of the organic molecule via covalent bonding. Common examples include nitriles, such as acetronitrile (CH_3CN) or cyanobenzene (C_6H_5CN), which are used as industrial solvents and as raw materials for making nylon products and pesticides. Other organocyanide compounds of interest include cyanocobalamine, also known as vitamin B_{12} (Evans et al., 1985; Knowles, 1976).

2.4.2 Reactivity of cyanide in water and soil

The reactivity, fate and toxicity of cyanide in water and soil are highly dependent on the chemical speciation. In the environmental systems, wastewaters and wastes, cyanide is usually found in free and complexed forms. Because of reactive electronic arrangement, cyanide anions can readily form metal-cyanide complexes with most metal cations (Dzombak, 2006).

Free cyanide (HCN, CN^-)

HCN formation and dissociation

In aqueous solutions of simple alkali cyanides, the cyanide is present as CN^- and molecular HCN.
The ratio of these forms depends on pH and dissociation constant (see Figure 2.2). In most natural waters, HCN greatly predominate. It is formed in solutions of cyanide by hydrolytic reaction of CN^- in water (Doudoroff, 1976; Flynn and Haslem, 1995; Moran, 1998).

$$CN^- + H_2O \rightarrow HCN + OH^- \qquad \text{(Reaction 2.7)}$$

HCN has a very low boiling point (25.7°C) and is volatile in water under environmental conditions. The equilibrium air-water partitioning of HCN can be described by Henry's law:

$$P_{HCN} = K_{H,\,HCN}\,[HCN]$$

where P_{HCN} is the partial pressure of HCN_{gas}. $K_{H,\,HCN}$ is the Henry's constant.
[HCN] is the equilibrium aqueous phase concentration of HCN.

Free cyanide hydrolysis

Free cyanide can react with molecular water under alkaline conditions and high temperature to yield formate and ammonia (Robuck, 1988; Smith and Mudder, 1991):

$$CN^- + 2H_2O \rightarrow HCOO^- + NH_3 \qquad \text{(Reaction 2.8)}$$

At low pH values, HCN can also be hydrolyzed, yielding formic acid and ammonia:

$$HCN + 2H_2O \rightarrow HCOOH + NH_3 \qquad \text{(Reaction 2.9)}$$

Under acidic conditions the reaction is also very slow.

Free cyanide oxidation

Free cyanide can be oxidized to cyanate CNO^- (Reaction 2.2). The oxidative conversion on CN^- to CNO^- in alkaline chlorination is often exploited for rapid treatment of free cyanide in water. The general reactions for alkaline chlorination are as follows (Palmer, 1988):

$$CN^- + Cl_2 \rightarrow CNCl + Cl^- \qquad \text{(Reaction 2.10)}$$

At alkaline pH, CNCl hydrolyses in CNO^- cyanate

$$CNCl + 2NaOH \rightarrow CNO^- + 2Na^+ + Cl^- + H_2O \qquad \text{(Reaction 2.11)}$$

CNO^- can be oxidized with chlorine at a nearly neutral pH to CO_2 and N_2

$$2CNO^- + 6\,NaOH + 3Cl_2 \rightarrow 6Cl^- + 2HCO_2^- + N_2 + 6Na^+ + 2H_2O \qquad \text{(Reaction 2.12)}$$

CNO^- also will be converted on acidification to NH_4

$$2NaCNO + H_2SO_4 + 4H_2O \rightarrow (NH_4)_2SO_4 + 2NaHCO_3 \qquad \text{(Reaction 2.13)}$$

Cyanogen is highly toxic gas of limited solubility; the toxicity may exceed that of equal concentration of $CN.^-$ At pH = 9, with non excess chlorine present, CNCl may persist for 24 h. Its break down is pH and time dependent.

Metal cyanide-complexes

The metal – cyanide complexes can be classified into weak and strong metal-cyanide complexes depending upon the strength of the metal-cyanide bonding.

Weak metal-cyanide complexes

The cyanide anion can form weak metal cyanide complexes with many transition metals, the most common among them being Ni, Cu, Cd, Zn, Hg and Ag (Sharpe, 1976; Sehmel, 1989). The metal-cyanide bonds in these complexes are mostly arranged in tetrahedral or square planar forms with relatively weak bonding energy existing between the heavy metal atom and the cyanide ligand as compared to the strong cyanide complexes with Fe, Co and Pt. Because weakly bonded metal-cyanide complexes dissociate under weakly acidic pH conditions ($4 < pH < 6$), they are commonly termed weak acid dissociable (WAD) complexes (APHA, 1998). For comparable reaction stoechiometry, the higher the value of the formation equilibrium constant (K), the greater is the energy of formation and stability of the metal-cyanide complex. Table 2.1 lists the measured and calculated stability constants for the formation of weak metal-cyanide complexes:

Table 2.1 Equilibrium constants for formation of selected weak metal-cyanide complexes (Sehmel, 1989):

Reaction	log K (at 25ºC, I = 0)
$Ag^+ + CN^- + H_2O = AgCN(OH)^-$	-0.56
$Ag^+ + 2CN^- = Ag(CN)_2^-$	20.38
$Ag^+ + 2OCN^- = Ag(OCN)^-_2$	5
$Cd^{2+} + CN^- = Cd(CN)^+$	5.32
$Cd^{2+} + 2CN^- = Cd(CN)_2^0$	10.37
$Cd^{2+} + 3CN^- = Cd(CN)_3^-$	14.83
$Cd^{2+} + 4CN^- = Cd(CN)_4^{2-}$	18.29
$Cu^+ + 2CN^- = Cu(CN)_2^-$	24.03
$Cu^+ + 3CN^- = Cu(CN)^{2-}_3$	28.65
$Cu^+ + 4CN^- = Cu(CN)^{3-}_4$	30.35
$Ni^{2+} + 2CN^- = Ni(CN)_2^0$	14.59
$Ni^{2+} + 3CN^- = Ni(CN)_3^-$	22.63
$Ni^{2+} + 4CN^- = Ni(CN)_4^{2-}$	30.13
$Zn^{2+} + 2CN^- = Zn(CN)_2^0$	11.07
$Zn^{2+} + 3CN^- = Zn(CN)_3^-$	16.05
$Hg(OH)_2^0 + 2H+ + CN^- = HgCN^+ + 2H_2O$	24.17

The work of Sehmel, (1989) was performed for the USEPA and incorporated the metal-cyanide complexation constants in the thermodynamic database of the general chemical equilibrium program MINTEQ (Kunz et al., 2001).

An example of zinc speciation in aqueous solution is presented in Figure 2.3.

The dissociation properties of weak metal-cyanide complexes in aqueous solutions depend on their stability constants, pH, temperature and the redox potential of the solution. Their dissociation may be described by:

$$M(CN)_x^{n-} \leftrightarrow M^+ + xCN^- \qquad \text{(Reaction 2.14)}$$

Because of the labile nature of weak metal-cyanide complexes, mildly acidic conditions (pH 4 to 6) can result in the dissociation of many of these complexes.

Weak metal-cyanide complexes generally are readily oxidized by oxidizing agents such as chlorine or ozone.

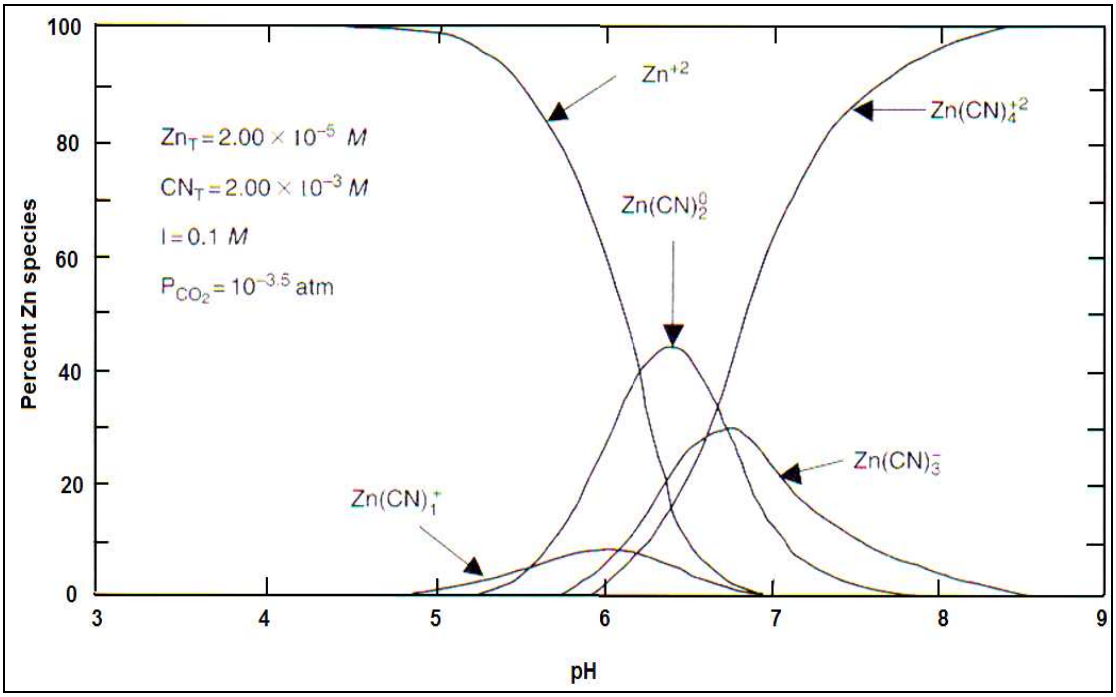


Figure 2.3 Calculated aqueous speciation of zinc (II) in the presence of excess cyanide (Theis and West, 1986)

The more strongly bonded complexes in the WAD category, such as Ni, Ag and Hg cyanide complexes, oxidize more slowly; the more weakly-bonded complexes, including those of Cd, Cu and Zn decompose rapidly in the presence of oxidizing agents. In some cases, the presence of weak metal-cyanide complexes can enhance the rate of free cyanide decomposition through catalysis by the metal. This has been demonstrated for copper cyanide complexes (Gurol, 1988).

The following reaction was proposed:

$$2Cu(CN)_4^{3-} + 3CN^- + 5O_3 \rightarrow 2CuCN + 9CNO^- + 3O_2 \qquad \text{(Reaction 2.15)}$$

The rate of this reaction is accelerated by the presence of Cu(I).

Strong metal-cyanide complexes

The cyanide anion can form strong complexes with a number of transition heavy metals; the most common being Co, Pt, Au, Pd and Fe. The metal-cyanide bonds in these complexes are arranged in tetrahedral or octahedral forms with strong bonding energy existing between the heavy metal atom and the cyanide ligand (Sharpe, 1991). Because they can only dissociate under strongly acidic pH conditions (pH < 2), they are referred to as strong acid dissociable complexes (SAD), or simply as strongly-complexed cyanide (APHA, 1980).

As some of these species are formed very slowly, it is difficult to determine the equilibrium formation constants. Formation data determined by direct thermodynamic methods are available only for complexes of Au(I) and Pd(II).

For other metals, like iron, the formation constant can be determined from measurement of redox potentials. Table 2.2 lists the equilibrium constants for the reversible formation of iron-cyanide complexes, which are of primary interest with respect to cyanide in the environment:

Table 2.2 Equilibrium constants for formation of selected strong metal-cyanide complexes (Sehmel, 1989)

Reaction	**log K (at 25ºC, I = 0)**
$Fe^{2+} + 6CN^- = Fe(CN)_6^{4-}$	45.61
$Fe^{2+} + H^+ + 6CN^- = HFe(CN)_6^{3-}$	50.00
$Fe^{2+} + 2H^+ + 6CN^- = H_2Fe(CN)_6^{2-}$	52.45
$Fe^{3+} + 6CN^- = Fe(CN)_6^{3-}$	52.63
$2Fe^{2+} + 6CN^- = Fe_2(CN)_6^{0}$	56.98
$2K^+ + Fe^{2+} + 6CN^- = K_2Fe(CN)_6^{2-}$	48.98
$K^+ + Fe^{2+} + 6CN^- = KFe(CN)_6^{3-}$	48.12
$Na^+ + Fe^{2+} + 6CN^- = NaFe(CN)_6^{3-}$	47.99

Equilibrium with hydrous ferric oxide, the common amorphous iron oxide, typically is important because $Fe(OH)_{3(S)}$ serves as the source of iron that becomes dissolved, which in turn regulates the cyanide speciation. Figure 2.4 presents a species predominance diagram for dissolved cyanide species in a system in equilibrium with hydrous ferric oxide. The diagram was calculated with MINEQL+ (Schecher, 1998). In the area denoted $Fe(CN)_6$(tot), cyanide is predicted to exist at equilibrium primarily as the iron cyanide species $Fe(CN)_6^{3-}$ (oxic conditions) or $Fe(CN)_6^{4-}$ (anoxic conditions). In the remaining area HCN is the predominant form of dissolved cyanide, except for a small region at pH > 9.2, the pKa for HCN, above which CN^- dominates free cyanide speciation. Dissociation of iron-cyanide complexes in the dark is very slow (Meussen, 1999).

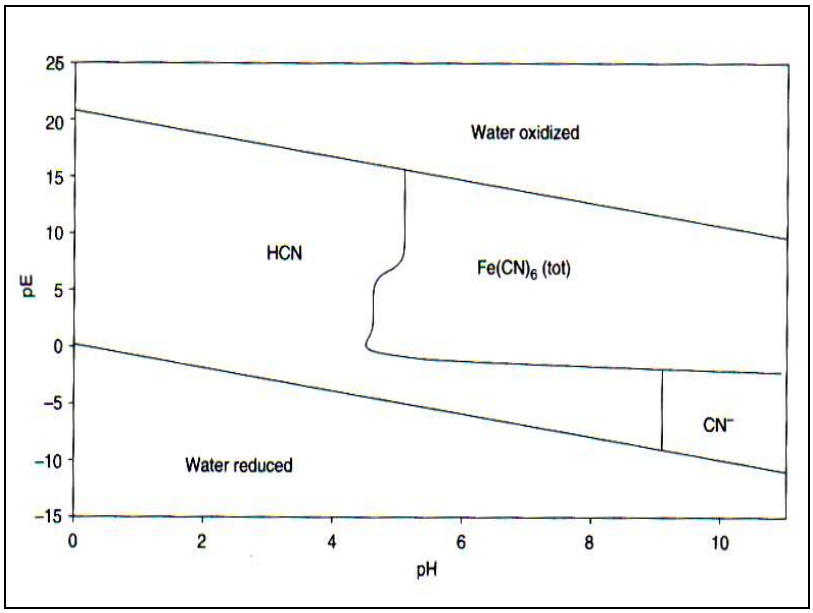


Figure 2.4 Predominance diagram for dissolved cyanide species in equilibrium with hydrous ferric oxide at T = 25°C, as calculated with MINEQL+ (Schecher et al., 1998)

Like weak metal-cyanide complexes, the dissociation properties of iron-cyanide complexes in aqueous solutions are functions of their stability constants, pH,

temperature and redox potential of the solution. Meussen et al. (1999) studied the dissociation of ferrocyanide, $Fe(CN)_6^{4-}$ in 1 mM solutions in dark at 15°C.

Based on the results, they projected half-lives ranging from 1 year under reducing conditions (pE ≈ 5) at pH 4 to 1000 years at the same pH under oxidizing conditions (pE ≈ 10). Some proposed photo dissociation pathways for ferro- and ferricyanides are shown in Figure 2.5.

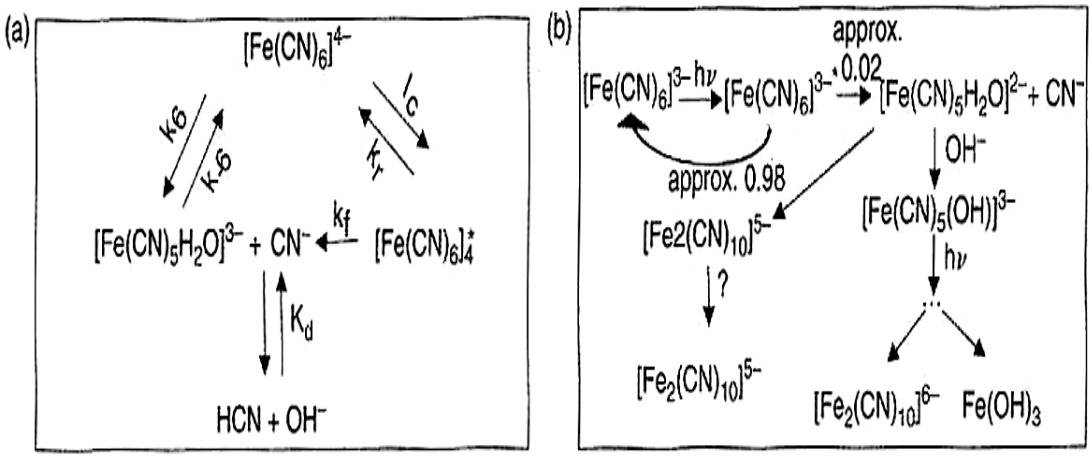


Figure 2.5 Ferro-(a) and ferricyanide (b) photo dissociation reaction pathways (Cherryholmes, 1983)

Ferricyanide can be readily reduced to ferrocyanide by a variety of reducing agents. Ferrocyanide can be oxidized to ferricyanide by molecular oxygen in the dark, but the kinetics of this reaction is slow. Asperger et al. (1969) determined the first order rate constant for this reaction to be 10^{-4} sec^{-1} in the dark at 40°C and pH 4.5. In absence of UV light, only very strong oxidants like ozone, persulfate and permanganate can oxidize ferrocyanide ion in acidic solutions to ferricyanide. It is difficult to oxidize ferrocyanide under neutral to alkaline pH conditions without UV light (Cyanamid, 1953).

For example, the photocatalytic dissociation of ferrocyanide and subsequent oxidation of free cyanide and cyanate (Shaefer, 1996) is as follows:

$Fe(CN)_6^{4-} + 3H_2O + h\nu \rightarrow 6CN^- + Fe(OH)_{3(S)} + 3H^+ + e^-$ (Reaction 2.16)

$CN^- + \text{oxidant} \rightarrow CNO^-$ (Reaction 2.17)

$CNO^- + \text{oxidant} \rightarrow NO_3^- + CO_2$ (Reaction 2.18)

2.5 Behaviour of cyanides in soil and ground water

The most common source of cyanide contamination in soil and ground water is former gas work sites; however, cyanide contamination is also associated with electroplating factories, road salt storage facilities, tailing ponds containing gold mine wastes and others. The chemical behaviour of cyanides in soil and ground water is extremely complex, because cyanides have the potential to undergo many chemical processes (precipitation, dissolution, adsorption, complexation and degradation) as shown in Figure 2.6. Under aerobic conditions, microbial activity can degrade cyanide to ammonia, which then oxidizes to nitrate (Zagury et al, 2004). This process has been shown effective with cyanide concentration of up to 200 ppm. Although biological degradation also occurs under anaerobic conditions, cyanide concentration greater than 2 ppm is toxic to this micro organism. Figure 2.6 provides an illustrative reference for the following discussion regarding the chemical behaviour of cyanides. The arrows indicate the potential reactions pathways.

In a simplistic manner, three cyanide forms (free cyanide, WAD cyanides and SAD cyanides) are common in gold mining process waste solutions (Zagury et al., 2004). There are, of course, many other compounds derived from cyanide that are present in process waste solutions such as cyanate, cyanogen chloride and thiocyanate, the reaction of cyanate with sulfides can also occurs (Souren, 2000).

Free cyanide is not persistent in the tailings environment and will degrade through physical, chemical and biological processes, into other less toxic chemicals.

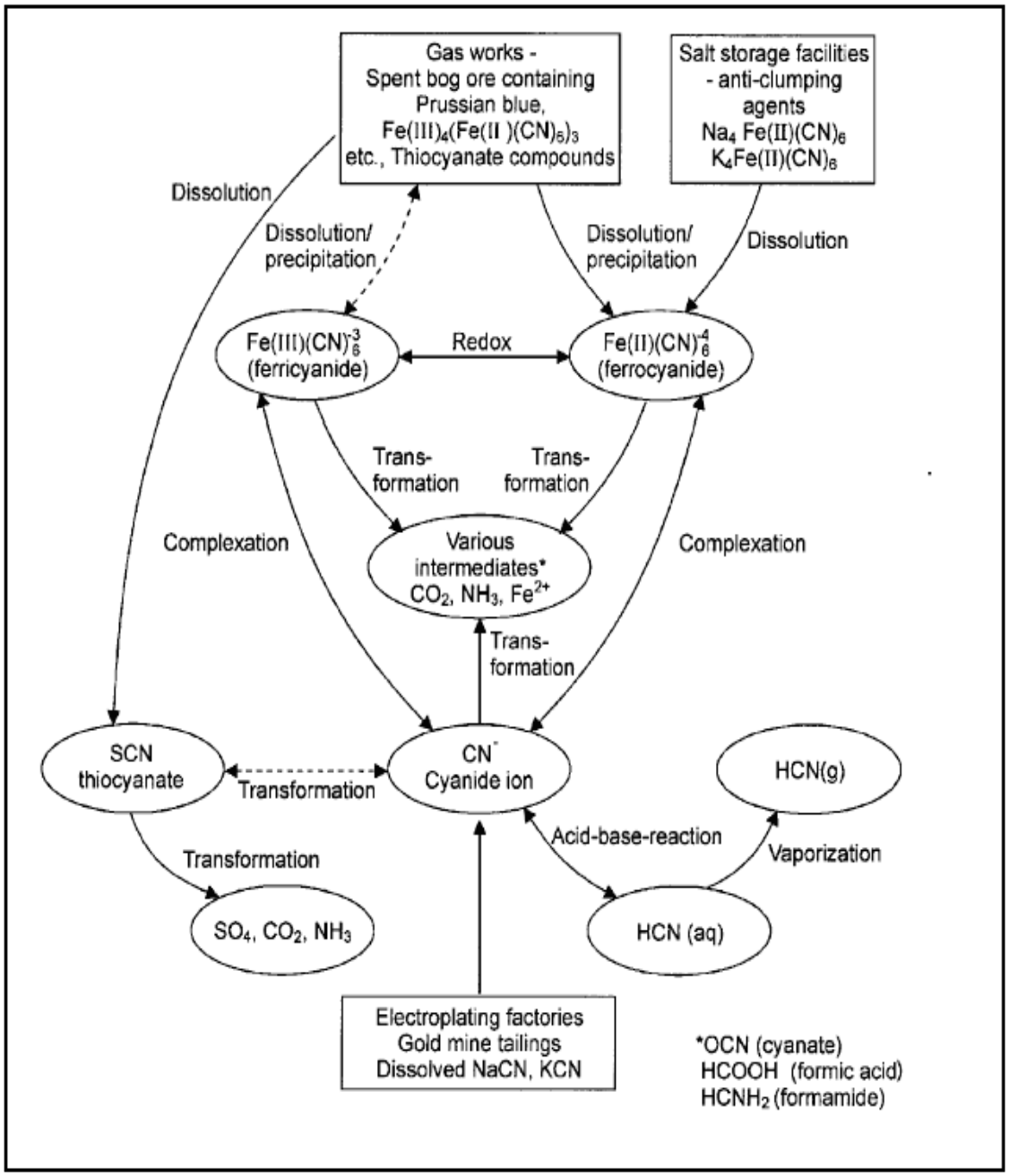


Figure 2.6 Overview of the most important cyanide species, and the processes that govern their behaviour in soil and ground water (Kjelden, 1998)

Natural degradation, primarily by volatilization of cyanide in tailings storage facilities (TSFs), is the most common method of removing cyanide in the gold

mining waste. Heavy metals react with free cyanide to form metal cyanide complexes which are characterized by their stability, insolubility or being slightly soluble. Copper and zinc cyanide complexes are insoluble in water but soluble in ammonia which is present in tailings dams.

The solubility of cyanide and its complexes contribute to its bioavailability to biota that is exposed to them (Franson, 1992; Klenk et al., 1996).

Bioavailability and cyanide concentrations also vary considerably in the tailings environment due to varying concentrations of metals in ore gold extraction recovery targets, ore blending and changing tailings dam environmental conditions (www.epa.gov).

2.6 Environmental fate of cyanide

Once released into the environment, the reactivity of cyanide provides numerous pathways for its degradation and attenuation. These represent a range of competing reactions or processes that often occur simultaneously, depending on the prevailing conditions. Figure 2.7 depicts the main attenuation mechanisms playing a role in tailings storage facilities. All the attenuation processes are to some extent reversible and could result in fluctuating levels of free cyanide in solution or in the atmosphere depending on the specific circumstances. Volatilisation into open air is by far the most important mechanism by which cyanide is irreversibly removed from aqueous solution (Lötter, 2006). Cyanide removal by precipitation or complex formation is typically reversible, as the products do not leave the solution, and are thus available as sources of cyanide, should the conditions favour the reserve reactions (Huiatt et al., 1983).

Photolysis during daylight hours may typically increase the free cyanide by decomposition of cyanide complexes, initiating either the loss of cyanide from solution through volatilisation or by the formation of other complexes (Smith and Mudder, 1991; Lötter, 2006).

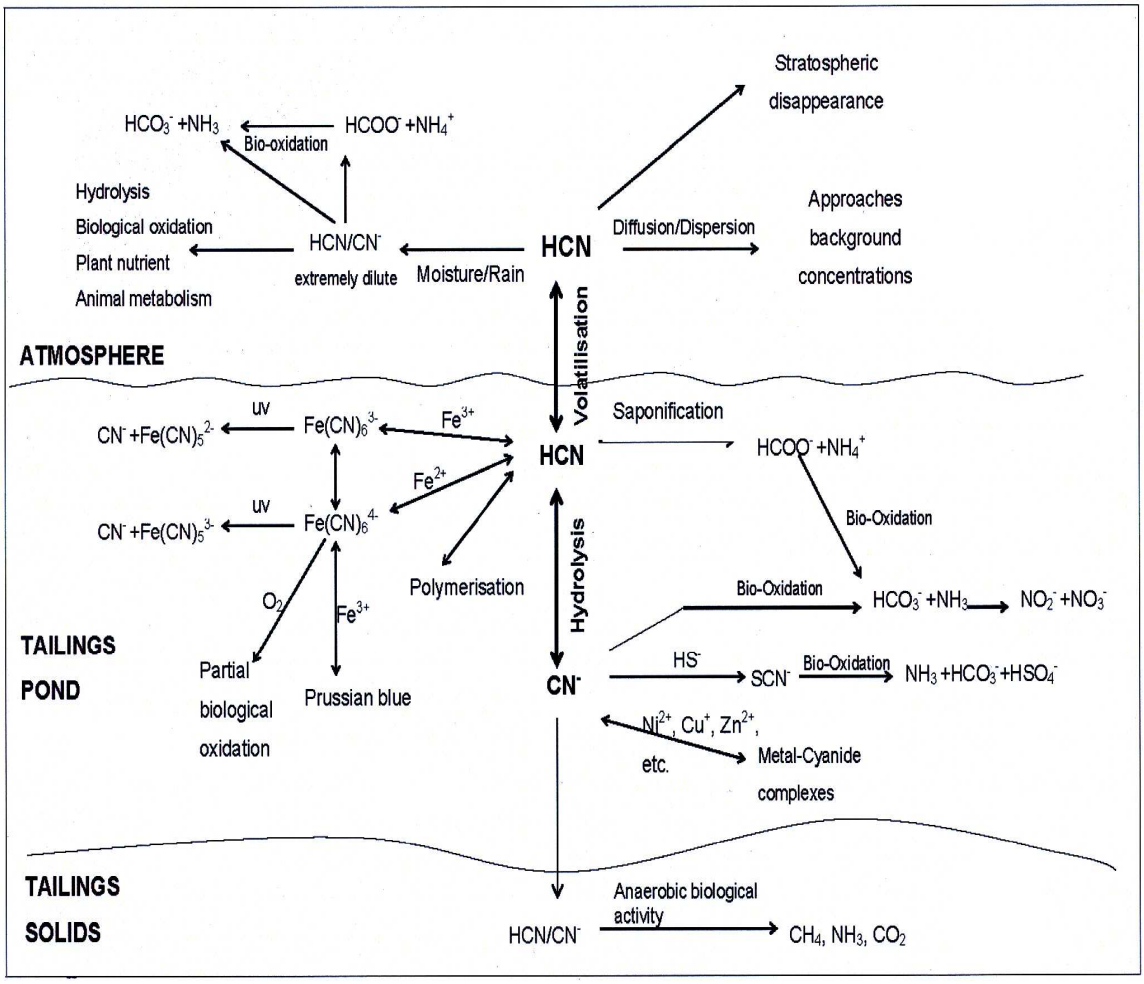


Figure 2.7 Attenuation mechanisms for tailing storage facilities (Smith and Mudder, 1991)

Free cyanide adsorption to soil and sediment

Free cyanide (HCN, CN-) adsorbs weakly on soils and sediment. The cyanide anion can be retained by soils with anion exchange capacity but in the pH range 4 to 9 of interest for most soils, HCN is the dominant form of cyanide and CN^- concentrations are very low.

HCN adsorbs weakly or not all to inorganic soil components such as iron oxide, aluminum oxide, clay and sand. However, HCN has been shown to adsorb

significantly to soils with appreciable organic carbon contents (Theis et al., 1986; Higgins, 2005). The magnitude of cyanide adsorption onto soils tested by Chatwin et al. (1988) showed excellent correlation with organic carbon content.

Available data for free cyanide adsorption onto mineral surfaces, however, indicates that the free cyanide adsorption in Figure 2.8 is likely to be substantially over predicted. Free cyanide has been observed to exhibit little to no adsorption on mineral surfaces, including the crystalline iron oxide goethite, across arrange of pH (Theis et al., 1986).

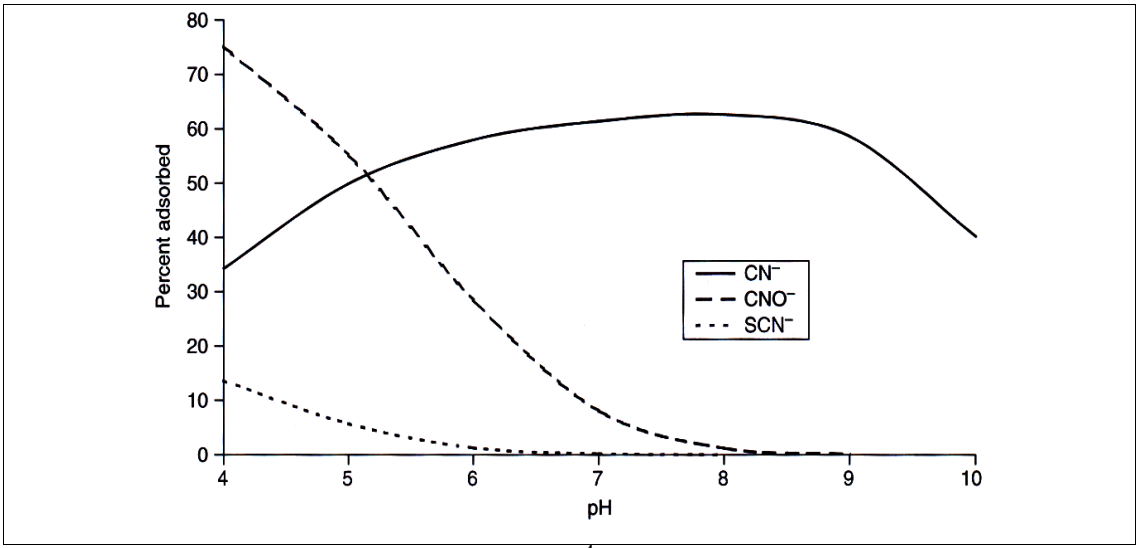


Figure 2.8 Predicted adsorption of 10^{-4}M CN^-, CNO^- and SCN^- on hydrous ferric oxide as a function of pH (Theis et al., 1986)

Weak metal-cyanide complexes adsorption on soil and sediment

Weak metal cyanide complexes can adsorb on common soil and sediment components such as iron, aluminium, silicon, manganese oxides and clays which in most systems will inhibit their aqueous transport (Theis, 1986; Chatwin, 1988; Higgins, 2005).

However, complexation of metals by cyanide can also serve to hold them in solution, inhibiting their adsorption and retention.

Theis and Richter demonstrated that $Ni(CN)_4^{2-}$ must bond at specific surface sites on goethite($FeOOH_{(s)}$), in surface complexation reactions that involve high free energies of interaction. Batch adsorption experiments were conducted in 0.01 M $NaClO_4$ aqueous solutions containing $10^{-4.77}$ M total nickel (Ni_T) and amounts of total free cyanide (CN_T) of 10^{-5}, 10^{-4} and 10^{-3} M. Calculated plots of the equilibrium distribution of nickel species as a function of pH in aqueous solution with no solids present are the speciation plots of Figure 2.9:

In the systems with $CN_T = 10^{-4}$ and 10^{-3} M, adsorption of nickel is enhanced at lower pH values, and inhibited at higher pH values. The goethite surface is positively charged up to about pH 6, or even higher, so electrostatic attraction of $Ni(CN)_4^{2-}$ explains in part its adsorption at lower pH values.

The meal-cyanide complexes may interact with the surface to a great extend or lesser extend than the metals alone. An interrelated, complex group of factors governs metal-cyanide species adsorption, and it is difficult to form generalizations (Dzombak, 2006).

Strong metal-cyanide complexes adsorption on soil and sediment

Strong complexes such as ferro and ferricyanides can adsorb on common soil and sediment components such as iron, aluminium, manganese oxides and clays (Theis et al., 1986). Adsorption of metal-cyanide complexes occurs through a combination of electrostatic attraction and surface complexation (Theis, 1986).

Based on the test conducted by Alesii and Fuller (Alesii, 1976), it was concluded that soil properties, such as low pH (pH < 5), free iron oxide content, kaolin, chlorite and gibbsite type clay (high anion exchange capacity) material increased adsorption of iron-cyanide complexes to soil material. It has been demonstrated in a number of studies that aluminum and iron oxides, two very common and surface-reactive components of soils and sediments can adsorb iron-cyanide species significantly, especially at lower pH values (<7) (Theis, 1986).

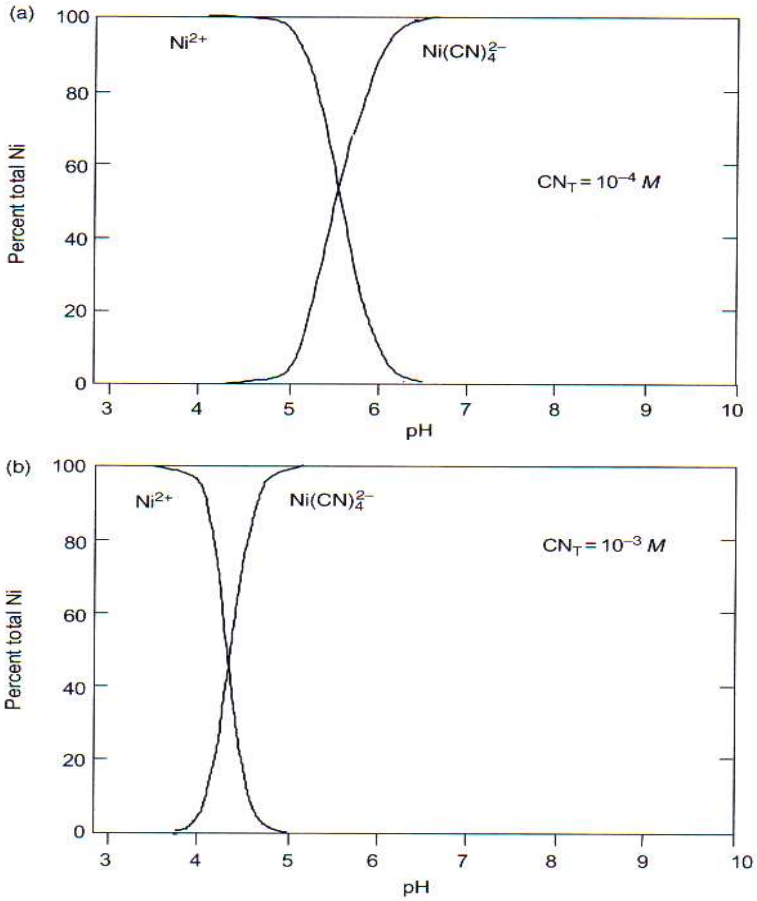


Figure 2.9 Theoretical distribution of nickel in the presence of (a) 10^{-4} M cyanide ($Ni_T = 10^{-4.77}$ M , I = 0.01M), and (b) 10^{-3} M cyanide ($Ni_T = 10^{-4.77}$ M, I = 0.01M) (Theis and Richter, 1980)

2.7 Microbial activity

Various species of bacteria, fungi, algae, yeasts and plants possess the ability to convert cyanide (CN^-) which acts as a carbon and nitrogen source, to ammonia and carbonate. The requirement for aerobic conditions plays a major role in the effectiveness of metabolisation as an attenuation process, as was concluded from a review done by Chatwin and Trepanowski (1987).

Simple cyanides, in particular, are relatively easily degraded, especially under aerobic conditions. Degradation of iron cyanides under aerobic conditions also occurs, but a slower rate than that of simple cyanide degradation (Oudjani et al., 2002). There is evidence that cyanide biodegradation under anaerobic conditions may represent a secondary reaction or cometabolism, depending on the form of reduced carbon present in the system and the microbial consortium (Fedorak et al., 1989; Raybuck, 1992).

Cyanide bioavailability and solubility in soil-water systems is a determining factor for cyanide biodegradation (Aronstein et al., 1994).

Aerobic degradation of CN^-involves the following steps:

Oxidation of cyanide to cyanate

$$CN^- + \tfrac{1}{2} O_2(aq) \rightarrow OCN^- \qquad \text{(Reaction 2.19)}$$

Hydrolysis of cyanate which requires a pH below 7

$$OCN^- + 3 H_2O \rightarrow NH_4^+ + HCO_3^- + OH^- \qquad \text{(Reaction 2.20)}$$

Aerobic degradation of CN_{SAD} is mediated by a number of organisms, generally Pseudomonias bacteria (Young & Jordan, 1995; Zagury et al., 2003; Akcil et al., 2003). The relevant reaction is:

$$M(CN)_x^{y-x} + 3 H_2O + x/2\ O_2(aq) \rightarrow M^{y+} + NH_4^+ + HCO_3^- + OH^- \qquad \text{(Reaction 2.21)}$$

Thiocyanate is also subject to bacterially-mediated aerobic degradation:

$$SCN^- + 3H_2O + 2O_2(aq) \rightarrow SO_4^{2-} + NH^{4+} + HCO_3^- + H^+ \qquad \text{(Reaction 2.22)}$$

Anaerobic biodegradation of free cyanide is restricted to the moderately to strongly reduced portions of the environment and can only occur if HS^- or $H_2S(aq)$

are present. The sulphur species present will depend on pH. At a pH value greater than 7, HS^- is the dominant species. At a lower pH, H_2S (aq) will be present. These equations illustrate the anaerobic biodegradation of cyanide:

$$CN^- + H_2S(aq) \rightarrow HCNS + H^+ \qquad \text{(Reaction 2.23)}$$

$$HCN + HS^- \rightarrow HCNS + H^+ \qquad \text{(Reaction 2.24)}$$

The HCNS will be hydrolyzed to form NH_3, H_2S and CO_2. In comparison with the aerobic biodegradation of cyanide, anaerobic degradation is much lower and anaerobic bacteria have a cyanide toxicity threshold of only 2 mg l^{-1} compared to 200 mg l^{-1} for aerobic bacteria (Smith and Mudder, 1991). Consequently anaerobic biodegradation would be a less effective cyanide removal mechanism.

2.8 Toxicity of cyanide

Cyanide is a chemical well known to the public as a highly toxic agent. A number of reviews have examined the toxicological effects of cyanide and its related compounds (Huitt et al., 1983; AMIRA, 1997; Zagury et al., 2003). Free cyanide CN^- and HCN are the most toxic form of cyanide and among CN_{free} , HCN is more toxic.

The salts of Na, K, Ca cyanides are also quite toxic as they are highly soluble in water and thus readily dissolve to form free cyanide. Weak or moderately stable cyanide complexes (Cd, Cu, Zn) by themselves are much less toxic than free cyanide. Their dissociation releases free cyanide as well as the metal cation which can also be toxic. Even in neutral pH range of most surface water, WAD metal cyanide complexes can dissociate to release free cyanide (Doudoroff, 1976; Moran, 1998; Zagury et al., 2003).

Cyanide forms complexes with Au, Hg, Co and Fe very stable even under mildly acidic conditions. Exposure to cyanide is by inhalation of HCN_{gas}.

Once cyanide is inhaled, it interferes with the organism's oxygen metabolism and can be lethal within a short time. Initial symptoms of cyanide poisoning can occur from exposure to 20 to 24 ppm. The lethal toxicity of free cyanide for humans is 1 – 2 mg kg^{-1} and 0.028 – 2.295 mg kg^{-1} for fresh water invertebrates (Huitt et al., 1983). Brief exposures to lower levels may result in shortness of breath, convulsions and loss of consciousness. Exposure to high levels for short periods may result in:

- irritation of the eyes, nose and throat
- headache
- pounding of the heart
- shortness of breath
- harm to the central nervous system, respiratory system and the cardiovascular system
- quickly lead to death

Long term exposure to low levels of cyanide may cause deafness, vision problems and loss of muscle coordination. Cyanide does not bio-accumulate in animals because sublethal doses are rapidly metabolized and excreted and there is no evidence that it bio-accumulate in ecosystems or atmosphere (Huitt et al., 1983). Acute toxicity is the principal hazard posed by poisoning in wildlife.

The best known example of human cyanide poisoning from a natural source involves the ingestion of cyanogenic plants and particularly cassava in several African countries (Dzombak, 2006). SCN^- is approximately 7 times less toxic than HCN, however, exposure to it can lead to lung irritation. It can be chemically and biologically oxidized into carbonate, sulphate and ammonia (Ingles and Scott, 1987; U.S.EPA, 1986).

Greater environmental concern is the exposure of domestic and wild animals to cyanogenic plants and to cyanide containing devices placed in the ground and used to control nuisance predators (Mudder and Botz, 2004).

For migratory birds and other waterfowl, a level of 50 mg l^{-1} WAD cyanide in the tailing slurry entering an impoundment has been employed as a regulatory guideline providing protect of animals coming in contact with stored process solution (Minerals Council of Australia, 1996; Mudder, 1997; NTB, 1998).

2.9 Environmental incidents related to cyanide and mining

Much of the process material and the waste generated during the leaching process may be exposed to the environment, with a potential for contaminant transport. If water leaches or dams break, cyanide can be released into watersheds resulting in catastrophic consequences. Examples are the killing of fish over a stretch of 700 km in the Szamos/Tisza/Danube river system in Europe in January 2000, due to release of cyanide from the Baia Mare gold mine, Romania (UNEP/OCHA, 2000), and more recently in Ghana and China October 2001 (MEM, 2001).

In recent years, some environmental pollution problems of cyanide-related leaks, discharges, and accidents have been reported. These accidents raise questions about the current operating practices, monitoring, and enforcement at cyanide-related mine sites worldwide. Same of these accidents are presented here.

Pegasus Corporation (Montana, U.S.A.) recently closed the Zortman-Landusky gold mine in Montana. Opened in 1979, it was the first large-scale cyanide heap leach mine in the United States. The mine experienced repeated leaks and discharges of cyanide solution throughout its operating life, resulting in wildlife deaths and severe contamination of streams and groundwater (Cyanide Uncertainties, 1998).

In 1994 in South Africa, the Merriespruit tailings dam failed by overtopping as a consequence of heavy rains causing a slide flow (static liquefaction) of part of the embankment. Water mismanagement was to blame that caused 600,000 m^3 of tailings (1.2 Million tones) to mobilise out of the impoundment where the flows eventually stopped 2 km away in the town of Merriespruit. 17 people were killed

and scores of houses were demolished; cyanide spillage was not quantified (Cyanide Uncertainties, 1998).

Guyana: In 1995, more than 860 million gallons of cyanide-laden tailings were released into a major river in Guyana when a dam collapsed at Cambior mining company's Omai gold mine (Cyanide Uncertainties, 1998).

On 9 October 1997 a pipeline, normally used to transport the tailings to a storage dam, ruptured at the Ballarat East Gold Mine. Mine tailings containing cyanide from the gold extraction process flowed onto land near the Yarrowee River. The tailings material was later washed into the Yarrowee River where it killed many types of fish and aquatic life, posed a serious threat to public health and had the potential to kill or injure birds and other wildlife (EPA, 1998)

Spain: A dam at the Los Frailes zinc mine in southern Spain ruptured in April 1998, releasing an estimated 1.3 billion gallons of acid, metal-laden tailings into a major river and over adjacent farm lands. While news reports of the associated massive fish kill did not mention cyanide or related compounds in the wastes, their presence seems likely given the nature of the metals extracted at this site (Cyanide Uncertainties, 1998).

Kyrgyzstan: On May 20, 1998, a truck transporting cyanide to the Kumtor mine in Kyrgyzstan plunged off a bridge, spilling almost two tons of sodium cyanide (1,762 kilograms) into local surface waters (Cyanide Uncertainties, 1998).

On 30 January 2000, a tailings pond burst at a facility near the city of Baia Mare, Romania which was reprocessing old mining tailings and re-depositing the waste sludge into a new tailings pond.

This led to approximately 100,000 m^3 of waste water containing up to 120 tons of cyanide and heavy metals being released into the Lapus River, then travelling downstream into the Somes and Tisa rivers into Hungary before entering the Danube.

On 2000, there was failure of gold tailing dam in Baia Mare, Romania. The resulting leak proceeded to let out over 130,000 m^3 of water tainted with cyanide.

The water made its way into the Lupes, Somes, Tisza, and Danube Rivers, killing fish, birds, and other species of animals.
The effects of the pollution were felt throughout three countries and affected over 400 kilometers of waterways (Cyanide Issues, 2000).

2.10 Environmental legislation concerning cyanide

There are many legitimate questions about environmental and human health impacts related to the use of cyanide at mining operations that mine operators, regulators, and health officials are simply unable to answer at this time. Legislation for cyanide management has had a history of non-uniformity amongst countries, and this is currently still the case (Lye, 1999).
The mineral Policy Center has produced Cyanide Uncertainties to help industry, government regulators, and local citizens begin the process of assessing these very real and very serious uncertainties related to cyanide (Minerals and Research Institute of Western Australia, 2000; ICMC, 2001).
Based on various experimental studies especially animal studies, various organizations and states have come up with different allowable limits for cyanide in water (free cyanide). These limits are presented in Table 2.3.
Although soil contamination can occur through residues from tailings seepage, soil quality is rarely taken into account in legislation. Figure 2.10 represents the current legislation in place with regards to required maximum cyanide levels in aquatic systems in South Africa (Lotz and Wright, 2000).
In South Africa, atmospheric HCN emission monitoring is currently self-regulatory, with the emphasis on safety and health. The occupational Safety and Health threshold limit value (TLV) for HCN in air is currently set at 10 ppm in South Africa and Australia.

Table 2.3 Free cyanide limits in drinking water according to various legislative authorities (U.S.Environmental Protection , 1999).

ORGANISATION	ALLOWABLE LIMIT
1. Department of Water Affairs and Forestry (DWAF)/South Africa	< 0.02 mg l^{-1}
2. Department of Health (DOH)/South Africa	0.07 mg l^{-1}
3.United States Environmental Protection Agency (USEPA)	0.2 mg l^{-1}
4.European Union Directives	0.05 mg l^{-1}
5.World Health Organization (WHO)	0.07 mg l^{-1}

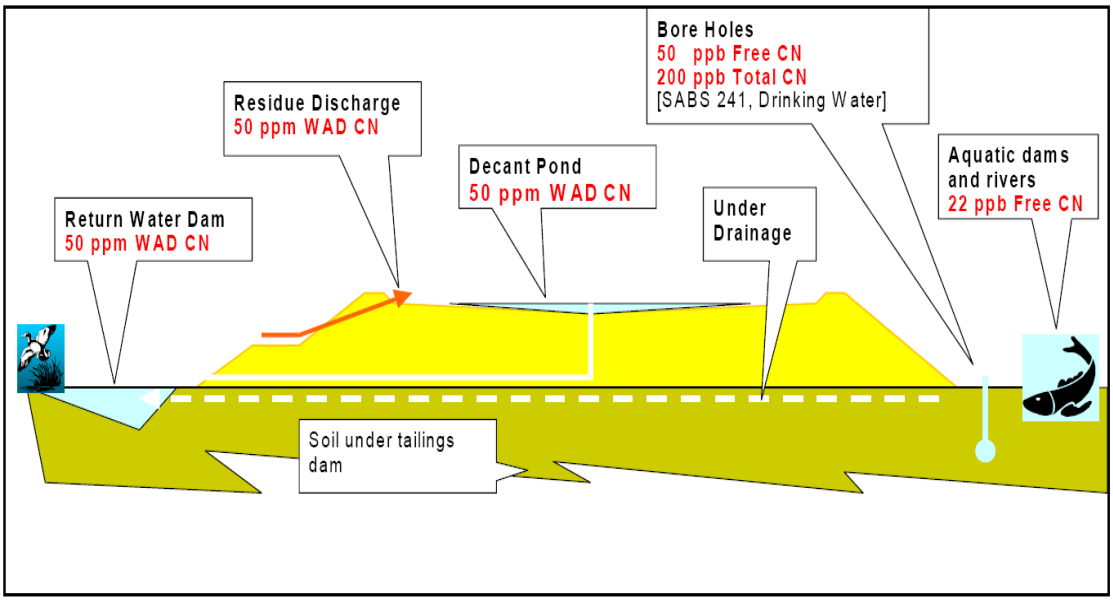


Figure 2.10 Legislation for aquatic cyanide in South Africa (www.cyanidecode.org. 2000)

The few available data of free cyanide in soil-air and in ambient air in situation of historical cyanide soil contamination showed that concentration of 1 – 2 mg free CN/m^3 can occur (Hoppener et al., 1983; Jans, 1999).

These concentrations are 5 – 10 times below the permissible cyanide concentration in air at workplaces (11 mg HCN/m^3), but exceed the tolerable concentration in air of 0.025 mg HCN/m^3. Consequently, the concentration of free HCN in the ambient air should be taken into consideration for the intervention value of cyanide. However, this does not seem possible as at present a relationship between cyanide in soil and/ or groundwater and free cyanide in air has not been identified (RIVM report, 2001).

Stringent safeguards and standards exist to regulate the manufacture, transport, storage, use and disposal of cyanide. For example, the International Cyanide Management Institute (ICMI) is a voluntary program of companies involved in the production of gold using cyanide and companies producing and transporting this cyanide. It was developed under the auspices of the United Nations Environment Programme. Recently in South Africa, the Sasol Polymers' Cyanide Production Plant and Anglo Gold Ashanti were certified under this code.

The ICMC provides principles and standards of practice on cyanide use and specifies that 50 mg l^{-1} WAD is an appropriate discharge concentration. The code intends to complement existing operational regulatory requirements (The International Cyanide Management Institute, 2005).

CHAPTER THREE – SAMPLING METHODS AND ANALYTICAL TECHNIQUES

This chapter gives an overview of the general sampling strategies and the theory of instrumental techniques used in this study.

3.1 Sampling

The first step in any environmental analysis is to design a sampling plan that will provide answers to the question being asked about the site. Collection and analysis of samples should provide representative data about the problem under investigation. The sampling plan is a framework for developing clear study objectives and collection of data that will lead to the resolution of the objectives. A plan has to be flexible enough to adjust to changing conditions and new information while providing a logical framework (Kegley and Andrews, 1996). In order to obtain satisfactory outcomes in environmental analysis, sampling has to be carried out with care and competence (Wagner, 1995). Random errors, which cause poor precision, can be expected in some of the steps of sampling, sample preparation and measurements. For example, the definition of the sampling area, number of samples, sample mass, sub samples and calibration analysis can produce random errors. There also a tendency to produce systematic, absolute or qualitative errors in other steps such as transportation, packaging, storage, washing which cause inaccuracy of results.

The sampling plans and protocol involve (after Barnard, 1995):

- Development of sampling and analysis plans (including sampling patterns such as simple, random, grid, or nested sampling).
- Sampling and data collection (includes sample amounts, preservation procedures, field measurements and observations).
- Data analysis (this entails the interpretation of the data after collection such as graphs, mapping, statistics and modeling).

Historical data is essential in sampling; this gives information on the site and an insight into the behavior of pollutants. Three basics approaches (Figure 3.1) are typically used in taking environmental samples (Kegley and Andrews, 1996):

- Judgmental sampling - is done where the concentration of pollutants is thought to be high or low. It gives a “worst case” or “best case”

scenario of a pollutant source. There is a bias of the sampler.

- Systematic sampling - involves dividing the site into equal-sized areas and sampling each area. A grid or regular pattern is normally constructed which provides an easy way of setting up a systematic sampling scheme.
- Random sampling - this entails selection of sample sites with no particular pattern or reason. The choice of sites is a random process. Combinations of random sampling with judgemental or systematic sampling can also be carried out.

The details of sampling protocols for tailings, water and sediment samples are given in Chapter 5.

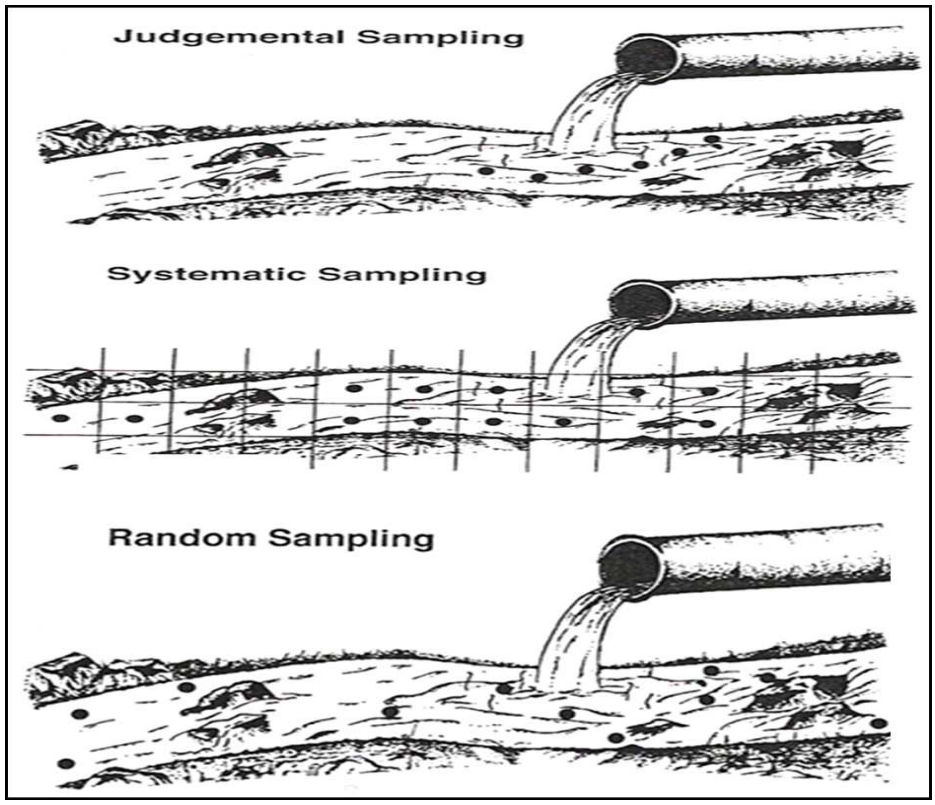


Figure 3.1 The three basic sampling approaches. The solid dots represent sample sites (Keith, 1991).

3.2 Analytical techniques

This section provides a summary of the description of analytical techniques used in the project.

3.2.1 Ion Selective Electrode (ISE)

The Ion Selective Electrode (ISE) is a sensor for the potentiometric determination of ionic species and one of the most frequently used devices during laboratory analysis in industry, process control, physiological measurements, and environmental monitoring. Other ions that can be measured include anions such as, F^-, Br^-, I^-, CN^-, NO_3^-, NO_2^-, the cations such as, Pb^{2+}, K^+, Ca^{2+}, Cu^{2+} and Na^+, and gases in solution such as NH_3, CO_2, N_2 and O_2.

Principle

Diffusion of analyte ions out of the membrane (Figure 3.2) creates a slight charge imbalance (an electric potential difference) across the interface between the membrane and the analyte solution. Changes in analyte ion concentration in the solution change the potential difference across the outer boundary of the ion selective membrane. By using a calibration curve; we can relate the potential difference to analyte concentration. To be more precise, the term 'concentration' should really be replaced by 'activity' or 'effective concentration'. This is an important factor in ISE measurements. In order to measure the electrode potential developed at the ion-selective membrane the ISE/pH electrode must be immersed in the test solution together with a separate reference system and the two must be connected via a milli-volt measuring system. At equilibrium, the electrons added or removed from the solution by the ISE membrane (depending on whether it is

cation or anion sensitive) are balanced by an equal and opposite charge at the reference interface. This causes a positive or negative deviation from the original stable reference voltage which is registered on the external measuring system.

The relationship between the ionic concentration (activity) and the electrode potential is given by the Nernst equation:

$$E = E^{o} + (2.303RT/ nF) \times \log(A) \qquad \text{(Equation 3.1)}$$

Where E = the total potential (in mV) developed between the sensing and reference electrodes.

E^{o} = is a constant which is characteristic of the particular ISE/reference pair.

(It is the sum of all the liquid junction potentials in the electrochemical cell)

R = the gas constant (8.314 J/K.mol).

T = the absolute temperature.

n = the charge on the ion (with sign).

F = the Faraday constant (96 500 C).

(A) = the logarithm of the activity of the measured ion.

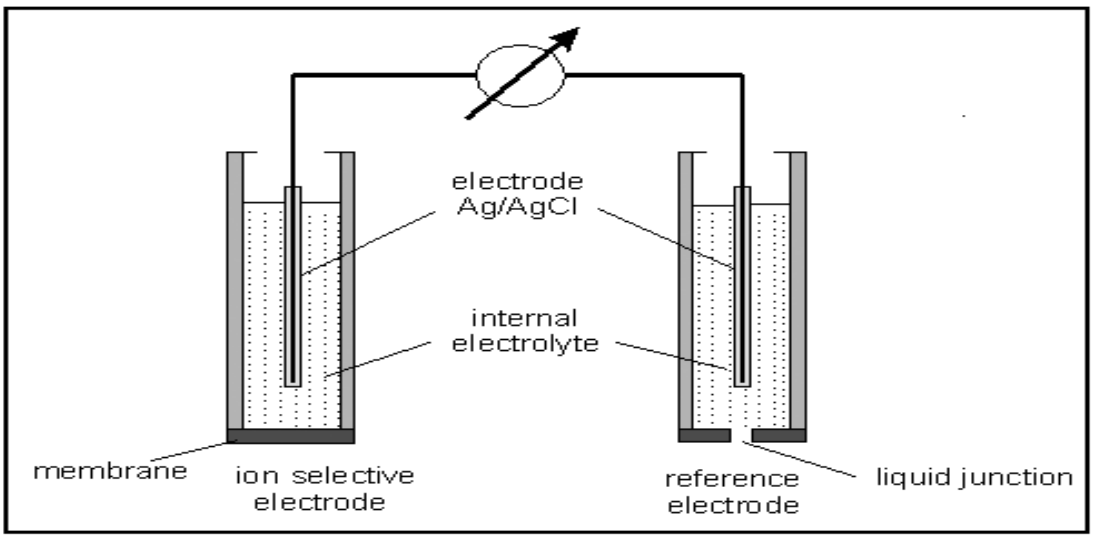


Figure 3.2 The electrochemical circuit for an Ion Selective Electrode measurement (www.chemistry.nmsu.edu).

Note The straight line plot of E versus log(A) is the basis of ISE calibration graphs and the slope of the line is 2.303RT/nF. This is an important diagnostic characteristic of the electrode; generally the slope gets smaller as the electrode gets old or contaminated, and the smaller the slope the higher the errors on the sample measurements.

An ISE (with its own internal reference electrode) is immersed in an aqueous solution containing the ions to be measured, together with a separate, external reference electrode. (NB: this external reference electrode can be completely separate or incorporated in the body of the ISE to form a combination electrode).

The electrochemical circuit is completed by connecting the electrodes to a sensitive milli-volt meter using special low-noise cables and connectors. A potential difference is developed across the ISE membrane when the target ions diffuse through from the high concentration side to the lower concentration side (Figure 3.2).

Reference electrodes are used to provide a stable voltage at electrolytic contact to permit a voltage gradient to be measured across a measurement membrane such as an ISE.

Some advantages of the ISE method are:

i) It is considerably less expensive than other analytical techniques, such as Atomic Absorption Spectrophotometry (AAS) or Ion Chromatography (IC).

ii) It is simple to use and measurement is quick. It has a large range of applications and can be used over a wide concentration range.

iii) It is robust and durable and ideal for use in either field or laboratory environments.

iv) Accuracy and precision levels of ± 2% for some ions compare favorably with analytical techniques which require more complex and expensive instrumentation.

Membrane electrodes are called ion selective electrodes because of their high selectivity.

The membranes must have minimal solubility, electrical conductivity, and selective reactivity with the analyte of interest. Several types of sensing electrodes are commercially available (Orion Research).

The main problems with Ion Selective Electrode measurements are the effect of interference from other ions in solution, the effect of the ionic strength of the solution reducing the measured activity relative to the true concentration at high concentrations and potential drift during a sequence of measurements. A total Ionic Strength Adjustment buffer (TISAB) is normally added to samples and standards in order to solve these problems.

Types of ion selective membrane electrode

Crystalline membrane electrode:

- Single crystal: LaF_3 for F^-
- Polycrystalline or mixed crystal: Ag_2S for S^{2-} and Ag^+

Non crystalline membrane electrode

- Glass: Silicate glasses for Na^+ and H^+
- Liquid: Liquid ion exchangers for Ca^{2+} and neutral carriers for K^+
- Immobilized liquid in a rigid polymer: Polyvinyl chloride matrix for Ca^{2+} and NO_3^-.

The cyanide ion-selective electrode has a solid-state crystal membrane, designed for the detection of cyanide ions (CN^-) in aqueous solutions and is suitable for use in both field and laboratory applications. It was used in this study for the determination of free and total cyanides.

3.2.2 Ultraviolet and visibly spectroscopy (UV-Vis)

Many molecules absorb ultraviolet or visible light. The absorbance of a solution

increases with attenuation of the beam. Absorbance is directly proportional to the path length and the concentration of the absorbing species.

Principle

Ultraviolet and visible (UV-Vis) absorption spectroscopy is the measurement of the attenuation of a beam of light after it passes through a sample or after reflection from a sample surface. Absorption measurements can be at a single wavelength or over an extended spectral range. Ultraviolet and visible light are energetic enough to promote outer electrons to higher energy levels, and UV-Vis spectroscopy is usually applied to molecules or inorganic complexes in solution and UV-Vis spectra have broad features that are of limited use for sample identification but are very useful for quantitative measurements. The concentration of an analyte in solution can be determined by measuring the absorbance at some wavelength and applying the Beer-Lambert law (Asimov, 1972; Ingle and Crouch, 1988).

The Beer-Lambert law states that the absorbance of a solution is directly proportional to the solution's concentration. Thus UV/Vis spectroscopy can be used to determine the concentration of a solution. It is necessary to know how quickly the absorbance changes with concentration. This can be taken from references (tables of molar extinction coefficients), or more accurately, determined from a calibration curve.

UV/Vis spectroscopy is routinely used in the quantitative determination of solutions of transition metal ions and highly conjugated compounds. The method is most often used in a quantitative way to determine concentrations of an absorbing species in solution, using the Beer-Lambert law:

$$A = - \log_{10} (I / I_0) = \varepsilon c L \qquad \text{(Equation 3.2)}$$

Where A is the measured absorbance, I_0 is the intensity of the incident light at a given wavelength, I is the transmitted intensity, L the path length through the sample, and c the concentration of the absorbing species. For each species and wavelength, ε is a constant known as the molar absorptivity or extinction coefficient.

Ultraviolet-visible spectroscopy (UV = 200-400 nm, visible = 400-800 nm) corresponds to electronic excitations between the energy levels that correspond to the molecular orbitals of the systems. Solutions of transition metal ions can be coloured (i.e., absorb visible light) because electrons within the metal atoms can be excited from one electronic state to another. The color of metal ion solutions is strongly affected by the presence of other species, such as certain anions or ligands. For instance, the colour of a dilute solution of copper sulfate is a very light blue; adding ammonia intensifies the color and changes the wavelength of maximum absorption (λ_{max}). A UV/Vis spectrophotometer may be used as a detector for HPLC. The presence of an analyte gives a response which can be assumed to be proportional to the concentration.

For accurate results, the instrument's response to the analyte in the unknown should be compared with the response to a standard; this is very similar to the use of calibration curves. The response (e.g., peak height) for a particular concentration is known as the response factor.

The UV/Vis spectrophotometer measures the intensity of light passing through a sample (I), and compares it to the intensity of light before it passes through the sample (I_o). The ratio I / I_o is called the transmittance, and is usually expressed as a percentage (%T). The absorbance, *A*, is based on the transmittance (en.wikipedia.org, 2007).

$$A = - \log (\%T) \qquad \text{(Equation 3.3)}$$

The basic parts of a spectrophotometer are a light source (usually a deuterium discharge lamp for UV measurements and a tungsten-halogen lamp for visible and NIR measurements), a holder for the sample, a diffraction grating or monochromator to separate the different wavelengths of light, and a detector (figure 3.3). The detector is typically a photodiode or a charge-coupled device (CCD). Photodiodes are used with monochromators, which filter the light so that only light of a single wavelength reaches the detector. Diffraction gratings are used with CCDs, which collects light of different wavelengths on different pixels.

The detector in single-detector instruments is a photodiode, phototube, or photomultiplier tube (PMT). Most commercial UV-Vis absorption spectrometers use one of the three overall optical designs: a fixed or scanning spectrometer with a single light beam and sample holder; a scanning spectrometer with dual light beams and dual sample holders for simultaneous measurement of P and P_o; or a non-scanning spectrometer with an array detector for simultaneous measurement of multiple wavelengths. In single-beam (Figure 3.3) and dual-beam spectrometers, the light from a lamp is dispersed before reaching the sample cell. In an array-detector instrument, all wavelengths pass through the sample and the dispersing element is between the sample and the array detector (Rendina, 1976).

A spectrophotometer can be either single beam or double beam. In a single beam instrument (such as the Spectronic 20), all of the light passes through the sample cell. I_o must be measured by removing the sample. This was the earliest design, but is still in common use in both teaching and industrial labs (Figure 3.3).

In a double-beam instrument, the light is split into two beams before it reaches the sample. One beam is used as the reference; the other beam passes through the sample. Some double-beam instruments have two detectors (photodiodes), and the sample and reference beam are measured at the same time. In other instruments, the two beams pass through a beam chopper, which blocks one beam at a time. The detector alternates between measuring the sample beam and the reference beam (Skoog et al., 1992).

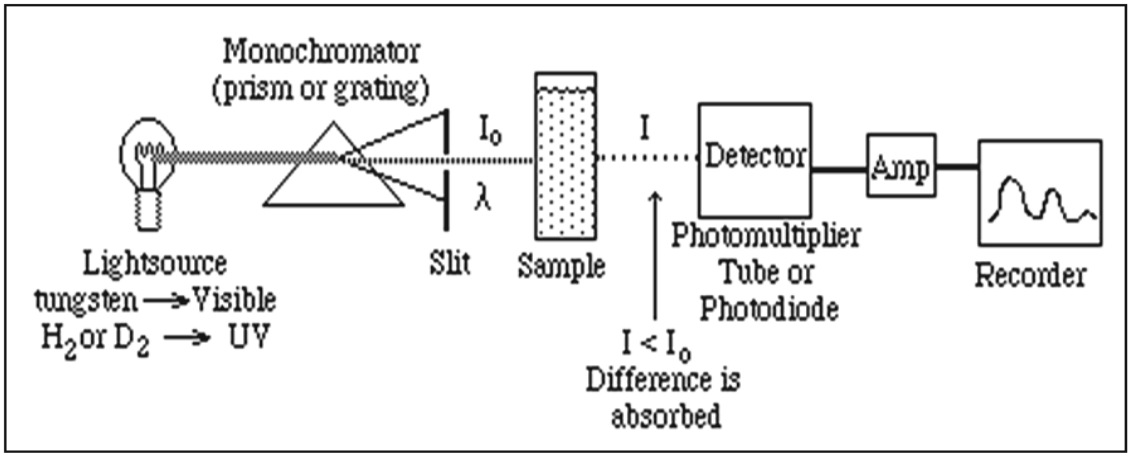


Figure 3.3 Schematic of a wavelength-selectable, single-beam UV-Vis spectrophotometer (www.chem.vt.edu)

3.2.3 Ion chromatography

Ion chromatography (Figure 3.4) is used for the separation and determination of ionic solutes in water in general, especially in environmental industrial processes, metal industry and industrial waste water in biological systems in pharmaceutical samples in food .Ion chromatography provides a single instrumental technique that may be used for rapid and sequential measurement. It is often used for the analysis of common anions such as bromide, chloride, fluoride, nitrate, nitrite, phosphate and sulphate to characterize water quality (Hamish, 1989; Joachim, 2005).

Suppression in ion chromatography is needed when conductivity detectors are used and the mobile phase is intensively conducting, saturating the detector's response. A device, called the suppressor, is inserted between the ion-exchange separator column and the detector. The packing consists of small polymer beads carrying acidic protons (H^+) on their surface.

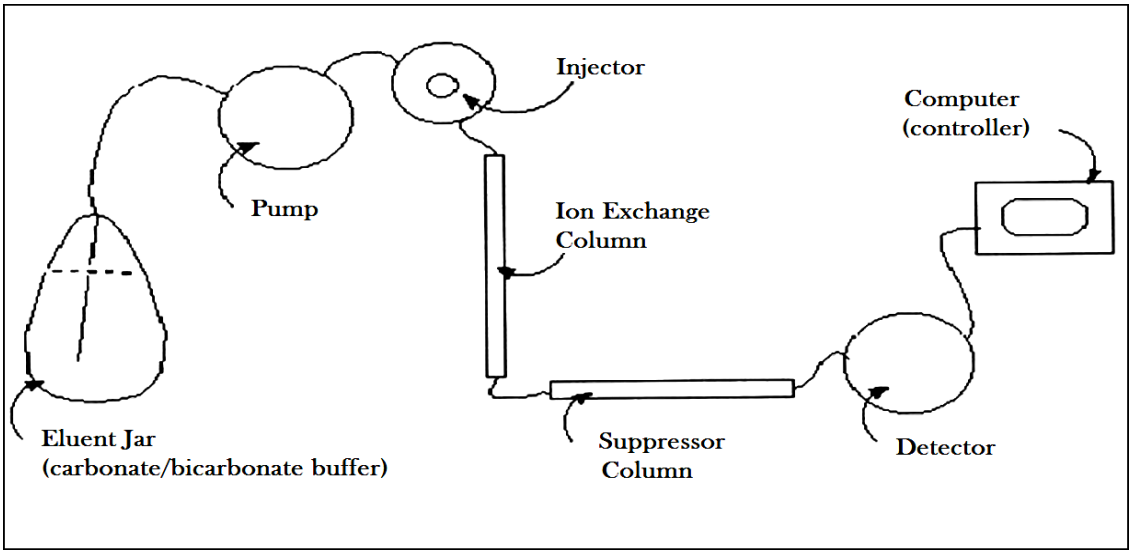


Figure 3.4 Basic components of ion chromatography (Piers, 2003)

The anions of interest are separated on the basis of their relative affinities for a low capacity, strong basic anion exchanger (guard and separator columns). The separated anions are directed through a membrane suppressor where they are converted to their highly conductive acid forms and the carbonate-bicarbonate eluent is converted to weakly conductive carbonic acid. The separated anions in their acid forms are measured by conductivity. They are identified by their retention time as compared to standards (Metrohm Ltd, 1999; Piers, 2004).

In ion chromatography, the support material is a polystyrene/divinylbenzene (PS/DVB) based resin (Joachim, 1986). The column material (resin) is synthesized to serve as cation exchange or anion exchange columns. The most common site on anion exchanger is the tertiary amine group $-N(CH3)_3^+$, OH^- , a strong base and the sulphonic acid group $-SO_3^- H^+$ for a cation.

Anion-exchange resin

The anion-exchange resins used by Dionex are composed of a surface sulphonated PS/DVB core (10-25 μm) and a totally porous latex particle which is completely

aminated. The latex particles have a considerably smaller diameter of about 0.1 μm and carry the actual ion exchange function $-NR_3^+$. The structure of the anion exchange resins used by Dionex and developed by Small is illustrated in Figure 3.5.

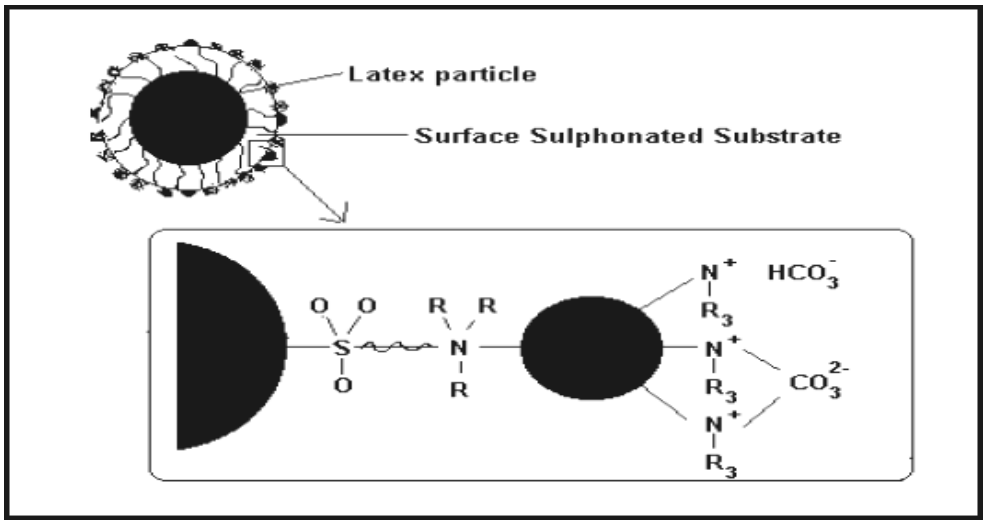


Figure 3.5 The structure of the anion exchange resins (Weiss, 1986)

The exchange process of a solution, which contains an anion, A^{X-} on an anion exchange column, is described by the following reaction:

$$xN(CH_3)_3^+OH^- \text{ (solid)} + A^{X-} \text{ (solution)} \leftrightarrow (N(CH_3)_3^+)_xA^{X-} \text{ (solid)} + xOH^- \text{(solution)} \quad \text{(Equation 3.4)}$$

The affinity of the resin for the anion relative to OH^- ion is $SO_4^{2-} > C_2O_4^{2-} > I^- > NO_3^- > Br^- > Cl^- > HCO_2^- > OH^- > F^-$. These conditions depend on various factors, such as the type of resin, size or the hydrated ion, and so on.

Cation exchange resin

The stationary phase of a cation exchange column is based on inert, surface sulphonated, cross-linked polystyrene (Figure 3.6).

The exchange process for a cation, M^{x+}, can be described by the equilibrium:

$xRSO_3^-H^+$ (solid) + M^{x+} (solution) ↔$(RSO_3^-)xM^{x+}$ (solid)+xH^+ (solution) (Equation 3.5)

Since the core of a cation exchange resin is strongly hydrophobic, the diffusion into the resin of highly dissociated and hydrated species such as Na^+, K+, and Mg^{2+}, can be neglected. Consequently, the diffusion paths are short and high efficiencies are achieved (Fritz et al., 2000).

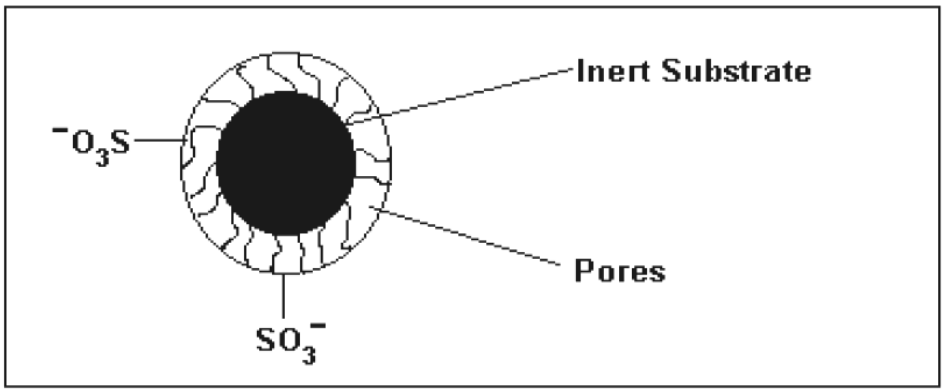


Figure 3.6 The structure of a cation exchange resin (Weiss, 1986).

Detection and suppressor column

The detection mode that is used is a major factor that determines the types of mobile phases suitable for the desired separation. The detector signal obtained by the background, i.e., the mobile phase itself must not be too high otherwise it would be difficult to obtain linearity, wide dynamic range and stability of the baseline.

As the solution from the analytical column flows into the suppressor column, the carbonate and bicarbonate ions combine chemically with the proton on the polymer surface forming carbonic acid which, being unstable in aqueous solution decompose to carbon dioxide gas and water. In this way the carbonate and bicarbonate ions are removed from the solution (Piers, 2003):

$HCO_3^{-1} + H^+ \rightarrow [H_2CO_3] \rightarrow H_2O + CO_2$ (Equation 3.6)

$CO_3^{2-} + 2\ H^+ \rightarrow [H_2CO_3] \rightarrow H_2O + CO_2$ (Equation 3.7)

For the analysis of cations, the analytical column is made of anions (usually RSO_3^- groups) chemically bound to a polymer resin (Metrohm Ltd, 1999).

3.2.4 High-performance liquid chromatography (HPLC)

High-performance liquid chromatography (HPLC) is liquid chromatography which has been optimized to provide rapid high resolution separations. It evolved over nearly a century from the early work of Tswett in the late 1900s to the highly sophisticated reliable and fast liquid chromatography (LC) techniques in common use today. HPLC is probably the most universal type of analytical procedure; its application areas include quality control, process control, forensic analysis, environmental monitoring and clinical testing. In addition, HPLC also ranks as one of the most sensitive analytical procedures and is unique in that it easily copes with multi-component mixtures. It has achieved this position as a result of the constant evolution of the equipment used in LC to provide higher and higher efficiencies at faster and faster analysis times with a constant incorporation of new highly selective column packing (Simpson et al., 1987).

Principle

The sample to be analyzed is introduced in small volume to the stream of mobile phase and is retarded by specific chemical or physical interactions with the stationary phase as it traverses the length of the column. The amount of retardation depends on the nature of the analyte, stationary phase and mobile phase composition. The time at which a specific analyte elutes (the retention time) is considered a reasonably unique identifying characteristic of a given analyte. The use of pressure increases the linear velocity (speed) giving the components less

time to diffuse within the column, leading to improved resolution in the resulting chromatogram. Common solvents used include any miscible combinations of water or various organic liquids (the most common are methanol and acetonitrile). Water may contain buffers or salts to assist in the separation of the analyte components, or compounds such as trifluoroacetic acid which acts as an ion pairing agent (Simpson et al., 1987)

Types of HPLC

Adsorption chromatography

Separation is based on repeated adsorption-desorption steps:

Normal phase chromatography

Also known as normal phase HPLC (NP-HPLC) was the first kind of HPLC chemistry used, and separates analytes based on polarity. This method uses a polar stationary phase and a non-polar mobile phase, and is used when the analyte of interest is fairly polar in nature. The polar analyte associates with and is retained by the polar stationary phase. Adsorption strengths increase with increase in analyte polarity, and the interaction between the polar analyte and the polar stationary phase (relative to the mobile phase) increases the elution time. The interaction strength not only depends on the functional groups in the analyte molecule, but also on steric factors and structural isomers are often resolved from one another. Use of more polar solvents in the mobile phase will decrease the retention time of the analytes while more hydrophobic solvents tend to increase retention times. Particularly polar solvents in a mixture tend to deactivate the column by occupying the stationary phase surface. This is somewhat particular to normal phase because it is most based mainly on an adsorptive mechanism (the interactions are with a hard surface rather than a soft layer on a surface).

Reversed phase chromatography

Reversed phase HPLC (RP-HPLC or RPC) consists of a non-polar stationary phase and an aqueous, moderately polar mobile phase. One common stationary phase is silica which has been treated with RMe_2SiCl, where R is a straight chain alkyl group such as $C_{18}H_{37}$ or C_8H_{17}. The retention time is therefore longer for molecules which are more non-polar in nature, allowing polar molecules to elute more readily. Retention time is increased by the addition of polar solvent to the mobile phase and decreased by the addition of more hydrophobic solvent. Reversed phase chromatography is so commonly used that it is not uncommon for it to be incorrectly referred to as "HPLC" without further specification (IUPAC, 2008; Horvath, 1967).

RPC operates on the principle of hydrophobic interactions, which result from repulsive forces between a polar eluent, the relatively non-polar analyte, and the non-polar stationary phase. The binding of the analyte to the stationary phase is proportional to the contact surface area around the non-polar segment of the analyte molecule upon association with the ligand in the aqueous eluent. This solvophobic effect is dominated by the force of water for "cavity-reduction" around the analyte and the C18-chain versus the complex of both. The energy released in this process is proportional to the surface tension of the eluent (water: 7.3×10^{-6} J/cm², methanol: 2.2×10^{-6} J/cm²) and to the hydrophobic surface of the analyte and the ligand respectively.

The retention can be decreased by adding less-polar solvent (MeOH, ACN) into the mobile phase to reduce the surface tension of water. Gradient elution uses this effect by automatically changing the polarity of the mobile phase during the course of the analysis (IUPAC, 2008).

Structural properties of the analyte molecule play an important role in its retention characteristics. In general, an analyte with a larger hydrophobic surface area (C-H, C-C, and generally non-polar atomic bonds, such as S-S and others) results in a

longer retention time because it increases the molecule's non-polar surface area, which is non-interacting with the water structure. On the other hand, polar groups, such as –OH, $–NH_2$, COO^- or $–NH_3^+$ reduce retention as they are well integrated into water. Very large molecules, however, can result in an incomplete interaction between the large analyte surface and the ligands alkyl chains and can have problems entering the pores of the stationary phase (IUPAC, 2008).

Another important component is the influence of the pH since this can change the hydrophobicity of the analyte. For this reason most methods use a buffering agent, such as sodium phosphate, to control the pH (IUPAC, 2008).

A volatile organic acid such as formic acid or most commonly trifluoroacetic acid is often added to the mobile phase, if mass spectrometry is applied to the eluent fractions. The buffers serve multiple purposes: they control pH, neutralize the charge on any residual exposed silica on the stationary phase and act as ion pairing agents to neutralize charge on the analyte. The effect varies depending on use but generally improve the chromatography (IUPAC, 2008; Horvarth, 1976).

Ion exchange chromatography

In Ion-exchange chromatography, retention is based on the attraction between solute ions and charged sites bound to the stationary phase. Ions of the same charge are excluded. Some types of Ion Exchangers include (a) polystyrene resins- allow cross linkage which increases the stability of the chain, higher cross linkage reduces swerving, which increases the equilibration time and ultimately improves selectivity; (b) cellulose and dextrin ion exchangers (gels), these possess larger pore sizes and low charge densities making them suitable for protein separation; (c) controlled-pore glass or porous silica.

In general, ion exchangers favour the binding of ions of higher charge and smaller radius.

An increase in counter ion (with respect to the functional groups in resins) concentration reduces the retention time. An increase in pH reduces the retention time in cation exchange while a decrease in pH reduces the retention time in anion exchange.

This form of chromatography is widely used in the following applications: in purifying water, preconcentration of trace components, ligand-exchange chromatography, ion-exchange chromatography of proteins, high-pH anion-exchange chromatography of carbohydrates and oligosaccharides.

There are many types of detectors that can be used with HPLC, some of the more common detectors include: Refractive Index (RI), Ultra-Violet (UV), Fluorescent, Radiochemical, Electrochemical, Near-Infra Red (Near-IR), Mass Spectroscopy (MS), Nuclear Magnetic Resonance (NMR), and Light Scattering (LS) (DiCesare et al. 1981; Brown, 1995).

3.2.5 Inductively coupled plasma - Optical emission spectroscopy (ICP-OES)

ICP-OES technique was used in this work for the quantification of metals in water and soils samples.

Principle

ICP-OES (Figure 3.7) makes use of the fact that the atoms of elements can take up energy from inductively coupled plasma, their electrons become are thereby excited and then fall back into their ground states, emitting characteristic radiation. The identification of this radiation permits the qualitative analysis of a sample. A quantitative determination takes place on the basis of the proportionality of radiation intensity and element concentration in calibration and analysis samples. The energy transfer for electrons when they fall back to the

ground state is unique to each element as it depends upon the electronic configuration of the orbital (Bauer and O'Reilly, 1978; Alcock, 1995).

The apparatus for the ICP-OES is composed of three main sections: the nebulizer, the torch and the detection system (Tyler and Horiba, 2000.ICP-OES) as shown in Figure 3.7.

The energy transfer, E, is inversely proportional to the wavelength of electromagnetic radiation:

$$E = hc/\lambda \qquad \text{(Equation 3.8)}$$

where h is Planck's constant, c the velocity of light and λ is the wavelength, and hence the wavelength of light emitted is also unique (Skoog et al., 1992).

An energy source is needed in order to atomize and ionize the samples to allow radiation emission. In the ICP-OES, plasma is used as an energy source, producing heat of 5500 K- 8000 K and up to 10 000 K in some regions, enough to ionize and excite most analyte atoms. Molecular interferences are greatly reduced with this excitation source but are not eliminated completely.

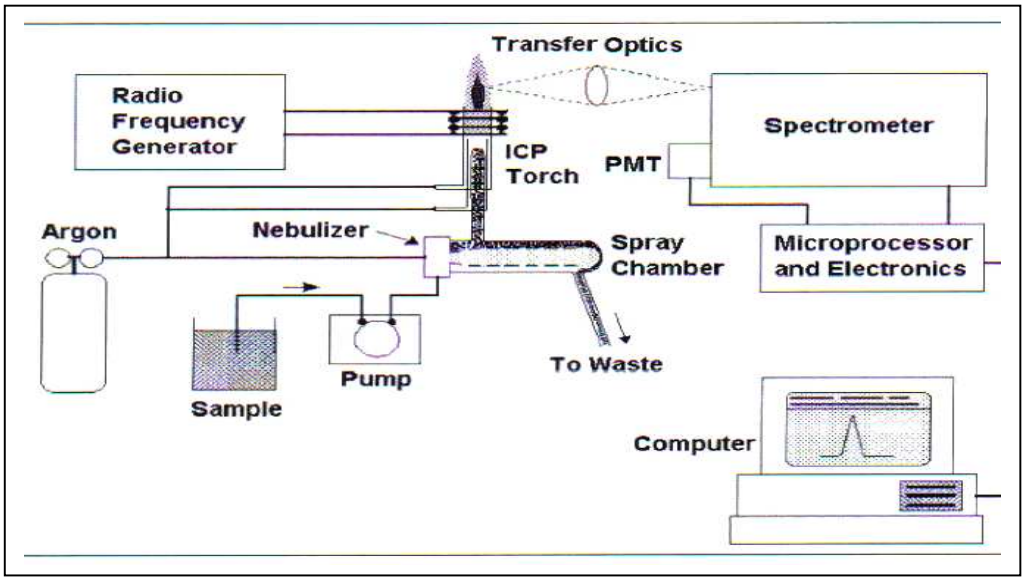


Figure 3.7 ICP-OES schematic diagram (Arcinus, 2000)

ICP sources are used to excite atoms for atomic-emission spectroscopy and to ionize atoms for mass spectrometry.

The element type is determined based on the position of the photon rays, and the content of each element is determined based on the ray's intensity (Alcock, 1995). Argon gas is supplied to the torch coil, and high frequency electric current is applied to the work coil at the tip of the torch tube in order to generate plasma. Using the electromagnetic field created in the torch tube by the high frequency current, argon gas is ionized and plasma is generated. Solution samples are introduced into the plasma in an atomized state (Boumans, 1996).

ICP process

The sample being analyzed is introduced into the plasma as a fine droplet aerosol. The processes, which occur while the aerosol moves up through the plasma, are described in Figure 3.8 (Moore, 1989).

The hot plasma removes any remaining solvent and causes sample atomization followed by ionization. The aerosol droplets introduced to plasma after nebulization is desolvated to solid salt particles and vaporized to produce gas-phase molecular species. These species subsequently undergo dissociation to free atoms, namely atomization. With sufficient energy, these free atoms are excited to higher energy stages and further to higher states of thee ions called excitation and ionization. At this condition, most elements emit light of characteristic wavelengths, which can be measured and used to determine the concentration. The following reactions are shown the main reaction of the processes occurred in the plasma (Figure 3.8).

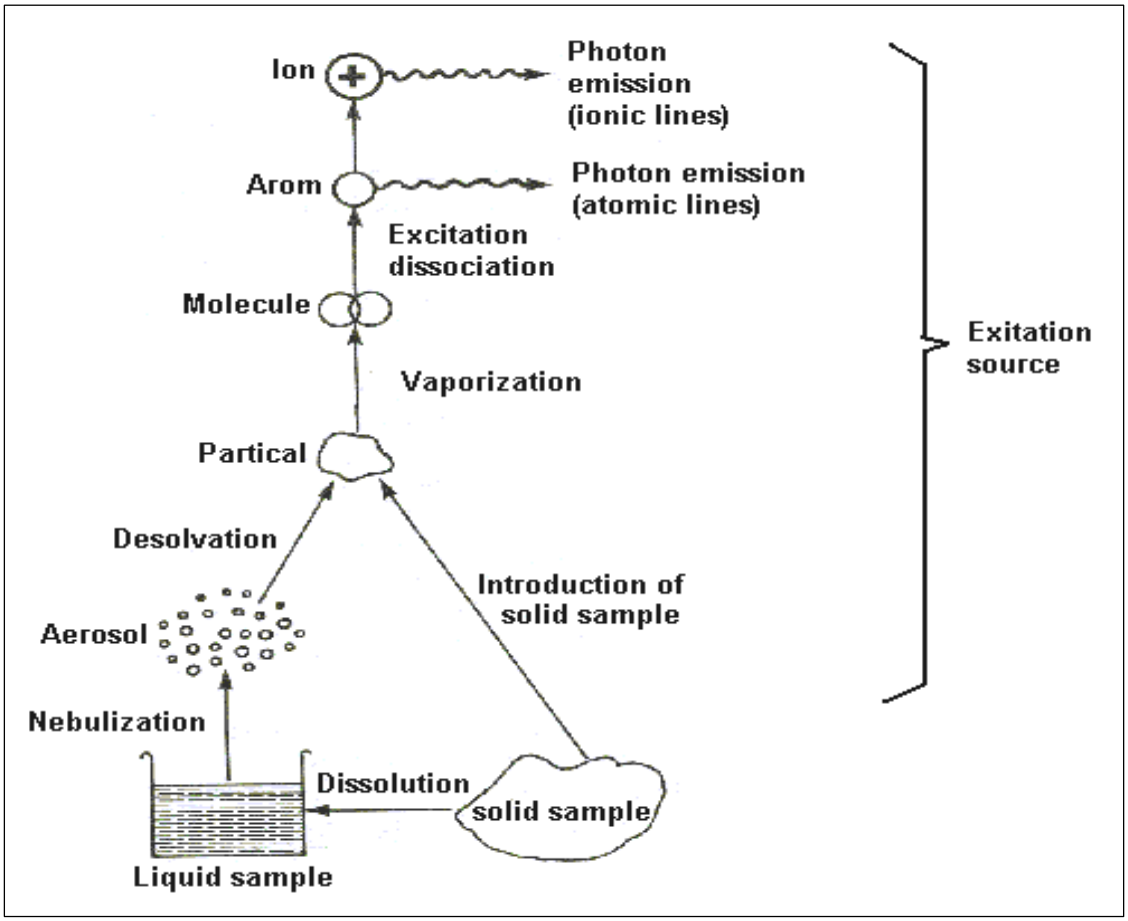


Figure 3.8 ICP process (Moore, 1989)

There are three types of detectors, namely sequential, simultaneous multi-channel and Fourier transform. Sequential instruments are usually programmed to move from the line for one element to that of a second, pausing long enough at each to obtain a satisfactory signal-to- noise ratio. In contrast, multi-channel instruments are designed to measure the intensities of emission lines for a large number of elements (up to 50 or 60) simultaneously, or nearly so (Goodfellow, 2003).
Multichannel instruments normally use a Rowland circle in a Paschen-Runge arrangement (Figure 3.9). Spectral dispersion of polychromatic radiation and focusing is achieved simultaneously through a grating scratched in a concave

surface. The focusing takes place on the Rowland circle (with a radius which is half the curvature of the grating). There are two types of multi-channel instruments: polychromators and array-based systems.

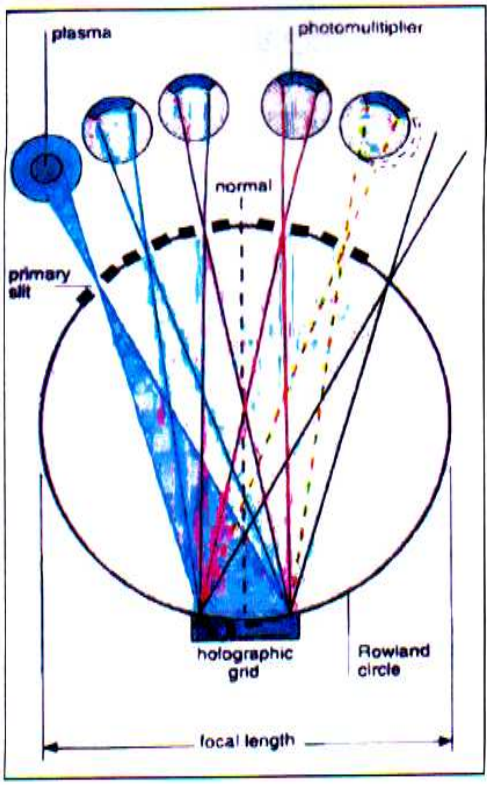


Figure 3.9 Multichannel instrument with a Rowland circle (Schwedt, 1997)

CHAPTER FOUR – MOTIVATION AND OBJECTIVES OF THE STUDY

4.1 MOTIVATION

The use of cyanide in gold extraction is of concern. This pollutant is discharged with effluent and tailings from gold extraction based on the assumption it will decompose within a relatively short period of time.

The cyanide is from leaching residues of the adsorption of gold and is transferred to the liquid phase as an anionic cyanide complex ion during the leaching operation. Depending on the pH of the tailings slurry, the free cyanide may exist as aqueous HCN that can escape to the atmosphere as $HCN_{(g)}$ or occur as soluble cyanide ions (CN^-) that can be leached by infiltrating water to the sub-surface environment. Additionally, the presence of pyrite minerals in the Witwatersrand Basin makes them susceptible to acid drainage.

The free cyanide (CN^-) ions or simple cyanide compounds giving free CN^- ions readily and weak metal-cyanide complex ions, that can be present in leaching wastes, are highly toxic. For instance, the cyanide in very stable complex structures such as $Fe(CN)_6^{4-}$ can be degraded or decomplexated only under very specific conditions (e.g. by photodecomposition, low pH, etc..) to yield $HCN_{(g)}$.

Water quality information from the Rand Water Board, Water Research Commission and Crown Gold Recovery shows that the drainage systems have been affected by acid mine drainage and high salt loads from tailings spillages, runoff as well as seepage from mine tailings. Water emanating from the tailings dams contains cyanide. This can seep into the groundwater which is accessed by many people through wells and boreholes. The utilization of this underground water can be harmful to these people.

Also, the shallow groundwater contaminated as a result of mining activities is contributing to the quality of water emanating from the Witwatersrand watershed. Our concern is justified by the presence of cyanide in tailings dams and streams which can affect the drinking water source.

4.2 OBJECTIVES

This research was a quantitative assessment of cyanide pollution on the East and Central Rand Goldfields of the Witwatersrand Basin. The following environmental

compartments were studied: tailings, sediments, ground and surface water. These environments were studied so as to address the following specific objectives:

- to assess the transport and fate of cyanide
- to study the speciation of cyanide, namely: CN_{free}, CN_{WAD}, CN_{SAD}
- to study the distribution of various transformation species of cyanide e.g. cyanate, thiocyanate and ammonium
- to predict the speciation of cyanide by use of geochemical modelling techniques

CHAPTER FIVE - SAMPLING, SAMPLE PREPARATION AND STORAGE, ANALYTICAL METHOD, OPTIMISATION AND QUALITY CONTROL

5.1 Introduction

This chapter provides a summary of the preparative steps before the analysis of samples. These include: the collection of tailings sediments and water samples; in situ measurements of physical-chemical parameters and the pre-treatment of the samples. The sampling techniques applied are also discussed. The analytical techniques used in this study as well as the optimisation and the quality control are described.

5.2 Sampling

5.2.1 Tailings sampling

The sampling of the tailings dams had the objective to collect representative and

sufficient material for the assessment of the hazard potential, especially the cyanide species. Samples were collected from representative tailings in the study area.

The samples were collected both vertically and laterally. Near surface samples were collected by means of shovels (after scrapping off the oxidised layers) while the subsurface samples were collected by means of hand augers. Sample disturbance and contamination were minimised, for instance, subsurface environments are often chemically reducing and so a significant source of sample disturbance and contamination is exposure to air. Samples were thus collected into black polythene bags and the air inside removed. The samples were oven-dried and pulverised. Field parameters were immediately measured which include pH, temperature, redox potential (Eh) and electrical conductivity (Ec).

Water and sediment samples from the pond were directly placed in a polypropylene container and tailings samples collected at each location and at each depth were placed immediately in plastic bags and stored in the dark at $4^{o}C$.

The coordinates of the sampling points were measured with a Global Positioning System (GPS).

Geochemical parameters of the tailings were also determined, mainly by inserting the appropriate probe into the slurry in situ. Where the slurry was not immediately available, it was made by mixing a portion of the tailings (50 g) with about 50 ml of deionised water and the measurements taken of the resulting slurry (Smith, 1995; USGS, 2004).

The cycle periods have to be known along with many other factors of influence in an environmental system. A typical example would be the sampling of tailings surface liquid (or solids), decant liquids or return dam bulk liquid. All of these systems undergo massive cyclic fluctuations through the influence of chemical and physical changes from process management tailings, surface events and seasonal climatic conditions.

5.2.2 Sediment sampling

Sediments included stream sediments and wetland sediments. The stream sediment survey was done by collecting a composite sample of fine-grained sediment on a transverse perpendicular to the stream course. Some background samples were also collected in order to determine the best contrast between background element concentrations and contamination.

About 500 g of sample were collected into black polythene bags and oven-dried in the laboratory (at about 50 ^{o}C). The samples were pulverised to fractions of < 60 μm and stored in small polystyrene sample bottles prior to analysis (Ndasi, 2004).

In the case of wetland sediments, augers were used for sampling at about 30 cm depth intervals. Where the sediment profiles had been exposed (for example at Fleurhof dam, Figure 1.6), sampling was done by scrapping off the oxidised outer layers and sampling the unoxidised layers following the profile layout.

Geochemical parameters of the sediments were also determined, mainly by inserting the appropriate probe into the slurry in situ. The coordinates of the sampling points were measured with a Global Positioning System (GPS).

5.2.3 Water sampling

The water samples were collected according to commonly accepted sampling procedures (Mugo *et al*., 1993; Hermond and Fechner-Levy, 2000; USGS, 2004. Water resources). The samples were collected into acid-washed and conditioned polypropylene (PP) 1litre bottles. Surface water samples were taken from the main streams along the thawed and ground water samples were collected mainly from stream banks. In streams, samples were collected in the main stream flow away from the banks and where wading into the stream was involved, samples were taken upstream of the wading path.

Drill holes were made by use of augers and sufficient time was allowed for flushing out and equilibration. A point sampler consisting of a Perspex rod and a PP cup was used to draw out the sample. Water samples were also collected from a reprocessing tailings dam. Drain water was taken from the pipe.

The PP bottles were rinsed with the water to be sampled just before the water samples were collected and the rinse water was discarded away from the sampling point. This was done to equilibrate the sampling equipment to the sample environment and to help ensure that all cleaning-solution residues had been removed before commencing with sampling. (USGS, 2004. Water resources).

The PP bottles were filled with water leaving no air space and the geochemical parameters were measured in the field before tightly closing the containers to prevent any leakage. Each bottle was then marked with the date of sampling and a sample description, placed into cooler boxes and transported to the laboratory.

The geochemical or physical-chemical parameters were measured directly at the sampling sites and include: temperature (^{o}C), pH, Ec and Eh. These measurements were carried out with the portable kit Multi Line F/Set 3 of the Wissenschaftlich-Technische Werkstatten, Weiheim (WTW, Germany) equipped with a pH electrode, an integrated temperature probe (SenTix 41), a standard conductivity cell (Tetra Con 375) and an oxidation-reduction potential probe (SenTix ORP). The pH electrode was calibrated according to IUPAC recommendations against two buffer solutions pH 4 and pH 7. Redox potentials were obtained from Pt electrodes versus Ag/AgCl. The electrodes were checked using a standard buffer solution and all reported potentials were corrected relative to the standard hydrogen electrode (SHE).

5.3 Sample preparation

5.3.1 Water samples

In the laboratory, each sample was divided into three parts: the one was unfiltered and unacidified and tested for the anions (Cl^-, Br^-, F^-, NO_3^-, NO_2^-, PO_4^{3-} and SO_4^{2-}) using ion chromatography; the other was filtered (using a 0.45 μm filter), acidified and analysed for major and trace metal elements using ICP-OES techniques. Acidification was done with 1 vol. % HNO_3 (55%) Merck to pH < 2; the third portion was filtered using a 0.45 μm cellulose nitrate filter paper and then the pH raised to 12 by adding a solution of 1 M NaOH after removing oxidising matter as well as sulphide. The pH was raised in order to avoid the loss of molecular HCN by volatilisation. It was analyzed for cyanides species using ISE, UV-Vis spectrophotometer and HPLC techniques.

Samples were refrigerated at 4ºC and covered with black plastic prior to analysis to avoid U.V.light (ferrocyanide and ferricyanide complexes of cyanide undergo photodecomposition with ultraviolet light).

The adsorption of CN- and its complexes on the colloids was also studied by analysing a filtered and non filtered sample.

5.3.2 Leaching test

All cyanide forms were leached by a caustic solution since very alkaline conditions make even strongly complexed cyanides, soluble (Theis et al., 1994). Therefore, cyanide content in the sodium hydroxide solution represents the maximum extractable quantity of cyanides from the tailings and sediments. 10 g of solid tailings in 250 ml of 1 M NaOH extractant solution were shaken at 170 rpm for 16 hrs on a shaker (Labcon, CJ Labs) and then centrifuged using a Mistral 1000 centrifuge (20 x 100 rpm).

Free cyanide was then analyzed in the leachate. For CN_T and CN_{WAD}, leaching was performed using 500 mg: 500 ml of 10 % w/v NaOH solution. The resultant leachate was distilled (reflux) with 50 ml of H_2SO_4 (1:1 v/v H_2SO_4 for CN_T and 1: 9 v/v CH_3COOH for CN_{WAD}) and the distillate collected into 10 ml of 1 M NaOH. Leaching with water was also performed with the purpose to compare the results with the alkaline leachate. Thiocyanate (SCN^-) and cyanate (CNO^-) were determined in the water leachate (10 g of solid material: 200 ml deionised water according to standard methods (Clesceri et al. 1989). Ammonium (NH_3/NH_4^+) was performed in water leachate using Nesslerization method. Thiosulphate ($S_2O_3^{2-}$) was determined in water leachate using UV -Vis spectroscopy. Total metals in the water leachates (2 g of solid material: 200 ml deionised water) were determined by ICP-OES. Metal-cyanide complexes were analysed in alkaline leachate (2 g of solid material: 100 ml of 0.01 M NaOH) using reversed ion-pair HPLC method.

5.3.3 Total digestion

Total digestion for the determination of total metal concentration was done using a mixture of hydrofluoric acid (HF) and aqua regia (3: 1 by volume of HCl: HNO_3). HF dissolves the silicate minerals. The dissolving power of aqua regia is derived mainly from the ability of chlorine and nitrosyl chloride to oxidize the metals which are then transformed to stable complex anions by reaction with the chloride ion (Rauret et al., 2000).

An Anton Paar GmbH Multiwave microwave with Rotor 6MF 100 was used to digest samples. The maximum microwave power was 1400 W. The temperature measurement range is from 0^oC to 300^oC. The closed vessel technique helps to speed up reactions by allowing higher temperatures while preventing the loss of volatile analytes and minimize exposure to corrosive gases and hazardous solvent vapour.

5.3.4 Cation exchange capacity (CEC)

The cation exchange capacity (CEC) of a soil is simply a measure of the quantity of sites on the soil surface that can retain positively charged ions (cations) by electrostatic forces. Cations retained electrostatically are easily exchangeable with other cations in the soil solution and are thus readily available for plant uptake. It is also an index of the clay activity and mineralogy, which is important for calculating mineralization rates, leaching rates and interaction with pollutants.

CEC is important for maintaining adequate quantities of plant availability calcium (Ca^{2+}), magnesium (Mg^{2+}) and potassium (K^{+}) in soils. Under acidic conditions pH < 5.5, aluminum (Al^{3+}) may also be present as an exchange cation. Soil CEC can be expressed two ways:

- the number of cation adsorption sites per unit weight of soil
- the sum total of exchangeable cations that a soil can absorb.

Two different, but numerically equivalent sets of units are used: meq/100g (milliequivalents of charge per 100 g of dry soil) or $cmol_c/kg$ (centimoles of charge per kilogram of dry soil).

CEC is influenced by the strength of adsorption and the relative concentration of the cation in the soil solution.

In the procedure of determining CEC (Allen et al., 1974), the cations particularly Na, K, Ca and Mg are displaced from the exchange sites on the material colloids and replaced by a cation from the extractant. After the washing stage the adsorbed cation is then displaced by a leaching solution in which it is subsequently determined. Almost all procedures in use for CEC have this sequence.

5.3.5 Particle size distribution

The measurement of particle size is important since the stability, chemical reactivity, opacity, flowability and material strength of many materials are affected by the size and characteristics of the particles within them.

The measurements of particle size were performed on dried samples using the Malvern Mastersizer Hydro 2000. The results for particle size distribution in the slimes tailings are given in Chapter 6.

5.4 Method development and optimisation

5.4.1 Instrumental analysis

(a) Ion selective electrode

A cyanide- electrode was used to determine free cyanide and total cyanide. Cyanate was determined using an ammonia- electrode.

Free and total cyanides

The CN-concentration was measured using a CN-Electrode (crystal membrane, Metrohm 6.0502.130) in combination with an Ag/AgCl single junction Reference electrode connected to the read out device, a pH meter (Beckman ϕ 50 pH meter). The technical specifications are followed:
Preconditioning / Standard solution: 1000 mg l^{-1} CN^- as KCN
Preconditioning time : 5 minutes
Optimum pH range : pH 11 - pH 13
Temperature range : 5°C - 80°C
Recommended ISAB : 10 M NaOH (Add 2% v/v)
Recommended reference electrode : double junction (ELIT 002)
Reference electrode outer filling solution : 0.1 M KNO_3
Electrode slope at 25°C : 56±5 mV/decade
Concentration range : 0.01 to 260 mg l^{-1}
Response time : < 10 seconds (Defined as time to complete 90% of the change in

potential after immersion in the new solution).

Time for stable reading after immersion: < 1 to > 5 minutes, depending on concentration, use of ISAB, nature of sample and stabilisation time of liquid junction potential of reference electrode.

Potential drift (in 1000 mg l^{-1}): < 3 mV/day (8 hours), measured at constant temperature and with ISE and reference electrode continually immersed.

A 1000 ppm CN^- stock solution was prepared by dissolving 2.57 g of KCN (pro analysis, Merck) in a 1000 ml volumetric flask with deionised water containing 10 ml of 10 M NaOH as ionic strength buffer adjuster (ISAB). The stock solution was stored in a polypropylene bottle at 4ºC. Standards at the required concentration were prepared daily by appropriate dilution of the stock solution.

Accurate calibration is an important factor in the determination of analyte concentration in any analytical technique. In the case of ISE methods, calibration is carried out by immersing the electrodes in a series of solutions of known concentration and then plotting the graph of the voltage versus the log of the activity. For a full calibration, 100 ml of solutions containing 0.01, 0.05, 0.1, 0.5 and 1 mgl^{-1} CN^- (as KCN) were prepared. An example of a calibration curve for CN^- is shown in Figure 5.1.

NB: 2 ml 10 M NaOH buffer solution must be added to each standard and mixed thoroughly to ensure a correct pH level for electrode operation and eliminate any possibility of toxic HCN fumes. Polypropylene beakers were used for measurements, glass beakers were avoided for contamination of cyanide on the wall of the glass.

Sample preparation

2 ml of buffer solution must be added to 100 ml of each sample and stirred well before measurement.

Direct measurement

It is important to note that, the electrodes must be washed and dried between each sample, to avoid cross contamination, and sufficient time must be allowed (2 or 3 minutes), before taking a reading after immersion, to permit the electrode signal to reach a stable value. For the highest precision, frequent recalibration is recommended. Buffer solution has been added equally to standards and samples then the results will not need adjusting because they will all be affected by the same dilution factor. Detection limit was 0.01 mg l^{-1}.

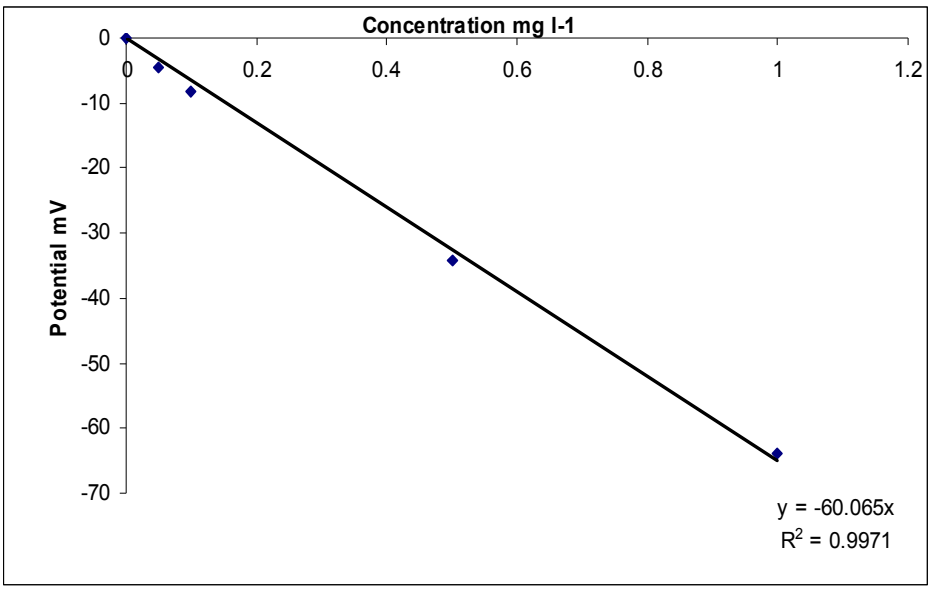


Figure 5.1 Calibration curve for CN^- (r^2=0.9971; RSD = 4.568)

Cyanate

The ammonia content before and after hydrolysis of cyanate was measured by ammonia selective electrode. A solution of NH_4Cl was used as standard.
Ammonia content was estimated from the calibration curve.

Calculations:

mg NH_3-H derived from CNO^- /l= A – B

where, A = mg NH_3-H /l found in the acidified and heated sample portion

B = mg NH_3-H /l found in untreated portion

mg CNO^- /l = 3.0 x (A – B)

Detection limit was 1 to 2 mg l^{-1}.

(b) Ion chromatography

Anions in water and in water leachate samples were analysed by ion chromatography. The eluent was a solution of 2.0 mM $NaHCO_3$ and 1.3 mM Na_2CO_3. The eluent was degassed by filtration through a 0.45 μm filter paper.
The metrohm 761 Compact Ion Chromatograph (Metrohm, Switzerland) with a Metrosep A Dual 2 (6.1006.100) 4.6 x 75 mm analytical column was used.
All solutions were prepared with purified water obtained by passing deionised water through a Milli-Q water purification system.

(c) UV vis spectroscopy

CN_{WAD}, thiocyanate, thiosulfate as well as ammonium were analysed using UV-Vis spectroscopy. The Jenway 6300 Spectrophotometer (U.K), single beam, was used and each compound was determined at various wavelengths. Standard solutions were prepared for each species to be analysed and then calibration curve were constructed after analysis of the standards.

Weak acid dissociable cyanide (CN_{WAD})

CN_{WAD} was determined in the distillate obtained after acid reflux distillation using a zinc acetate/ acetate buffer. Measurement of CN^- was done at 578 nm, 8 minutes

after adding the pyridine-barbituric acid reagent. CN^- in the alkaline distillate is converted to CNCl by reaction with chloramines-T at pH □ 8 without hydrolyzing to CNO^-. After the reaction is complete, CNCl forms a red-blue dye on addition of a pyridine-barbituric acid reagent.

Method detection limit (MDL) for CN_{WAD} was 0.5 mg l^{-1}.

Thiocyanate (SCN^-)

At an acidic pH (pH 2), ferric ion (Fe^{3+}) and SCN^- form an $Fe(SCN)^{2+}$ complex, an intense red colour suitable for colorimetric determination.

A series of standards containing between 0.02 g and 0.40 mg l^{-1} of SCN^- were prepared by pipetting measured volumes of standard KSCN solution. The acidified sample (pH 2) and another portion of standard were passed through the resin column at a flow rate not to exceed 20 ml/ min. Ferric nitrate solution (2.5 ml) were added to the collected eluates. Absorbances were measured at 460 nm against a reagent blank within 5 minutes.

Thiosulfate ($S_2O_3^{2-}$)

0.1 M of thiosulfate standard solution was prepared by dissolving a known amount of sodium thiosulfate pentahydrate in oxygen-free water containing a small amount of sodium carbonate (0.01% w/v) as stabilizer. This solution was standardized by iodometry.

Working standard solutions of thiosulfate were prepared by suitable dilution of standard solution with oxygen-free oxygen.

The standard iodate-iodide was added to the sample as well as to the thiosulfate standard solution prior to measurement the absorbance of the solutions at 350 nm. An iodate-free reagent blank was substracted from all absorbances measured.

A standard iodate-iodide solution was prepared by adding 50 ml of 1.0 x 10^{-2} N standard iodate to a solution containing 0.2 g of sodium carbonate and 72.6 g of potassium iodide, and diluting it to 500 ml to give 1.0 x 10^{-3} N iodate in a 0.87 M iodide solution (0.04% w/v sodium carbonate). An iodate-free iodide (0.87 M) solution was prepared and used for correcting the air-oxidation of iodide.

Ammonium

The principle of the determination of Ammonia by Nesslerisation is based on the formation of an orange-brown complex when an ammonia sample is reacted with an alkaline Nessler reagent according to the following reaction:

$$2K_2[HgI_4] + 2NH_3 \rightarrow NH_2Hg_2I_3 + 4KI + NH_4I \qquad \text{(Reaction 5.1)}$$

The formation of $NH_2Hg_2I_3$ is fairly fast but not instantaneous. It has been observed that the colour change is slowest after about 20 minutes.

Standards and samples reacted with alkaline Nessler's reagent at 20^{o}C and the absorbance was measured with a spectrophotometer at 420 nm. The colour production in this reaction follows Beer's law as long as the concentration of ammonia in between 0.2 to 10 ppm range. Below 0.2 ppm the method becomes insensitive and above 10 ppm there is rapid development of turbidity due to formation of mercuric iodide.

This will make absorbance readings deviates from the Beer's law where the concentration will be no longer proportional to ammonia present in the sample.

To obtain a calibration curve, standards of varying ammonia concentration were prepared ranging from 0.2 ppm to 10 ppm using ammonium sulphate.

To get the concentration of ammonia in the sample, each sample reacted with the nessler's reagent incubated at 20^{o}C and the absorbance read after 20 minutes.

The corresponding concentration of ammonia in the sample was read from the calibration graph.

(d) Reversed – Phase High performance Liquid Chromatography

Metal-cyanide complexes were determined by reversed - phase ion- interaction chromatography. A pairing-ion, hydrophobic, was also added to the mobile phase. Samples from this mode of separation are ionisable and can form an ion-pair with the pairing-ion. In the case of separation of metal-cyanide anions ($M(CN)_n^{z-ny}$, where ny > z), the pairing-ion present in the mobile phase is a cation, and its typically a quaternary ammonium ion.

The HPLC system consisted of a Metrosep isocratic pump (pressure 1.5 x 1000 psi) and a UV spectrophotometer (Lambda-max model 481) operated at 214 nm. The peak simple chromatographic was used. A silica-based C_{18} column (Supelcosil, 250 x 4.0 mm, 5 µm particle size) was used in this study. Mobile phases were prepared using water purified with Millipore Milli-Q water treatment system, a LC-grade acetonitrile (77: 23 v/v), an appropriate ion-interaction reagent and an inorganic modifier. The ion-interaction reagent used was tetra-n-butyl ammonium hydrogen sulphate (4 mM or 1.358 g l^{-1}).

The adjustment to the ionic strength of the mobile phase was made by adding NaH_2PO_4 (1.25 mM or 0.1499 g l^{-1}). The pH value of the mobile phase was adjusted to 8 by using a phosphate buffer ($H_2PO_4^-$ and HPO_4^{2-}). The mobile phase was filtered immediately prior to use trough 0.45 µm Millipore-type membrane filters and degassed before use.

The retention time and selectivity of metal complexes are depended on the composition of mobile phase and in particular, on its organic solvent. Retention time also change with the type of pairing-ion.

Standards solutions of the cyanide complexes of Ni (II), Co (III), Fe (II) and Fe (III) were prepared by dissolving weighed amounts of the respective potassium

salts (Table 5.1) in 0.01 M NaOH. Solution containing Cu (I) complex was prepared by dissolution of CuCN with a stoichiometric amount of KCN in 0.01M NaOH. The standards were supplied by industrial analytical (SA).

Standard solutions containing mixtures of the metal-cyanide complexes were prepared from the individual standard solutions. Standard solutions were kept at an alkaline pH and stored in darkness to minimize degradation.

Table 5.1 Preparation of metal cyanide standard stock solution 1000 mgl^{-1}

Anion	Compound	Mass (g)	Stability (days)
$[Cu(CN)_3]^{2-}$	Cu(CN)and Na(CN)	0.0632	1
$[Ni(CN)_4]^{2-}$	$K_2Ni(CN)_4.\ H_2O$	0.1591	1
$Co[(CN)_6]^{3-}$	$K_3Co(CN)_6$	0.1546	30
$[Fe(CN)_6]^{3-}$	$K_3Fe(CN)_6.3H_2O$	0.1993	30
$[Fe(CN)_6]^{4-}$	$K_4Fe(CN)_6.3H_2O$	0.1993	30

All the standards were run at a column temperature of 30^oC with a flow rate of 1 ml min^{-1} and an injection volume of 20 μl. Detection limit is in the mgl^{-1} range.

Results indicated that most complexes could be resolved except those of Cd(II) and ZN(II) which are very weakly absorbing at 215 nm and at the same time decompose in the mobile phase. The calibration curve peak area versus concentration for copper and nickel cyanide complexes is shown as an example in Figure 5.2.

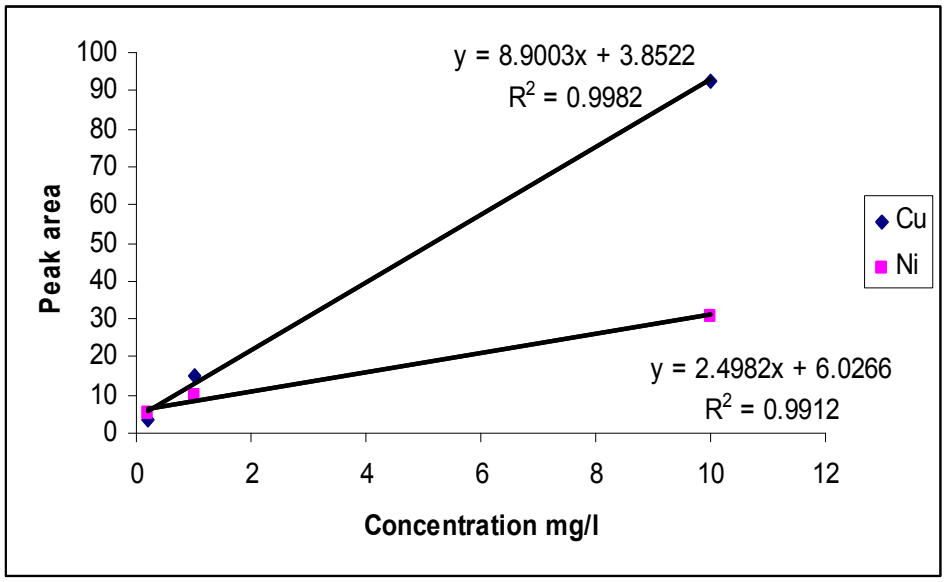


Figure 5.2 Calibration curve for $Cu(CN)_3^{2-}$ and $Ni(CN)_4^{2-}$

An example of chromatogram obtained after a run of a mixture of standard is given in Figure 5.3.

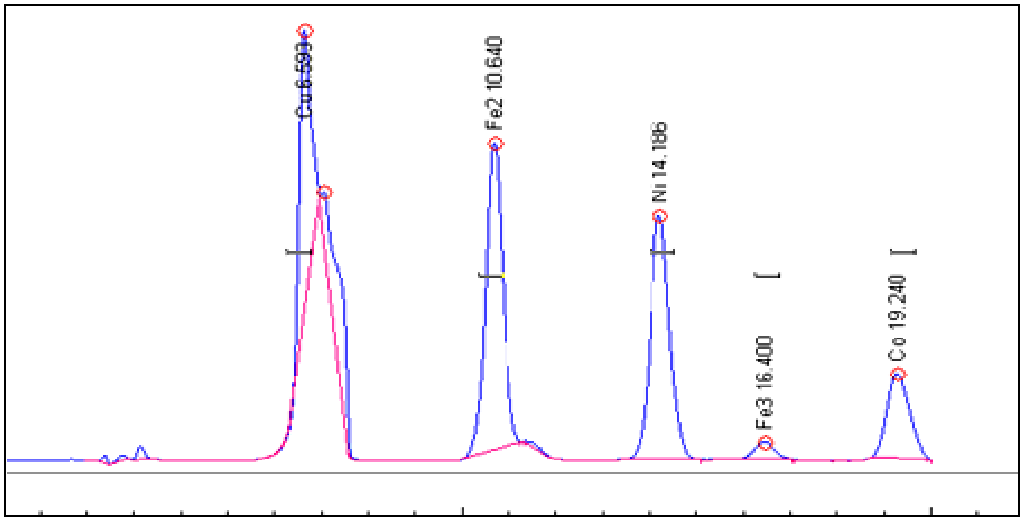


Figure 5.3 Chromatograms for cobalt-cyanide, copper-cyanide, Iron (II) and Iron (III)-cyanides and nickel-cyanide complexes.

(e) ICP-OES

Total metal concentrations in water and acid digested samples were obtained by ICP-OES (Kleve, Germany) with a coupled charge detection (CCD) system. The parameters in Table 5.2 were used and each element was determined at various wavelengths. The standards, supplied at a concentration of 10 mg l^{-1} were used to make working standards of concentration 0.05, 0.1, 0.2, 0.5 and 1 mg l^{-1}. Calibration curves were then constructed after the analysis of these standards.

Table 5.2 Table of parameters of ICP-OES

Parameter	Value
Plasma power	1400 W
Coolant flow	14 ml min^{-1}
Auxiliary flow	1 ml min^{-1}
Nebulizer flow	1 ml min^{-1}
Type of nebulizer	Cross-flow
Injector tube diameter	0.889 mm

Modelling software

MEDUSA (Making Equilibrium Diagrams Using Sophisticated Algorithms, Royal Institute of Technology, Sweden) software was used to construct models and predict cyanide speciation.

5.4.3 Analytical figures of merit

Limits of detection (LOD)

The limit of detection, expressed as the concentration or the quantity, is derived from the smallest measure that can be detected with reasonable certainty for a given analytical procedure.

Formally, the limit of detection is defined as the concentration of analyte required to give a signal equal to the background (blank) plus three times the standard deviation of the blank. So, before any calibration or sample measurement is performed, you must evaluate the blank. Detection limits are calculated as three times the standard deviations of a reagent blank.

Accuracy

The accuracy of the instrument was assessed by comparison of measured and recommended values for reference materials.

Precision

Three measurements were used to assess the precision or the reproducibility of analysis.

An average was determined and from this value the potential of a blank was subtracted. This gave the true value and by using the equation derived from the calibration curve, the concentration was determined. (In the case of UV-vis, absorbance of the blank was subtracted).

Percentage recoveries

This was calculated mainly by ion selective electrode using a certified reference material.

5.3.6 Quality control

The use of glassware or Polyvinylchloride (PVC) containers was avoided during determination of free cyanide to prevent reaction of CN^- and metals on the glass surface or the chloride and metals from the PVC. Sample containers and other glassware were cleaned with metal free non ionic detergent solution, rinsed with tap water, soaked in 50% HNO_3 acid for 12 hours and then rinsed with deionised water from Milli-Q-water purification system as recommended by Arienzo and Scrudo, (2001). All sample containers were rinsed again with deionised water prior to use. All blanks were subject to similar sample preparation and analytical procedures. All chemicals were of analytical grade obtained from Sigma-Aldrich, Industrial Analytical and Merck.

CHAPTER SIX – RESULTS AND DISCUSSION

Gold mining resulted in many tailings dumps around the Witwatersrand Basin pose an environmental threat through dust and polluted water plumes emanating from them.

Cyanide is one pollutant of concern emanating from the tailings dumps. While the general perception is that this pollutant degrades after treatment with chemicals as well as naturally, the results from most studies point to the contrary (Bernd, 2003; Lötter, 2006). During rainfall, oxygenated water accumulates in ponds at the top of the tailings dumps leading to percolation and surface run-off. This results in pollutants from the tailings entering the ground and the surface water systems.

Gold mine tailings have contributed significantly to water pollution as a result of AMD. The stream is contaminated by seepage of acidic waters containing a high content of metals and other substances. Water quality is affected by mine tailings

and spillages, especially from active slimes dams, reprocessed tailings, as well as from footprints left behind after reprocessing.

As the contaminated water flows from the stream into wetlands, the pollutants are sorbed onto suspended sediment particles which ultimately settle at the bottom resulting in removal of pollutants from the water column. The wetlands serve as a sink for pollution where polluting metals and cyanide are trapped in sediments and peatlands. The presence of organic matter provides complexing ligands which tend to bind strongly with heavy metals as well as cyanide (Tutu, 2005).

Case studies of tailings dumps, natural stream within and wetland in the East and Central Rand were considered, namely: (a) two types of representative tailings were studied: tailings rehabilitation facility and actives slimes, (b) a natural stream within an area of concentrated tailings dumps (the Natalspruit) and (c) a wetland (the Fleurhof Dam).

This chapter focuses on the determination of cyanide species, its transport and fate in tailings, wetlands and water systems.

The metal-cyanide complexes were also studied as well as the likelihood of their persistence in the environment. The results obtained were used for the geochemical modelling of its speciation.

6.1 Tailings

The tailings pumped from plant operations are stored in the TSF where cyanide levels are reduced by numerous mechanisms. These include biodegradation, volatilisation, adsorption onto solids, and seepage through the sediments at the base of the impoundment, photolysis and dilution through rainfall.

Tailings were studied for cyanide species (free cyanide, total cyanide, weak acid dissociable cyanide, strong acid dissociable cyanide, metal - cyanide complexes); related secondary compounds (thiocyanate, cyanate, and ammonium), anions (sulphate, chloride) and metals.

6.1.1 Tailings undergoing rehabilitation

The tailings dam is essentially a large sink in which slimes deposition is done by means of spigots which is located around the dam. The slimes are pumped from the reprocessing plant via pipes which feed interspersed spigots from which the tailings are released in the form of a slurry spray. The slurry flowed down the catena to the central sump or pond. A catena is a sequence of soil or sediment profiles that occur down a slope (Kirby *et al*., 1996). A penstock placed in the middle of the pond collects overflow water. This water is normally pumped to a water return reservoir, but at the Brakpan tailings facility some of this water is evaporated at the foot of the dam by spraying into the atmosphere. At the foot of the tailings dam is a toe paddock or a solution trench into which surface run-off from the slopes collects. The slopes (top, middle and bottom) are divided by berms as shown in the Figure 6.1.

A berm is a ledge or shelf along the top, middle or bottom of a slope. The berms are wide enough and provide access (by means of dirt roads) around and to the top of the dam for maintenance and monitoring. They also allow for control of rainfall run-off (Tutu, 2006).

Deposition of waste slurry has been discontinued and the dump is being prepared for phytoremediation. As such, the dump presents a suitable case for studying the chemical evolution of cyanide and its complexes over a period of time.

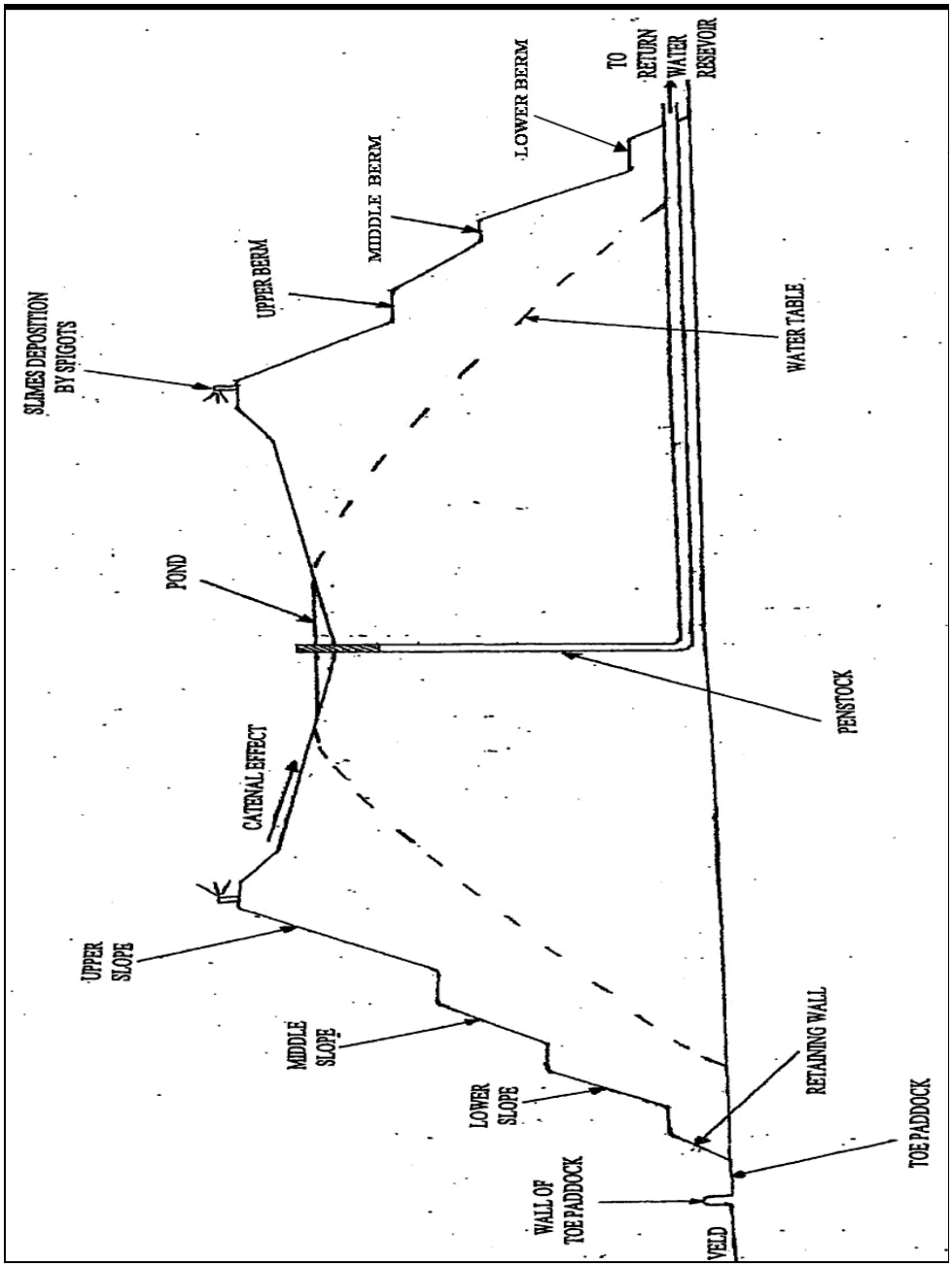


Figure 6.1 General section of the ERGO tailings dams (Weiersbye and Tutu, 2005)

Sampling strategy

Sampling was carried out in December 2006 and July 2007 at a tailing storage facility located at 26° 20'S and 28° 25'E. This tailings dam is generally an expanse of tailings with a central pond at the top (Figure 6.2.a).

(a)



(b)

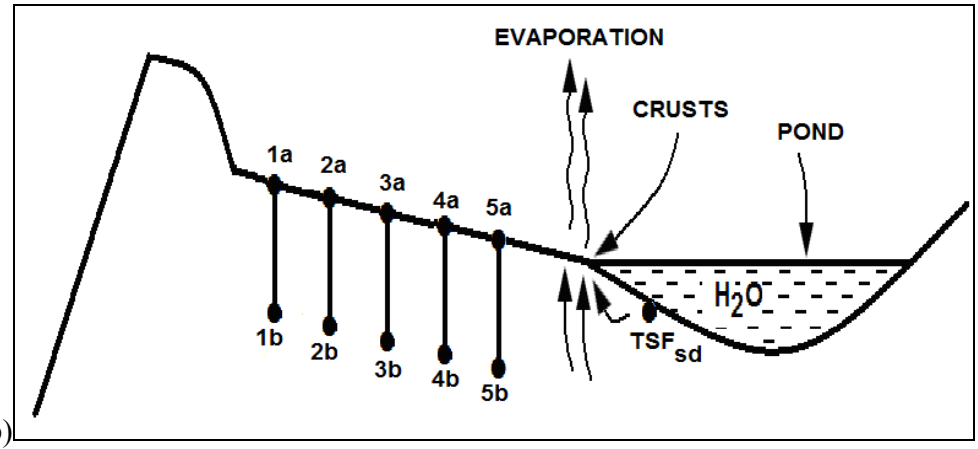


Figure 6.2 (a) Tailing dam with a central pond at the top (the transect is shown in red), (b) Sampling points along the transect

Samples were collected along a transect extending from the edge of the dam to the central pond in the dump at depths of 0-20 cm and 40-60 cm at each drill core using an auger as shown in Figure 6.2.b.

A total of 28 samples (5 sampling points x 2 sampling depths, 6 samples of crust salts, 2 samples of pond water) were collected.

Temperature, pH, redox potential and conductivity were measured on the field. Metal concentrations in samples were determined using ICP-OES (Spectro, Kleve, Germany), with concentration in solid samples recalculated for dry mass. The most important anions in aqueous solution were determined using ion chromatography (IC 761, Metrohm, Switzerland) with conductivity detection and concentration in solid samples was recalculated for dry mass.

The sampling techniques, sample treatment, sample storage and analytical procedures have been discussed in Chapter 5.

Results and discussion

Physical characterization

The physical-chemical parameters (pH, T^o, Eh, EC, moisture, CEC) results obtained are presented in Table 6.1.

The samples were collected along a transect (from 1, close to the edge of the dump to 5, close to the pond). The results for the physical-chemical properties presented in table 6.1 showed an increase in pH with the distance from the edge of the dump towards the central pond. This could be due to the flow of limed slimes towards the central pond. During deposition, the dominant transport of tailings solids is lateral towards the central pond due to gravitational flow.

Table 6. 1 Physical-chemical properties of the tailings collected in 2007

Sample	Depth	T^{o}	pH	Eh	EC	Moisture	CEC
	cm	^{o}C		mV	mScm^{-1}	%	cmol.kg^{-1}
1a	0 - 20	15.6	2.69	594	3.99	19.8	21.85
1b	40 - 60	13.8	3.66	567	2.808	22.1	22.89
2a	0 - 20	11.3	5.69	302	1.446	17.5	24.12
2b	40 - 60	11.1	6.76	77	0.46	20.6	23.03
3a	0 - 20	9.8	6.35	165	0.763	29.3	23
3b	40 - 60	10.3	7	134	1.216	21.8	30
4a	0 - 20	11.5	7.04	287	0.850	24.2	25.22
4b	40 - 60	11.9	7.01	267	0.634	22.2	23.88
5a	0 - 20	10.7	8.27	127	1.36	10.4	24.55
5b	40 - 60	12.5	8.67	257	0.79	22.6	28.64
C1	solid white crust		4.2	n.a	n.a	4.6	45.22
C2	yellowish crust		n.a	n.a	n.a	5.1	38.68
C3	yellow crust		n.a	n.a	n.a	5.3	55.45
TSFsd		13.6	5.25	377	1.788	37.58	25.42

n.a: not analysed

An average pH of 8.10 was obtained for the slurry emanating from the spigots during deposition. The elevated pH is attributed to the addition of lime during gold extraction. This is done to keep the cyanide in solution as it escapes at low pH and can pose a toxicity problem. The mildly alkaline pH of the tailings is attributed to the weathering effects resulting from acidic water (due to oxidation of pyrite). This causes the deterioration of the buffering capacity of the tailings. The pH values for the two sampling periods (2006 and 2007) are presented in Figure 6.3.

The trend shows a decrease in pH within the year. This could be attributed to the generation of AMD which is accelerated by the discontinuation of disposal of fresh tailings (of higher pH).

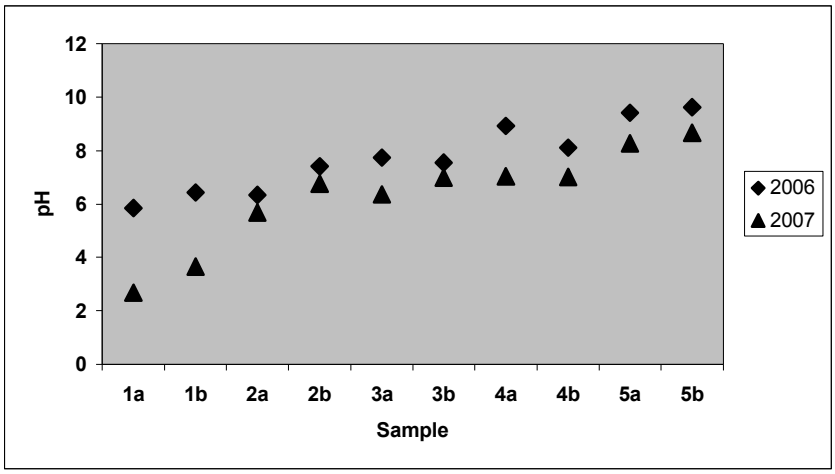


Figure 6. 3 pH values of the tailings for 2006 and 2007

Also, over time, the tailings' pH gradually decreases due to neutralisation of the alkaline environment during rainwater infiltration and also because of carbon dioxide uptake (Simovic et al., 1985; Smith and Struhsacker, 1987). Zagury et al. (2003) found a more alkaline pH 10.6 for recently discharged (3 months) tailings compared to pH 7.6 for aged ones (6 – 9 years). Low pH was observed in the pond water (3.79) and sediment (5.25) due to the weathering effects.

High potential redox was found for the samples collected at the edge of the tailings. This could be due to the easy oxidation of coarse material settled at the edge of the dump during deposition. The potential redox increases with decreases of pH. The same trend was observed for the conductivity. Relative high conductivity was found at the edge of the tailings dams compare to the pond. This could be the evidence of dissolution of metals when the pH drops and the presence of soluble salts on the top of the tailings dams (NaCl, $MgSO_4$ and $CaSO_4$), leading to high values of conductivity.

Prior to characterization, average moisture content approximately 21.05% was measured in the tailings except for the crusts salts with average moisture of 5%

and the pound sediment with a moisture content of 37.58%. The moisture in the tailings could be due to water table in them but that water was evaporated in the salts crusts. This become evident when the tailings are disturbed as is the case during rehabilitation activities. Hsu et al. (1995) states that it is important to maintain the moisture content at between 16% and 20%. If the dump is too moist, the air access is not possible. On the other hand, if the dump is dry, then bacterial action cannot take place effectively because migration of bacteria throughout the material is difficult.

Cation exchange capacity values for tailings collected in 2007 were high and ranged from 21.5 to 30 cmol kg^{-1}. Crusts solid salts have an average CEC value of 46.45 cmol kg^{-1}. These values indicate a high capacity of tailings materials to adsorb metals. Normal CEC ranges from 3 cmolkg-1, for sandy soils low in organic matter to > 25 cmol kg^{-1} for soils high in certain types of clay or organic matter (Evangelou, 1998).

The size distribution of tailings is presented in Table 6.2. The tailings comprised of sand-sized particles ranging from 1000 to 75µm, silt-sized particles ranging in from < 75 µm to 2 µm and clay sized particles < 2 µm. During deposition, the dominant transport of tailings solids is lateral towards the central pond due to gravitational flow. Size and density segregation in the flowing material are expected with coarser material settling near the edge and finer material settling towards the central pond. At the edge, the tailings are mostly sandy and towards the pond, tailings are silly.

The results obtained showed coarser material settling near the edge (low pH) and the finer material settling towards the central pond (high pH).
The coarse material is easily oxidised compared to the finer one that is why the potential redox is higher for the tailings from the edge of the dump.

Table 6.2 Size distribution of tailings dams material

samples	Depth	Sand	Silt	Clay
	cm	%	%	%
1a	0 - 20	81	14	5
1b	40 - 60	80	14	6
2a	0 - 20	86	12	2
2b	40 - 60	87	10	3
3a	0 - 20	0.4	91	8
3b	40 - 60	6	85	9
4a	0 - 20	1.6	97.5	0.9
4b	40 - 60	5	85	10
5a	0 - 20	0	88	12
5b	40 - 60	3	90	7
C1	crust solid white	95	4	1
C2	yellowish crust	83	15	2
C3	yellow crust	1	88	11

Chemical characterization

Metals Metal concentrations were determined in the tailings using ICP-OES after acid digestion and leaching with deionised water. Results obtained by acid digestion for trace metals are shown in Figure 6.6 for (a) Fe, (b) Ni, (c) Cu, (d) Zn and (e) Co. The full table for metals analysis is given in Appendix A.

In general, the concentration of Fe, Ni, Cu, Zn and Co obtained by acid digestion in tailings increases between 2006 and 2007, except for the samples 5a & 5b. This could be due to the generation of AMD with the subsequent release of heavy metals and metalloids.

In fact, with the decrease of the pH with time, AMD is generated and this could result in the dissociation of metal complexes which release metal.

Samples 5a and 5b with alkaline pH, showed a decrease of metal concentration after a year. Metal could be leached out and the release of metal from metal complexes could have been limited by the alkaline pH. Weak metal-complexes can not dissociate at this pH range.

An increase of concentration between 2006 and 2007 was respectively 17.31% for iron, 21.66% for nickel, 19.29% for zinc and 20.32% for cobalt. A decrease of 3.01% was observed for copper.

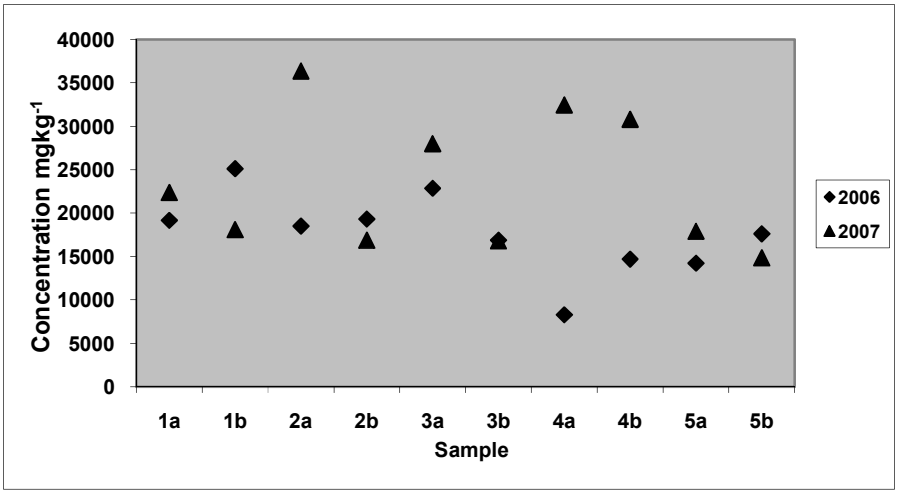
Concentration of iron is high in both cases (2006 and 2007) as it is one of the major elements in the ores. Iron concentration in most tailings analyzed range from 2.0 – 4.0% as Fe_2O_3 (Mphephu, 2004).

At the edge of the dump, concentrations of Fe, Ni, Zn and Co for both periods are low at the surface, profile (a) 0 – 20 cm compare to those obtained for the profile (b) 40 - 60 cm. The trend shows a decrease in metals concentrations for tailings collected in 2006 from the edge to the pond. A similar trend was observed for the tailings collected in 2007.

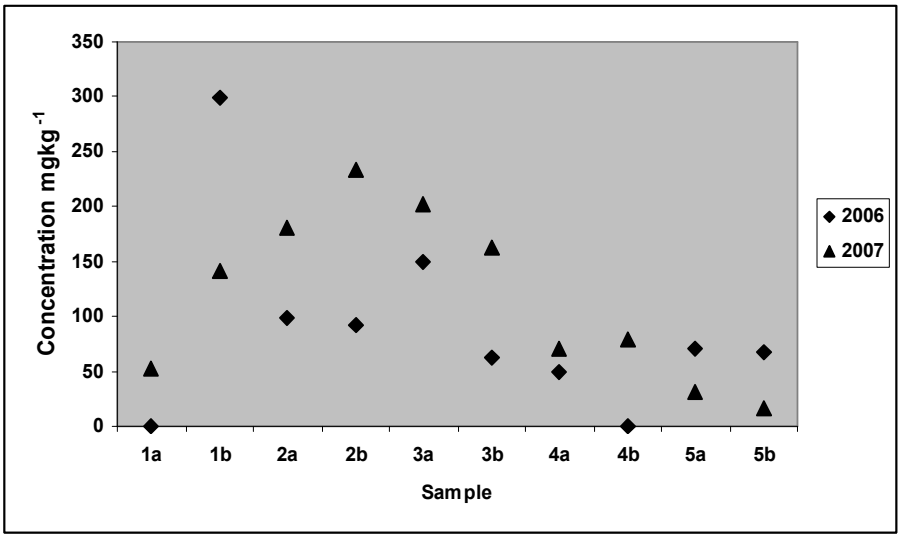
The concentration of nickel was under detection limit in samples 1a & 4b in 2006 but as evidence of dissociation of metal-complexes, the concentration increases in 2007, 52 mg kg^{-1} for 1a and 31 mg kg^{-1} for 4b. The concentration of cobalt in tailings was lower compared to the other metals analysed.

The concentrations of Fe, Co, Ni, Cu and Zn were very high in salt crusts, since efflorescence is composed of water soluble salts in addition to dominant iron hydroxides and sulphates. Salt crusts are also enriched in concentrations of several metal including Co, Ni, Cu and Zn. Efflorescence is secondary source of pollution.

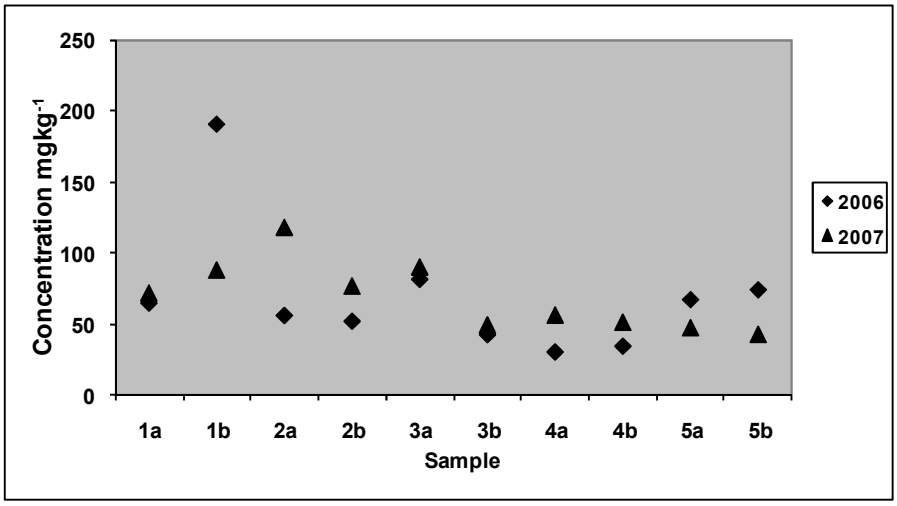
High concentration of Ca, Na and K was obtained at the surface for the samples collected in 2006. During reprocessing Ca, Na and K are added as CaCN (170 ppm), NaCN and KCN.


40000
35000
30000
25000
20000
15000
10000
5000
0
Concentration mgkg-1
1a
1b
2a
2b
3a
3b
4a
4b
5a
5b
Sample
2006
2007

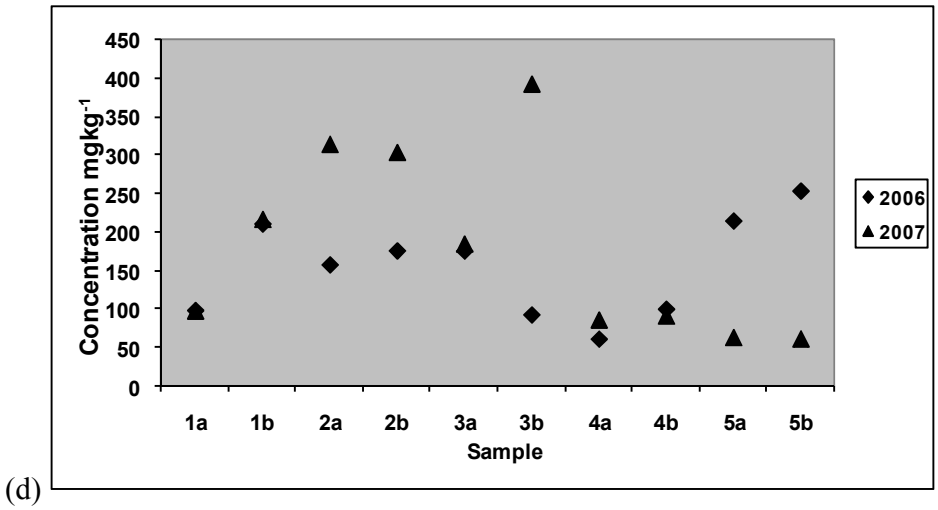
(a)


350
300
250
200
150
100
50
0
Concentration mgkg-1
1a
1b
2a
2b
3a
3b
4a
4b
5a
5b
Sample
2006
2007

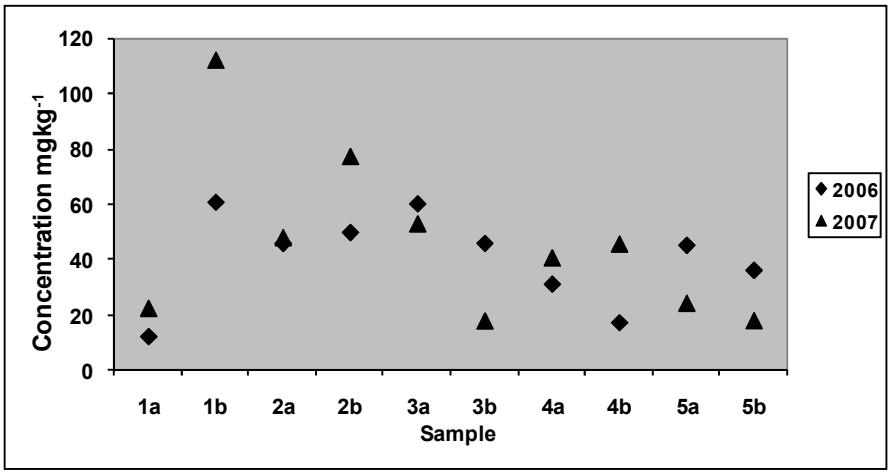
(b)


250
200
150
100
50
0
Concentration mgkg-1
1a
1b
2a
2b
3a
3b
4a
4b
5a
5b
Sample
2006
2007

(c)



(d)



(e)

Figure 6.4 Total concentration of (a) Fe, (b) Ni, (c) Cu, (d) Zn and (e) Co in tailings for profile: a) 0 – 20 cm; b) 40 -60 cm.

Lime was also used to raise the pH above 11 during the operation to avoid the volatilisation of cyanide, so the tailings materials contain high concentration of Ca, Na and K. These metals can be leached out with time, since they are very soluble in water and tend to be conservative ions. The concentrations of Fe, Ni, Zn and Co in crusts (H9a and H10) collected in 2006 were higher than the crusts (C1, C2 and C3) collected in 2007 except for copper. The decrease in metal concentration in crusts could be due to evaporation or dissolution. The sediment (TSFsd) collected at the bottom of the pond, contains almost the same concentrations of metals for both periods because there was no change in the pH

(5.25). High concentration of Ca was obtained in the sediment. During tailings deposition, the slurry (containing quite high amount of lime) flows towards the pond and then the finer particles reaching the pond precipitate to form sediments. The precipitation leads to deposition and adsorption of metals onto sediment, this could also explain the high concentration of metals found in the sediment.

Metal concentrations were also determined in the tailings using ICP-OES after leaching with deionised water. Results obtained are given in Appendix B. The general trends show low concentration of heavy metals(mainly Co, Zn, Cu, Ni) in water leachate compared to the concentration obtained after acid digestion, except on top surface from the edge (sample 1a). The concentration of Ca was high in water leachate. In the tailings, $CaSO_4$ is the most abundant form of Ca and it is readily soluble in water. Iron was very low. Co, Zn, Cu and Ni were also low except on the top surface from the edge.

These metals are likely to be from efflorescence and they are relatively insoluble at that pH of water. The study done by Rosner and Schalkwyk (2000) revealed that the top soil of slimes dumps after reclamation to the east of Johannesburg was highly acidified and contaminated with heavy metals, notably Co, Ni and Zn.

The concentrations of metals were high in crusts and sediment. This could mean that the low pH allows an increase in dissolution of metal complexes.

Between 2006 and 2007, a decrease of Na, K and Fe was observed. The concentration of Co, Zn, Ni, and Cu increases for the samples collected at the edge of the tailings (1a, 1b and 2a).

An increase in Na, K and Ca was found in crust with time whilst the concentration of heavy metals decreases. In the sediment, the concentration of heavy metals increases with time Na, K and Fe whilst the one for Na, K, Ca and Fe decreases.

Anions (SO_4^{2-} , $S_2O_3^{2-}$, Cl^-) The concentrations of major anions (thiosulphates, sulphates and chlorides) in the tailings are shown in Figure 6.5.

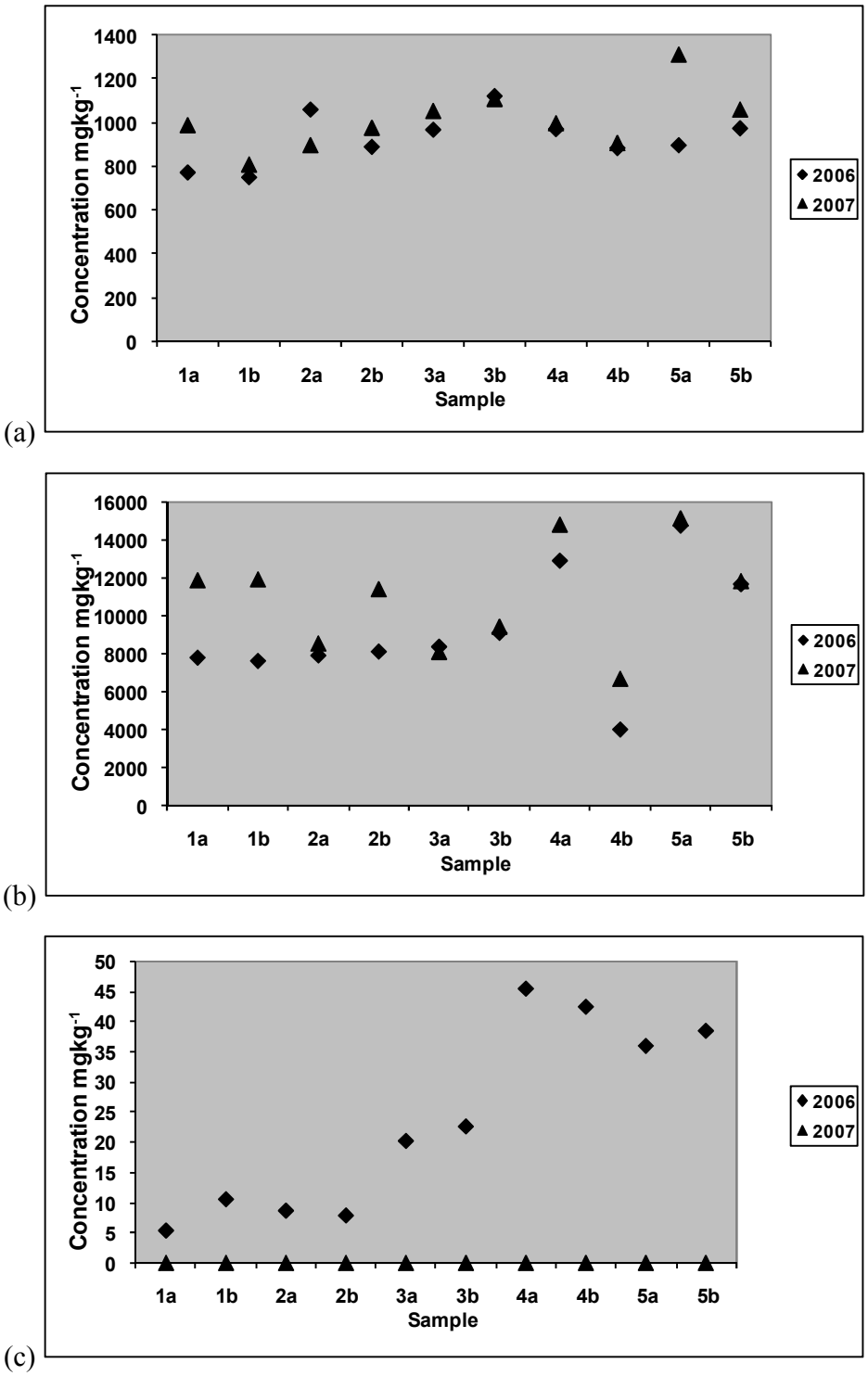


Figure 6.5 Results for (a) thiosulphate (b) sulphate and (c) chloride in tailings

The trend shows a general increase in thiosulphate and sulphate concentrations between 2006 and 2007. The weathering of pyrite generates sulphuric acid and hence high concentration of sulphates.

Chlorides were found in very low concentration in tailings. The values vary between 5.2 $mgkg^{-1}$ and 45.4 $mgkg^{-1}$ in the samples collected in 2006. For those collected in 2007, chlorides were not detected as well as in the TSFsd. This could serve as evidence that gold tailings are not treated with chloride based reagents before discharge (pers. comm. Weirsbye, 2008).

The concentration of chloride is relatively high (100 - 200 mg kg^{-1}) in salts crusts collected in 2006.

Anions concentrations in salt crusts and TSFsd are given in Table 6.3.

Concentrations of thiosulphate in the salt crusts are in the same magnitude as in the tailings but those for sulphates are by far greater. The study done by Naicker et al. (2002) revealed that salt crusts affected by AMD contain gypsum ($CaSO_4.2H_2O$). This could enhance the concentrations of sulphate in salt crusts.

TSFsd collected in 2007, has high concentrations of thiosulphates as well as sulphates. During deposition, for instance, the dominant transport of tailings solids is lateral towards the central pond. The same trend was observed for AMD flowing towards the pond and likely seeping in the bottom sediment. This could explain the low pH of the sediment, hence, more sulphate.

Table 6.3 Concentration of thiosulphate, sulphate and chloride in tailings

Sample	$S_2O_3^{2-}$	SO_4^{2-}	Cl^-
	$mgkg^{-1}$	$mgkg^{-1}$	$mgkg^{-1}$
H9a	897.4	91561	117.8
H10	1966	14785	201.3
TSF	1113	13185	n.d
C1	1309	65152	n.d
C2	1013	60235	14.4
C3	743.4	4575	n.d
SED	1304	15024	n.d

Cyanide species and related compounds Free cyanide, weak acid dissociable cyanide, total cyanide, thiocyanate, cyanate and ammonium were analysed in the tailings. The analytical procedures are described in Chapter 5.

Results, presented in Figure 6.6, are a comparative assessment between samples collected in 2006 and the ones collected in 2007. The average content of CN_{free} (Figure 6.6a) for samples collected in 2006 was lower 2.382 $mgkg^{-1}$ than the average (9.659 mg kg^{-1}) for samples collected in 2007.

It is well known and proved by previous studies (Lötter, 2006) that CN_{free} can be lost by volatilisation, biodegradation and complexation. CN_{free} can be converted into cyanates and thiocyanates depending on the environmental conditions.

The high value of CN_{free} obtained in 2007 could be due to the dissociation of CN_{WAD} and CN_{SAD} when the pH of the tailings drops due to the weathering effects. In fact, CN_{WAD} can dissociate at pH range from 4-5 to release CN_{free} when CN_{SAD} required strong acidic condition pH < 2 to dissociate.

This can be observed by the decrease of CN_{WAD} and CN_{SAD} with time. Tailings collected in 2006 contains an average of 19.06 mg kg^{-1} and 98.53 mg kg^{-1} for CN_{WAD} and CN_{SAD} respectively (figure 6.6b and c), whereas, the average of 5.767 mg kg^{-1} and 32.22 mg kg^{-1} was obtained for tailings collected in 2007.

Total cyanides (Figure 6.6d) were higher in 2006 with an average of 120 mg kg^{-1} and 50.85 mg kg^{-1} in 2007. A corresponding trend was observed for CN_{WAD} as well as CN_{SAD}. This could be attributed to the fact that during deposition of tailings pH values are high and cyanide complexes are stable. As pH decreases, the complexes begin to dissociate releasing CN_{free} as stated in the previous case.

CN_{SAD} content was high in all tailings compare to CN_{WAD}; this indicates the predominance of strong complexes in the tailings.

The high concentration of iron in tailings suggests a higher proportion of strong cyanide complexes.

Discrepancies were observed with high CN_{free} in profiles 1b and 5b compared to profiles (40 - 60 cm) 1a and 5a (0 – 20 cm) in 2007. This could be due to the lost

of CN_{free} in profile 1a with the lowest pH (2.69). The same reason could be attributed to sample 5, since HCN (volatile) is the predominant form of CNfree at pH < 9.

CN_{WAD} was higher in profile 5a in 2007. This could be explained by the high concentrations of heavy metals (Co, Zn, Ni and Cu) in profile (a), these metals form weak metal- complexes with cyanide (Chapter 2).

The samples with high heavy metals concentrations (Zn, Ni, and Cu) did not necessary have high CN_{WAD}.

The concentrations depend strongly on the stability of each complex. The same observation was done for CN_{SAD}.

The average thiocyanate (SCN^-) concentrations (Figure 6.6e) are observed to be higher in 2007 (95.13 mg kg^{-1}) than 2006 (27.27 mg kg^{-1}). This observation is consistent with that done by Plumlee et al. (1995) that relatively high concentrations of thiocyanate may persist in the presence of acidic solutions. CN_{free} released from the complex metal cyanide, reacts with active sulphur species (Reaction 2.5 and 2.6) to produce thiocyanate, SCN^-. Thiocyanate also reacts with metals to form metal-thiocyanate complexes.

High concentrations of SCN^- were found in 3(a) and (b) but this doesn't mean high values of thiosulphate in these samples. This could be due to reaction of CN_{free} with polysulfides (Reaction 2).

Cyanate (OCN^-) (Figure 6.6f) concentrations do not seem to differ significantly in the two periods. Average concentrations of 18.33 mg kg^{-1} and 22.4 mg kg^{-1} were found respectively for 2006 and 2007. This could be due to exposure of CN^- to similar oxidation conditions (largely atmospheric oxygen).

Cyanate hydrolyses under acidic conditions to form NH_3 which then reacts with SO_4^{2-} present in tailings to form NH_4^+, also, thiocyanate SCN^- can be transformed to CO_2, NH_4^+ and SO_4^{2-}.

Ammonium NH_4^+ concentrations (Figure 6.6g) were higher in samples collected in 2007 than in the ones from 2006. Ammonium concentration was higher for the

tailings collected at the pond (5a & 5b). The average of ammonium content is respectively 49.87 mg kg^{-1} and 26.58 mg kg^{-1}. This difference could be explained by high concentration of sulphate in tailings collected in 2007 which is susceptible to react with ammonia.

This could explain also the low concentration of cyanate. Cyanate could give the indication of the amount of CN_{free} that is oxidized. This is important as cyanate is far less toxic than CN_{free} and this would have a positive impact on the environment if the conversion is occurring at a rapid rate. The relative high concentration of NH_4^+ in tailings contributes to the cation exchangeable content.

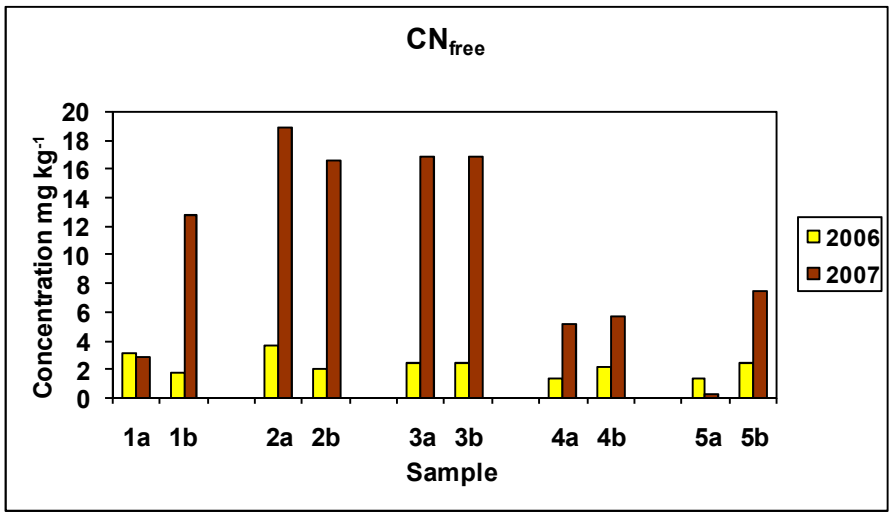
In salt crusts, the same trend as in tailings was observed for the concentrations of CN_{free}, CN_{WAD}, CN_{SAD} and CN_T. An increase of $CN_{free}$was observed whilst CN_{WAD} and CN_{SAD} decreased.

The crusts have higher concentration of SCN^- in 2007 due to the presence of high concentration of sulphate. Also due to the fact that microbial degradation is responsible for SCN^- production, these microorganisms can also aerobically degrade CN^- to OCN^-. This can also explained the higher concentration of ammonium in the salt crusts collected in 2007.

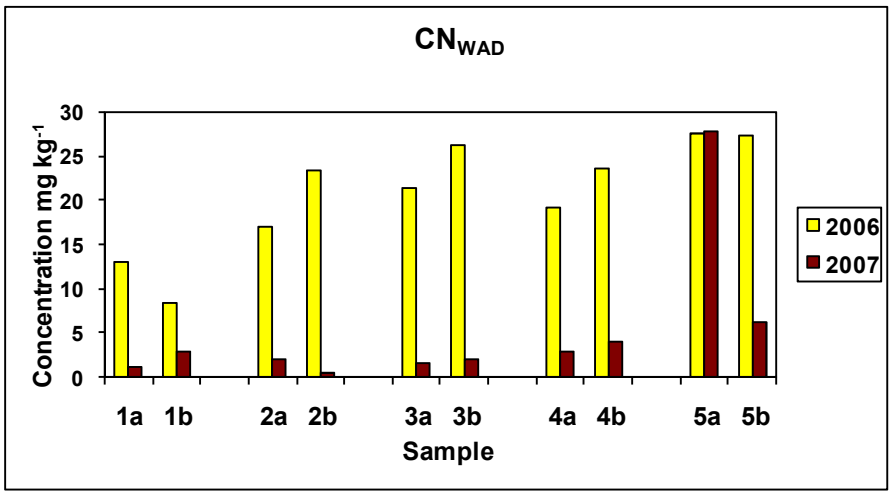
Very low concentration of cyanate was found in the pond sediment (TSFsd) collected in 2006 and it was not detected in sediment collected in 2007. Pond sediment is in reducing conditions and cyanate is produced by the oxidation of CN_{free}. This could explain the low concentrations of CNO^- and also the very low pH of the sediment probably means that high losses of cyanide occur through volatilization.

The concentration of NH_4^+ was very low in sediment; this could be due to the low concentration of cyanate obtained, since ammonium is a byproduct of cyanate.

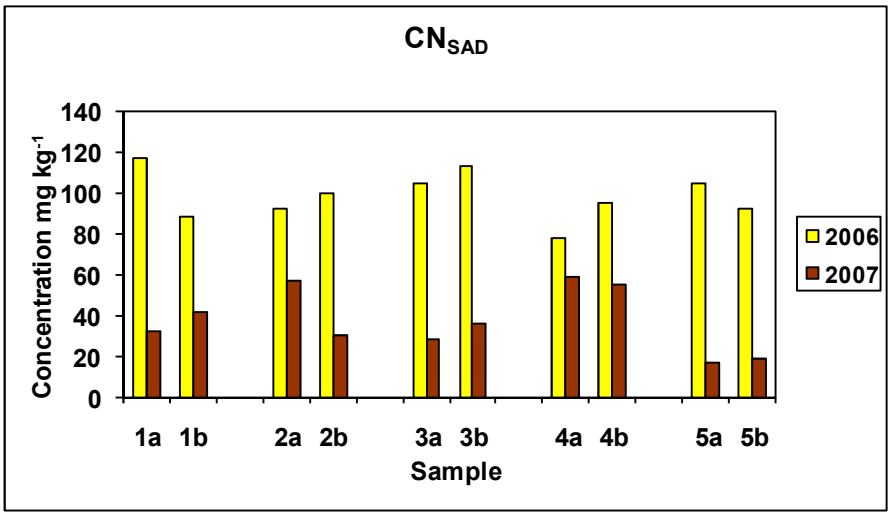
The correlation between metals and cyanide species depends of several parameters. Metal forms also complexes with other anions, depending on the environmental conditions, e.g. Cu forms complexes with CN^-, SCN^-, OH^-, SO_4^{2-}. There is a competition of these anions towards Cu.


CNfree
Concentration mg kg-1
20
18
16
14
12
10
8
6
4
2
0
1a 1b 2a 2b 3a 3b 4a 4b 5a 5b
Sample
2006
2007

a)

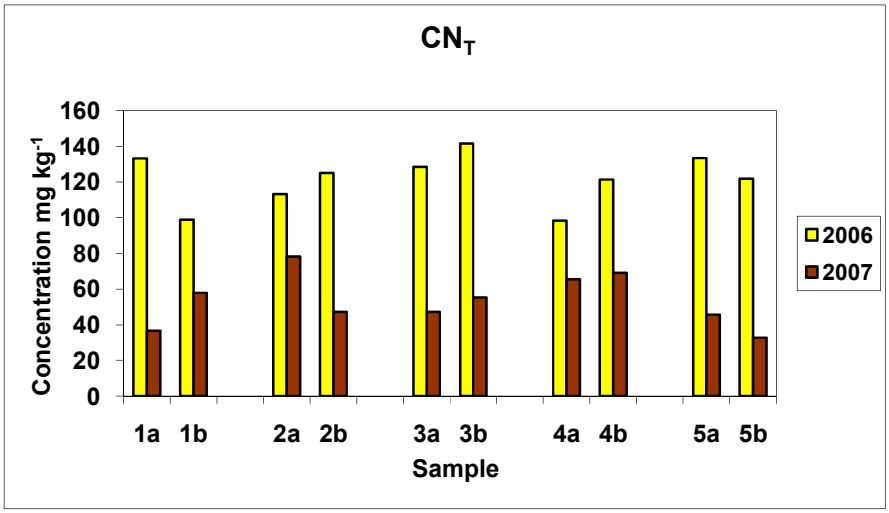

CNWAD
Concentration mg kg-1
30
25
20
15
10
5
0
1a 1b 2a 2b 3a 3b 4a 4b 5a 5b
Sample
2006
2007

b)

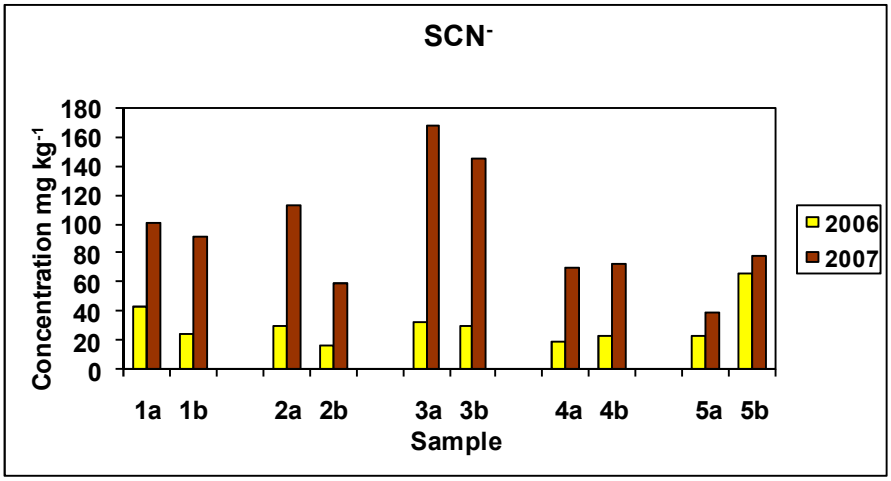

CNSAD
Concentration mg kg-1
140
120
100
80
60
40
20
0
1a 1b 2a 2b 3a 3b 4a 4b 5a 5b
Sample
2006
2007

c)

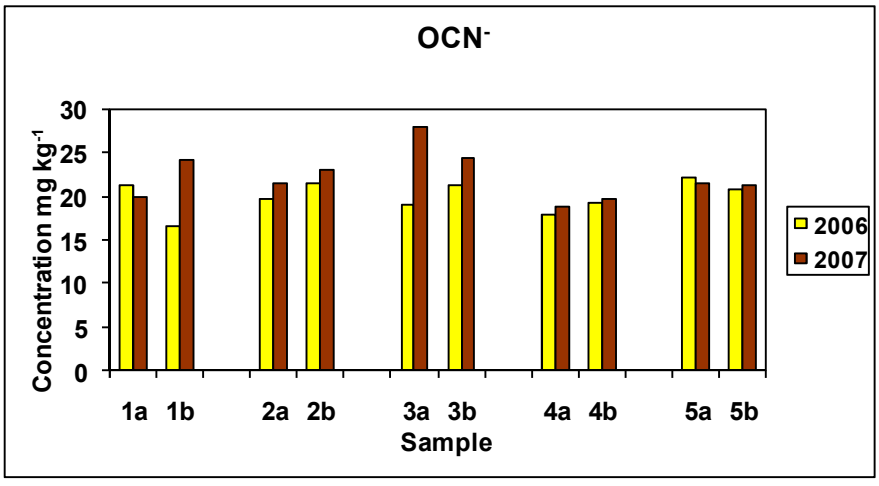
d)


CN$_T$
Concentration mg kg^{-1}
160
140
120
100
80
60
40
20
0
1a 1b 2a 2b 3a 3b 4a 4b 5a 5b
Sample
2006
2007

e)


SCN$^-$
Concentration mg kg^{-1}
180
160
140
120
100
80
60
40
20
0
1a 1b 2a 2b 3a 3b 4a 4b 5a 5b
Sample
2006
2007

f)


OCN$^-$
Concentration mg kg^{-1}
30
25
20
15
10
5
0
1a 1b 2a 2b 3a 3b 4a 4b 5a 5b
Sample
2006
2007

g)

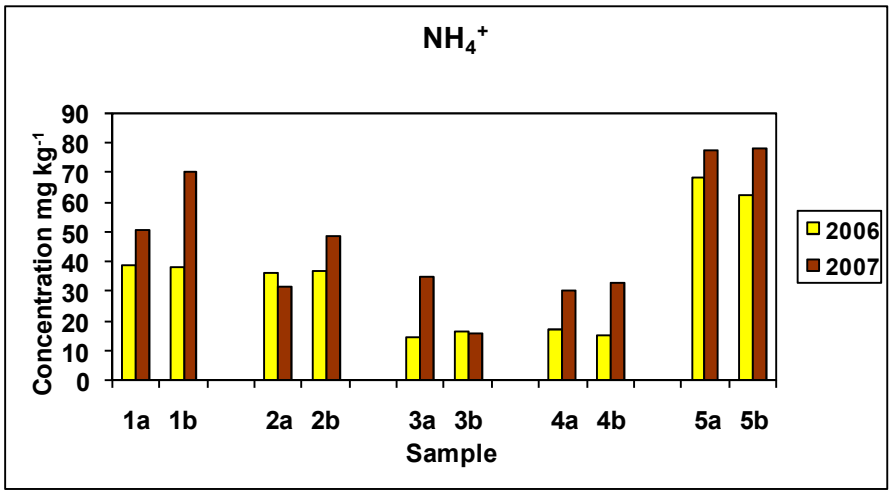


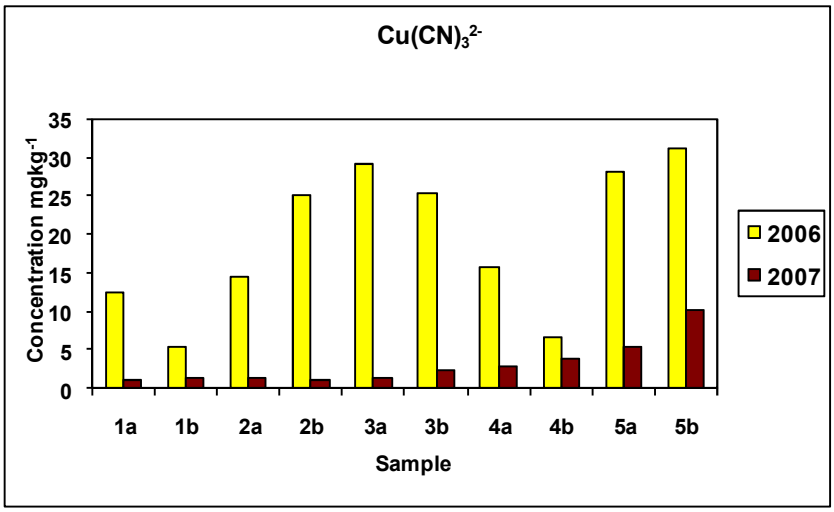
Figure 6. 6 Results for (a) CN_{free}; (b) CN_{WAD}; (c) CN_{SAD}; (d) CN_T; (e) SCN^- ; (f) CNO^- and (g) NH_4^+ in profiles.

Metal cyanide complexes

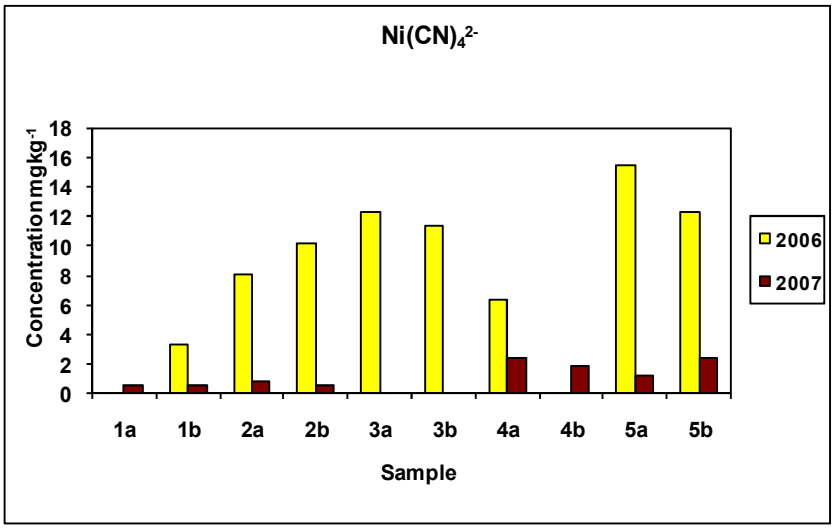
CN_{free} bonds with metals to form metal- cyanide complexes. The results obtained for such complexes in tailings are shown in Figure 6.7, except for $Zn(CN)_4^{2-}$ which is only weakly absorbing at the wavelength used and is not stable (labile) under the chromatographic conditions.

The general trend showed a decrease in the concentrations of Cu, Ni, Co and Fe - cyanide complexes with time. In figures (a) and (b), samples 1a to 3b show very low concentration of Cu and Ni complexes in 2007.

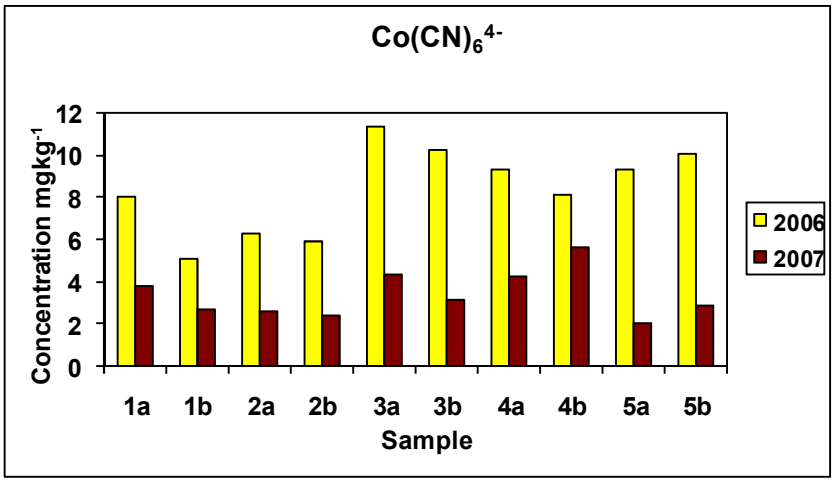
The average concentration of Cu and Ni was respectively 17.94 mg kg^{-1} and 7.948 mg kg^{-1} in 2006; 4.85 mg kg^{-1} and 2.006 mg kg^{-1} in 2007. The pH values for these samples range from 2.69 to 7. The decrease of pH within time could explain the drastic decrease of the Cu & Ni complexes which are weak complexes, unstable in slightly acidic conditions and then can be dissociated at pH 4 – 6. The stability constants are log k = 28.65 for $Cu(CN)_4^{3-}$ and 30.13 for $Ni(CN)_4^{2-}$.


Cu(CN)3 2-
Concentration mgkg-1
35
30
25
20
15
10
5
0
1a 1b 2a 2b 3a 3b 4a 4b 5a 5b
Sample
2006
2007

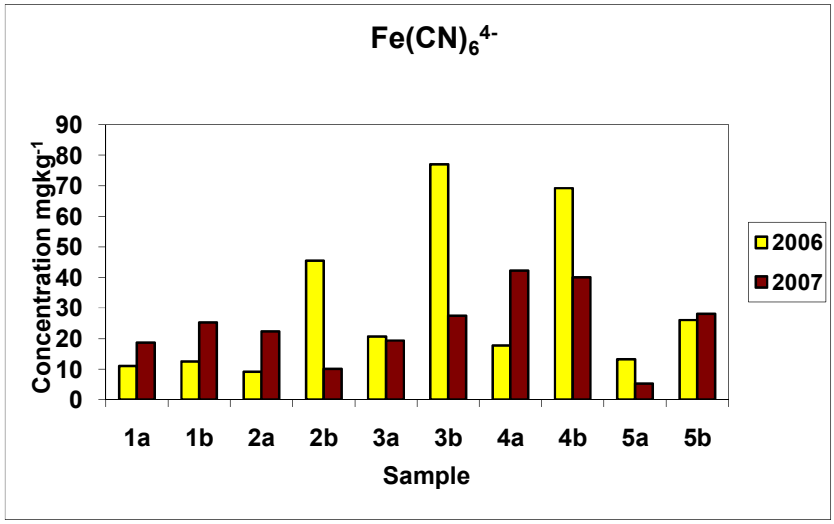
(a)


Ni(CN)4 2-
Concentration mgkg-1
18
16
14
12
10
8
6
4
2
0
1a 1b 2a 2b 3a 3b 4a 4b 5a 5b
Sample
2006
2007

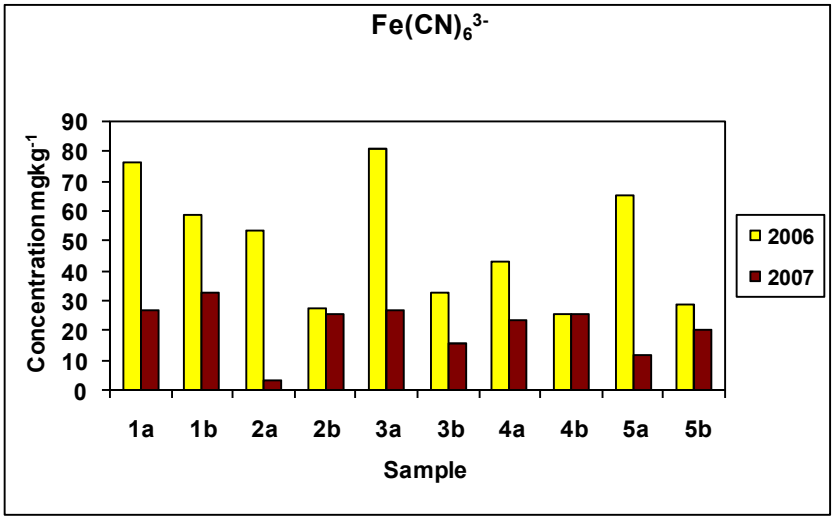
(b)


Co(CN)6 4-
Concentration mgkg-1
12
10
8
6
4
2
0
1a 1b 2a 2b 3a 3b 4a 4b 5a 5b
Sample
2006
2007

(c)



(d)



(e)

Figure 6.7 Results for (a) $Cu(CN)_3^{2-}$, (b) $Ni(CN)_4^{2-}$, (c) $Co(CN)_6^{4-}$, (d) $Fe(CN)_6^{4-}$ and (e) $Fe(CN)_6^{3-}$

At high pH, these complexes may be stable as observed in the models created using MEDUSA (Figure 6.8). Cu and Ni more or less resemble one another (both CN_{WAD}) and so do Co and Fe (both CN_{SAD}). They have fairly significant concentrations in 2007 to compare with Ni & Cu. However, the concentrations are significantly low to compare with those for 2006.

CN_{SAD} are stable and can be only dissociate at pH < 2, and the tailings analyzed have a pH above 2, hence the disparity between the two periods is not significant. The stability constants for Fe species are log K = 47 for $Fe(CN)_6^{4-}$ and 52 for $Fe(CN)_6^{3-}$.

Indeed, the average concentration of $Co(CN)_6^{4-}$ was 8.375 mg kg^{-1} in 2006 and 3.156 mg kg^{-1} in 2007.

The Fe-cyanide complexes were present in two forms: $Fe(CN)_6^{4-}$ and $Fe(CN)_6^{3-}$ with the latter being more stable (table 2.2).

Fe (II) and Fe (III) cyanide complexes are the most important complexes found in tailings in term of concentration. Even the Mössbauer spectroscopic analysis pitched iron-cyanides complexes and also suggested a different Fe(II)/Fe(III) ratio for samples analyzed.

In figure 6.7d, Fe (II) complex is high in samples 2b, 3b, 4b and 5b for 2006. The profile b (40 – 60 cm) has low redox potential compare to profile a (0 -20 cm). Besides, Fe (III) complex in figure 6.7(e), is high in samples 1a, 2a, 3a and 5a. The redox potential was high in profile (a) than in profile (b). Thus, Fe (II) is likely to be high in reducing condition and Fe (III) in the oxidizing one.

Geochemical modeling

The models for copper and iron in tailings are shown in Figure 6.8 and Figure 6.9.

The models below predict the formation of cyanide complexes. For instance, the predominance rea of $Cu(CN)_3^{2-}$ is between pH 4 – 8 and $Fe(CN)_6^{3-}$ can be found in ranges of pH and at high pE. The introduction of major anion (e.g SO_4^{2-}) does not affect the equilibruim of the complex.

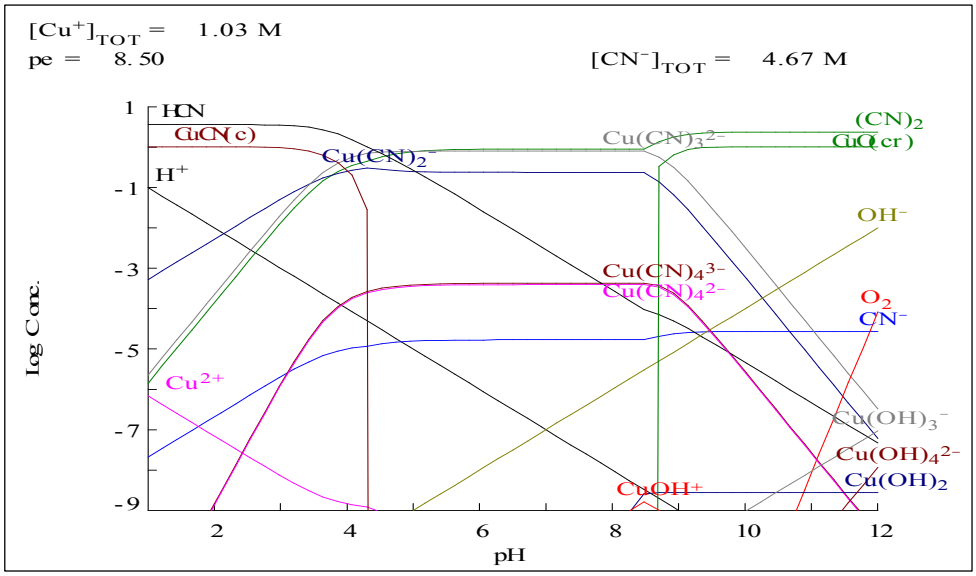
At lower pH values, H^+ out competes Cu^+ for complexation with CN^- as H^+ becomes more abondant and forms HCN.

At higher pH, soluble copper hydroxide complexes form but in this system, CN^- outcompetes OH^- in the pH range shown. Concentration of dissolved copper

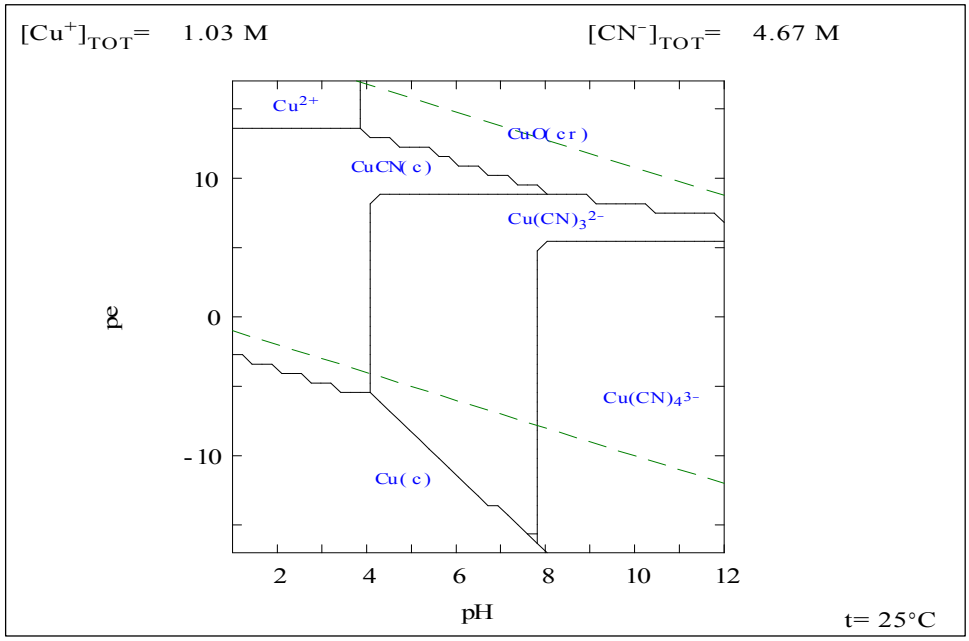
hydroxide species are very small and their influence on Cu speciation is not significant.

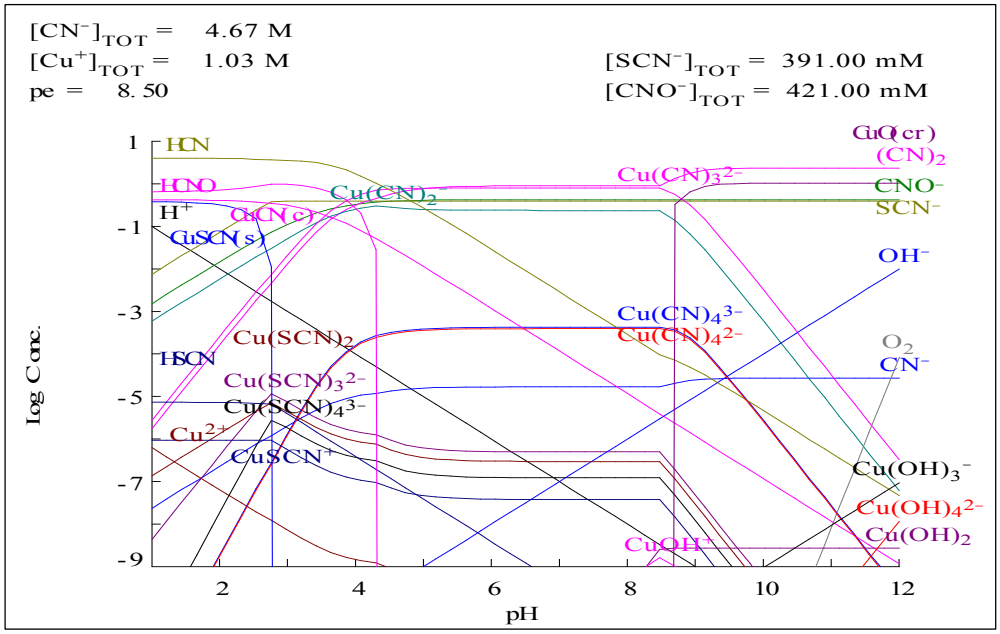
Dfferents copper cyanide species predominate in different pH regions, with $Cu(CN)_c$ at pH < 4; $Cu(CN)_3^{2-}$ at pH 4 – 8 and $Cu(CN)_4^{2-}$ at pH > 8.

(a)

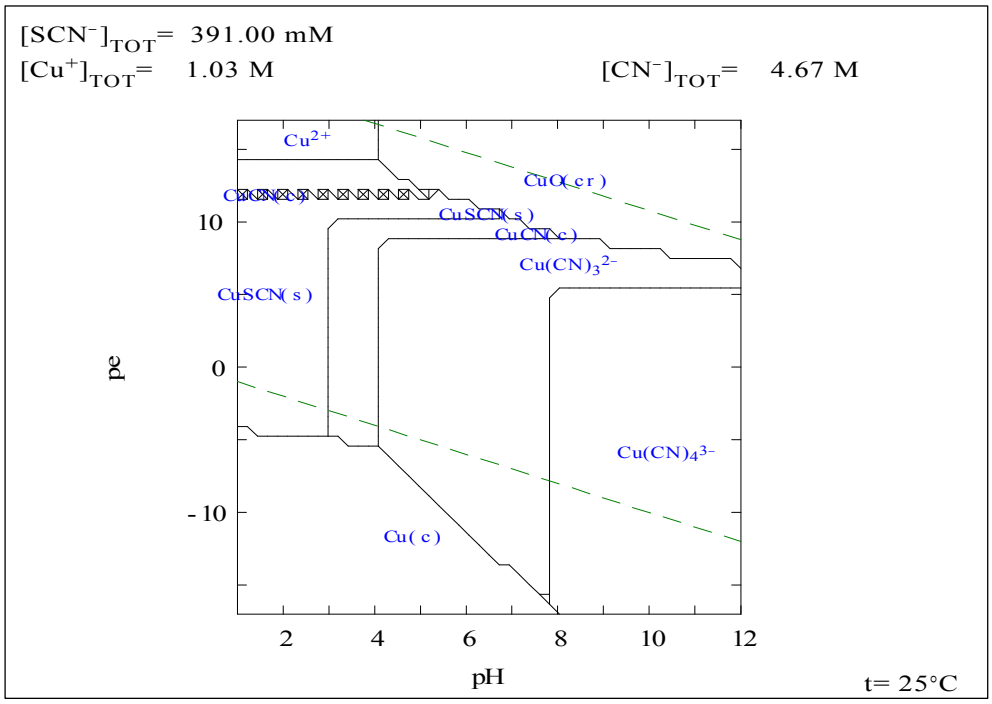


(b)



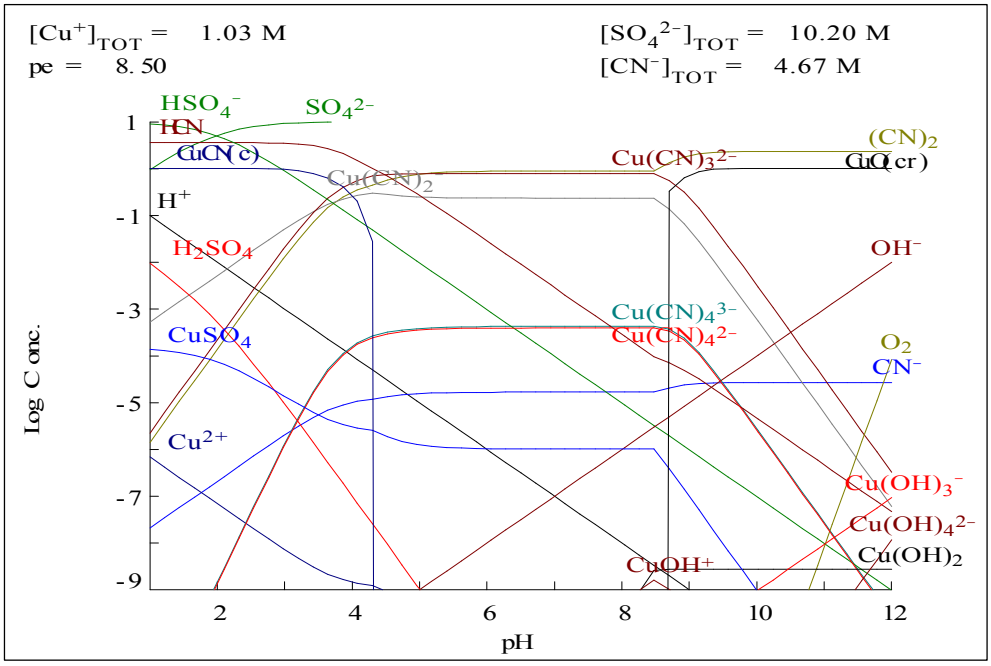

[CN⁻]TOT = 4.67 M
[Cu⁺]TOT = 1.03 M
pe = 8.50
[SCN⁻]TOT = 391.00 mM
[CNO⁻]TOT = 421.00 mM
Log Conc.
pH
HCN
HCNO
H⁺
CuSCN(s)
Cu(CN)2
Cu(CN)(c)
Cu(SCN)2
HSCN
Cu(SCN)3 2-
Cu(SCN)4 3-
Cu2+
CuSCN+
Cu(CN)3 2-
Cu(CN)4 3-
Cu(CN)4 2-
CuO(cr)
(CN)2
CNO-
SCN-
OH-
O2
CN-
Cu(OH)3-
Cu(OH)4 2-
Cu(OH)2
CuOH+

(c)


[SCN⁻]TOT= 391.00 mM
[Cu⁺]TOT= 1.03 M
[CN⁻]TOT= 4.67 M
pe
pH
t= 25°C
Cu2+
CuO(cr)
CuSCN(s)
Cu(CN)(c)
Cu(CN)3 2-
Cu(CN)4 3-
Cu(c)

(d)

(e)



(f)

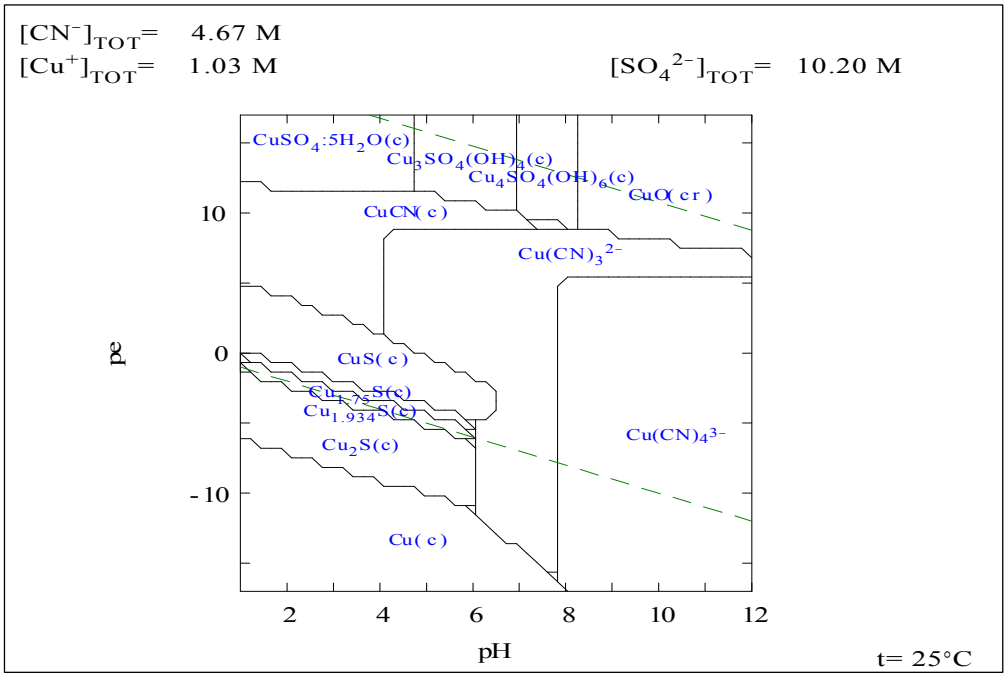
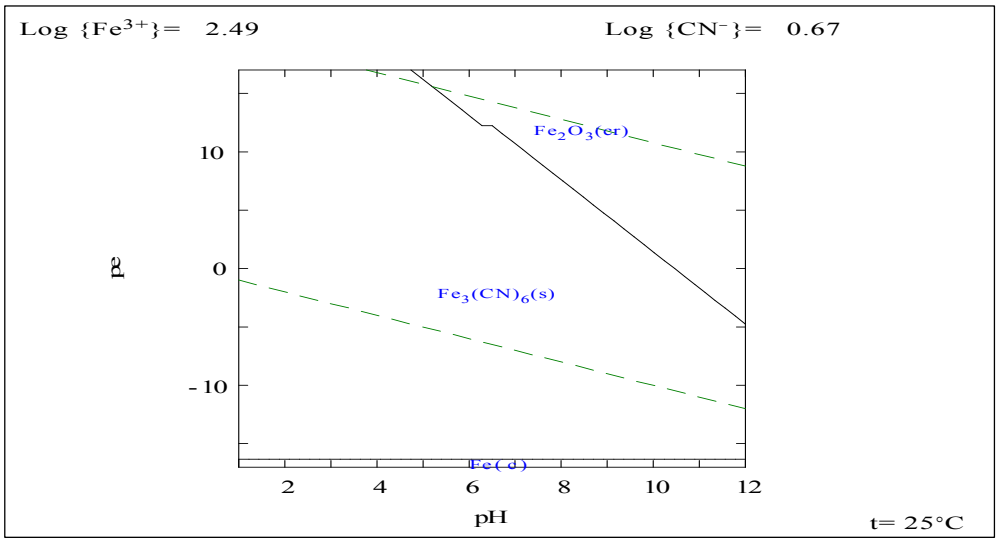


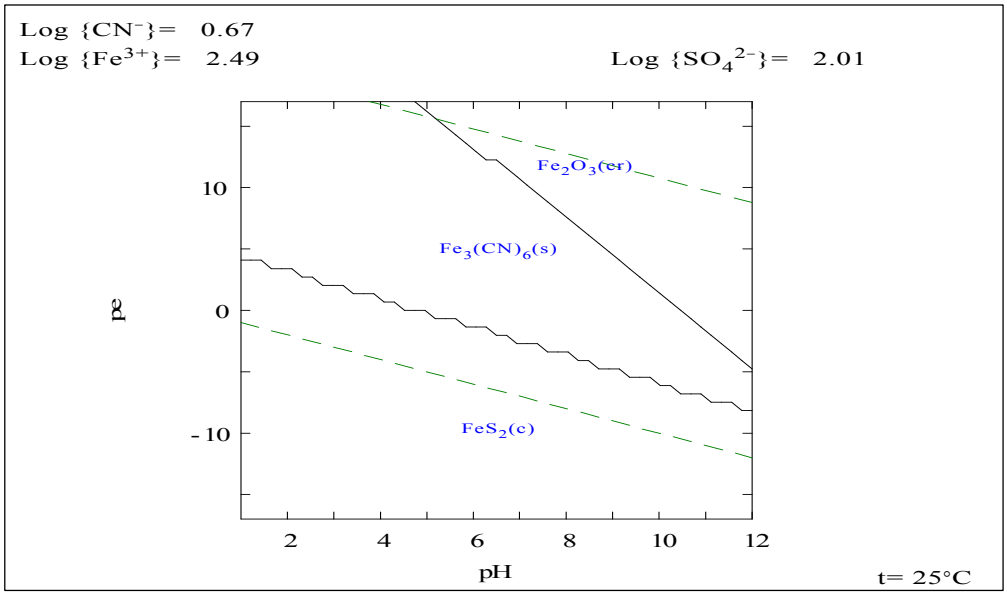
Figure 6.8 Predominance diagrams of Cu(I) in presence of (a)&(b) CN_T (b)&(c) SCN^- and CNO^- (e) &(f) SO_4^{2-}.

The introduction of major anions for instance SCN^- and SO_4^{2-} does not affect the dissociation of the copper-cyanide complex as seen in Figure 6.8f.

The model for iron species is shown in Figure 6.9.



(a)



(b)

Figure 6.9 Predominance diagram of Fe(III) species in presence of (a) CN_T and (b) SO_4^{2-}

As indicated in the equilibruim species predominance diagram, $Fe(OH)_3$ serves as the source of iron that becomes dissolved, which regulates the cyanide speciation. In the area dominated by $Fe_3(CN)_6$, cyanide is predicted as $Fe(CN)_6^{3-}$ (oxic conditions) or $Fe(CN)_6^{4-}$ (anoxic condition).

Conclusion

The application of cyanide in gold processing in South Africa is an issue for the Environment Scientist. This pollutant is discharged into the environment with the assumption that it will decompose with in a relatively short period of time. The distribution and fate of cyanide in the environment upon release from the tailings dumps depends on its physical-chemical speciation.

This study describes the characterisation of cyanide in the superficial deposits of a re-processed gold tailings dump and its fate in the environment. Sampling was done in 2006 and 2007 to assess the impact of tailings acidification on cyanide release over that period.

The results indicated a decrease in metal-cyanide complex concentrations over a short period after deposition. The acid generated due to sulphide oxidation promotes the dissociation of these complexes releasing free metal ions and cyanide. During deposition of tailings pH values are high and cyanide complexes are stable. As pH decreases, the complexes begin to dissociate releasing CN_{free}.

On contact with AMD, cyanide is released to form other cyano-species including thiocyanate and cyanate. These species, although less toxic than the free cyanide, they have the tendency to form soluble complexes with metals and, as such, are important for their mobility. The metal-cyanide complexes (CN_{WAD} and CN_{SAD}) are generally persistent in the tailings, their stability depends strongly on the extent of acid generation, and therefore on the tailings management regime during reclamation and post-deposition.

Fe-cyanide complexes are common in waste from mine waste and this is because these two complexes are very stable, but can be dissociated at very low pH and by photolysis.

The drop of pH leads to dissolution of metals as well as dissociation of metal cyanide complexes with release of CN_{free}. CN_{free} released is subject at several chemical mechanisms, namely: volatilization, oxidation, biodegradation. CN_{free} can be converted to thiocyanate or\ and oxidized to cyanate. These related compounds were found to be less toxic than CN_{free}.

The size distribution shows that these tailings are sandy at the edge and silly at the pond. High cation exchange content was obtained, these permit tailings to hold metals.

Pond water

The physical - chemical parameters as well as metals in the pond water are shown in Table 6.4.

The trend shows a decrease in pH with time due to weathering effects. An increase in conductivity was observed. This could be explained by an increase in dissolved metals with the generation of AMD.

An increase in heavy metal (Fe, Co, Ni, Zn and Cu) concentrations was observed with time due to the decrease of pH as explained previously.

Results obtained for cyanides species and related compounds are shown in Figure 6.10.

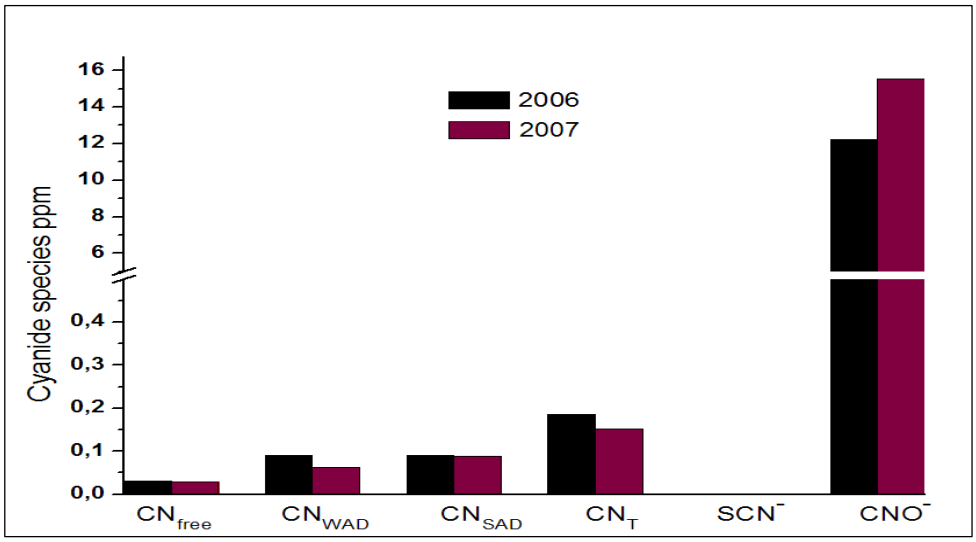


Figure 6.10 Cyanides species and related compounds in pond water

The concentration of CN_{free} was constant in pond water for both samples; this could be due to the continual release of CN^- since the pH of pond water decreases. Weak and strong-metal cyanide complexes release CN_{free} in acidic pH condition which may be lost as HCN. Concentration of CN_{WAD} decreases while that for CN_{SAD} remain the same since CN_{SAD} can be dissociated only at a pH < 2 and the pH in 2007 was 3.79. This value was not far from pH 4.5 found in 2006. Thiocyanate has not been detected in pond water since it is highly soluble in water or the concentration may be below the detection limit. Further investigations by Flynn and al. (1995) revealed that the region of thiocyanate stability decreases in Eh as the pH increases. Elevated concentrations of cyanate were found in samples collected in 2007. Oxidation of CN_{free} forms cyanate. As pH drops in the tailings, CN_{free} is released from CN_{WAD} complexes and collects in the pond. The oxidizing conditions in the pond result in the formation of cyanates. Concentrations of chlorides were respectively 365.8 mg l^{-1} in 2006 and 361.8 mg l^{-1} in 2007. These concentrations were by far high compare to those found in the tailings. The dissolution of salt crusts release ions and metals that can leach over time and accumulate in pond, this could explain the high conductivity of the pond water.

Table 6.4 Physical-chemical properties and metal concentrations in the pond water

	pH	T^{O}	ORP	EC	Al	Ca	Co	Cr	Fe	K	Mg	Zn	Mn	Na	Ni	Pb	U	Cu
		°C	mV	$mScm^{-1}$	mgl^{-1}	mgl^{-1}	mgl^{-1}	mgl^{-1}	mgl^{-1}	mgl^{-1}	mgl^{-1}	mgl^{-1}	mgl^{-1}	mgl^{-1}	mgl^{-1}	mgl^{-1}	mgl^{-1}	mgl^{-1}
2006	4.5	24.4	543.2	4.9	27	0.163	0.044	0.004	0.352	50	1.077	26	13.7	n.d	3.9	0.05	0.186	0.219
2007	3.79	13.3	512.6	5.48	30.12	0.175	0.052	0.015	0.461	45.36	1.122	28.55	12.27	0.844	4.121	0.03	0.154	0.284

n = 3, rsd □ 10

The results showed an increase of the concentrations of Fe and Cu in samples collected in 2007. This is the effect of weathering, since a decrease of pH was observed. The pond acts as an accumulation point or reservoir. Salt crusts also dissolve and contribute to the pollution load. They are very soluble in water and contain very high concentrations of metals. Low concentration of CN_{free} was found in the pond. CN^- is released from cyanide complexes and partly flows into the pond (it is also leached to the ground water). The low pH in the pond results in volatilization of CN^- as HCN. The Eh region (above 500 mV) is likely to result in oxidation of CN^- to CNO^-. The volatilization of CN^- was not assessed in this study, but results from a study by Lötter (2006) point to the confirmation that 9% of cyanide lost from the TSF could be attributed to HCN volatilization.

The low concentrations of CN_{WAD} in the pond water also point to the likelihood of dissociation of these complexes.

The high metal load could point to two possibilities relating to their release, namely: metal leaching from the tailings due to AMD and metals released from cyanide complexes. The former could be released from host minerals (Fe_2O_3, UO_2, U_2TiO_6, FeAsS etc) while the latter would be from cyanide complexes specifically ($Fe(CN)_6^{3-}$, $Ni(CN)_4^{2-}$ etc).

Metal-cyanide complexes

The results for metal-cyanide complexes are presented in Figure 6.11. The trend showed a decrease in the complexes with time. Copper-cyanide complex was found lower compared to nickel-cyanide complex, both being weak cyanide complexes. The dissociation of these complexes in aqueous solution depends on their stability constant, pH, temperature and the redox potential. The stability constant of nickel complex is higher than that for copper complex. The higher the stability constant, the more limited the dissociation in CN_{free}. The pond water was found to contain both iron-cyanide complexes, that is, $Fe(CN)_6^{4-}$ and $Fe(CN)_6^{3-}$. The predominance of $Fe(CN)_6^{3-}$ could be due to the relative high redox potential.

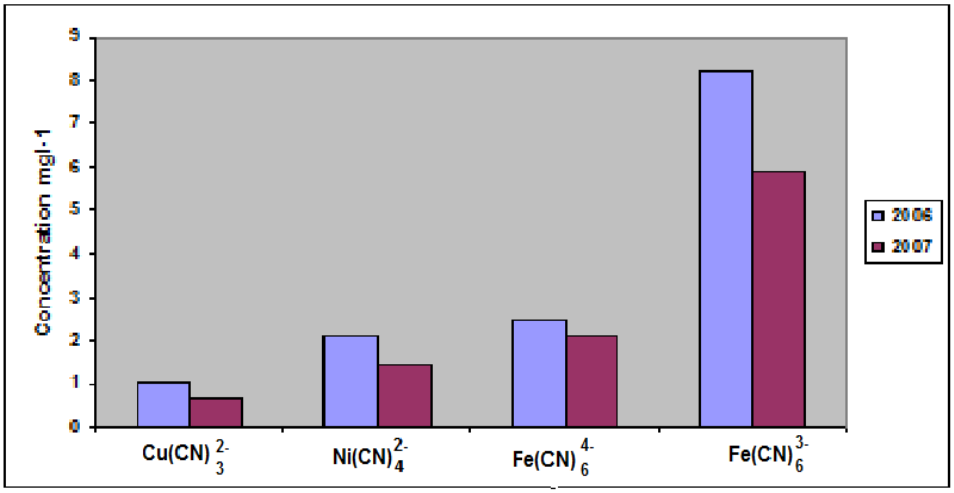


Figure 6.11 Metals-cyanide complexes in pond water.

Conclusion

During tailings deposition, the slurry flows towards the central pond. The coarser particles settled at the edge and water flows at the pond. This study revealed that the pound water contains CN_{free}, which remains constant with time. Weak and strong-metal cyanide complexes release CN_{free} in acidic pH condition, this lead to a continual release of CN^- since the pH of pond water decreases. CN_{free} may be lost as the volatile HCN or can seep into the groundwater with detrimental consequence.

6.1.2 Active slimes dam

An active slime dam is a dam where deposition from retreatment operation takes place. Sampling was carried out in January 2008 at an active slimes dam to assess the potential release of cyanide and related by product from such facility. The study site was one of three active slimes dams located in Nasrec, South west of Johannesburg (see Figure 6.12). The aerial view is given in appendix C.

Water was collected from pipes draining from the top of the dump as well as from a solution trench in which the water from the pipes and seepage points collects and flows to

water return dam. The samples were collected according to the standard procedure described in Chapter 3.

Algae were also collected in a plastic bag. The algae were wet at the time of sampling signifying saturation. Solid samples collected included salt crusts and tailings. Figure 6.13 shows the sites where samples were collected.

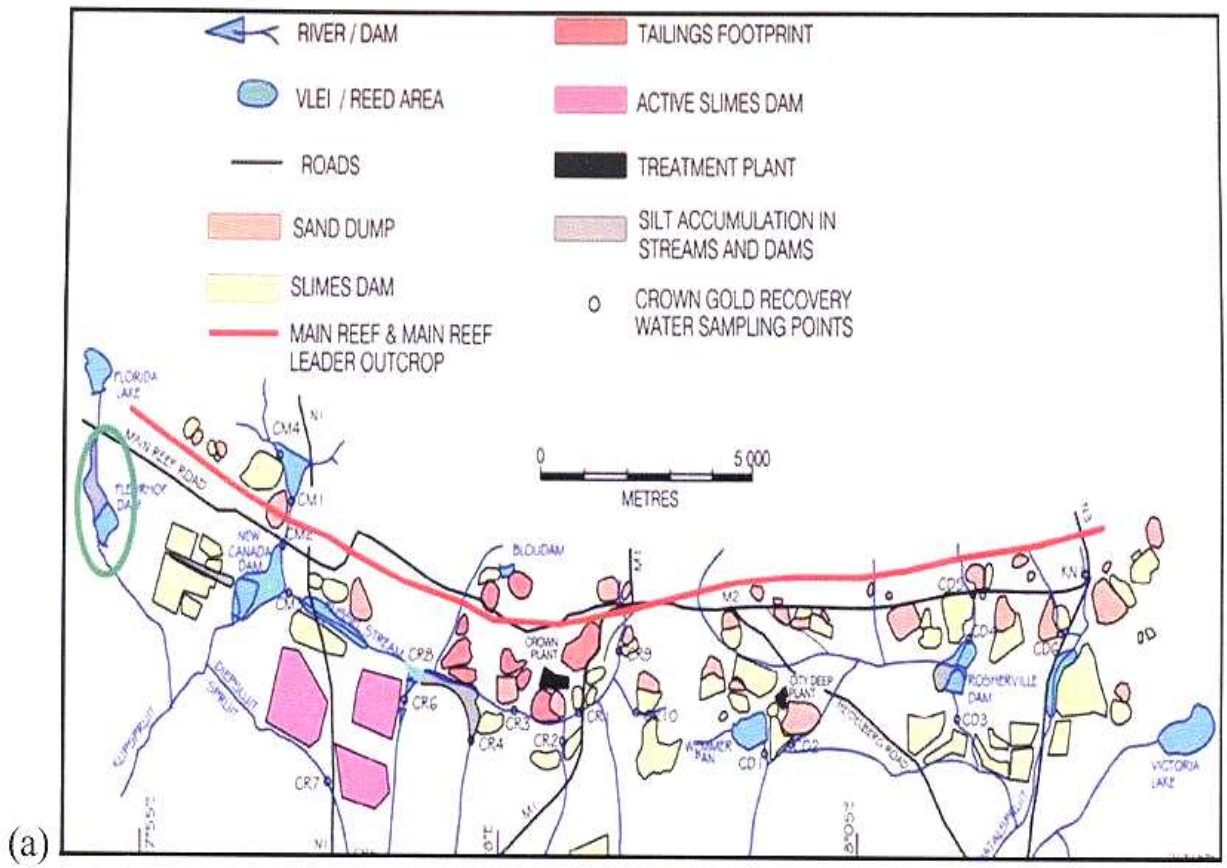


Figure 6.12 Location of tailings dams in the Witwatersrand basin

(a)



(b)



(C) 

Figure 6.13 (a) Side view of Nasrec active slimes (b) Bluish-green efflorescence along a solution trench (c) Sampling water from a pipe draining from the tailings (Photograph by author).

Results and discussion

Physical – chemical properties, anions and metals

The results obtained for metals, anions as well as the physical- chemical properties are given in Table 6.5.

The pH values were low for water collected from pipe. The trench samples had elevated pH (particularly sample C3). The slightly elevated pH values could be attributed to dilution effects. It should be recalled that the trench consists of water collected from source with different types of chemistry, namely: water draining from the pond; water spilling from spigots (i.e. from the slurry coming from the reprocessing plant); rainwater flowing down the slope of the tailings dam (samples were collected during the rainy season); and seepage water. The heterogeneity of trench water is observed from the ORP

values that are lower than those for the water collected from pipes. The concentrations of pollutants (as well as conductivity values) are also generally lower for the samples collected from the trench.

Elevated concentrations of metals (Fe, Co, Zn, Ni and Cu) were found in the samples C1 & C2, collected from the pipe. The low pH recorded in these samples could be the evidence that the water is from the pond. It is known that at low pH, metals are dissolved; this could explain the high metals content in these samples. Conductivity increases with an increase in metal concentration and this is because the most metal salts that are dissolved in the water, the higher the conductivity.

The same trend was observed for sulphate concentrations, being high in samples C1&C2, due to generation of AMD at low pH. Elevated sulphate concentrations corresponded with the low pH recorded.

Elevated iron concentration was recorded for water collected from pipes. Sample C2 had a particular high iron concentration (1745 mg l^{-1}). This could be attributed partly to the nature of the pipe, (a metal pipe). The sample was also visibly different from the others, being brownish in colour (as typically signifying the corrosion and leaching of iron, Figure 6.14).



Figure 6.14 Water samples from Nasrec dam.

Iron concentrations were drastically reduced in water collected from the trench. This could be attributed to a combination of dilution and precipitation effects.

The elevated pH of trench water is likely to contribute to precipitation of iron. Atmospheric oxidation is also increased in the trench water. Fe^{2+} quickly oxidises to the insoluble Fe^{3+}.

The pH value recorded for the algae was as low as the one from sample C2. The ORP and the conductivity were also high, this could lead to more metals dissolved and an algea provides a large surface area for adsorption of the metals ions and other pollutants. High concentration were obtained for Fe (56970 mg kg^{-1}) and Cu (450 mg kg^{-1}) but Co, Zn and Ni were not detected. This could be attributed to the oxidation of Fe according to the following reaction:

$$4Fe^{3+} + 12H_2O \rightarrow 4Fe(OH)_3\downarrow + 12H^+ \qquad \text{(Reaction 6.1)}$$

In this reaction, Fe^{3+} precipitates as hydroxides, $Fe(OH)_3$, resulting in a decrease of the pH. During the precipitation of Fe^{3+}, colloids are formed and these trap heavy metals which co-precipitate with iron.

The similar trend was observed with the bluish-green crusts. Low pH, high ORP as well as conductivity were recorded. High concentration of metal was obtained in the crust, for instance 61950 mg kg^{-1}, 150 mg kg^{-1} and 120 mg kg^{-1} were obtained for Fe, Zn and Cu respectively. This could be due to the composition of salt crusts or efflorescence which contains: water soluble salts (Na, K, and Ca), iron hydroxides and sulphates. It is also enriched with several metals including Co, Ni, Cu, and Zn. Co and Ni were not detected in the salt crusts for the same reason as observed in algae.

The concentration of thiosulphates and sulphates were high in algae and in the crusts. In the algae, the elevated concentration of sulphate could be due to the contamination by AMD and for the crusts, sulphate may have various sources probably, generation of AMD at low pH and $CaSO_4$ from the efflorescence.

Table 6.5 Field parameters and chemical composition of water emanating from the active slimes dam at Nasrec

sample	Description	T°	pH	Eh	Ec	$S_2O_3^{2-}$	SO_4^{2-}	Cl^-	Na	K	Ca	Fe	Co	Zn	Ni	Cu
		°C		mV	$mScm^{-1}$	$mg\ l^{-1}$	$mg\ l^{-1}$	$mg\ l^{-1}$	$mg\ l^{-1}$	$mg\ l^{-1}$	$mg\ l^{-1}$	$mg\ l^{-1}$	$mg\ l^{-1}$	$mg\ l^{-1}$	$mg\ l^{-1}$	$mg\ l^{-1}$
C1	Plastic pipe	20	4.28	436.3	6.1	280	5083.7	80.3	91.65	33	520.5	1412	6.45	10.95	15.45	0.6
C2	Metal pipe	20.2	2.41	648.3	9.31	405	8736.8	56.7	55.35	4.5	578.4	1745	4.5	13.8	24.45	4.2
C3	Trench	19.7	7.17	326.9	2.89	360	1575.8	33.9	62.7	10.65	626.8	5.4	2.1	nd	8.85	7.95
C4	Trench	18.2	5.6	287.9	3.6	320	1818.4	86.3	64.95	24.15	466.6	74.1	0.9	nd	0.3	0.9
C5	Plastic pipe	18.8	4.28	441.5	4.56	320	3002.5	73.5	73.5	30.45	534.5	730.4	2.7	3.9	6	0.15
Algae		20.3	2.39	653.5	6.63	1254	8985	85.85	9300	10950	18450	56970	nd	nd	nd	450
M1	Bluish-green crusts	20.2	3.44	604.4	1.611	1158	15564	100.2	54900	58350	13950	61950	nd	150	nd	120

Cyanide species and secondary compounds in water and solid samples

The results obtained for cyanide species in the active slime dams are given in table 6.6.

Table 6.6 Cyanide species and related compounds in water and solid material samples

Sample	CN_{Free} mg l^{-1}	CN_{WAD} mg l^{-1}	CN_{SAD} mg l^{-1}	CN_T mg l^{-1}	SCN^- mg l^{-1}	CNO^- mg l^{-1}	NH_4^+ mg l^{-1}
C1	3.492	5.635	0.807	9.934	97.57	105.9	31.25
C2	7.544	8.244	0.922	16.71	99.98	142.5	32.55
C3	15.95	35.47	6.540	57.96	94.43	100.5	33.88
C4	7.492	7.965	3.613	19.07	99.86	98.56	25.17
C5	1.428	8.525	9.057	19.01	94.88	114.3	34.05
Alg	10.45	14.24	0.470	25.16	213.4	301.6	85.02
M1	15.73	85.92	96.75	198.4	247.9	333.2	78.09

CN_{free} concentrations are low (except in C3), thus suggesting a possible loss. Due to the low pH values it is expected that the concentration declines rapidly due to the volatilization of cyanide in the form of HCN gas. CN_{free} present in the colloids (as seen in table 6.7) can be deposited onto the sediments and this would affect the CN_{free} as well as the CN_{tot}.

CN_{free} is higher in C3 with relatively high pH value compared to the other samples; this could limit the volatilisation of CN_{free}.

This trend is likely to be followed in terms of the cyanide complexes (both CN_{WAD} and CN_{SAD}). This is due to the fact that CN_{WAD} complexes dissociate at the pH range from 4.5 to 6 and CN_{SAD} complexes dissociate below pH 2.

Elevated concentration of CN_{WAD} and CN_{SAD} was obtained for sample C3. The pH of C3 is between 7 and 8. At this pH it is expected that volatilization of cyanide should be minimal and the complexes, even CN_{WAD} complexes should not dissociate within this pH range.

Elevated concentration of CNO^- was obtained. C2 had the higher concentration of CNO^- due to the high Eh value.

CNO^- also point to another possible attenuation process, namely the hydrolysis (Reaction 2.2) and oxidation of CN_{free}. The presence of NH_4^+ further suggests that CNO^- could be converted to NH_3 (reaction 2.4) which in turn is converted to NH_4^+ according to Reaction 2.13.

The results show a relatively high concentration of CN_{free} in algae compared to those obtained in water.

Very low concentration of CN_{SAD} was found in algae, despite the high concentration of Fe. This is likely due to the low pH 2.39, CN_{SAD} complexes dissociate below a pH of 2.5.

The concentration of SCN^- was high due to the presence of high concentration of sulphur species (thiosulphate).

Elevated concentration of OCN^- was obtained in the algae. The high potential redox recorded (653.5 mV) may lead to a chemical conversion of cyanides to cyanates.

Solid materials (M1) displayed a very high concentration of CN_T with a predominance of CN_{SAD}. This could be due to precipitation or adsorption of metal-cyanide complexes in crusts. The elevated concentrations of CN_{SAD} and Fe could suggest the presence of Prussian blue. The bluish-green colour of the crusts further substantiates this. In fact, Prussian blue is the complex ferri-ferro cyanide $Fe_4(Fe(CN)_6)_3(s)$ and can only exist under acidic pH and oxic conditions. Its solubility is very low and controlled by the pH and redox potential. The intense colour of Prussian blue arises due to charge transfer between the metal ions present in different oxidation states (Robin, 1962). The x-ray diffraction analysis would be necessary to confirm the suggestion.

It can be seen that CN_{free} concentration is high and this is due the low pH and subsequent dissociation of complexes, as mentioned previously.

The table above shows that the concentration of CN_{SAD} is comparatively high and this is because the low pH leads to dissociation of CN_{WAD} complexes and the free cyanide forms other complexes which are stable even at low pH values.

Adsorption of cyanide onto colloids was assessed on the filter membrane by analysing filtered (through a 0.45 μm cellulose nitrate membrane) and unfiltered water samples. The results showed in Table 6.7 revealed significant concentrations (up to 34 %) of CN_{free}

being adsorbed onto the colloids. Colloids in this case can be viewed as proxy to the salt crusts and partly reveal why accumulation occurs in the solid phases. The tendency of accumulation and adsorption is also prevalent for metals.

Table 6.7 Adsorption of cyanide onto colloids

	CN_{free}		
Sample	**Non filtered**	**Filtered**	**Adsorbed by colloids**
	mg l^{-1}	**mg l^{-1}**	**mg l^{-1}**
C1	4.492	3.914	0.578
C2	8.544	7.482	1.062
C3	15.95	15.22	0.73
C4	7.492	4.944	2.548
C5	1.428	0.274	1.154

Metal-cyanide complexes in water and solid samples

The results obtained for metal-cyanide complexes are presented in Table 6.8.

The field measurements given in Table 6.5, show that the pH of the water samples is between 2 and 7. At this pH range, it is expected that dissociation of cyanide complexes CN_{WAD} even CN_{SAD} will occur. Copper and iron cyanide complexes were the most complexes found in the water samples.

The results show high concentrations of Cu-cyanide complex in C4. Ni-cyanide complex was not detected in C1& C5 whilst relative higher concentration was obtained for C2& C3, indeed, elevated concentration of Ni was found in C2. The iron-cyanide complex ($Fe(CN)_6^{4-}$) is high in sample C2. This could be attributed in part to Fe released from the metal pipe. The Fe discharged from the pipe is likely to be Fe (II) and hence the prevalence of Fe (II) cyanides. The presence of Fe $(CN)_6^{3-}$ in the solid material (M1) is an evidence of the presence of Prussian-blue. The solid material contains quite high

concentration of metal-cyanide complexes. This could be due by accumulation of complexes in the crusts, recalled that this material is a mixture of tailings and salt crusts.
Cobalt and iron (III) cyanide complexes were not detected in water samples. However, elevated concentrations of these were obtained in crusts (M1).
Fe-cyanide (II) was the higher complex obtained in the algae. Fe-cyanide (III) was not detected, despite the high potential redox.

Table 6.8 Metals-cyanide complexes in water emanating from an active slime dam

Sample	$Cu(CN)_3^{2-}$	$Fe(CN)_6^{4-}$	$Ni(CN)_4^{2-}$	$Fe(CN)_6^{3-}$	$Co(CN)_6^{4-}$
	mg l^{-1}	mg l^{-1}	mg l^{-1}	mg l^{-1}	mg l^{-1}
C1	6.49	15.58	n.d	n.d	n.d
C2	13.44	53.79	32.77	n.d	n.d
C3	15.44	47.04	46.75	n.d	n.d
C4	22.28	13.98	7.914	n.d	n.d
C5	14.29	17.37	n.d	n.d	n.d
Alg	15.39	20.75	7.156	n.d	n.d
M1	54.21	50.41	13.36	20.45	5.423

Conclusion

Drainage water from the active slimes dams is acidic, hence, contains high concentration of cyanide species as well as metals. The low pH allows complexes to dissociate and to release CN_{free} which may form other complexes. Besides, metals are also release which can leach and contaminate the groundwater or being adsorb in sediment.
The study revealed a contamination of the environment of the reprocessing plant by heavy metals and more stable cyanide complexes.

6.2 Wetland sediments

Wetlands refer to lowlands covered with shallow and sometimes temporary or intermittent waters. Wetlands are lands transitional between terrestrial and aquatic

systems where the water table is usually at or near the surface or the land is covered by shallow water. Wetlands must have one or more of following three attributes:
(1) periodically, the land supports predominantly hydrophytes; (2) the substrates is predominantly undrained hydric soil; and (3) the substrate is non soil and is saturated with water or covered by shallow water at some time during the raining season of each year.
The Fleurhof Dam in the Central Rand presents a case of wetland sediments where surface runoff led to an accumulation of sediments along the river bed and in the dam. It is a good illustration to study the fate of cyanide from the surrounding tailings dam to the wetlands sediments through the stream sediment.

6.2.1 Sediments of the Fleurhof Dam wetland

Site description

The Fleurhof Dam is over a hundred years old and is one of the many dams on the Central Rand Goldfield that were constructed to supply water to the gold mining industry. Surface erosion of exposed and poorly managed tailings dumps in the vicinity of these dams over the years has led to siltation. This has also affected most streams, for example the Russel Stream and the Upper Klipspruit which are major tributaries draining through the area. This phenomenon, describing closely the situation relating to the Fleurhof Dam, is captured in Figure 6.15 which shows a sketch of spillage or surface erosion of tailings into a stream and eventually into a dam.
The sediments in the Fleurhof Dam present a peculiar case in that gold concentrations were found in very high (> 30 $mgkg^{-1}$) to compare with ordinary extractable concentrations in most ores of around 2 $mgkg^{-1}$. This resulted in the company carrying out mining operations in the area, i.e. Crown Gold Recovery draining water out of the dam and dredging the gold-rich sediments for reprocessing, a development seen to be far more profitable to compare with reprocessing of normal tailings. The excavation

activities left an exposed face of the sediments (see Figure 6.16) measuring close to 134 m in length and up to 1200 m in depth.

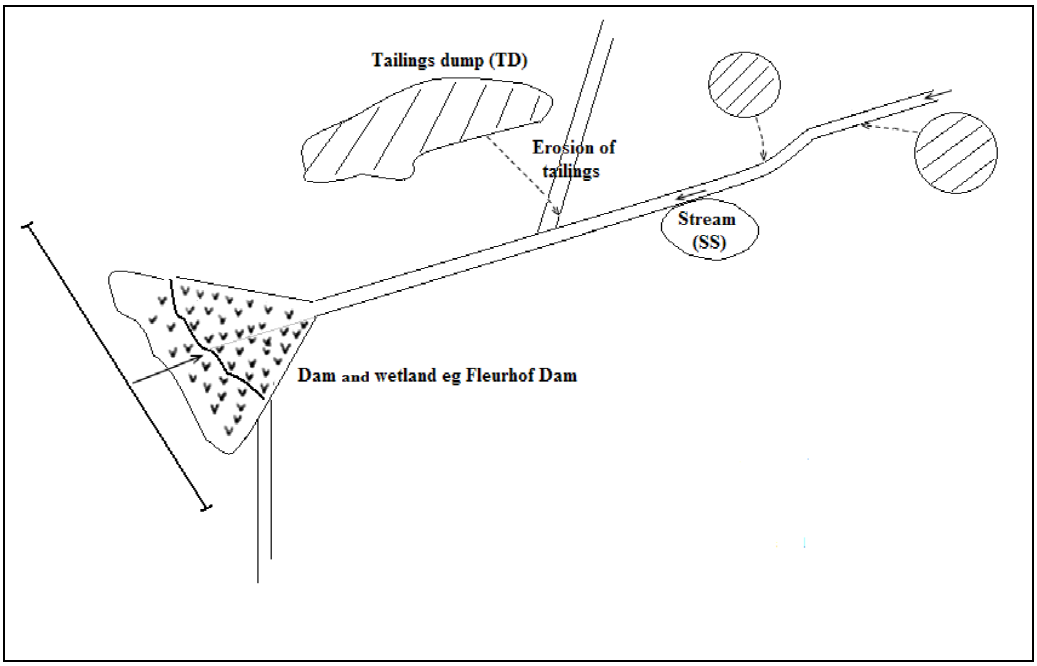


Figure 6.15 Sketch of tailings dumps and dam

The deposition of the sediments in the dam has been cited by Ndasi (2004) as resembling the Mississippi-type of delta formation in which sediments were deposited horizontally with well-defined strata. The formation is such that coarser sediments are deposited first due to gravity and then the finer sediments and organic matters suspended in the water and are deposited later in the inner parts of the dam (Tutu, 2006). Figure 6.17 shows a sketch of this process and also points out the sequence of segregation of material based on their size.



Figure 6.16 Section of sediment in Fleurhof Dam left exposed after dredging (Ndasi, 2004)

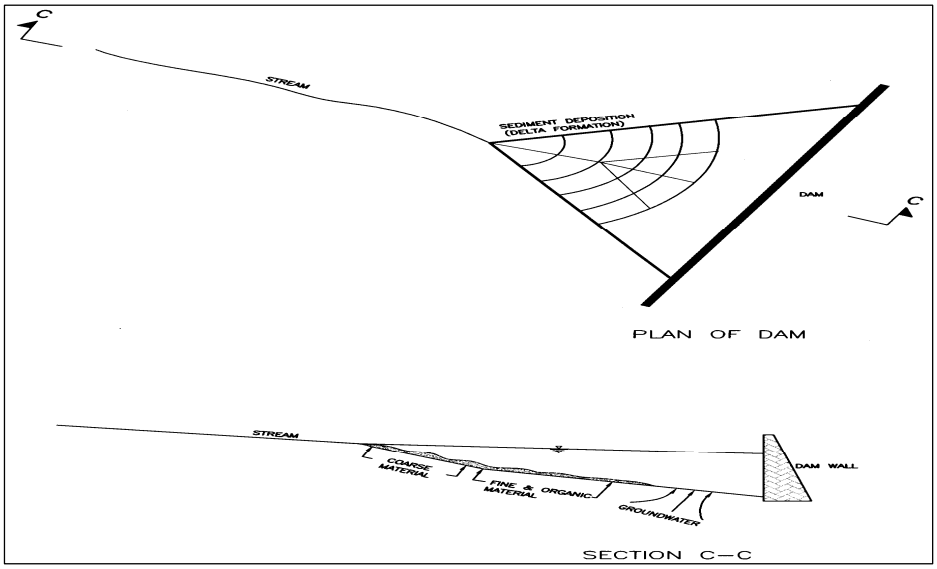


Figure 6.17 Schematic diagram of delta formation and section showing sedimentation in a dam (Ndasi, 2004)

Sampling strategy

Sampling was carried out along the exposed face (shown in Figure 6.16) and through the face at selected profiles. The profiles, namely: FA, FE and FH are described in Figure 6.18 which shows them as columns.

Sampling of stream sediment (SS) was carried out along the bed of the Upper Klispruit stream up to just below Floride Lake to obtain background concentrations. SS1 – SS6 are samples from different points along the inlet streams to the dam.

Tailings dams (TD) samples were collected from surrounding mine tailings dumps, from a depth of about 20 cm in the tailings dumps. TDA, TDB1-3, TDC, TDD and TDE are tailings dumps and SDB1 and SDB2 are sand tailings dumps.

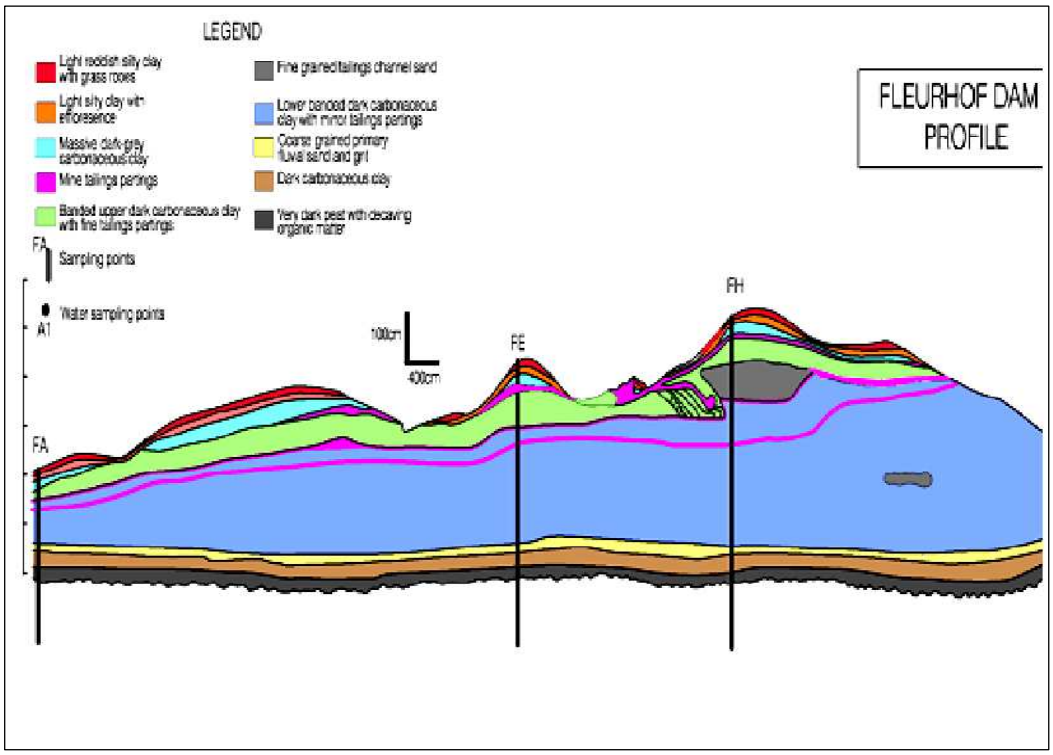


Figure 6.18 Stratigraphic profile of exposed face of unmined sediment in the Fleurhof dam (Ndasi, 2004)

Results and discussion

Stream sediment and surrounding tailings

Metals

The ICP - OES results done by Ndasi in 2004 are given in Table 6.9.

The general trends show increases of the average concentration of metals such as Fe, Co, Zn, Ni and Cu from the surrounding tailings dam to the stream sediments. The increase was respectively 15.42% for Fe, 62.29% for Co, 83.03% for Ni, 76.67% for Zn and 31.59% for Cu. Na, K, Ca showed low values in stream sediments than in tailings. This could be attributed to the solubility of those metals, which are also part of the fine clay component. They are very soluble and constantly been washed away by flowing waters and hence cannot be held in the stream sediments.

The metal concentration was low in sample SS1, close to the Fleurhof dam.

High metal concentration was obtained in sample SS2. This point could hold the material from the tailing dam located at the Bird Reef Open Cast as well as from a small tributary, where SS3 was sampled. Along this tributary lied two tailing dams. The materials eroded from these tailings could be held either at SS3 or SS2. SS6, close to the Florida Lake, contains high concentration of iron.

The sand tailings dams (SDA) contain low concentration of metal (Fe, Co, Zn, Ni and Cu). Iron and copper are higher in tailings dams compared to cobalt, zinc and nickel.

Clays have a high cationic exchange capacity and absorb metals like Fe, Al and Mn, causing them to precipitate. Metal concentrations are generally higher in the clays than in the sands and increases with the clay content.

The others metals like Ni, Cu and Zn can co-precipitate with Fe, Al, Mn, and will have high concentrations in the clays.

Table 6.9 Results of ICP-OES analysis for samples collected the in the stream sediment and surrounding tailings. Concentrations are given in $mgkg^{-1}$ dry weight

Sample	Na	K	Ca	Mg	Al	Mn	Fe	Co	Zn	Ni	Cu
	$mgkg^{-1}$	$mgkg^{-1}$	$mgkg^{-1}$	$mgkg^{-1}$	$mgkg^{-1}$	$mgkg^{-1}$	$mgkg^{-1}$	$mgkg^{-1}$	$mgkg^{-1}$	$mgkg^{-1}$	$mgkg^{-1}$
SS1	370.8	1684	544.8	2250	9434	168.8	13240	19	43.22	35.2	50.96
SS2	370.04	4902	1144	1030	14280	1566	37680	192.4	426.2	217	120.4
SS3	263.8	1458	2374	11138	19200	249	19960	17.2	496.4	57.14	78.68
SS4	305.4	1614	888.6	2362	14380	246	27940	25	195.8	77.74	58.06
SS5	417.3	2060	511.4	1544	17660	128.8	17160	14.38	42.52	102.7	38.02
SS6	372.66	3640	495.6	880.6	22540	152	32800	0.98	65.1	61.18	63.88
TDA	384.8	2454	586.4	1988	12740	162.8	15380	2.9	2.8	2.88	20.94
TDB1	455.66	2022	7038	2154	44100	157	28780	3.1	36.5	10.5	33.84
TDB2	600	13660	580.4	2052	42310	155.6	22480	8.24	45.46	18	44.88
TDB3	354.78	3534	672.34	2155	45322	162.7	20996	12.53	53.68	22.78	40.96
TDC	1278.4	23260	1418	2162	48240	452.4	25540	38.1	68.06	3.06	176.4
TDD	908.44	1132	762.4	1838	10420	135.4	11320	2.58	24.16	9.88	10.1
TDE	785.63	4124	1850	1384	12080	395.4	38680	7.63	48.21	53.94	27.16
SDA	167.2	1062	314.8	1350	8928	138	9714	5.22	17.65	5.88	7.6
SDB1	3590	8888	3858	2629	29140	207	18080	43.28	40.38	16.6	57.92
SDB2	3466	58380	11020	2716	35380	225.4	18740	45.44	156.6	12.4	47.56

Note: SS –Stream sediments

TD –Tailings dumps

Cyanide species and secondary compounds

The results for cyanide species and secondary compounds are given in Table 6.10.

Table 6. 10 Concentration of cyanide species and secondary compounds in stream sediment and surrounding tailings dams

Sample	CN_{free}	CN_{WAD}	CN_{SAD}	CN_T	SCN^-	CNO^-	NH_4^+
	$mgkg^{-1}$	$mgkg^{-1}$	$mgkg^{-1}$	$mgkg^{-1}$	$mgkg^{-1}$	$mgkg^{-1}$	$mgkg^{-1}$
SS1	4.615	5.595	62.67	72.88	21.35	24.22	28.11
SS2	15.81	2.69	71.35	89.85	23.33	17.91	33.54
SS3	9.704	5.546	68.87	84.12	33.13	34.99	33.54
SS4	5.584	5.066	61.38	72.03	26.4	23.17	23.31
SS5	8.049	7.431	47.89	63.37	7.07	17.12	26.98
SS6	8.176	10.074	53.29	71.54	24.55	21.59	23.66
TDA	2.364	3.203	6.063	11.63	29.69	16.89	5.244
TDB1	7.353	3.197	28.59	39.14	10.22	22.38	3.006
TDB2	5.602	6.848	25.79	38.24	55.65	28.95	9.081
TDB3	8.328	2.322	23.02	33.67	12.27	42.35	45.21
TDC	4.748	10.492	33.93	49.17	18.26	20.01	31.78
TDD	2.983	1.253	5.834	10.07	0.198	11.86	8.121
TDE	2.467	3.221	12.342	18.03	12.23	23.96	2.046
SDA	3.989	6.671	70.08	80.74	38.99	16.07	28.05
SDB1	5.981	3.674	69.875	79.53	27.99	19.49	28.11
SDB2	4.969	5.261	73.07	83.3	22.53	22.64	26.02

The general trend shows elevated concentration of cyanide species in stream sediment compared to tailings dams. CN_{free} is higher in stream sediment than in tailings. This is likely due to the dissociation of CN_{SAD} and CN_{WAD} under acidic condition to release CN_{free}. In this case, the low concentration of CN_{WAD} in tailings and stream sediments could be due to dissociation and we assume that the pH in the tailings is slightly acidic.

Sand tailings dams (SDA, SDB1& SDB2) contain low concentration of CN_{free}. In fact, CN_{free} is weakly adsorbs in sand.

Along the inlet stream, SS2 contains high concentrations of CN_{free} and CN_{SAD}.

CN_{WAD} concentration was higher in SS6. High concentration of CN_{SAD} was obtained in stream sediments. This could be due to the presence of high concentration of metal such as iron and cobalt which form the strong complex with CN_{free}.

Beside, high concentration of CN_{SAD} was obtained in the sand tailings dumps (SDA, SDB1 and SDB2) compared to tailings dumps.

The CN_{tot} increases in stream sediment and this is due to deposition and adsorption of the cyanide and cyanide complexes to the soil particles (i.e. enrichment of cyanide). From Table 6.10 above, it can be seen that elevated concentrations of all forms of the cyanide in the stream sediment. This could be due to the deposition onto the sediments. In the tailings, TDC contains higher concentrations of CN_{WAD} and CN_{SAD}.

Concentration of CN_{free} is relatively high in samples TDB1 and TDB3. CN_{WAD} are high in TDB2 and TDC. CN_{SAD} are high in TDB1, TDB2, TDB3, TDC and TDE.

SCN^- concentration is relatively high in stream sediment than in tailings dumps, except for TDB2. Sulphur species is mostly found in sediment because of the reducing conditions with low potential redox. CN_{free} is converted to SCN^- and the latter is deposited and adsorbed onto sediment.

Sand dumps contain higher concentration of SCN^- compared to tailings dumps. SCN- is retained on soils with significant anion exchange capacity (Dzombak, 2006).

High concentration of thiocyanate was found in TDA and TDB2. TDD contains very low concentration of thiocyanate. CNO^- concentration is similar in stream sediment than in tailings dumps and sand dams. Only TDB3 contains higher concentration of cyanate, hence, high concentration of ammonium.

Concentrations of cyanates are high in all samples. This could be due to the oxidising conditions of these tailings.

The general trend for ammonium concentration shows high concentration in stream sediment than in the tailings, except for TDB3 &TDC.

Metal cyanide complexes

Metal-cyanides complexes were analysed in the tailings dumps and stream sediments. The results obtained are shown in Table 6.11.

Table 6.11 Metal cyanide-complexes in samples collected in the stream sediment and surrounding tailings dams

Sample	$Cu(CN)_3^{2-}$	$Ni(CN)_4^{2-}$	$Co(CN)_6^{4-}$	$Fe(CN)_6^{4-}$	$Fe(CN)_6^{3-}$
	$mgkg^{-1}$	$mgkg^{-1}$	$mgkg^{-1}$	$mgkg^{-1}$	$mgkg^{-1}$
SS1	3.042	2.98	15.09	30.12	38.22
SS2	1.88	1.21	30.05	37.51	33.07
SS3	2.988	3.125	18.05	36.88	32.97
SS4	2.504	2.014	14.52	31.02	37.62
SS5	4.05	4.685	10.15	24.83	28.55
SS6	5.668	6.332	1.203	32.79	35.31
TDA	2.03	0.855	1.204	4.124	1.255
TDB1	2.362	0.942	5.428	15.02	20.32
TDB2	3.512	1.022	4.25	18.31	16.54
TDB3	1.095	0.758	4.361	14.45	10.06
TDC	9.247	4.322	8.595	19.13	14.82
TDD	0.99	0.788	0.542	3.258	1.522
TDE	2.314	0.925	1.023	7.524	5.841
SDA	2.103	1.691	2.504	46.88	40.32
SDB1	1.98	2.134	21.13	34.42	30.01
SDB2	2.041	2.58	19.05	35	42.28

From Table 6.11 above, it can be seen that high concentrations of metal-cyanide complexes are obtained in the stream sediment as expected.

The concentration of weak complexes $Cu(CN)_3^{2-}$ & $Ni(CN)_4^{2-}$ is very low in tailings as well as in stream sediment. This is consistent with the low concentration of CN_{WAD} obtained. Weak complexes dissociate under slightly acidic condition to release CN_{WAD}. Their stability constant is also low.

Also most of the complexes present in the sediments are strong complexes and by looking at the ICP-OES results for the sediments it can be seen that Fe is present and it is most likely that the Fe-cyanide complexes are present in very high concentration. $Fe(CN)_6^{2-}$ and $Fe(CN)_6^{3-}$ are the most important complexes in the samples analysed. They are very stable even under acidic conditions. Strong complexes adsorb strongly in sediment. Iron complexes are high in sand tailings. This correlate with the high CN_{SAD} obtained. The trend revealed high concentration of copper and nickel cyanides complexes in TDC. Fe (II) and Fe (III) cyanides complexes as well as cobalt cyanide complex showed high values in TDB1, TDB2, TDB3 and TDC.

Iron- cyanide complexes are the most important complexes found in the stream sediment. SDA contains higher iron cyanide complexes (Fe II and Fe III). SS1 – SS5 contain relative high concentration of cobalt cyanide complex. Nickel and copper cyanides complexes are low in all samples.

It is likely an enrichment of metal - cyanide complexes in the sediment, mainly the strong complexes.

Profiles (FA, FE & FH)

The results for Eh and pH measurements for the sediment profiles are presented in Table 6.12.

Table 6.12 Eh and pH measurements for sampling points FA, FE and FH of Fleurhof Dam.

Profile FA			**Profile FE**			**Profile FH**		
Sample	**pH**	**Eh(mV)**	**Sample**	**pH**	**Eh (mV)**	**Sample**	**pH**	**Eh (mV)**
FA1	4.23	437	FES	2.6	740	FHS	2.8	680
FA2	3.78	538	FE4	4.3	340	FH4	3.3	430
FA3	6.3	220	FE5-7	7.6	20	FHS'	2.4	721
FA4	5.6	376	FE8	6.7	122	FH5-7	7.4	-175
FA5-7	6.26	66	FE9	6.9	-100	FH8	6.7	162
FA8	5.56	151				FH9	6.9	-100

pH values were higher in the strata that are rich in organic matter. Organic material tends to reduce iron hydroxides thus removing acidity as illustrated in reaction 6.2.

$$Fe(OH)_3^0 + 3H^+ + e^- \rightarrow Fe^{2+} + 3H_2O \qquad \text{(Reaction 6.2)}$$

Metals

Analytical results for selected metals on the profiles FA, FE and FH are given in Table 6.13.

High metal concentrations were found in the stratum FA2, FE2 and FH2. This could be attributed to the precipitation of metals during formation of efflorescence. pH values in this stratum were significantly low(< 4). This is evidence of acid generation during weathering of pyrite containing material. The iron concentration varied down the profiles. This could be attributed to changes in redox equilibrium. High values of metal concentrations were found in the stratum FA3, FH3 & FH3. This stratum revealed high pH (> 6). This could be due to relative high value of organic matter. Both organic and clay particles can hold on to metals electrochemically because of their negatively charged structures and high surface areas.

An increase in metal concentrations was observed in the stratum FA5 -7, FE5-7, and FH 5-7. This could be attributed to the presence of organic matter. High concentrations of copper concentration were recorded in some sediments (FA3) (>1000 $mgkg^{-1}$), evidence of enrichment of metals in sediments. A decrease in metal concentrations was observed in the stratum FA8, FE8 and FH8. This could be due to the composition of the layer (the layer consists of coarse-grained primary fluvial sand and grit).

This is evidence that the wetland sediments are a sink for heavy metals washed from the tailings dams.

Table 6.13 Metal concentrations in the Fleurhof Dam sediments (Ndasi, 2004)

Sample	Na	K	Mg	Ca	Al	Mn	Fe	Co	Zn	Ni	Cu
	$mgkg^{-1}$	$mgkg^{-1}$	$mgkg^{-1}$	$mgkg^{-1}$	$mgkg^{-1}$	$mgkg^{-1}$	$mgkg^{-1}$	$mgkg^{-1}$	$mgkg^{-1}$	$mgkg^{-1}$	$mgkg^{-1}$
FA1	499.8	3026	3206	1084	18000	434.8	27080	117.8	566.2	441.8	183.4
FA2	544.6	11420	7022	3166	8982	2138	71120	751.6	1770	3362	922
FA3	2200	13100	12280	5078	9800	3338	78320	1750	3326	7126	1490
FA4	696.5	11680	4572	3122	36680	820	55340	411.4	1144	1692	687.4
FA5	890.6	7584	2268	1680	52140	257.8	35440	137.7	396	761.8	300.6
FA6	1570	11140	1696	1136	26020	266.8	37720	146.8	441.2	791	283
FA7	466.2	9695	882.7	760.5	13154	112.4	29076	133.2	1058	658.5	599.6
FA8	309.2	13120	1000	980.5	29980	142	13200	5.960	48.34	18.80	11.48
FA9	1230	17760	1174	237	20344	179.6	22300	16.80	493.8	60	63.66
FA10	660.4	13140	530	322.4	14360	251	28000	127.2	5966	339.4	182.6
FES	365.4	17440	2396	1252	52880	273.2	22800	66.98	84.58	35.44	115.8
FE1	529.6	4470	660.2	459.4	18300	310.4	73980	203.6	1166	718.2	741.4
FE2	1032	7070	1730	2352	33460	540	33820	105.6	250	246.2	245.8
FE3	899.2	48760	8665	3786	45876	3058	73600	2298	4860	8240	1538
FE4	1580	44960	12840	3396	89900	665.2	42960	529.6	1274	1894	719.8
FE5	595.6	15280	2058	744.6	33300	365.6	29500	166	103.8	142	73.8
FE6	969.4	5288	3150	1474	30740	357.4	43800	230.8	590.4	1166	269.8
FE7	349.6	1096	19840	887.8	77960	660.6	32540	165.6	964	533	438.2
FE8	446.2	1634	996.6	613.2	13233	137.2	9098	24	54.72	28	25.16
FE9	444.7	2766	696.4	927.4	15120	214.2	27900	29.08	1802	136.4	105.2
FE10	556.7	3166	2572	683	34080	325	19260	25.88	1516	82.9	36.42
FHS	883.6	977.2	1812	1146	10420	179.6	11560	67.68	229.4	232.5	97.44
FH1	776.2	9290	993.4	705.4	26520	183.6	63420	133.5	673.6	509.8	728.2
FH2	647.2	18680	12380	3700	42780	263.8	30540	143.8	390.6	732	290.2
FH3	708.9	37920	18760	3708	47540	2612	77000	3174	4972	1026	1478
FH4	988.3	2172	2288	1900	17280	393.2	29400	206.4	536.2	891.8	252.2
FHS'	216.2	1186	1672	627.8	10320	186.6	15440	31.3	161.2	137.4	140.6
FH5	247.4	8880	4266	884.4	30420	450.4	33560	190	524.6	1028	240.8
FH6	456.7	4216	1450	1350	18840	314.6	37460	140.32	596.6	648.6	388.4
FH7	1122	6190	876.4	921.6	83680	337.8	33260	133	735.2	416.4	502
FH8	756.5	621.2	1018	509	16360	83.66	9696	8.04	138.2	30.8	29.18
FH9	356.3	23960	800.6	758.8	43040	244.4	22880	27.62	1222	114.8	93.2
FH10	416.8	5534	447.4	654.4	10080	372.6	11340	42.3	240.2	111.3	79.96
FP-BR	427.8	1232	1992	793.6	7522	188	16420	4.9	29.58	18.8	21.04

Results for carbon analysis are given in Table 6.14. The values are for total organic carbon obtained after removing inorganic carbon (carbonates) by reaction with sulphuric acid.

Table 6.14 Carbon analysis results for selected sections of profiles (Tutu, 2006)

Sample	FE2	FE3	FE10	FA1	FA3	FA6	FA9	FA10	FH2	FH3	FH10	FHS	TDD
% carbon	0.445	4.358	20.24	0.460	3.358	0.550	1.866	19.21	0.885	3.471	14.03	0.193	0.036
standard deviation	0.042	0.010	0.288	0.021	0.079	0.027	0.013	0.091	0.043	0.011	0.266	0.018	0.004
RSD	10.33	2.792	1.446	4.601	2.383	5.181	0.712	0.470	5.005	2.347	1.859	8.789	10.75

High carbon values were obtained in the stratum for FA10, FE10 and FH10. The organic matter in this stratum is accumulated in form of peat. The stratum for FA3, FE3 and FH3 also revealed relatively high values of carbon. This stratum consisted of dark-grey carbonaceous clay and also revealed elevated metal concentrations with a pH value > 6.
Most heavy metals tend to be trapped in the iron and manganese colloids and form complexes with organic ligands.
Organic matter contribute to the cation exchange capacity (CEC) of the soil, hence, soil with high organic matter, has high CEC. And the latter depends on the pH.

Cyanide species and secondary products

Cyanide species (CN_{free}, CN_{WAD}, CN_{SAD}, and CN_T) and secondary compounds (SCN^-, CNO^-, NH_4^+) were analysed in profiles FA, FE, & FH. The results obtained are given in Figure 6.19 below.
The general trend shows high concentration of CN_{free} for the profiles FE and FH. Concentration of CN_{free} is high for the strata FE1 and FH1 and is almost the major form of cyanide. These are likely to be CN_{free} in efflorescent crusts which accumulated in these layers. High concentration of CN_{free} was recorded for layers FA3, FA9, FA10; FH3, FH9,

FH10; FE3, FE9, FE10. These strata revealed relatively high values of organic carbon and also elevated metal concentrations. On the other hand, the pH was observed to increase in these strata (> 6). They all consisted of dark-grey carbonaceous clay with the higher carbon content. Previous studies showed that CN_{free} adsorbs significantly on organic carbon and under near-neutral pH conditions, its adsorption on soils is correlated with organic matter (Dzombak et al., 2006).

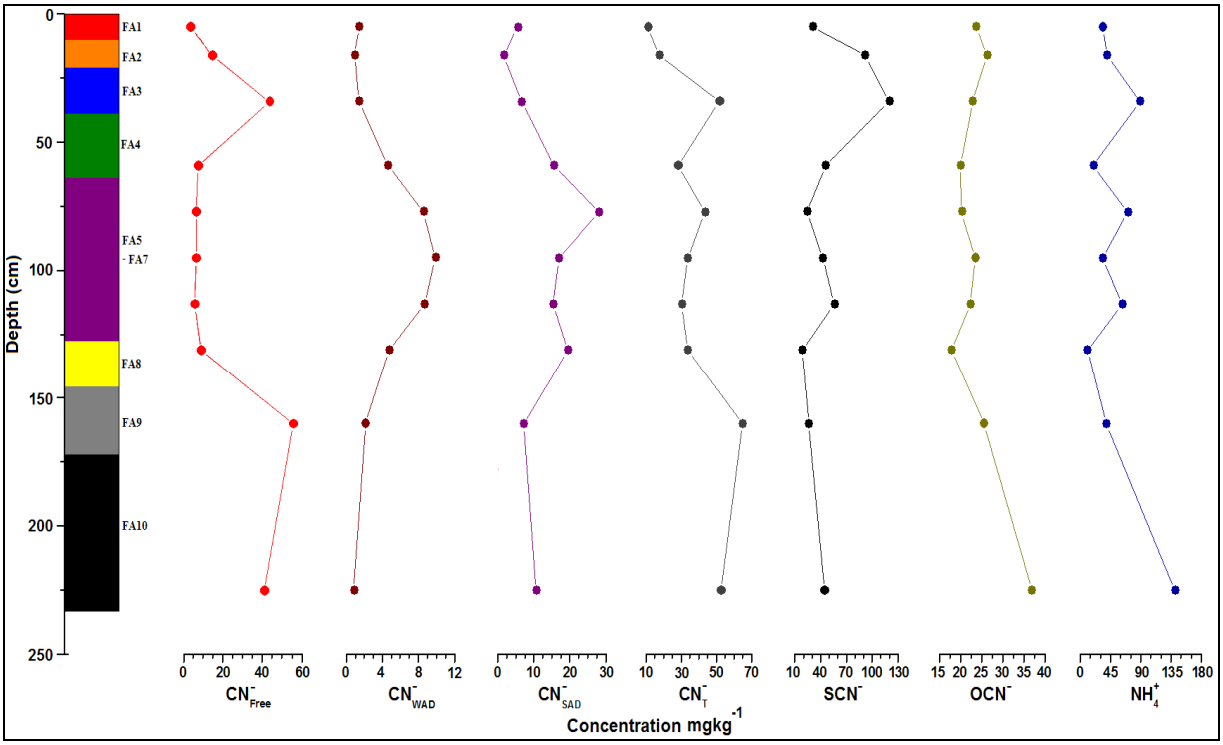
At the neutral pH range of interest, HCN is the dominant form of cyanide and CN^- concentrations are very low. HCN adsorbs weakly or not at all to inorganic soil components such as iron oxide, aluminium oxide, clay and sand. However, HCN has been shown to adsorb significantly to soils with appreciable organic carbon content (Dzombak et al., 2006).

Literature showed an adsorption capacity of about 1 to 2 mg of CN_{free} per gram of carbon while similar tests performed with soil organic carbon revealed an adsorption capacity of 0.5 mg of CN_{free} per gram of carbon (Chatwin et al., 1988). On the contrary, our calculations of grams of carbon versus CN_{free} differ from the literature. More than 0-5 mg of CN_{free} might be adsorbed.

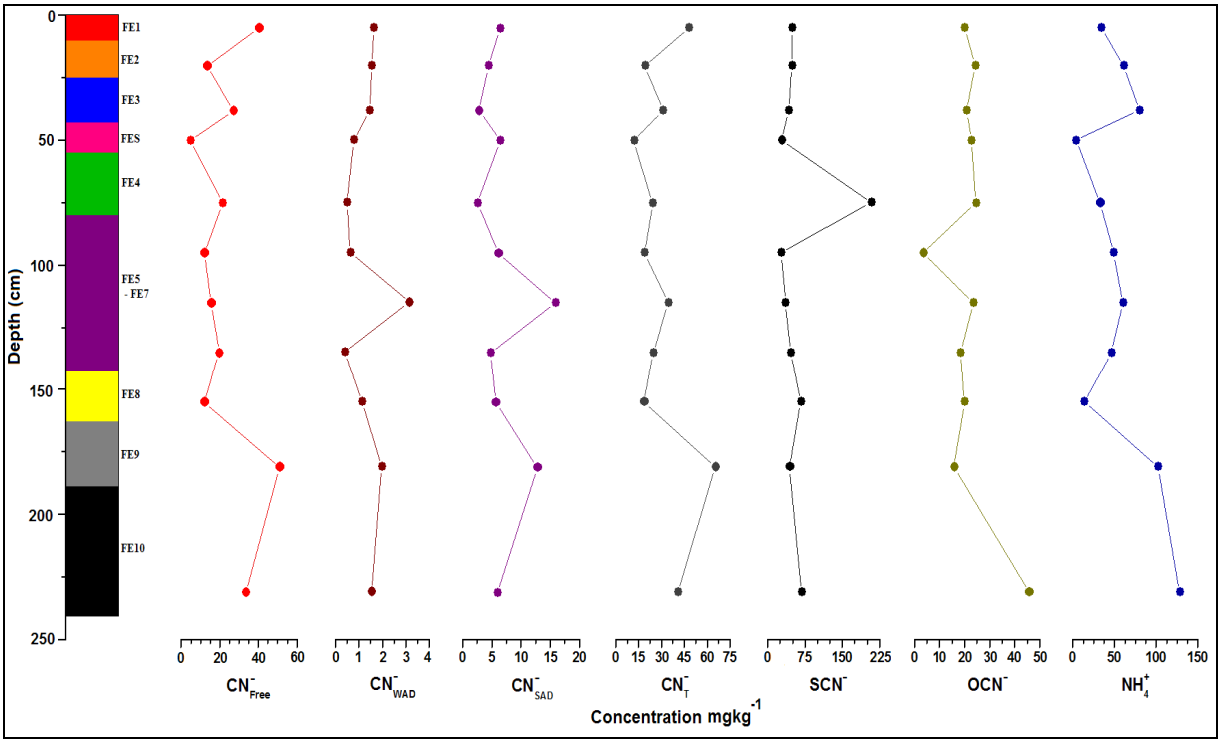
Organic matter usually possesses a variable charge surface (both negative and positive charges). Thus it can adsorb both cations and anions. On the other hand, sand consists largely of SiO_2 which on hydration becomes Si-OH or $Si\text{-}O^-$. Thus cations are adsorbed instead of anions (James and Barrow, 1981).

Concentrations of CN_{WAD} were high for the layers FH4 – FH8. These strata consist of carbonaceous clay except for FH8 that consist of sand and grit.

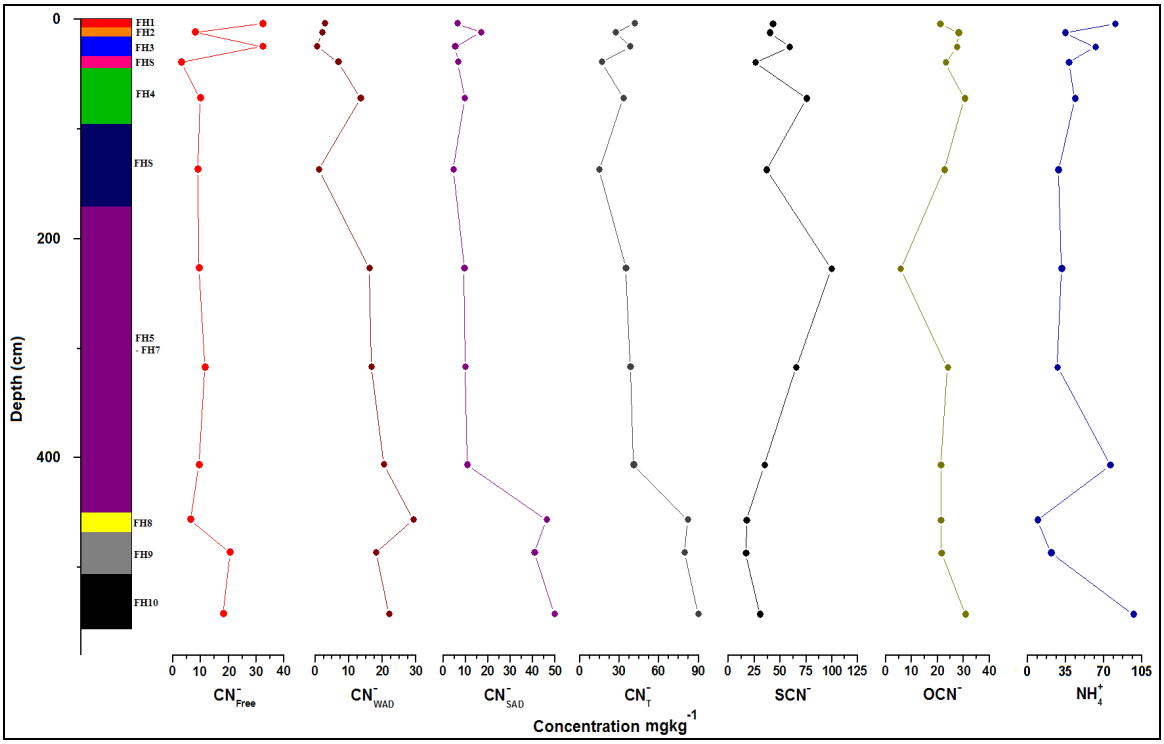
High values of CN_{SAD} were obtained in the stratum FA4 –FA8, FH8 –FH10 and FP –Br.



Profile FA



Profile FE



Profile FH

Figure 6.19 Results of cyanide species and secondary compounds in profiles FA, FE and FH

Secondary products

The results for SCN^-, CNO^- and NH_4^+ given in Figure 6.19, shows a similar trend in profiles FA, FE and FH. The concentrations of thiocyanate were by far greater than those for cyanate. Very high concentrations were recorded for the strata FA2 (91.97 mg kg^{-1}), FA3 (120.1 mg kg^{-1}), FE4 (209.6 mg kg^{-1}) and FH5 (99.81 mg kg^{-1}). Thiocyanate is high in the strata FA3, FE4 and FH5, since these strata consist of carboneous clay. SCN is known to be stable at low potential redox. Ammonium is formed by hydrolysis of cyanate (Reaction 2.4). High concentrations of ammonium (> 100 mg kg^{-1}) were obtained for the layers FA10, FE9, FE10 and FH10. These layers recorded high content of organic matter. The concentration values of CNO^- range from 20 mg kg^{-1} to 30 mg kg^{-1}, except for the layers FE5 and FH5 with concentrations of 3 mg kg^{-1} and 6 mg kg^{-1} respectively.

A high concentration of 45.76 mg kg^{-1} was recorded for the layer FE10. This could be due to high organic carbon content (20.24%) in that layer which could be adsorbing CNO^-.

Metal cyanide complexes

The results obtained for metal-cyanide complexes are given in Table 6.15. CN_{free} reacts with transition metals to form metal-cyanide complexes. The formations of these complexes depend on the formation constants.

The general trend shows higher concentration of metal-cyanide complexes in profile FH. Also during the sediment deposition, coarser sediments are deposited first due to gravity and then the finer sediments and organic matter remain suspended in the water and are deposited later in the inner parts of the dam. The profile FH might content fine particles and organic matter which can hold on metal complexes.

Elevated concentration of $Cu(CN)_4^{3-}$ was obtained in the strata FH4– FH10, the concentration range from 10.55 mg kg^{-1} to 20.85 mg kg^{-1}. The $Cu(CN)_4^{3-}$ concentration was low in the profiles FA and FE except for the strata FA5 –FA7. The stratum consisted of dark-grey carbonaceous clay. Both organic and clay particles can hold on to metal-cyanide complexes. Similar trend was observed for $Ni(CN)_4^{2-}$. This could explain the low concentration of CN_{WAD} observed in these profiles. At the pH of most of the sediment (3.78 – 6.3 for FA; 2.6 – 7.6 for FE and 2.4 – 7.4 for FH), the weak complexes dissociate to release CN_{free} and the metals.

Weak metal-cyanide can adsorb on sediment component such as iron, aluminium, silicon and manganese oxides, and, clays, which in most systems will inhibit their aqueous transport. However, complexation of metals by cyanide can also serve to hold them in solution, inhibiting their adsorption and retention. The enhancement or inhibition of adsorption depends on the metal-cyanide species, the adsorbent, and the solutions conditions. Ni $(CN)_4^{2-}$,which dominates nickel speciation in sediment and soil systems, has no affinity for the SiO_2(s) surface.

Table 6.15 Results of metal-cyanide complexes in profiles FA, FE & FH

Sample	$Cu(CN)_3^{2-}$	$Ni(CN)_4^{2-}$	$Co(CN)_6^{4-}$	$Fe(CN)_6^{4-}$	$Fe(CN)_6^{3-}$
	$mgkg^{-1}$	$mgkg^{-1}$	$mgkg^{-1}$	$mgkg^{-1}$	$mgkg^{-1}$
FA1	1.502	1.428	1.104	2.008	3.352
FA2	1.004	0.945	0.702	0.802	1.002
FA3	1.021	0.907	1.254	2.121	4.503
FA4	3.142	2.98	2.102	8.552	9.014
FA5	5.203	2.104	6.255	22.31	10.22
FA6	5.122	3.251	2.224	12.181	5.042
FA7	5.412	4.524	3.122	11.58	4.114
FA8	3.251	2.124	3.224	10.05	8.227
FA9	0.957	1.203	0.998	4.201	1.852
FA10	1.204	0.805	1.101	5.503	2.502
FE1	1.448	1.209	1.245	2.101	3.5
FE2	1.335	1.121	0.995	1.858	2.571
FE3	1.022	0.899	0.752	1.001	0.852
FE4	0.82	0.732	0.705	1.011	0.703
FE5	0.805	0.721	1.104	2.1	4.205
FE6	1.145	1.028	2.104	11.54	6.142
FE7	0.75	0.681	0.889	3.223	0.959
FE8	1.121	1.009	1.102	4.502	1.018
FE9	1.022	0.875	1.213	10.014	4.221
FE10	1.182	1.312	1.001	4.315	1.201
FH1	1.195	1.091	0.101	2.185	4.512
FH2	1.12	0.989	2.721	6.202	10.952
FH3	0.812	0.755	1.001	3.415	2.202
FH4	10.55	8.432	2.201	3.122	7.021
FH5	11.88	8.95	2.19	6.887	3.112
FH6	11	10.02	1.985	6.554	3.028
FH7	14.75	12.28	2.011	6.699	3.152
FH8	20.85	15.99	16.55	23.83	20.71
FH9	13.44	12.12	14.04	25.55	15.42
FH10	12.82	13.04	15.72	30.72	16.85

$SiO_2(s)$ surface is negatively charged at pH > 2, so electrostatic repulsion of negative Ni $(CN)_4^{2-}$ species is in part responsible for the absence of surface binding. Adsorption of nickel is enhanced at lower pH values, and inhibited at higher pH values. The goethite surface is positively charged up to about pH, or even higher, so electrostatic attraction of

$Ni(CN)_4^{2-}$ explains in part its adsorption at lower pH values. Electrostatic attraction alone is not sufficient to explain the extent of removal observed, however.

Copper and Zinc-cyanide species have no affinity for the goethite surface at the neutral to alkaline pH values. At lower pH values, adsorption of Zn, Cu was unaffected by the free cyanide, above pH 6.5 to 7, adsorption of metals was inhibited by the presence of the cyanide. At the higher pH values, metal-cyanide complexes dominate the speciation of the metals.

High concentrations of $Co(CN)_6^{4-}$ were obtained in the stratum FH8 – FH10. These strata consisted of coarse fluvial sand for FH8, dark carboneous clay for FH9 and dark peat with decaying organic matter for FH10. $Co(CN)_6^{4-}$ is a strong complex, then the dissociation in dark is very low and besides, this complex adsorbs strongly on sediment with organic matter.

High concentrations of Fe are present and it is most likely that they are the most abundant, with Fe (II) cyanide being dominant in most of the layers. This could be due to the reducing conditions in the wetland sediments. Fe-cyanide complexes are very stable, but can be dissociated at very low pH and by photolysis.

The concentration of iron-cyanide complexes is higher in the stratum FH8 – FH10 due to the composition of the layers. In general, soils with iron, manganese and aluminium oxides, clay minerals and organic matter provide anion exchange sites (Dzombak et al., 2006). Fe-cyanide complexes are anionic, and then can be absorbed on soils with high anion capacity exchange.

The pH also affects the extent of adsorption of metal-cyanide complexes. For instance, soil type clay with low pH (< 5) increases adsorption of Fe-cyanide complexes.

In the profile FA, is high in the strata FA4 – FA8. These strata consist of carboneous clay and fluvial sand for FA8.

In the profile FE, elevated concentration of $Fe(CN)_6^{2-}$ is obtained for the layers FE6 & FE9. As seen, the concentrations of $Fe(CN)_6^{3-}$ were lower than those for $Fe(CN)_6^{4-}$. These concentrations are significant in FA4, FA5, FA8 and FH2. These layers have either carboneous clay content or clay with efflorescence.

The change in the redox potential could be the reason of high concentration of $Fe(CN)_6^{3-}$. Ferrocyanide adsorb to a somewhat greater extent than ferricyanide on goethite. Sulphate and adsorbing anion competes for adsorption sites on oxides, and the adsorption of the iron-cyanide complexes. At the pH range 3.5 to 8, iron-cyanide complex adsorption was strongly dependent on sulfate concentration and vice versa. Iron-cyanide complex adsorption decreased by the presence of the sulphate, especially at lower pH values.

Sulphates were not analyzed in these samples but from the sulfur results, we can deduct the concentration of sulphates. An average of 1.69 % of sulphur was obtained. High concentration of sulphur was observed in FA10 & FE 10. This could be another reason of low adsorption of iron-cyanide complexes in these layers. Besides, the sulphur was low in FH 8 -10 and high adsorption of these complexes was observed in these strata.

Soil organic matter can have an important role in enhancing the adsorption of both iron-cyanide complexes, possibly by reaction between the iron-cyanide nitrogen and reactive functional groups of surface organic matter.

From the results obtained, it can be observed that the extent of adsorption of metal-cyanide complexes depends strongly on the particular metal cyanide species, mineral adsorbent and solution conditions. pH is an especially important governing parameter. The metal cyanide complexes may interact with the surface to a greater or lesser extent than the metals alone. An interrelated, complex group of factors governs metal cyanide species adsorption and it is difficult to form generalizations.

FES, FHS and FHS' represent channel sands and the results obtained cyanide species, secondary compounds and metal-cyanide complexes are given in Table 6.16.

Low values for CN_{free}, CN_{WAD} and CN_{SAD} were recorded for FAS, FES, FHS and FHS' compared to those obtained for other layers. These layers represent channel sands with very low pH owing to their high leachibility and low CEC. The low value could be due to the weak adsorption of cyanide species on sand.

The strata FAS, FES and FHS present low concentration of cyanide species (12mg kg-1 CN_T). These layers have low concentration, FES have very low pH (2.6) and high Eh (740mV). FES, FHS and FHS' represent channel sands and therefore are expected to

show very low pH owing to their high leachability and low CEC (3.652 cmol.kg^{-1} for FAS, 5.615 cmol.kg^{-1} for FES, 3.101 cmol.kg^{-1} for FHS and 3.102 cmol.kg^{-1} for FHS').
FP-Br is the main channel stream between the different profiles FA, FE, FH. This channel has the highest concentration of CN_T 102 mg kg^{-1} and from which 90 mg kg^{-1} are CN_{SAD}.

Conclusion

The main source of pollution would be from the surrounding tailings dams, from where the tailings have been eroded, transported by streams, especially the Klipspruit and deposited into the Fleurhof dam.
The fleurhof dam is a case where the materials are washed from the tailings dams to the wetlands sediments through the stream sediment.
The results obtained showed an increase of metal concentrations in the sediments. The enrichment of metals in the sediments could be the effect of organic matter which might complex and precipitate the metals.
The fate of cyanide species was also studied and the findings revealed higher concentration of cyanide species, include, CN_{Free}, CN_{WAD}, CN_{SAD}, metal-cyanide complexes in the stream sediment. The presence of organic matter tends to sorb the metal-cyanide complexes onto the sediment, mainly the iron-cyanide complexes. Sorption is attributed to interactions of iron-cyanide and reactive functional groups of soil organic matter. Low concentration of cyanide species was obtained in wetland sediment contrary to what we were expecting. We expected higher concentration of cyanide species and complexes due to the enrichment in the wetland sediment but the finding revealed higher concentration in the stream sediment. Natural attenuation, includes, biodegradation, photo dissociation, precipitation and chemical conversion of cyanide species and complexes could have happened in the wetland sediment.

Table 6. 16 Results of cyanide species, secondary compounds and metal-cyanide complexes obtained for FAS, FES, FHS and FP-Br

Sample	CN_{free}	CN_{WAD}	CN_{SAD}	CN_T	SCN^-	CNO^-	NH_4^+	$Cu(CN)_3^{2-}$	$Ni(CN)_4^{2-}$	$Co(CN)_6^{4-}$	$Fe(CN)_6^{4-}$	$Fe(CN)_6^{3-}$
	$mgkg^{-1}$	$mgkg^{-1}$	$mgkg^{-1}$	$mgkg^{-1}$	$mgkg^{-1}$	$mgkg^{-1}$	$mgkg^{-1}$	$mgkg^{-1}$	$mgkg^{-1}$	$mgkg^{-1}$	$mgkg^{-1}$	$mgkg^{-1}$
FAS	7.725	2.715	1.61	12.05	28.32	22.55	19.63	1.03	1.1	0.71	0.881	1.012
FES	4.855	0.796	6.508	12.16	29.2	22.64	4.125	1.112	0.92	0.988	1.203	5.502
FHS	3.098	6.952	6.8	16.85	26.36	23.43	37.54	3.5	4.135	0.201	2.991	5.308
FHS'	9.157	1.203	4.74	15.1	37.49	22.9	27.95	0.898	1.005	0.882	1.602	3.505
FP-Br	3.361	8.879	90.56	102.8	12.13	19.22	26.02	4.95	5.222	25.55	50.82	40.24

6.3 Natural stream

Site description

Streams form an important component of the drainage system in the study area. They drain through industrial areas, residential areas, old mine workings as well as areas of active mining, largely tailings reprocessing sites. They also receive recharge from groundwater as well as surface run-off. Most streams in the study area are perennial.

The Natalspruit headwaters lie in an area in which tailings dumps around, but one small tributary aisle to the north of the mining belt. The stream is perennial over all of the reaches sampled, and also susceptible to severe flash flooding during summer thunderstorms. During the dry season, discharge in the stream is sustainable by ground water emerging through the bed of the stream, and by seepage through the banks.

In this section, cyanide speciation and fate was studied in relation to the Natalspruit, a tributary of the Klip River. The part of the stream studied was adjacent to a tailings reprocessing facility (Figure 6.20).



Figure 6.20 The Natalspruit with tailings reprocessing activities on the background. On the foreground are salt crusts along the capillary fringe.

Sampling

Sampling was carried out along the Natalspruit, downstream of the mining area. Both surface water and groundwater samples were collected according to standard protocols mentioned in Chapter 3. Groundwater samples were collected from drill cores on the stream bank. Seepage water was collected at the site where it had formed shallow puddles on the bank, which were sufficiently deep to collect samples.

At the time of sampling, efflorescent crusts were observed along the capillary fringe on the stream bank (Figure 1.7c). A study by Naicker et al. (2003) in the same area identified such crusts as containing gypsum ($CuSO_4.2H_2O$). Water samples were collected from streams in August 2007. Figure 6.21 is a map showing the study site and sampling points. The surface water samples (labelled as S) were taken from the middle of the stream; seepage water was sampled at the site where it had formed shallow puddles on the bank, which were sufficiently deep to collect samples. Ground water samples (labelled as GW) were collected using an auger holes. Crusts salts were collected from the bank of the stream.

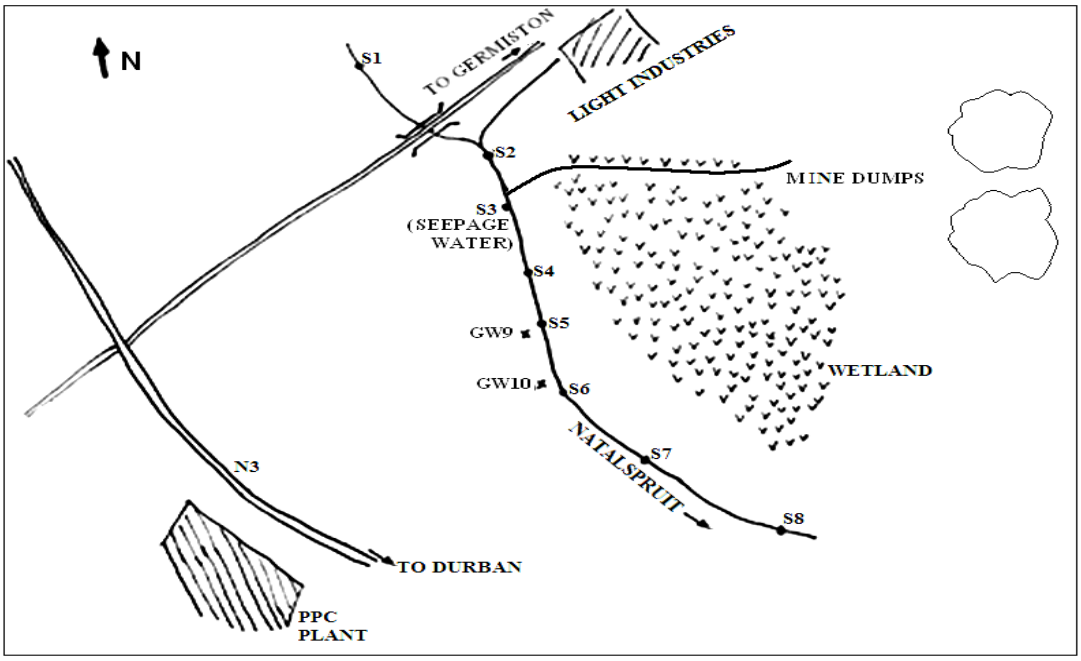


Figure 6.21 Map showing the sampling points along the Natalspruit

Results and discussion

The physical - chemical characteristics, anions and cations concentration of surface and groundwater from the Natalspruit are shown in Table 6.17.

The results pointed to a variation of chemistry of surface and groundwater. Samples collected upstream and the seepage areas have neutral pH, relatively low conductivities and low redox potential.

Samples collected downstream have low pH, relatively high conductivities and high redox potential. These samples generally have elevated sulphate, iron and trace metal concentrations. The ground water has much higher dissolved solid concentration, conductivities and lower pH relative to surface water.

Groundwater is known to preserve its composition (Naicker, 2003). The groundwater recharching the Natalspruit at this point is likely to be originating from the adjacent tailings dumps that are undergoing reprocessing. In this instance, the stream acts as a mixing zone with all the above-mentioned water types accounting for the observed chemical variability.

From the trends, it is evident that the water samples cluster into three groups; Group 1 (S1 – S4) surface water collected upstream of the mining area and the seepage area, Group 2 (S5 –S8) surface water collected downstream with low pH (4.26 -4.48) and Group 3 (GW9 & GW10) groundwater with pH 3.55 - 3.56.

The white surface crust, which develops along the banks of the stream during winter, was identified in previous studies (Naicker, 2003; Tutu, 2005) as mainly consisting of gypsum ($CaSO_4.2H_2O$). The analysis of the crusts indicated relatively high concentrations (2000-5000 ppm) of several metals including Co, Ni and Zn (Naicker et al., 2003).

Crusts were not analysed in this study, otherwise the results would be identical to those for crusts from Brakpan tailing facility. The crusts are formed from the capillary evaporation of groundwater. The groundwater has low pH and is laden with pollutants. These pollutants would typically be deposited in the crusts.

Table 6.17 Physical-chemical characteristics, anion and cation concentrations of water sample from the Natalspruit

sample	Description	Temp.	pH	ORP	Cond	$S_2O_3^{2-}$	SO_4^{2-}	Cl^-	Na	K	Ca	Fe	Co	Zn	Ni	Cu
		°C		mV	$mScm^{-1}$	mgl^{-1}	mgl^{-1}	mgl^{-1}	mgl^{-1}	mgl^{-1}	mgl^{-1}	mgl^{-1}	mgl^{-1}	mgl^{-1}	mgl^{-1}	mgl^{-1}
S1	surface water	12.1	6.8	324	0.425	360.4	3308	nd	3.769	2.033	30.61	0.568	0.131	0.128	0.125	0.011
S2	surface water	15.5	6.38	285	0.492	330.1	1803	nd	4.179	2.231	31.67	5.498	0.554	0.423	0.448	0.018
S3	seepage water	11.8	6.72	268	0.515	85.02	2475	nd	4.240	5.933	30.38	6.952	0.305	0.486	0.333	n.d
S4	surface water	17.9	6.25	270	0.385	320.1	2066	nd	2.300	1.500	22.50	4.500	0.288	0.169	0.192	n.d
S5	surface water	15.6	4.48	506	0.891	370.2	5601	nd	4.946	4.625	42.20	14.53	3.173	1.959	2.459	0.166
S6	surface water	16.2	4.44	514	0.929	320.0	4695	nd	5.040	3.560	43.48	13.72	3.284	2.167	2.636	0.214
S7	surface water	14.9	4.46	508	0.800	320.5	4530	67	4.768	4.162	39.69	7.146	2.501	1.667	1.987	0.151
S8	surface water	16.4	4.26	538	0.814	315.3	3945	nd	4.662	2.957	39.21	6.910	2.558	1.704	2.048	0.154
GW9	Ground water	11.1	3.55	484	4.860	330.1	7751	20	13.85	5.144	172.9	125.6	25.68	18.644	21.98	4.151
GW10	Ground water	11.6	3.56	470	4.610	340.0	7751	22	11.26	4.474	171.4	156.7	22.86	16.784	19.34	3.047

n.d – not detected

Seepage water (S3) in the study area is characterised by near - neutral pH, high sulphates as well as metals concentrations and low thiosulphate. This could possibly be indicative of ingress of a mixed type groundwater. It's likely that at that point, the polluted groundwater plume could be diluted by unpolluted groundwater and exuding as the lesser polluted water to compare with the groundwater samples GW9 and GW10.

Upstream of the mining area, the surface water (S1& S2) was near – neutral pH with low metals concentration and relatively low conductivity. This was expected as there are no tailings facilities and reprocessing activities upstream that are likely to contribute to pollution.

Adjacent to the mining area, the pH of water falls to 4. Heavy metals and sulphate concentrations rise due to the ingress of acidic ground water.

The metal concentration increases towards downstream (except for S4) because of the tributary from the mine dump which drains to the same mixing point at S2. This observation is consistent with the increase of the conductivity. Conductivity increases with an increase in metal concentration and this is because the less metal salts that are dissolved in the water, the lower the conductivity. Sample S4, with low conductivity, has low metal concentration. It can be seen that the conductivity increases towards downstream.

The ICP-OES showed results of high Fe concentration compared to Co, Zn, Ni and Cu.

Samples from groundwater contain high concentration of metals; this could be due to deposition and precipitation. The average concentrations were calculated for metals in surface water (exclude S1 & S2 because they are upstream) and in groundwater. Decreases in concentration of 94% for Fe; 92% for Co, Zn as well as Ni and 97% for Cu were observed from groundwater to surface water. The concentration of thiosulphate was very low at the seepage point (85 mg l^{-1}) where as the average concentration for surface and groundwater ranges between 315 mg l^{-1} – 370 mg l^{-1}. On the other hand, there is a discrepancy in sulphate concentration between surface and groundwater, the latter has higher sulphate concentration. The ground water samples displayed low pH, high conductivity, elevated sulphate, iron and trace metal concentrations, this is the evidence

of pollution by acid mine drainage. Along the stream, sample S5 yields high concentration of thiosulphate as well as sulphates. This could be due to low pH and high potential redox. A similar trend is observed for samples S6 – S8.

Cyanide species and secondary compounds

The results for cyanide species and secondary compounds are given in table 6.18.

Table 6.18 Cyanides species and related compounds in the Natalspruit samples

Sample	CN_{free}	CN_{WAD}	CN_{SAD}	CN_T	SCN^-	CNO^-	NH_4^+
	mgl^{-1}	mgl^{-1}	mgl^{-1}	mgl^{-1}	mgl^{-1}	mgl^{-1}	mgl^{-1}
S1	0.065	0.088	0.073	0.161	n.d	17.65	1.173
S2	0.122	0.105	0.123	0.228	n.d	18.17	3.851
S3	0.304	0.325	0.329	0.654	n.d	17.38	9.627
S4	0.082	0.102	0.09	0.192	n.d	15.81	2.277
S5	0.023	0.12	0.065	0.185	n.d	16.86	1.629
S6	0.135	0.205	0.147	0.352	n.d	17.38	5.554
S7	0.011	0.099	0.022	0.121	n.d	18.43	8.707
S8	0.015	0.102	0.053	0.155	n.d	18.44	5.689
GW9	0.078	0.252	0.3	0.552	1.837	23.69	22.98
GW10	0.264	0.385	0.296	0.681	2.294	19.75	31.89

The trend shows low concentration of free cyanide (ranging from 0.065 mg l^{-1} to 0.122 mg l^{-1}) in surface and groundwater. This could be attributed to degradation and volatilisation of CN_{free}. At the pH of surface and groundwater (< 7), most of CN^- exists as $HCN_{(g)}$ hence volatile (Figure 2.2). Adsorption on colloids could be one of the reasons of low CN_{free}, as this can be seen further.

The concentration of CN_{free} is lower in samples S5 –S8, they were collected downstream and displayed low pH (4.26 – 4.48) due to the in flow from the tributary. The low concentration could be due to the volatilization with the acidic pH.

GW10 showed a higher concentration of free cyanide compared to GW9. This could be explained by the presence of soluble cyanide which could be coming from the dissociation of metal-cyanide complexes due to low pH.

In ground water, cyanides exist mainly as complexes which can dissociate under weakly or strongly acidic conditions to yield CN_{free} as explained previously. High concentration of CN_{free}, CN_{WAD} and CN_{SAD} were found at the seepage point. This could be likely in put from the tributary which drains water from the mine dumps to some mixing point after S2. On the other hand, S3 is a mixture of surface, groundwater as well as the contaminated water from the mine dumps. At this point, the concentration of CN_{WAD} is similar to CN_{SAD}.

As shown in Table 6.18, CN_T concentration at the seepage point, is similar to that obtained in ground water. CN_{WAD} & CN_{SAD} were higher in groundwater samples, implying higher CN_T content. The CN_T results are consistent with results obtained for CN_{free}, except for GW9 with low CN_{free} but high CN_T due to dissociation of complexes (WAD and SAD) at low pH.

No thiocyanate was found in surface water as expected because of the presence of thiosulphate ($S_2O_3^{2-}$). In the presence of thiosulphate, CN_{free} can be converted in SCN^- as explained in chapter 2. SCN^- in these samples could likely be diluted since thiocyanate is highly soluble in water and can leach deep into the groundwater.

A small amount of thiocyanate was found in ground water. This is likely due to SCN^- leaching from dumps as complexes with metals. Also, chemical decomposition in groundwater has very slow kinetics (Dzombak, 2006).

The concentration of cyanate was similar in the surface and groundwater samples. GW9 has higher concentration of cyanate compare to GW10. This could be seen with the low concentration of CN_{free}. Assumption could be that CN_{free} was oxidised since potential redox in GW9 is higher than GW10.

The concentration of ammonium was high at the seepage point compare to the other surface water samples. This could likely be the in put from the groundwater. Groundwater samples have higher content of ammonium (an average of 27.43 mg l^{-1}) compares surface water (with an average of 5.58 mg l^{-1}).

Metal-cyanide complexes

The results for metal-cyanide complexes are given in Table 6.19 below.

The general trend for the metal-cyanide complexes shows higher concentration of copper-cyanide and iron-cyanide complexes in surface and ground water. As expected from the ICP-OES results with high concentrations of Fe, it is most likely that the iron cyanide complexes are present in relative high concentration mostly in ground water. Both iron- cyanides Fe (II) & Fe (III) are present in surface water collected downstream and in groundwater. Ferro-cyanide was analysed in all the samples but ferri-cyanide was only detected in the samples collected downstream (from S5). Fe (III)-cyanide complex was not detected in surface water collected upstream.

The ground water contains both iron-cyanide complexes with Fe(II) being predominant. Cobalt cyanide was only detected in groundwater and in S3, this could be an input from the ground water and/or from the tributary.

The study carried out by Ghosh (1999) revealed that metal-cyanide complexes typically dominate aqueous speciation of cyanide in groundwater systems, with iron-cyanide complexes often most abundant.

Table 6.19 Metal-cyanide complexes in the Natalspruit samples

Sample	$Cu(CN)_3^{2-}$	$Ni(CN)_4^{2-}$	$Fe(CN)_6^{4-}$	$Fe(CN)_6^{3-}$	$Co(CN)_6^{4-}$
	mgl^{-1}	mgl^{-1}	mgl^{-1}	mgl^{-1}	mgl^{-1}
S1	9.461	1.609	3.419	n.d	n.d
S2	3.871	1.942	10.152	n.d	n.d
S3	15.84	1.661	14.89	n.d	0.504
S4	14.66	1.755	9.848	n.d	n.d
S5	10.69	2.405	10.12	10.67	n.d
S6	9.779	2.033	12.01	9.544	n.d
S7	9.931	1.566	7.342	5.877	n.d
S8	9.089	2.405	7.541	6.655	n.d
GW9	10.92	9.305	22.14	10.25	1.132
GW10	10.55	8.519	23.85	11.05	1.205

The ferrocyanide complex usually dominates groundwater, due to reducing conditions. The redox potential also controls the dissolved iron cyanide complex speciation in groundwater. CN_{free} in the groundwater will first form a dissolved iron-cyanide complex. The iron-cyanide complexes either formed from CN_{free} or already existing in the water then react further with iron to form iron-cyanide solid. Some of the solids formed from reaction between the elemental iron and the dissolved iron-cyanide complexes include Prussian Blue precipitate, which forms at lower pH values (pH <6), the Berlin Green precipitate, which forms at neutral pH values, and the Berlin White precipitate, which also forms at neutral pH values. The formation of these various iron-cyanide precipitates is represented in the following reactions:

$$4\ Fe^{3+} + 3\ Fe(CN)_6^{4-} = Fe_4\ (Fe(CN)_6)_3\ (s)\ \text{(Prussian Blue)} \qquad \text{(Reaction 6.3)}$$

$$3\ Fe^{2+} + Fe^{3+}\ 3\ Fe(CN)_6^{3-} = Fe_4\ (Fe(CN)_6)_3\ (s)\ \text{(Prussian Blue)} \qquad \text{(Reaction 6.4)}$$

$$Fe^{3+} + Fe(CN)_6^{3-} = Fe(Fe(CN)_6\ (s)\ \text{(Berlin Green)} \qquad \text{(Reaction 6.5)}$$

$$2\ Fe^{2+} + Fe(CN)_6^{4-} = Fe_2\ (Fe(CN)_6)\ (s)\ \text{(3Berlin White)} \qquad \text{(Reaction 6.6)}$$

Of the iron-cyanide solids, Prussian Blue is the most widely known because of its vivid blue color and its application in inks and dyes preparations. Prussian Blue is a mixed oxidation state solid that requires moderately reducing conditions to form. Berlin Green forms under oxidizing conditions, and Berlin White forms under reducing conditions.

CN_{free} are the thermodynamically favorable species in solution, and degradation of iron cyanide compounds to the free cyanides can be accelerated by sunlight and microorganisms. Other types of iron-cyanide solids, including solids containing other metals, for example, copper(II)-iron-cyanide, can also be formed.

The decomposition rates of these complexes also are affected by water, temperature, pH, total dissolved solids, and complex concentration. Some metal-cyanide complexes

degrade more rapidly when exposed to sunlight, atmospheric carbon dioxide, and air. Finally, site-specific geochemical information, like pH and pE, were used as the key variables to develop semi quantitative predictions of cyanide concentrations in groundwater within or near source materials.

Cu – cyanide complex was relatively high at the seepage point and in water samples collected downstream. This could be due to the contamination by the water from the dumps. The concentration at the seepage was even higher than the one in the groundwater. The concentration of S2 was the lowest. At the pH < 5, Cu and Ni-cyanide complexes are dissociated to yield CN_{free}, we couldn't expect high concentration in S5 – S8 with low pH but the opposite was observed.

The model constructed using MEDUSA software shows the same observation (Figure 6.22). The model predicted the existence of copper cyanide complex at low pH (< 6).

Ni-cyanide complex was lower than Cu – cyanide. The concentration was higher in the samples S5 and S6.

Cyanide adsorption

Free cyanide was analysed in an unfiltered and filtered portion. Results in table 6.20 show that as far as 60 % of cyanide can be retained by the filter membrane. The removal of colloids leads to a decrease in CN_{free} concentration because filtering the sample removes the colloids and subsequently the free cyanide associated with these colloids. The difference between the unfiltered and filtered samples should give an indication of the free cyanide present in the colloids.

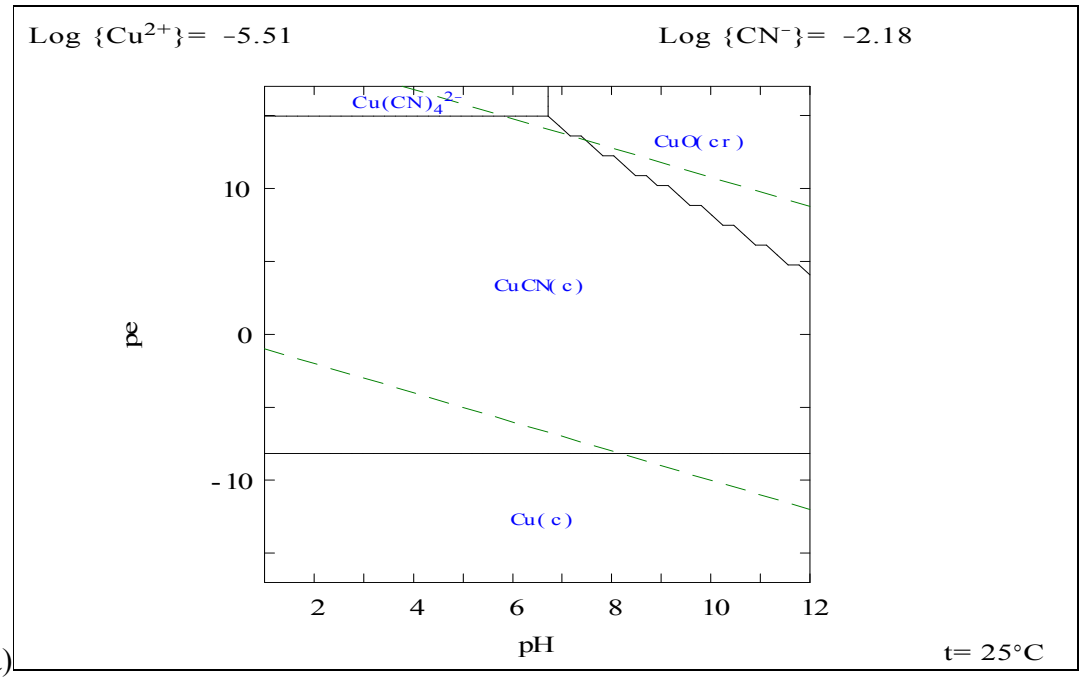
Table 6.20 Concentrations of CN_{free} in filtered and unfiltered water samples from Natalspruit

Sample	Non filtered	Filtered	particulate adsorbed	% adsorbed
	mg l^{-1}	mg l^{-1}	mg l^{-1}	
S1	0.122	0.065	0.057	46.72
S2	0.155	0.122	0.033	21.29
S3	0.344	0.304	0.04	11.63
S4	0.102	0.082	0.02	19.61
S5	0.052	0.023	0.029	55.77
S6	0.251	0.115	0.136	54.18
S7	0.088	0.011	0.077	87.75
S8	0.045	0.015	0.03	66.67
GW9	0.212	0.078	0.134	63.21
GW10	0.322	0.264	0.058	18.01

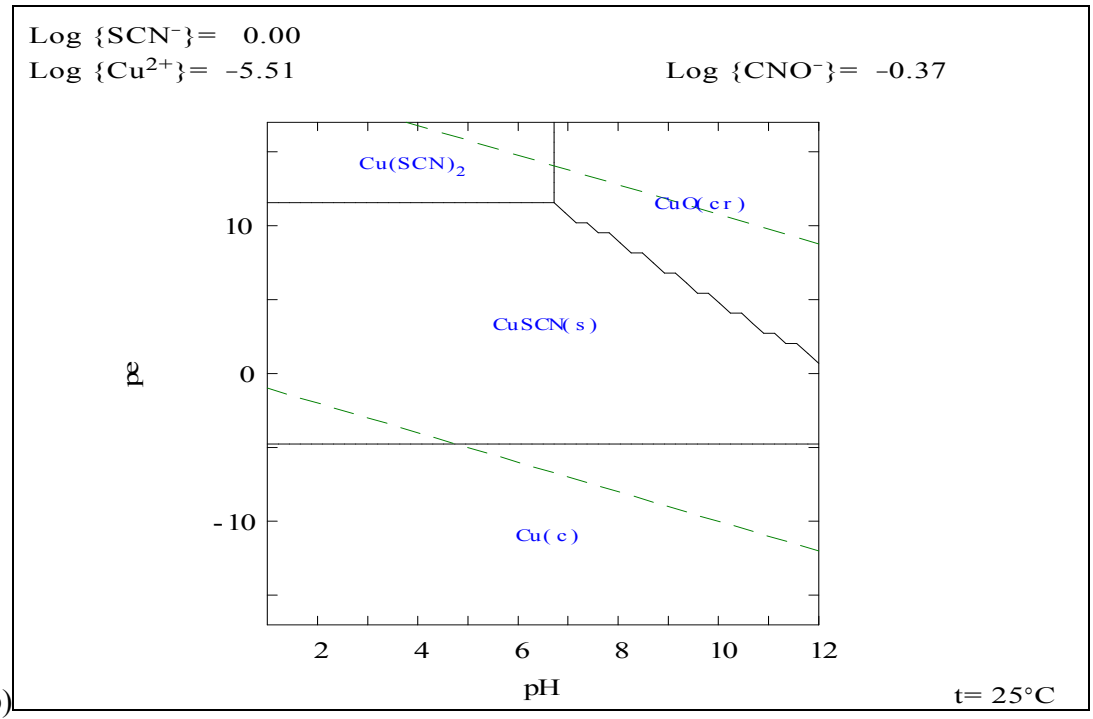
Geochemical speciation modelling

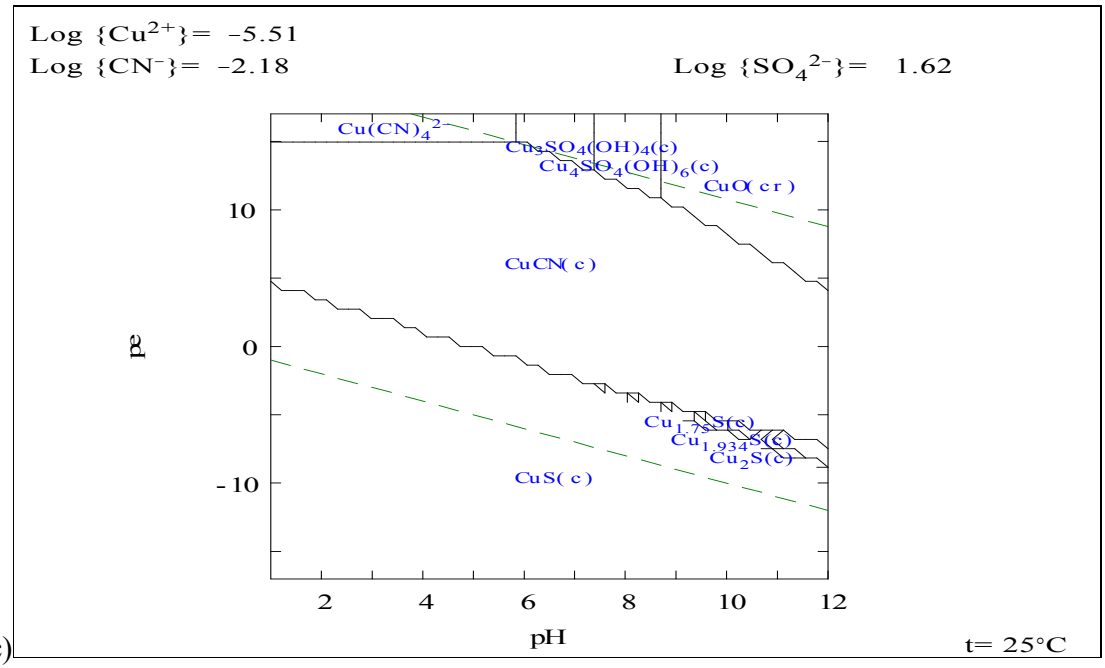
Computer modelling was done using the results of CN_{tot}; metal concentrations; SO_4^{2-}; SCN^- and fields measurements. The accuracy of the modelling results is dependent on the quality of the experimental results. As mentioned previously, the model predicts the formation of $Cu(CN)_4^{2-}$ at low pH (< 6) and in oxic condition, high pE. The introduction of major anion like SO_4^{2-} does not affect the formation of the copper cyanide complex as seen in Figure 6.21. At alkaline pH, there is formation of $CuSO_4(OH)_4$. In reducing condition, CuS forms. CuCN(c) exists at the all range of the pH. In the presence of thiocyanate, $Cu(CN)_4^{2-}$ is replaced by $Cu(SCN)_2$ complex.

a)


Log {Cu2+}= -5.51
Log {CN-}= -2.18
Cu(CN)4 2-
CuO(cr)
CuCN(c)
Cu(c)
10
0
-10
pe
2
4
6
8
10
12
pH
t= 25°C

b)


Log {SCN-}= 0.00
Log {Cu2+}= -5.51
Log {CNO-}= -0.37
Cu(SCN)2
CuO(cr)
CuSCN(s)
Cu(c)
10
0
-10
pe
2
4
6
8
10
12
pH
t= 25°C



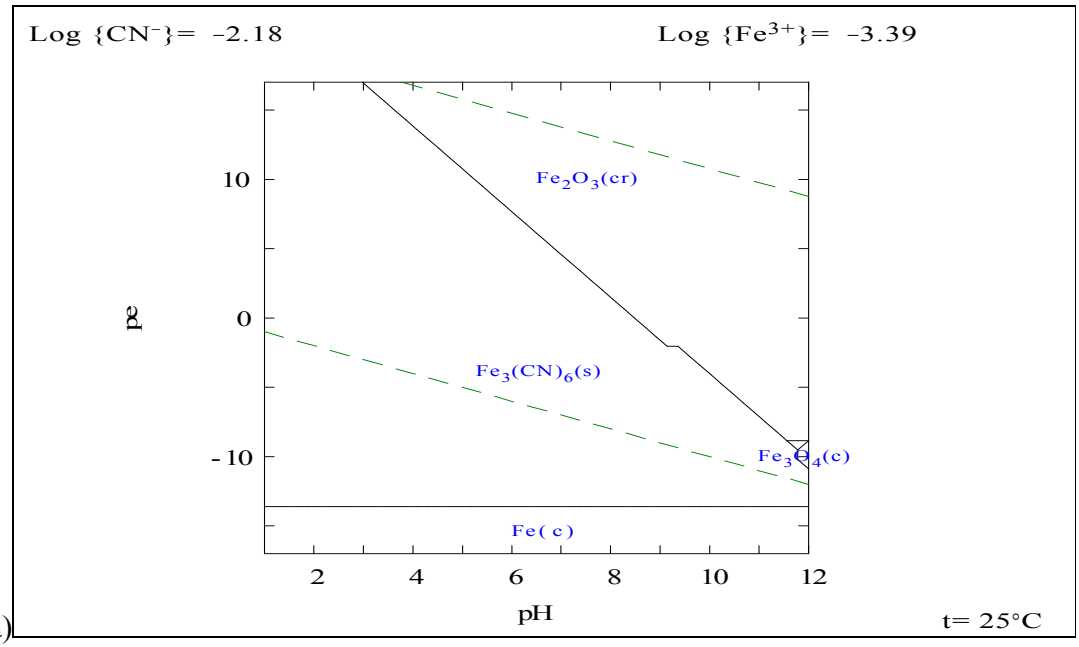
c)

Figure 6.22 Predominance diagram of Cu(I) in presence of (a) CN_T (B) SCN^- (C) SO_4^{2-}

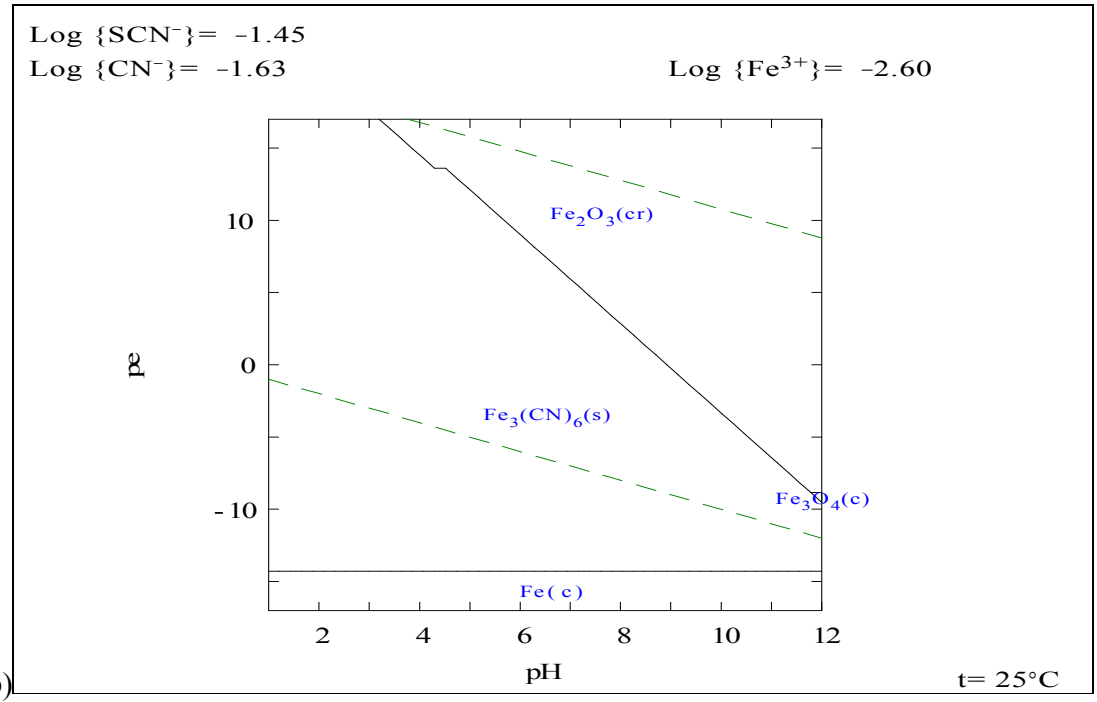
In Figure 6.23, the model predicts the formation of $Fe_3(CN)_{6(s)}$ at low pH (< 3), in anoxic and oxic conditions. As the pH increases, Fe_2O_3 forms and at very high pH (12) Fe_3O_4(s) forms at oxic and anoxic conditions. $Fe_{(c)}$ exists at very low pE.

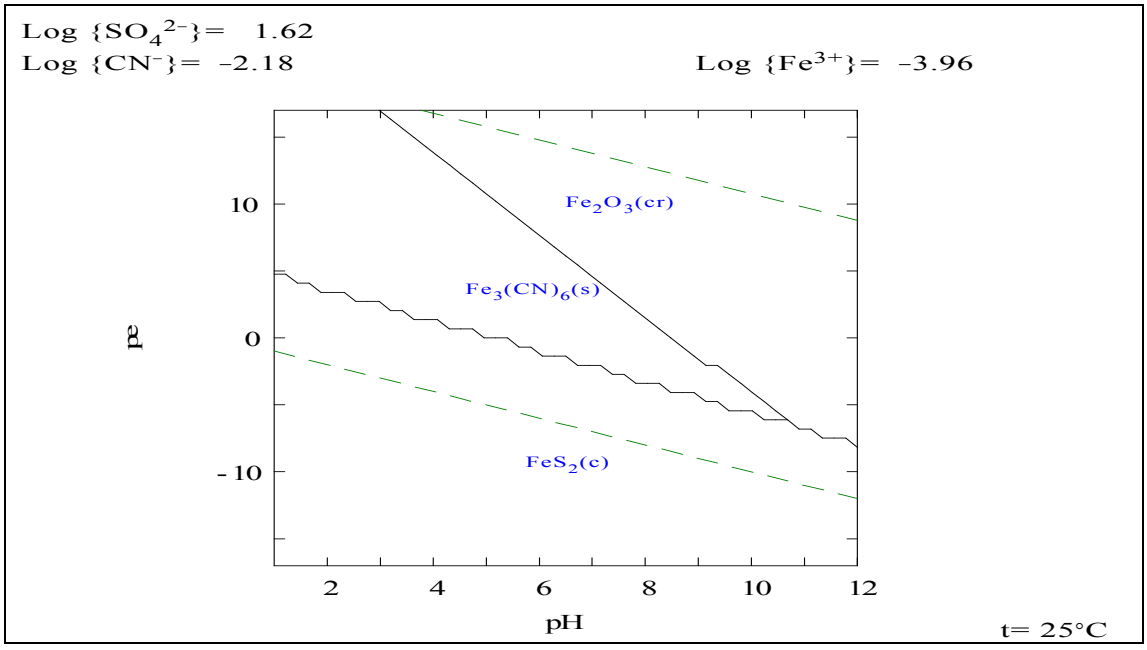
The introduction of major anions like SCN^- and SO_4^{2-} does not modify the equilibruim. When the sulphate is present, FeS_2 exists at reducing condition.

a)


Log {CN⁻}= -2.18
Log {Fe3+}= -3.39
Fe2O3(cr)
Fe3(CN)6(s)
Fe3O4(c)
Fe(c)
pe
10
0
-10
2
4
6
8
10
12
pH
t= 25°C

b)


Log {SCN⁻}= -1.45
Log {CN⁻}= -1.63
Log {Fe3+}= -2.60
Fe2O3(cr)
Fe3(CN)6(s)
Fe3O4(c)
Fe(c)
pe
10
0
-10
2
4
6
8
10
12
pH
t= 25°C



c)

Figure 6.23 Predominance diagram of Fe(III) in presence of (a) CN_T (B) SCN^- (C) SO_4^{2-}

Conclusion

The Natalspruit is contaminated by pollutants released from the mining activities. The groundwater is acidic with quite high concentration of cyanide total. It contains high concentration of sulphate as well as trace metals. In fact, the ground water within the mining area is heavily contaminated and acidified as a result of oxidation of pyrite (FeS_2) contained within mine tailings dumps, and has elevated concentrations of heavy metals (Fe, Co, Zn and Ni), cyanide total as well as metal-cyanide complexes. The latter dissociate under variable conditions to yield CN_{free}.

The polluted ground water discharges into the stream causing the decrease of the pH of the stream water (downstream). The contamination of water is enhanced downstream as seen with very low pH, high concentration of metals as well as metal cyanide complexes. Acidified water seeping from the mine tailing was found to contribute to stream flow by reducing the pH, increasing metal load and metal complexes. It should be noted here that

the dissolution of salt crusts on the surface can also contribute to pollution in water bodies. This leads to lowering of the pH, increase in solute loads and the subsequent release of pollutants in soluble phases.

Fe is present in high concentration in ground water, this would most probably mean that $Fe(CN)_4^{2-}$ and $Fe(CN)_6^{3-}$ are the most abundant. Fe-cyanide complexes are common in mine waste because these two complexes are very stable, but can be dissociated at very low pH and by photolysis.

The decomposition rates of metal cyanide complexes, mainly $Fe(CN)_6^{4-}$ and $Fe(CN)_6^{3-}$ are low in ground water. These complexes degrade rapidly when exposed to sunlight, atmospheric carbon dioxide and air. The decomposition is also affected by water temperature, pH and total dissolved solids. The breakdown of metal complexes releases CN_{free} resulting in sustained pollution form the groundwater to the surface water.

The concentration of cyanide in the stream can be affected by factors like: cyanide microbial degradation, adsorption, precipitation, photolysis and volatilization. Chemical conversion of CN_{free} to cyanates (OCN^-) and thiocyanates (SCN^-) also occurs.

The Natalspruit is tributary of Klipriver which flows into the Vaal Dam, where the drinking water is obtained and this water source can be affected by these small streams.

Fairly high concentration of cyanide was obtained in the Natalspruit. The law states that the allowed cyanide concentration (i.e. CN_{free}) in drinking water should be about 50 ppb, but the results obtained were far greater than the allowable value.

CONCLUSION

The fate and transport of cyanide species was studied in a representative tailings dam underdoing rehabilitation, an active slime dam, a wetland sediment and a natural stream within a mining area.

In this study, cyanide was characterised as free (CN_{free}), weak acid dissociable (CN_{WAD}) and strong acid dissociable (CN_{SAD}).

In the case of the tailings dump underdoing rehabilitation, deposition of waste slurry has been discontinued and the dump is being prepared for phytoremediation. As such, the dump presents a suitable case in studying the chemical evolution of cyanide and its complexes over a period of time.

Cyanide and its metal complexes were found to be instable following generation of AMD in the dump over a period of one year, resulting in the formation of secondary products (thiocyanates and cyanates). The tailings were predominantly contaminated by moderate to strong cyanide complexes, which are weakly dissociable. The stability of cyanide complexes such as CN_{WAD} and CN_{SAD} depends strongly on the extent of acid generation. On contact with acid mine drainage, the weak and strong cyanide complexes dissociate and release CN_{free}. CN_{free} evolves and form other cyano-species including thiocyanate (SCN^-) and cyanate (CNO^-).

High iron concentrations were measured in both tailings suggesting a higher proportion of strong cyanide complexes. The region of stability of iron metals cyanides is pH 4 to 8.5 which is the pH range of the tailings and the iron cyanide complexes have the highest stability constant (log K = 52).

Dissociation of iron-cyanide complexes in the dark is very slow and depends on the stability constants, pH, temperature, and redox potential.

Water from the active slime dam (Nasrec) as well as the solid materials collected in the surrounding of the dam contains high concentration of cyanide. This is a source of pollution for the surrounding environment and the groundwater.

High concentrations of cyanide were found in the sediments of the Fleurhof Dam wetland. The materials eroded from the surrounding tailings dumps were transported by the stream, the Klipspruit and deposited into the Fleurhof Dam. The study shows that the Fleurhof Dam sediments contain high concentration of cyanide with some cases recording more than 50 $mgkg^{-1}$ of free cyanide. This could suggest that cyanides are transported to sediments causing enrichment. The presence of organic matter provides complexing ligands which tend to bind strongly with cyanide.

Cyanide was found to be less in the Fleurhof Dam wetland than in the stream sediment. This is the consequences of physical-chemical conversion and microbial degradation of cyanide in the wetland.

Cyanide does not persist in natural stream but may persist for extended periods in ground water. At low pH, cyanide is lost by volatilization as HCN(g). In the natural stream, high concentrations of cyanide and metals were found downstream, after the seepage point, where the groundwater discharges in the stream. This is the evidence of the contamination of the ground water by the gold tailings dams nearby.

Natural degradation of cyanides in soil and tailings can be influenced by variables such as the cyanide species in solution and the relative concentration, pH, aeration, sunlight, presence of bacteria, pond size, depth, turbulence and chemical mechanisms which include volatilization, adsorption, precipitation, oxidation, and hydrolysis.

Although cyanide is ubiquitous in the environment, cyanide seldom remains biologically available in soils because it is either complexed by trace metals, metabolized by various microorganisms, or lost through volatilization. The fate of cyanide in water and soil would be pH dependent.

As a consequence, cyanide speciation will not only determine its toxicity, but also its complexes are observed in the sediment reactivity and fate as cyanide can undergo transformation and degradation in suitable environmental conditions.

Metal-cyanide complexes are generally thought to be less toxic than free cyanide but these complexes break up to yield hydrogen cyanide, which is the usual cause of toxicity.

Some metal cyanide complexes, including silver, copper and nickel cyanides, may themselves be toxic.

Medusa predicted the presence and the predominance of cyanide as HCN and metal-complexes. Iron-cyanide complex was found to be the most abundant in tailings and water even at very low pH.

Despite that many processes are available in order to treat cyanide in tailings dams (the probable source of cyanide in soil and groundwater), tailings waste in South Africa is not treated to convert cyanide to less toxic form like cyanate.

Recommendations for additional work

Further studies should be done to assess:

- The impact of the phytoremediation program on cyanide cyclisation: translocation of cyanide to plants and subsequent uptake of metals due to cyanide translocation.
- The impact on groundwater quality: requires a study of borehole water, particularly in areas where the borehole water is a source of drinking water and is also used for irrigation purposes.
- The natural attenuation of cyanide due to various mechanisms (e.g. microbial activities, oxidation, reaction with thiosulphates).
- The role of organic matter in cyanide sequestration (including identifying the most influential between fulvic and humic acids in this regard).

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APPENDIX

Appendix A Analysis results for metals in tailings dams

Table A1 Metals concentrations results obtained using ICP-OES after acid digestion in samples collected in 2006

Sample	Na	K	Mg	Ca	Al	Mn	Fe	Co	Zn	Ni	Cu	Cr	Hg	U	Pb
	$mgkg^{-1}$	$mgkg^{-1}$	$mgkg^{-1}$	$mgkg^{-1}$	$mgkg^{-1}$	$mgkg^{-1}$	$mgkg^{-1}$	$mgkg^{-1}$	$mgkg^{-1}$	$mgkg^{-1}$	$mgkg^{-1}$	$mgkg^{-1}$	$mgkg^{-1}$	$mgkg^{-1}$	$mgkg^{-1}$
1a	34260	15890	3108	17875	38033	52.60	19160	11.95	97.32	nd	64.55	11.92	17.87	nd	31.87
1b	938.3	35460	2400	35857	30300	400	25100	60.7	210.2	298.8	191.2	60.75	249	179.3	34.91
2a	950	7856	2500	13855	18465	150.4	20565	45.78	156.8	98.54	55.78	255.7	632.7	55.41	28.75
2b	920.5	7662	2900	13433	19500	100	19310	49.75	175.1	92.5	51.74	273.6	707.5	45.32	33.82
3a	5230	14980	3600	8973	48700	100	22850	60.13	174.8	148.9	81.41	444.9	602.2	87.91	28.72
3b	4040	5750	2000	14632	14400	100	16880	45.78	91.56	61.94	42.19	188.5	741.5	17.92	26.11
4a	812.2	4290	1600	9990	13000	90.51	8290	30.97	59.94	49.95	29.97	124.9	131.9	92.92	12.98
4b	23700	7600	9000	24700	23800	100	14700	17	99	nd	34	150	10	nd	27
5a	18000	1324	1205	9855	27000	99.8	16785	45.09	214	70	67	180.2	85.53	50.45	22.01
5b	17600	1340	1000	9600	27200	100	17600	36	253	68	74	224	107.4	nd	23
Crust H9a	27660	6370	7000	26567	11180	700	12940	186.1	275.6	269.5	11.94	505.5	595.1	nd	16.92
H10	67690	14810	8000	47117	33200	800	18490	237.6	141.2	418.5	37.77	70.64	515.9	77.52	418.5
TSF	380.2	1832	10770	13700	27000	1370	9624	63.52	65.22	147.2	62.31	198.6	18.22	100.7	145.4

Table A2 Metals concentrations results obtained using ICP-OES after acid digestion in samples collected in 2007

Sample	Na	K	Mg	Ca	Al	Mn	Fe	Co	Zn	Ni	Cu	Cr	Hg	U	Pb
	$mgkg^{-1}$	$mgkg^{-1}$	$mgkg^{-1}$	$mgkg^{-1}$	$mgkg^{-1}$	$mgkg^{-1}$	$mgkg^{-1}$	$mgkg^{-1}$	$mgkg^{-1}$	$mgkg^{-1}$	$mgkg^{-1}$	$mgkg^{-1}$	$mgkg^{-1}$	$mgkg^{-1}$	$mgkg^{-1}$
1a	28356	12054	1800	4725	44300	75	22372	22.18	97.39	52.07	71.36	489.2	190.2	46.51	19.55
1b	96657	25369	22800	51032	51900	155	18092	112.1	216.3	141.6	87.51	250.1	28.04	36.02	38.62
2a	19821	28187	800	796.8	67900	98	36354	47.81	313.7	180.3	117.5	455.2	15.32	30.02	15.42
2b	1734	5148	1200	953.3	12600	302	16873	77.22	303.1	232.6	76.26	571.3	10.05	36.32	19.53
3a	18924	13546	1400	11952	64200	64	27988	52.79	184.3	202.2	89.64	550.2	23.21	55.35	37.06
3b	26295	16618	1800	3910	42900	85	16813	17.59	391.9	162.3	48.87	229.5	38.55	33.71	52.92
4a	32455	5109	1650	4235	29400	83.24	28564	40.45	85.65	70.12	55.88	125.4	132.3	80.72	15
4b	31234	4812	1600	4549	28355	82.31	30796	45.49	90.99	78.74	50.74	140.1	15.45	10.21	22.08
5a	29594	7500	1900	7300	24100	96	17900	24	63	31	47	253.2	21.12	33.85	20.15
5b	5309	8849	1700	4916	27600	85	14847	17.69	60.96	16.72	42.28	216.2	25.65	28.22	15.72
C1	101055	21305	26100	50576	36100	368	9117	125.7	93.09	221.7	55.66	163.3	25.56	181.2	227.7
C2	1193	1349	67000	6294	3100	101	5894	68.93	65.93	164.8	29.97	94.42	13.32	115	149.5
C3	44389	35055	4300	37835	118880	89	77756	65.54	173.8	85.41	96.33	455.5	77.12	153.1	174.1
Pond sed	330.9	1545	1000	2000	8500	77	8364	60	53.64	129	50	183.2	12.52	178	126.6

Appendix B Results of metal in tailings dams from water leachate

Table B1 Metals concentrations in tailings dams from water leachate collected in 2006.

Sample	Na	K	Ca	Fe	Co	Zn	Ni	Cu
	$mgKg^{-1}$	$mgKg^{-1}$	$mgKg^{-1}$	$mgKg^{-1}$	$mgKg^{-1}$	$mgKg^{-1}$	$mgKg^{-1}$	$mgKg^{-1}$
1a	9993	1179	45438	2791	440	302	1020	196
1b	1552	541	58891	9	74	177	195	27
2a	5410	1285	7128	5	29	23	18	n.d
2b	4422	1389	69061	1	31	18	21	nd
3a	14550	2662	64067	2	52	129	123	nd
3b	3540	174934	6798	2095	80	366	20	78
4a	7752	823	107838	3	28	51	57	nd
4b	3475	690	30968	134	20	48	55	4
5a	2957	1603	76821	11	97	141	249	nd
5b	2633	31	114419	nd	15	31	39	nd
H9a	456045	63384	97553	60566	7208	1883	11618	59
H10	469619	26672	70255	162835	7718	3921	15605	954
Sed	5174	1944	132444	33	31	97	97	3

Table B2 Metals concentrations in tailings dams from water leachate collected in 2007.

Sample	Na	K	Ca	Fe	Co	Zn	Ni	Cu
	$mgKg^{-1}$	$mgKg^{-1}$	$mgKg^{-1}$	$mgKg^{-1}$	$mgKg^{-1}$	$mgKg^{-1}$	$mgKg^{-1}$	$mgKg^{-1}$
1a	826	303	72813	546.5	492	96	1577	526
1b	277	246	64565	980	767	3385	2673	77
2a	8699	667	80783	3	426	1660	1784	17
2b	8689	3815	77718	10	67	166	158	3
3a	8718	2334	61206	10	146	432	487	n.d
3b	3191	1336	88984	3	40	97	97	n.d
4a	1954	559	78641	4	23	18	35	n.d
4b	1756	654	63883	2	15	14	26	n.d
5a	2762	1355	59910	33	29	35	53	2
5b	2338	1034	74175	nd	17	16	12	n.d
C1	476883	75286	119032	839	2056	1468	4911	109
C2	77725	1335	336800	49594	1947	1667	3831	423
C3	54871	7441	264745	108	389	924	673	4
Sed	18317	988	32464	889	234	145	465	14

Appendix C Aerial photograph of the active slime dams (Nasrec)

