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EFFECTS OF OZONATION ON COOLING WATER SYSTEMS

Keneetswe Lilian Mosugelo

A research report submitted to the Faculty of Engineering and the Built Environment, University of the Witwatersrand, Johannesburg, in partial fulfilment of the requirements for the degree of Master of Science in Engineering.

Johannesburg, 2010

DECLARATION

I declare that this research report is my own unaided work. It is being submitted for the degree of Master of Science in Engineering to the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination to any other University.

……

(Signature of Candidate)

…… day of ……. 2010

ABSTRACT

Cooling water systems are needed to dissipate heat. The mist from open system cooling towers has been implicated as a source of infections of *Legionella pneumophila.* As a result biocide is added to cooling water systems, but the addition of biocide worsens biofouling, scaling and corrosion. Increasing environmental pressure has resulted in a move away from biocides which are usually chlorine based chemicals, so that the use of ozone instead has recently been reported as a way of controlling microbiological growth. This study aims to compare the corrosion rates (using calculated and measured surface areas) of different metals exposed to chemically treated and ozone treated cooling water in an industrial cooling water system. The types of corrosion were also observed and recorded. The scales from different components of the cooling systems as well as scale from chemically and ozone treated D tower water were characterized qualitatively using X-ray diffraction (XRD), Thermo gravimetric Analysis (TGA) and Atomic Absorption Spectroscopy. The D tower is a cooling water circuit in which the cooling water is from the Vaal River. As expected, the stainless steel has the lowest corrosion rate of 0.000 milli inches/year followed by brass with 1.531 milli inches/year and lastly mild steel (2.098 milli inches/year). Water quality rather than the presence or absence of ozone determines the corrosion rate. This confirms the findings reported in the literature. Scale from chemically treated water contains many different compounds while scale from ozone treated contains only different polymorphs of $CaCO_3$, which is present in the water source and magnesium calcite.

Key words: cooling water system, ozone, biocides, corrosion, biofouling, scaling, corrosion rate, X ray diffraction, Thermo gravimetric analysis

DEDICATIONS

I dedicate this research report to my husband, Keagatetse David Mosugelo, for his consistent support, encouragement, love and acceptance in helping me fulfil another dream in my life and to my lovely daughter, Ame, for understanding the reason for my absence during her first year at school and to the everlasting memories of my grandmother, Ditlhare Mary Mokgosi, for the great interest and wisdom she showed in my life and whom I wish I could share my achievements with.

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LIST OF SYMBOLS

K	corrosion decay for individual coupon, ($g.mm^{-2}$)
ρ	density of individual coupon (kg / m^3)
M_o	weight of coupon before exposure (g)
M_t	weight of coupon after exposure (g)
mpy	milli inches per year
S	Total surface area of coupon before exposure (mm^2)
t	time of exposure in weeks
V_u	Corrosion rate in milli inches / year

1.0 CHAPTER 1: INTRODUCTION

A cooling tower system is a device for the evaporative cooling of water in contact with air. This is achieved partly by an exchange of enthalpy of vaporization resulting from the evaporation of some of the circulating water, and partly by enthalpy change due to cooling (Mckelvey and Brooke, 1959).The direct contact of air and water provides a very effective means of temperature control of the cooling water, but also traps fine air-borne particles and bacteria thus upsetting the quality of water (Lin and Yeh, 1993).

The concern with respect to cooling tower exhaust is the mist. Mist drift from cooling towers has been implicated as a source of infections of *Legionella pneumophila.* Since a cooling tower uses sprays of water to cool the working liquid, the exhaust air from a cooling tower contains fine droplets of water; if bacteria, algae and viruses are present in the water, the mist will also contain these biological species, which may include *Legionella*. Thus a biocide is used and regular testing is done to ensure no *Legionella* is present.

The use of ozone in cooling tower systems as a biocide treatment has received a great deal of attention in recent years. The use of ozone in cooling water, particularly recirculating cooling water, has recently been advertised as a way of controlling microbiological growth in these recirculating water; it also reduces colour. It produces well oxygenated water but an ozone residual must be avoided since it is corrosive (Mugele and Wiseman, 1958). The control of microorganisms in open recirculating cooling water systems has been practiced for years. Without these controls, cooling tower systems will become septic quickly.

1.1 Concise problem

Cooling water systems are needed to dissipate heat, but the complications arising in doing so are maintenance headaches. Biofouling, scaling and corrosion are the main maintenance concerns with cooling systems (Lin and Yeh, 1993).

Air and water can transport many pathogens and are responsible for the *Legionella* found in cooling systems. The warm water in cooling towers supports micro flora and these can aggravate the problem of scaling and corrosion in the cooling system thereby creating a problem which requires maintenance. Deposits which accumulate in cooling tower systems reduce the efficiency of heat transfer and the carrying capacity of the water distribution systems.

Conventional methods of cooling water treatment consist of pH control for scale prevention, addition of chromates or zinc phosphate for corrosion control and chlorination by chlorine gas and hypochlorites for biofouling control. Due to increasingly stringent regulations governing the chlorine and chromate residues in cooling water, ozonation is now frequently used in water cooling systems (Lin and Yeh, 1993). According to Borenstein (1994), ozone is a very effective oxidizer that has powerful organism killing properties compared to other biocides used in these systems but its effects on the nature of scale formed and the corrosion rates on a plant cooling water system has not been investigated.

Therefore the purpose of this study is to compare corrosion rates in chemically treated and ozonated plant cooling water systems and to characterise the scales found in these two systems.

In each case the cooling water system was dosed with sufficient ozone or chemicals to control the bacteria in the system according to industrial operating procedures. The concentration of ozone or chemicals biocide was not varied in this work.

1.2 Conflicting views

Concerns regarding the environmental impact of chemicals like chlorine that have been used as biocides in water treatment have been raised. Therefore ozone is gaining acceptance as a viable alternative biocide.

It has been reported that ozone removes biological fouling and there are conflicting reports on whether it increases or inhibits corrosion. One view is that ozone is not a corrosion inhibitor *per se* as studies have shown that the higher concentration ratios resulting from the reduced volumes of water being treated raise the pH of the circulating water which in turn helps to protect the system from corrosion and according to Stanford and Hill (1967) all cooling water systems are potentially corrosive as there is a build up of dissolved and suspended solids which increases the electrical conductivity of the recirculated water, therefore enhancing corrosion risks. Complex aqueous chemistry needs to be considered with pH and water quality as determining factors. One important issue is the decreasing solubility of ozone with increasing temperature so that Parker (1995) recommends that it should be administered at controlled temperatures of not more than 57 °C, and the pH should be kept at around 8.4.

1.3 Justification

Due to the conflicting reports in the literature with respect to the effect of ozone on corrosion, the purpose of this work is to measure corrosion rates and characterize the scale in chemically treated and ozone treated plant cooling water.

1.4 Key research question:

The explanation of the following research question forms an integral part of the proposed study:

- How is the scale composition and corrosion rate of different metals affected by ozonation compared to chemical treatment in cooling water systems?

1.5 Research objectives

The overall objective of this study is to generate information to gain understanding of the impact of using ozone as a biocide on scaling and corrosion. Aims of the research are;

- To determine the type of corrosion experienced in stainless steel, brass and mildsteel as possible construction materials for cooling water systems.
- To compare the corrosion rates of stainless steel, mild steel and brass in ozone treated water and chemically treated water.
- To determine the composition of scale from two different cooling water systems.

1.6 Layout of research report

To achieve these objectives a detailed literature survey was conducted (see chapter 2) where different biocides as well as their effect on corrosion, scaling and biofouling were outlined; and the previous work on ozone application is analysed. The experimental procedures for corrosion identification, calculation of corrosion rates and scale identification done through Thermo Gravimetric Analysis (TGA) and X- Ray Diffractometry Analysis (XRD) are outlined in chapter 3. In chapter 4 the research report presents the results and their interpretation. The last chapters, chapter 5 and 6 will address the conclusion and the recommendations respectively.

2.0 CHAPTER 2: LITERATURE REVIEW

2.1 Cooling towers

Heat is a by-product of human activity. Comfort cooling, machines and industrial processes all generate a large amount of heat. Flowing water is a good medium to remove energy which is dissipated through evaporation (Touir et al., 2008). Cooling towers are widely used in many types of chemical processes for control of water temperature in cooling water systems. The cooling systems are either once through, closed circuit or recirculating; recirculating systems may be closed or open circuit (Lens et al., 2002).

In once-through systems large amounts of water are required since the water only passes through the system once. These are commonly found in thermal power plants (and other industrial plants) which have access to sea water for cooling. Due to their potential for environmental damage from thermal shock and pollution these systems are being phased out in some countries.

In a closed circuit cooling system the cooling water is completely confined within the system's pipes and heat exchangers. Examples of these systems are the cooling of gas engines, compressors and refrigeration systems. In these systems, water circulates in a closed loop and is subjected to alternate cooling and heating without air contact. The heat transferred to the water is transferred in a water-to-water exchanger to the recirculating water of an open recirculating (or a once-through) cooling system. In a closed circuit cooling system the water losses only occur due to leaks.

In open systems or direct contact systems hot water enters the system and it trickles down the tower. Direct contact between the water and air flows accomplishes heat

removal from the water by partial evaporation. Cooling water use and the associated evaporative losses constitute the highest consumption of water in most of these industries. This provides a very effective way of cooling the water, although it has the disadvantage of air borne bacteria and particles being trapped in the process (Lin and Yeh, 1993). According to Herro (1989), this system is mostly susceptible to high concentrations of suspended solids and precipitates. This will increase the concentration of nutrients and result in biological growth and fouling. Seneviratne (2007), states that water, more than any other medium, is used for cooling because it is readily available, cheap, has an ability to absorb large amounts of heat per volume (relative to air-cooled systems) and can be discharged easily to the public utility sewers.

2.2 Operational principles of a cooling tower

The principle of a recirculating cooling tower is the same whether it is in a power plant or is in an air conditioning system. The cold cooling water is recirculated by the recirculating water pump and heat is transferred to the water in heat exchangers (condensers). The hot water enters the cooling tower at the top. The water is sprayed through nozzles in order to disperse it into small droplets. In open recirculating cooling water systems, the water passes through the heat transfer equipment and is continuously reused. This cooling water circulates to operating units where it picks up heat as it cools the process stream and the resulting warm water is returned to the cooling tower. The main function performed by a cooling tower is to cool the warmed water. During this process, there is exchange of heat with the incoming air flow that is sucked into the cooling tower. Figure 2.1 below illustrates the general operation principle of the cooling tower.

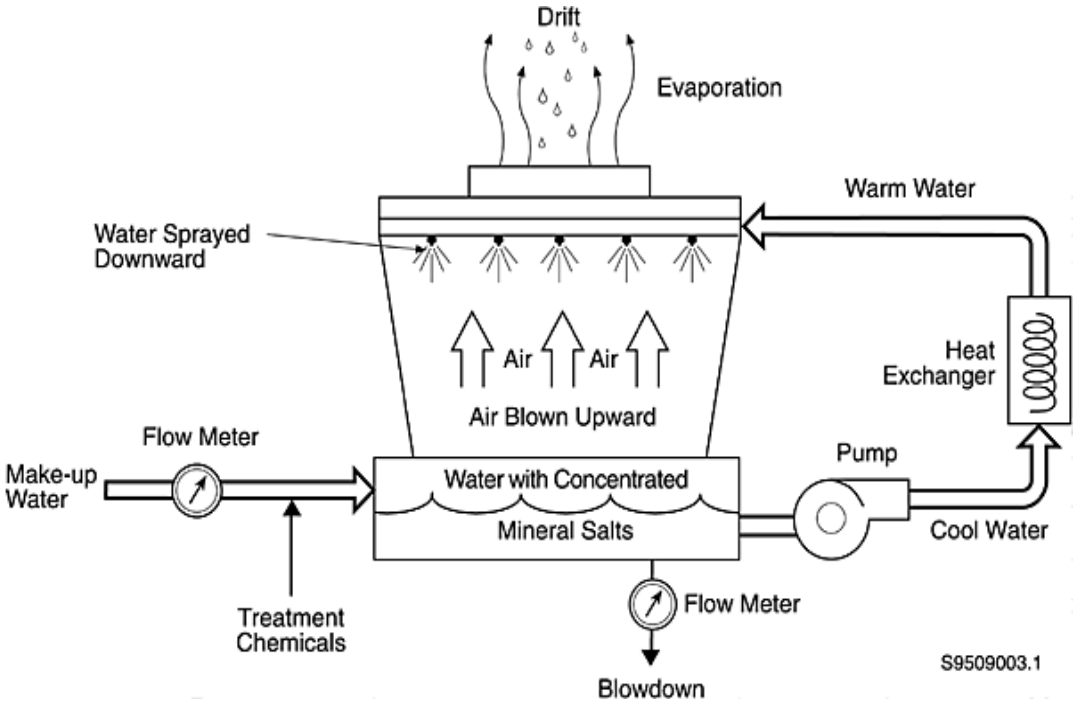


Figure 2.1: Typical Cooling Tower Operation (derived from Seneviratne, 2007:87)

2.3 Water quality of cooling tower system

If the water used in the cooling system was absolutely pure, no fouling, scaling or bacterial growth would occur, but as the water contains dissolved and suspended solids, dissolved and suspended organic matter, and dissolved gases fouling and scaling do occur over time. Kmec and Emerich (2001) are of the view that river water can be used in cooling systems. It contains dissolved inorganic salts and as some will be lost through evaporation, the concentration of salts will increase and, in the process, scales and deposits will be formed. These will promote underdeposit corrosion.

As the water volume in the tower is reduced through evaporation and drift, the concentration of the chemicals and their byproducts found in the water increases. Stanford and Hill (1967) revealed that water in cooling towers acquires hardness

either by flowing over deposits of gypsum or limestone. The water can also contain calcium carbonate which is insoluble in pure water but can be converted to soluble bicarbonate as it mixes with carbon dioxide from the atmosphere.

Since water is lost through evaporation, there is an increase in the concentration of dissolved solids which, according to James (1971), at high pH values may lead to high concentrations of sodium compounds which are liable to weaken the structure of the cooling system.

Cooling towers also pick up contaminants from the environment. In order to maintain chemical and contaminant concentrations at a minimum level, water is removed periodically from the system through a process known as blowdown. The blowdown water and the water lost through evaporation and drift are replaced with fresh water which will also contain minerals and other impurities (Touir et al., 2008).

Blowdown water, which is removed from the system, is discharged to a local wastewater treatment facility or to the streams or dams onsite. As the blowdown water contains little organic material, the local wastewater treatment facility or municipality will charge extra sewage fees for accepting and treating the water since treatment of such water is difficult. Discharge of the blowdown water to the environment, as surface water, is coming under increasing regulatory pressure due to stricter limits on the contaminants typically found in blowdown water.

2.4 Cooling tower problems:

Cooling tower water is tepid and open to the atmosphere, making it an ideal environment for growth of bioorganisms and due to evaporation during cooling, residual ions concentrate with time. Thus cooling towers are bound to experience

problems that can reduce heat transfer efficiency, lifespan and pose health risks to the community nearby. The problems encountered in cooling water systems are:"

2.4.1 Legionella

The direct contact of the water with the air during cooling traps fine particles and bacteria. The growth of biomass, especially bacteria, in the cooling system is supported by the increase of total dissolved solids, due to the increase of available nutrients. The main problems arising from the cooling circuits include fouling, corrosion and scaling. In addition, Domingue et al. (1988) state that epidemiological and environmental investigations have shown that cooling system water is a potential environment for the augmentation and spreading of micro organisms and has been implicated as the source of infectious *Legionella* species in some outbreaks of *legionellosis.*

According to Milne (2007) due to lack of awareness there have been only a few incidents of *legionellosis* reported in South Africa. The report goes on to state that this will change soon due to the increased awareness and environmental pressures from local and international bodies. Milne (2007) reported that *Legionella* is identified as a group 2, Hazardous Biological Agent (HBA) within the South African Regulations for Hazardous Biological Agents, and therefore ultimately demands acceptance of responsibility for control of exposure of individuals to *Legionella* by industries.

In order to cope with the problem of microorganisms, disinfectants known as biocides are used. These disinfectants should be harmless to humans and the environment, and they should be chemically stable and be easily soluble in water (Stanford and Hill, 1967). The application of these chemicals may be used on a continuous basis or irregularly depending on the severity of the problems. Generally

the frequency of dosing is related to the concentration of microorganisms. Some of the chemicals used for disinfection include, copper sulphate, chlorine and chlorine containing chemicals (calcium hypochlorite), ozone, chlorinated phenols, quaternary ammonium compounds, gluteraldehyde, polyamines and acridine dyes (Parkins, 1982). Unfortunately these biocides often accelerate corrosion and fouling.

i. Biocides

The main problems encountered from the direct air and water contact in the cooling water systems include corrosion, scaling and fouling and therefore treatment with biocides is necessary in order to maintain water quality of the cooling system at an acceptable level (Lin and Yeh, 1993; Brözel and Cloete, 1991) The reason for treating cooling water to limit the growth of mineral and microbial deposits is to prevent heat transfer efficiency from decreasing (Panjeshahi and Ataei, 2008).

According to Macchiarolo et al. (1981) biocides can be classified into oxidizing and nonoxidizing; oxidizing biocides cause irreversible oxidation of protein groups and polysaccharides in the micro organisms while the nonoxidizing biocides alter the permeability of the cell walls of the micro organism therefore interfering with their biological processes. In order to choose the product that is best for a particular application, the characteristics of the system to be treated, the operating conditions and the type of structural materials used in the system are considered (Videla, 2002).

A. Ozone treated cooling systems

i. Ozone Chemistry

Ozone, as a strong oxidizer, has a standard electrode potential of 2.07 V and it is an even stronger oxidizer than chlorine which has a standard electrode potential of only

1.36 V (Brown et al., 1992). Authors such as Brown and Duquette (1993) and Staehelin and Hoignē (1985) found that molecular ozone will either react directly with components in solution, or it may decompose to form secondary oxidants such as hydroxyl radicals, oxygen and hydroxide depending upon the pH of the solution in which it is dissolved (Brown and Duquette, 1993; Brown et al., 1992). The overall reaction is shown below:

$$2O_3 + H_2O + 2e^- \longrightarrow 2OH^- + 2.5\ O_2 \qquad (2.1)$$

The potential of a hydroxyl free radical is 2.80 V and this makes it a more powerful oxidizer than ozone. At pH values above 7.5, much of the ozone will decompose into hydroxyl radicals and will react rapidly with water contaminants but below this pH, molecular ozone is stabilized and only a small fraction of the ozone will be converted into hydroxyl free radicals. Increasing the pH above this value will cause the half-life of ozone to decrease significantly. According to Rice and Wilkes (1994) the disinfection with ozone is possible with molecular ozone only not hydroxyl free radical. This implies that if all the ozone is converted to hydroxyl free radicals at pH above 7.5 with their shorter half life, hydroxyl free radicals will not provide disinfection because their contact time will be insufficient.

ii. Ozone as a biocide

Environmental concern has led to legislation which encourages the replacement of toxic biocides widely used in the past, like chlorine, with effective, environmentally-safe biocides that are compatible with system operation (James, 1971). In their report Strittmatter et al. (1992) explain that two of the advantages of ozone over other chemicals are that there is minimal onsite chemical inventory, since it is used as it is generated, and because of its rapid decomposition it has little or no toxic discharge. In addition, it has a high biocidal efficacy, a wide antimicrobial spectrum (Ruiz et al., 2007) and it is generated on demand, 'in situ', without needing storage facilities.

Ozone is a practical oxidizing biocide because it is the fastest acting and the most efficient oxidizing agent against all microbiological organisms. Ozone works as a biocide by directly oxidizing the outer shell of microbes. Biological cells and their membrane components (proteins, lipids and polysaccharides) will also be oxidized and structurally modified resulting in cell lysis. Inactivation by ozone is a complex process that attacks various cell membrane and wall constituents and cell content constituents (Ruiz et al., 2007).

In their study Strittmatter et al. (1992) observed that ozone exhibited excellent microbiological control. They observed a difference in microbiological activity between ozone treated tests and those that were not treated with ozone.

The amount of ozone required to protect a system from microbiological infection is relatively small. For systems in which a biofilm layer is already in existence, a constant concentration of 0.2 to 1.0 mg/L ozone is required (Brown and Duquette, 1993). Smithee (1991) reported that ozone ruptures the cell walls of micro organisms and in order to maintain the protection, after the biofilm has been removed, only 0.02 to 0.05 mg/L ozone is required. The report highlighted that the residual concentrations of 0.1 mg/L will reduce the population of *Legionella pneumophila* in cooling systems by 80 % (Brown and Duquette, 1993).

The reaction of ozone with other molecules produces carbon dioxide, water and partially oxidized forms of the molecule involved in the reaction. Moreover during ozonation, organic contaminants are oxidized by directly reacting with dissolved chemicals and by decomposing to form OH radicals which will then oxidize the pollutant (Rosenfeldt et al., 2006). The residual ozone will recombine as molecular oxygen, in the process producing no toxins or carcinogenic byproducts.

a. Ozone application

Cooling tower ozone treatment systems include an air dryer, air compressor, water and oil coalescing filters, particle filter, ozone injectors, an ozone generator, and a monitoring or control system. The ambient air is compressed, dried, and then ionized in the generator to produce ozone. Ozone is then applied to cooling water through a side stream of the circulating tower water as is illustrated in Figure 2.2 below.

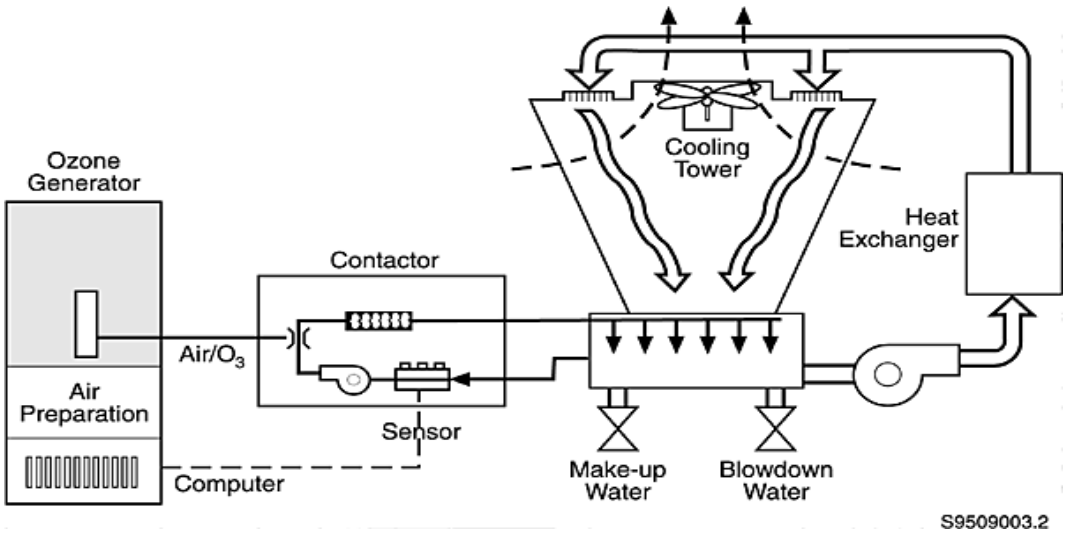


Figure 2.2: Process for ozone treatment of cooling tower water (Derived from Federal Technology Report, 5)

The ozone will dissolve quickly and will not be found in the blowdown water during discharge. This reduces the overall chemical load found in the discharged water, making it easier to comply with regulations.

There are other biocides that can be used in cooling systems besides ozone, these are:

B. Chlorine

According to Tchobanoglous and Schroeder (1985) and Favstritsky et al. (1990) when chlorine is added to water, hydrolysis and ionization occur. In most cases Chlorine is used in gaseous form which hydrolyses to form hypochlorous acid (HOCl) and hydrochloric acid (HCl).

$$Cl_2 + H_2O \leftrightarrow HOCl + HCl \qquad (2.2)$$

The hypochlorous acid is the active species and its concentration depends on the pH of the solution, since it dissociates according to the reaction given below.

$$HOCl \leftrightarrow H^+ + OCl^- \qquad pK_a = 7.6 \text{ at } 21\ ^\circ C \qquad (2.3)$$

When the pH is 7.6 the concentration of hypochlorous acid and its ions are equal. This implies that at pH < 7.6 most of the hypochlorous acid exists in its neutral form, HOCl, whereas at pH > 7.6 most of hypochlorous acid exists as hypochlorite ions, OCl^-. HOCl is known to be a more effective biocide than OCl^- (Kim et al., 2002; Favstritsky et al., 1990). The range from pH 6.5 to 7.6 is considered to be ideal for the action of chlorine as a biocide.

Chlorine is a good algicidal and bactericidal agent, despite evidence that the effective concentration of chlorine is considerably reduced following the penetration of bacterial biofilm (Videla, 2002). Videla (2002) reported that the measurements performed using selective microelectrodes showed that the chlorine concentration inside the biofilm represented only 20% of the concentration measured in the bulk liquid in contact with the biofilm. This is in agreement with the work of De Beer et al. (1994). This finding may be the explanation of why there is a decrease in chlorine biocidal efficacy when used on biofilm developed by different species of sulfate-reducing bacteria or by mixed bacterial consortia.

According to study done by Hamilton et al. (1996), chlorination can suppress but rarely eradicate *Legionella.* García et al. (2007) concluded that the reason why chlorine cannot eradicate *Legionella* was that an amoeba protects the bacteria from the disinfectant.

Instead of chlorine, sodium hypochlorite (NaOCl) or calcium hypochlorite (Ca $(OCl)_2$) may be added to the system. Their action is similar to that of gaseous chlorine as described above but their product, chlorine dioxide (ClO_2), does not form hypochlorous acid immediately when added to water and it is more effective at higher pH ranges than chlorine (Lutey, 1995). This biocide can be used in cooling water systems contaminated with ammonia or phenols as the presence of ammonia triggers the formation of mono- and di-chloramines and these reduce the efficacy of disinfection using chlorine (Shuval, 1977; Favstritsky et al., 1990).

Kim et al. (2002) note that corrosion is an important issue when chlorine is used as biocide. This is especially so at low pH (Videla, 2002).

C. Bromine and its derivatives

Bromine compounds form hypobromous acid (HOBr). According to Videla (2002) and Lutey (1995), the biocidal action of bromine compounds is effective over a wider pH range than hypochlorous acid. Kim et al. (2002) state that bromine exists as hypobromous acid in water in two forms, the HOBr and OBr^-. This is dependent on the pH. At a neutral pH, the HOBr is predominant over OBr^-. The pKa of HOBr is 8.8 which is 1.2 pH units higher than that of HOCl (Kim et al., 2002; Elsmore, 1994). Studies done by Thomas et al. (1999) indicate that bromine was less effective than chlorine against *Legionella pneumophila* as it only reduced *Legionella* and heterotroph populations in recirculating water failing to eliminate them totally.

Nonetheless they found that bromine reduced and controlled *Legionella pneumophila* populations as long as residual concentrations of 0.1 to 1.5 mg/L were maintained.

The popularity of bromine has also increased recently because of its superior biocidal activity in the presence of ammonia, lower volatility, which reduces loss of the product, and better compatibility with cooling water additives. A common method for applying bromine involves the use of solid brominated hydantoins.

According to a study reported by Videla (2002), both bromo-chloro-dimethyl-hydantoin and bromo-chloro-ethylmethyl-hydantoin have been shown to be effective at low concentrations for the control of planktonic bacteria and unlike chlorine-based biocides, their activity was not affected by ammonia. Further, it was found that brominated hydantoins were also effective against biofilm. In this case, the efficacy of brominated hydantoins increased in the presence of ammonia.

Nalepa et al. (2000) concluded from their study that bromine is less persistent than chlorine in aqueous systems but more effective against mature, more difficult to kill biofilms due to reduced reactivity with extracellular polysaccharides and other components of the biofilm matrix.

D. Hydrogen peroxide

This compound is reported by Videla (2002), as economically viable and relatively stable, especially in applications when water needs to be in contact with metals for a longer period, levels of 50 and 100 ppm are used as suitable agents of inhibition of microbial growth in those systems.

E. Non-oxidizing biocides

Other biocides used in cooling systems are non-oxidizing biocides. These can be more effective than the oxidizing biocides discussed above, owing to their overall control of bacteria, algae and fungi. Frequently, a combination of oxidizing biocides and non-oxidizing biocides is used to optimize the microbiological control. Chemical compounds such as gluteraldehyde, ammonium compounds and isothiazolone are included in this group (Videla, 2002).

i. Glutaraldehyde

Gluteraldehyde is used as an active ingredient and is mainly used in systems against troublesome bacteria and those associated with microbiological corrosion (Lutey, 1995). Videla (2002) reported that this compound is very effective in controlling bacteria especially sulfate reducing bacteria in bacterial films. It is active over a broad range of pH and temperature values. In the report by Videla (2002) it is reported that the functional group of gluteraldehyde reacts with basic constituents of proteins, groups such as –OH, –NH2, –COOH, and, –SH, present in cell membranes, cell walls and in cytoplasm of the micro organism.

According to Lutey (1995) gluteraldehyde is not effective alone therefore it is used in combination with other biocides which ought to comply with environmental regulations. Many of these compounds are toxic and they can have an impact on the environment into which they are discharged.

There are other non oxidizing biocides; these include organo-sulphur biocides. The mode of action of organo-sulphur biocides is the inhibition of cell growth by preventing the energy transfer through essential chemical reactions occurring within the cell. The disadvantage of using these biocides is that they are sensitive to pH so

that they undergo rapid hydrolysis at alkaline pH. Therefore organo-sulphur biocides are not recommended for use in cooling towers at pH above 8. This compound is active in the 6.5 to 8.0 pH range without any decrease in activity (Videla, 2002).

According to Videla (2002) this biocide is easy to handle and has a very low environmental toxicity, showing a good compatibility with other water treatment chemicals.

ii. Quaternary Ammonium Compounds

These form a class of cationic compounds (positively charged) which are used as biocides and corrosion inhibitors. Videla (2002) reports that they act on the microbial cells as detergents, dissolving lipids and thus causing the loss of cellular content and their detergent properties provide additional protection against the formation of polysaccharidic materials released during the process of bacterial colonization. Biocides containing quaternary ammonium compounds can contain a variety of additives, such as alcohol and water and the alcohol has a good penetrating ability (Videla, 2002).

Some of the advantages of using these compounds include (a) lower operational costs due to the lower concentration of the chemicals; (b) lower dosages which will result in fewer environmental control measures being required and (c) a simultaneous action on corrosion inhibition and bacterial adhesion (Viera et al., 2000). Some authors, Macchiarolo et al. (1981), see quaternary ammonium compounds being effective in alkaline pH ranges but they easily lose their activity when the system is fouled with dirt and debris. The author also reports that if the biocide is overdosed it can lead to foaming which will reduce the cooling efficiency of the system. Comparing a polymeric quaternary amine to glutaraldehyde, Kim et al. (2002), found

that the former is less effective against *Legionella* bacteria and its activity can be inhibited by high levels of calcium and chlorides.

iii. Isothiazolones

These products contain nitrogen, sulphur and oxygen and they are fast acting biocides inhibiting growth, metabolism and biofilm development of algae and bacteria. When dosed alone, isothiazolone biocides effectively control sulfate reducing bacteria under anaerobic conditions (Videla, 2002).

According to Viera et al. (2000) water-soluble, chlorinated or methylated formulations are generally used for microbiological control. The advantages of isothiazolones over chlorine are that: (a) they can be used over a broad pH range with no decrease in activity; and (b) they are compatible with other water treatment chemicals. Even though they are considered to be better than chlorine, one disadvantage is that they are deactivated by H_2S, and are therefore not effective in environments containing hydrogen sulphide.

Lutey (1995) report that isothiazolones are used as broad spectrum microbiocides and they persist over a wide range of pH. They are effectively used in the treatment of injection and cooling water (Videla, 2002). Thomas et al. (1999) concluded that isothiazolone was effective on planktonic *Legionella* bacteria in batch experiments and was less effective in a model cooling system. Lutey (1995) agrees with this and reports that isothiazolones effectively control aerobic and anaerobic bacteria and are also effective on adhering biomass. They reported that isothiazolones are less effective than glutaraldehyde. Similarly, Skaliy et al. (1980) found that isothiazolone was not as effective as chlorine, a quaternary amine and an alcohol (isopropanol), against planktonic *Legionella pneumophila.*

2.4.2 Corrosion

There are a wide range of construction materials, which includes wood, stainless steel, fiberglass, brass and mild steel among them and the selection of an appropriate material and its effective application is important. Defining corrosion, Shreir (1963) states that it is all the processes whereby a metal or alloy that is used as a material of construction is transformed from metallic form to the combined state with oxygen by interaction with its environment. And furthermore it can be described as the undesirable deterioration of a metal whereby the interaction of the metal and that of the environment adversely affects the metal properties which are desired to be preserved (Shreir, 1963).

According to Seneviratne (2007) the most common types of corrosion in cooling systems are general corrosion, pitting corrosion, galvanic corrosion, stress corrosion cracking and dezincification. In general corrosion the entire metal surface is uniformly attacked and the products are voluminous and they contribute to fouling and under deposit corrosion whereas in pitting corrosion the attack occurs over a small localised area where overall metal loss is negligible but can lead to heat exchanger failure. Furthermore galvanic attack occurs when two different metals are in contact with one another and they act as anode and cathode while stress corrosion cracking in cooling systems is due to chlorides and is mostly exhibited by austenitic stainless steels. Dezincification as the other type of corrosion is whereby the zinc is removed from a copper alloy leaving the metal brittle (Marshakov, 2005).

Metallic corrosion in water is a chemical reaction which is accompanied by the passage of an electric current. The metal ions leave the anodic site and enter the water leaving excess electrons behind which will be used in a balancing reaction at the cathodic site (Brandon, 1984). In an anaerobic environment, an alternative cathodic reaction is the reduction of hydrogen ions to hydrogen gas. This is shown by the following reactions:

1. Hydrogen evolution

$$2H^+ + 2e^- \longrightarrow 2H \longrightarrow H_2 \qquad (2.4)$$

2. Reduction of oxygen

$$O_2 + 2H_2O + 4e^- \longrightarrow 4OH^- \qquad (2.5)$$

3. Bacterial (anaerobic)

$$8H^+ + 8e + SO_4^{2-} \longrightarrow S^{2-} + 4H_2O \qquad (2.6)$$

If blowdown is not implemented correctly and dissolved and suspended solids build up in the water, Stanford and Hill (1967) explain that the electrical conductivity of the recirculated water will increase which will enhance the risk of corrosion.

i. Ozone treated water and corrosion

In recent years environmental considerations have lead to severe restrictions being imposed on the use of biocides besides ozone in particular chlorine compounds. Cooling water treatment by ozonization was first used by National Aeronautics and Space Administration, (NASA), in 1977 according to Lin and Yeh (1993). According to their report, ozone, a very strong oxidant was found to be capable of suppressing corrosion in a cooling tower. In view of this, ozone treatment provides an attractive alternative to other compounds as it has a low degree of aggression towards the majority of structural metals which is an important consideration for corrosion.

In ozonated cooling water systems the pH level stays between 8.5 and 9.0 and according to Videla (2002) this is where the corrosion rate of iron and steel approaches zero. According to Landolt (2007) a high pH at the metal surface

facilitates passivation. However, it must be taken into account that the corrosiveness of ozone towards metals depends on its concentration levels.

For cooling water environments, where temperatures range from 38 to 49°C, there have been reports of reduced corrosion rates of mild steels when exposed to ozone as compared to chemically treated water. Videla (2002), reported that Meier found that the corrosion rates of mild steel decreased from 28 mpy, when chlorine was used alone as a biocide, to 4.6 mpy when ozone alone was used. This decrease in corrosion rate is most likely due to the deposit of a protective layer of scale and corrosion product on the metal surface which was observed in the presence of ozone.

On the contrary, there have also been reports of ozone increasing corrosion rates in cooling water environments. Videla (2002) also described an experiment carried out by Lawson, who found that the addition of 0.1 mg/L ozone caused the corrosion rates of mild steel to range from 8 to10 mpy, which is higher than the corrosion rates reported for a traditional molybdate based water treatment program. In this case severe fouling and scaling were evident when ozone was used. Laboratory studies using ozone treated cooling water carried out by Strittmatter et al. (1992) found that low ozone concentrations of 0.1 mg/L had no effect on the corrosion rate of mild steel, while the addition of 1 mg/L increased the corrosion rates by a factor of five. Thus there are conflicting reports about the effect of ozone as a corrosion enhancer or inhibitor.

In their research, Strittmatter et al. (1992) and Smithee (1991) have come to the conclusion that the corrosion rates of mild steel in cooling water have little dependence on ozone, but are dominated by the water chemistry of the system. Rice and Wilkes (1994) associated the lowering of pH, which can be corrosive, with the presence of oxidizable organic materials which form organic acids and promote

corrosion. Further Littmann (1985) observed that in the presence of highly soluble ions like sodium and potassium, corrosion of metals will be high due to increased electrolyte concentrations resulting in increased electron flow which will automatically accelerate the electrochemical action of metals and corrosive agents in water.

In cooling tower environments, the corrosion rates of brass were found to be reduced by the presence of ozone at levels of 0.05 mg/L. In his research, Videla (2002) concluded that brass appears to undergo dezincification in aerated and low ozone conditions. In this process, there are two possible mechanisms: one mechanism involves the diffusion of zinc to the surface of the alloy where it undergoes preferential corrosion, leaving a copper rich residue and the other mechanism involves the corrosion of the alloy and redeposition of copper as a porous layer.

Videla (2002) attributed this effect to a thin protective layer forming on the metal surface. In another study of synthetic cooling water, Strittmatter et al. (1992) found that 0.1 mg/L of ozone has little effect on the corrosion rates of admiralty brass; however these corrosion rates increased when the concentration of ozone was increased. When the exposure time was extended, the composition of this surface layer changed, and this was indicated by a change in the colour of the corrosion product.

ii. Chlorine and corrosion

Chlorination is known to effectively control bacteria in cooling water systems (Rao et al., 1998). However laboratory studies have revealed that chlorination has very little biocidal action on iron bacteria (Satpathy et al., 1994 as referenced by Rao et al., 2000). The report also indicates that a study done by Pope concluded that

chlorination would increase crevice corrosion attack in pipelines covered by tubercles. This is possible as chloride concentration cells are created within the porous oxide layer of the metal and therefore the chloride ion would increase chemical corrosion potential which contributes to the net increase in corrosion rates of the metal. Excessive chlorine concentrations also tend to lower pH because of the formation of HCl in water (Favstritsky et al., 1990). The reaction is as follows;

$$Cl_2 + H_2O \longleftrightarrow HOCl + HCl \qquad (2.7)$$

iii. Non oxidizing biocide and corrosion

According to Landolt (2007) non oxidizing biocides are less critical in terms of corrosion because they do not accelerate the cathodic half reaction. As corrosion inhibitors, quaternary ammonium compounds form a protective layer on the internal parts of the treated system, thus reducing the exposure to oxidizing agents. As a biofilm-forming corrosion inhibitor, quaternary ammonium compounds have been tested to control or even prevent biocorrosion by inhibiting biofilm formation (Videla, 2002) and most of them tend to be active over a wide range of pH and temperatures.

2.4.3 Fouling

Fouling is a major problem in cooling systems. Fouling which is used interchangeably with scaling in this report refers to inorganic deposits and the formation of micro biological films on surfaces. According Wu and Chan (2003) fouling is mainly due to calcium carbonate deposits and its solubility in water decreases with increasing temperature.

This may be due to the fact that the cooling tower introduces two fouling considerations. Having the cooling tower open, firstly promotes microbiological

growth, and secondly allows particulate matter to enter the cooling water circuit. The source of the makeup water also contributes to its fouling potential. Fouling prevents biocides and corrosion inhibitors from reaching the microorganisms and the metal surface (Zdaniuk et al., 2006).

A. Mineral deposits

Fouling occurs due to suspended solids in the cooling water and forms deposits on the system's surface. Other authors like Zdaniuk et al. (2006) have categorized constituents of fouling into: salts, which may precipitate out of solution, suspended particles and residual water treatment components or substances added to the system after intake. They report that because of the variety of constituents, the use of cooling towers causes many water quality issues, which relate to fouling.

i. Particulate Fouling

According to Cho et al. (2003) particulate fouling is the deposition of particles carried by a flowing fluid as well as material generated in the solution. The scale produced in particulate fouling is much softer than the scale produced in crystallization fouling. Particles in this context may refer to particulate matter, bacteria, and corrosion products. The same authors categorized particulate fouling into three major steps; transport of the particles from the bulk fluid to the surface, the attachment of the particles to the surface, and re-entrainment of previously deposited particles from the surface back into the bulk fluid.

Particulate fouling differs from the crystallization fouling in that the former generally produces a soft sludge scale coating while the latter often produces persistent hardened scale. But the soft scale coating from the particulate fouling can become hardened scale if left on the heat transfer surface for extended periods. Wu and Chan

(2003) also observed that some ozone decomposes in the vicinity of the metal surface and it will generate small bubbles which will prevent calcium carbonate particles from settling on the surface. This will decrease the initial fouling rate of particulate fouling.

ii. Scaling

Another problem in circulating cooling tower water which requires prevention is mineral buildup. Circulating cooling water typically contains excess mineral ions such as calcium and magnesium due to the evaporation of water, thus making the water hard. According to Smithee (1991) when the concentration of these minerals reaches the solubility limit they will precipitate out of the water, forming scale and if a biofilm is present it will act as glue cementing the scale to the surface of the cooling tower system.

Such a hardened scale is common in heat transfer equipment using untreated water as a cooling medium. Factors affecting nucleation and subsequent crystal formation are the concentration of fouling materials (foulants), temperature, pH, pressure, time, flow velocity, mechanical motions, radiation and impurities (Cho et al., 2003).

Cho et al. (2003) observed that in cooling water, the precipitants are often inversely soluble salts that are calcium carbonate. In general, for precipitation to occur, the solubility limit at given conditions must be exceeded. The degree of supersaturation was found to affect the type of crystals that form. They also observed that calcium carbonate crystallizes in two forms; calcite and aragonite. Aragonite forms at higher supersaturation ratios and has a greater effect on the heat transfer resistance, whereas calcite forms at lower supersaturation ratios and has less of an effect on the heat transfer.

B. Biofilms

Any surface in contact with water can be colonized with microorganisms, resulting in the formation of biofilms. According to Johnston and Jones (1995) microorganisms can adhere to and colonise surfaces to form complex, structural layers known as biofilms. Many film-forming bacteria produce an extracellular polysaccharide polymer, known as the glycocalyx which aids with adhesion as well as giving protection from both antimicrobial agents and removal of cells by mechanical means (MacDonald and Brözel, 2000). According to Stanford and Hill (1967) if environmental conditions favour animal and vegetable microorganisms, they will multiply rapidly and cause fouling. Fouling creates an environment suitable for the blooming of pathogenic organisms (Pope et al., 1984).

Microbiological growth in recirculating water cooling systems poses a health hazard in the form of *Legionnaires'* disease. Cloete et al. (1998) state that it also results in biological fouling of these systems. These biofilms produce fouled pipelines, increase water circulation costs, cause and/or accelerate the corrosion of metal and reduce heat transfer (Pope et al., 1984).

3.0 CHAPTER 3: EXPERIMENTAL METHODS

The corrosion rates of different metals were measured in the cooling system and the scale found in the different sections of the cooling towers was analysed. Different experiments were carried out: these included looking at the corrosion rates of different metals used in cooling towers using the measured and calculated surface areas, corrosion rates of different metals exposed to ozone treated and chemically treated water, scale identification using X-Ray Diffraction (XRD) and Thermo Gravimetric Analysis (TGA) and the use of Atomic Absorption Spectroscopy (AAS) to try and quantify the scale components.

3.1 Corrosion rate

3.1.1 Experimental procedure

Different types of metal corrosion coupons were prepared from stainless steel, brass and mild steel. The coupons were mechanically cleaned and polished using a grinder to remove the surface oxide layer and were washed with distilled water followed by ethanol and later dried in the dessicator. Taking care not to contaminate the coupons, clean laboratory gloves were worn to prevent moisture and body oils present on the skin from coming into contact with the unexposed coupons. Later they were labelled. Their masses and dimensions were then determined using a balance and a vernier caliper.

Each coupon was placed in a labeled envelope and then was sent to a cooling water plant where they were exposed to cooling water that was either chemically treated with zinc phosphate or treated with ozone. The exposure time varied from one week to three months and corrosion coupons were exposed in two different cooling water circuits found in the industry namely the K501 which is the wastewater from the main treatment plant, and the D tower. The water in the D tower is from the Vaal

River while the K501 water contained a heavy load of ions from various industrial processes. The two circuits had different water qualities as for K501, wastewater from the main treatment plant is recycled back in the system to be used in cooling system and the cooling water in the D tower is from the river and sodium hypochlorite was used as a biocide. In the case of the mild steel coupons, a set of coupons was pretreated with zinc phosphate, a corrosion inhibitor, prior to insertion in the cooling water circuits. Corrosion coupons were only exposed to ozone treated water in the D tower for three months while for the other experimental setup they were exposed to chemically treated water.

After the exposure time had elapsed, the corrosion coupons were visually inspected in order to determine the type of corrosion which took place. They were then cleaned using a standard rubber stopper cleaning technique, whereby the corrosion coupon was vigorously scrubbed using the rubber stopper under running tap water, as described by Fontana (1986) and then they were weighed. The differences in the masses were used to calculate the corrosion rate (in $g/mm^2/yr$) as per the equation below, for each type of metal coupon taking care that all unit conversions are correct as per appendix A.

Corrosion decay for individual coupon:

$$K = (M_o - M_t) \times \frac{1}{S} \times \frac{1}{t} \times \frac{52\ weeks}{1\ year} \tag{3.1}$$

Where K is the corrosion decay for individual coupon, (g / mm^2)

M_o = weight of coupon before exposure (g)

M_t = weight after exposure (g)

t = time of exposure in weeks

S = Total surface of coupon before exposure (mm^2)

Corrosion rate, V_u in $g/mm^2/yr$ was computed as follows:

$$V_u = K \times \frac{1}{\rho} \tag{3.2}$$

ρ is the density of an individual coupon (kg / m^3)

In determining the surface areas of the corrosion coupons, two methods were used for comparison to estimate the experimental error.

i. Using the measured surface area

The dimensions of each corrosion coupon were measured using the vernier caliper, and these measurements were used to calculate the surface areas as follows:

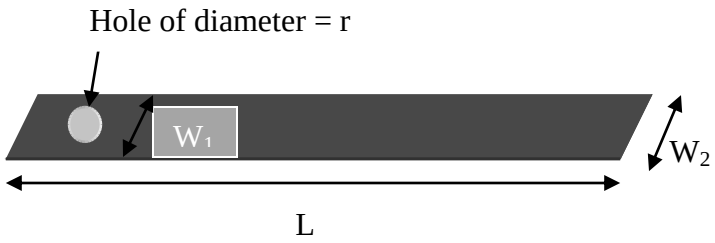


Figure 3.1: Drawing of corrosion coupon showing dimensions

$$S = \left[\frac{(W_1 + W_2)}{2} \times L\right] \times 2 - \pi r^2 \times 2 \tag{3.3}$$

W_1 = width 1 of the corrosion coupon (mm)

W_2 = width 2 of the corrosion coupon (mm)

L = length of the corrosion coupon (mm)

Лr^2 = area of the cut circular hole (mm^2)

Then corrosion rates were calculated using the measured surface areas.

ii. Using the calculated surface area

The surface area was calibrated from a graph which was prepared using paper rectangles with known dimensions and weight. The dimensions, the length and width of the paper rectangles were accurately measured using a ruler and these were later weighed using the balance. The masses of the paper rectangles were then plotted against their surface areas which resulted in a linear graph**.**

The real coupons were photocopied so as to get a paper copy which was weighed. The mass was used to read off their surface areas using the linear graph previously drawn from the paper rectangles. These surface areas for the corrosion coupons were then used to calculate corrosion rates (see appendix A for the corrosion rates calculations using calculated and measured surface areas).

3.2 Photographic images of coupons

After exposure to different water qualities, the corrosion coupons were photographed before and after washing so as to capture and record the type and the extent of corrosion experienced by each corrosion coupon. The pictures were edited using Canon picture editor.

3.3 Scaling

Samples of scale were collected from different places as indicated in the diagram below: i) two samples from the cooling tower packing, D tower which is chemically treated on one occasion and the other part of the experiment it was ozone treated, ii) the chiller unit, D tower, which is ozone treated iii) the sand filter backwash, a D tower circuit which is chemically treated and lastly iv) the air side of a heat exchanger which is on a different plant and the water is chemically treated.

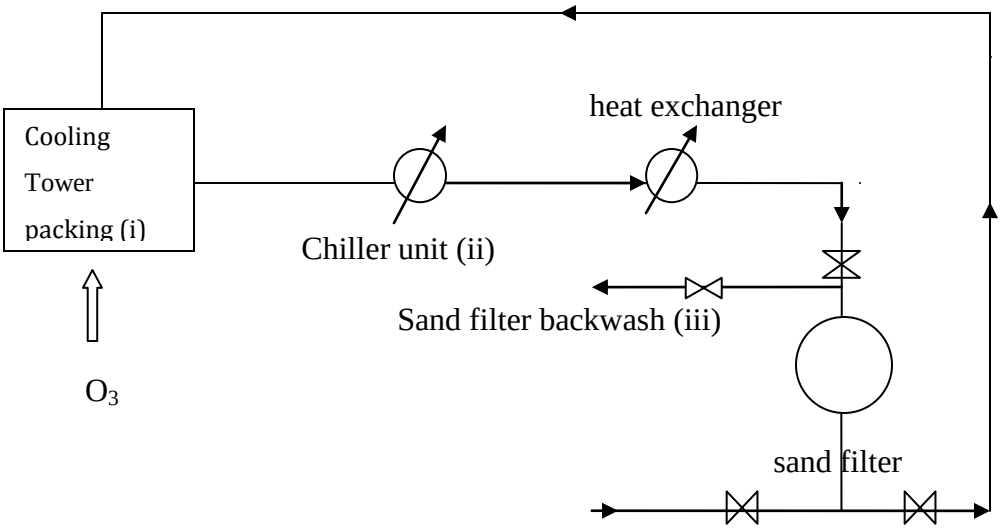


Figure 3.2: A schematic diagram of the cooling tower system

The sample from the sand filter backwash was a slurry suspension in water and the sample was filtered through a qualitative filter paper to get the residue which was air dried before analysis. The residue was mixed to get a representative sample. The scale sample from the heat exchanger was dry and it was ground to a fine powder. The sample was ground so as to get a representative sample, while the sample from the cooling tower packing was wet and it was air dried. Afterwards it was ground to a fine powder and a representative sample was used during analysis. The samples were then characterized using qualitative methods: X –Ray Diffraction and Thermo Gravimetric Analysis techniques and for quantitative analysis Atomic Absorption Spectrophotometer was used.

3.3.1 X - Ray Diffraction (XRD)

XRD was used to identify the powdered scale components. The instrument used was a Philips PW 1830 Diffractometer. Powder diffraction is mainly used for "finger print identification" of various solid materials.

Before using the x – ray diffractometer, the start position [°2Th.] and end position [°2Th.] in the computer system should be made to be 10.0000° and 80.0000° respectively at a step size of 0.020. For preparation of the XRD, the water valve was opened and the water meter was checked to make sure that the reading was in range of 50 to 60. The x – ray diffractometer was switched on and was operated at 40 mA and 40 kV.

The powdered scale sample was loaded into a sample holder and care was taken to make sure that the sample had a smooth, flat surface and that there was no contamination from the container. This was done in order to avoid experiencing noise in the graphs obtained at the end of the experiment.

The High Score Plus software was used for data capture and interpretation. The data stored in an ASCII format was presented as a graph, which was used for search / match purposes in order to identify the compounds. The peaks were matched with those stored in the Powder Diffraction file database created by the International Centre for Diffraction Data. The elements suspected to be in the sample were input in the computer and searched for. This is inconclusive and therefore atomic absorption spectrophotometry analysis was carried out in addition. After satisfactorily identifying the peaks, the chemical compounds were labelled and a word report was created.

3.3.2 Thermo Gravimetric Analysis (TGA)

TGA method used for analysis was the proximate analysis. The Simultaneous Thermal Analyzer, PerkinElmer STA 6000, was switched on for about an hour to warm up. The gas valves, oxygen and nitrogen valves were opened. When the analyzer had warmed up, the scale was zeroed before putting the sample in a pan.

The sample was then weighed until the weight % is between 99.999% and 100%. Care was taken in making sure that the sample weight did not go below 5 mg or above 15 mg. When the desired weight was achieved, the experiment was started.

The sample was held for 3 minutes at 30 °C which was the initial heating phase to remove the moisture from the sample. After that the sample was heated from 30 °C to 110 °C at a heating rate of 25 °C per minute to remove the adherent water moisture from the sample. After this phase of heating, the temperature was held at 110 °C for 3 minutes and heating resumed from 110 °C to 900 °C at a heating rate of 25 °C per minute whereby the organics were burned and other phase changes occurred. The temperature was held for 27 minutes at 900 °C and then it was allowed to cool to 30 °C at a cooling rate of 50 °C per minute.

The data from the experiment was used to plot the rate of weight loss (%) versus sample temperature (°C). The data was also used to draw up a derivative graph for each sample analyzed.

3.3.3 Atomic Absorption Spectrophotometer (AAS)

In order to determine the metal ion concentration in the scale samples, atomic absorption spectrophotometry (Spectra AA, 55B Varian model) was used. We attempted to dissolve the scale samples in hydrochloric acid according to their components as qualitatively determined using the XRD. The samples were left to stand overnight to allow the scale to dissolve before they were filtered. To obtain 1000 parts per million of stock solutions, the standard solutions of the metals to be analyzed, were prepared in 1000 mL volumetric flasks. The standards were prepared from the stock solutions based on the concentration expected from the scale samples.

The wavelength, slit width, lamp, and lamp current were chosen according to the metal being analyzed and the optimum working range required for the particular metal. Before every run, the equipment was cleaned and calibrated using the standard solutions until a curve which was in agreement with the calibration curve in the AAS manual was attained.

The filtrates were aspirated into the spectrophotometer, where metal ions from the filtrate were ionized in air and the acetylene flame environment until concentrations for each filtrate were read and recorded on the screen.

4.0 CHAPTER 4: RESULTS AND DISCUSSION

4.1 Corrosion rates

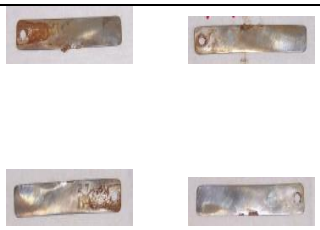
The results from the corrosion coupons exposed to a plant cooling water system are presented in this chapter. The photographs of corrosion coupons before and after cleaning and the corrosion rates of different types of corrosion coupons are presented.

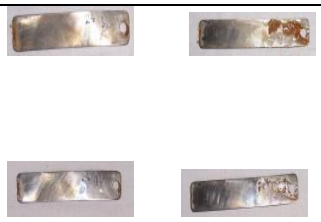
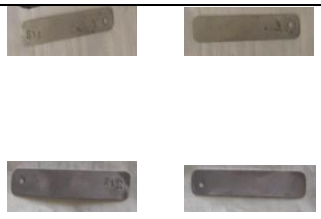
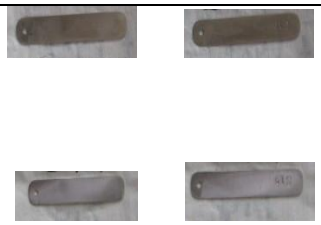
4.1.1 Visual Inspection and photography

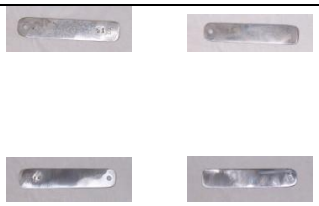
In this section the corrosion of the coupons was examined qualitatively by visual inspection after the exposure time had elapsed. The corrosion coupons were photographed before washing, (A) and after washing them (B). The results are presented in Tables 4.1, 4.2 and 4.3 below, for each coupon the top two photographs are for the coupons before washing and the second pair of photographs below shows the coupons after washing.

Table 4.1: Visual examination results for the corrosion coupons exposed to D tower

Coupon no.	**Period of exposure**		**Photograph**	**Description**
M38 Mild steel	1 week	A B		Localized corrosion, adherent corrosion product.

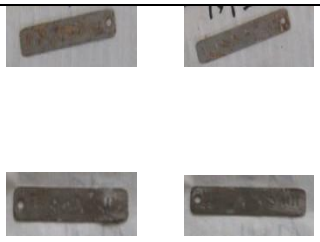
M 30 Mild steel	2 weeks	A B		Adherent corrosion product, localized pitting corrosion.
M 35 Mild steel	3 weeks	A B		Non-uniform corrosion, product can be easily removed
M 27 Mild steel	4 weeks	A B		Corrosion product adherent, localized corrosion observed
M 17 Mild steel	8 weeks	A B		Localized corrosion, corrosion product adherent
M 14 Mild steel	12 weeks	A B		Localized pitting corrosion. The corrosion product not easily removed
M 34 Mild steel Pretreated	1 week	A B		Corrosion product adherent

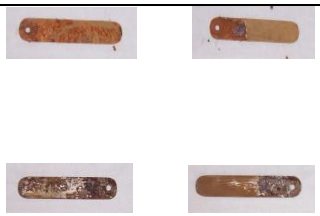
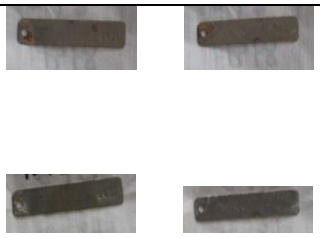
M 18 Mild steel Pretreated	2 weeks	A B		Adherent corrosion product, localized pitting corrosion
M 19 Mild steel Pretreated	3 weeks	A B		Corrosion product non-uniform and non adherent
M 24 Mild steel Pretreated	4 weeks	A B		Corrosion is localized and corrosion product can be easily removed
M 11 Mild steel Pretreated	8 weeks	A B		Corrosion product adherent. Corrosion localised
S 12 Stainless Steel	1 week	A B		No corrosion observed
S 19 Stainless steel	2 weeks	A B		No corrosion observed

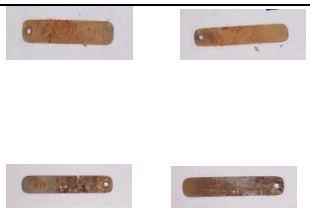
S 10 Stainless Steel	3 weeks	A B		No corrosion was observed
S 27 Stainless steel	4 weeks	A B		No sign of corrosion was recorded
S 15 Stainless steel	8 weeks	A B		No corrosion was observed
S 11 Stainless steel	12 weeks	A B		No corrosion was observed
B 16 Brass	1 week	A B		No changes observed
B 13 Brass	2 weeks	A B		Localized black coating which is adherent
B 10 Brass	3 weeks	A B		Black adherent coating was observed.

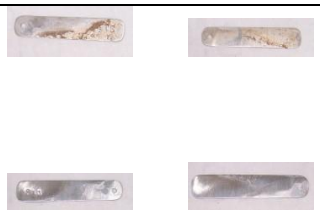
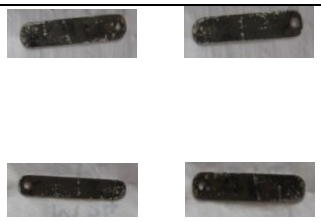
B 20 Brass	4 weeks	A B		No sign of corrosion
B 15 Brass	8 weeks	A B		No corrosion observed
B 19 Brass	12 weeks	A B		No corrosion observed

Table 4.2: Visual examination results for corrosion coupons exposed to K501

Coupon no.	**Period of exposure**		**Photograph**	**Description**
M 31 Mild steel	1 week	A B		Corrosion product readily removable, corrosion not uniform and it is pitting type
M 37 Mild steel	2 weeks	A B		Adherent corrosion product, uniform corrosion

M 39 Mild steel	3 weeks	A B		Corrosion product non-adherent and corrosion is non-uniform
M 21 Mild steel	4 weeks	A B		Non-localized corrosion with product which is non-adherent
M 10 Mild steel	8 weeks	A B		Corrosion uniform, corrosion product easily removed
M 16 Mild steel Pretreated	1 week	A B		Corrosion product can be easily removed, pitting corrosion
M 32 Mild steel Pretreated	2 weeks	A B		Loose corrosion product, corrosion is non-uniform.
M 33 Mild steel Pretreated	3 weeks	A B		Corrosion product non-uniform and non-adherent

M 26 Mild steel Pretreated	4 weeks	A B		Adherent uniform corrosion product
M 15 Mild steel Pretreated	8 weeks	A B		Uniform corrosion, corrosion product adheres
S 16 Stainless steel	1 week	A B		No corrosion observed
S 17 Stainless steel	2 weeks	A B		No corrosion was observed
S 18 Stainless steel	3 weeks	A B		No Corrosion product observed
S 20 Stainless steel	4 weeks	A B		No corrosion observed.

S 14 Stainless steel	8 weeks	A B		No corrosion observed.
S 13 Stainless steel	12 weeks	A B		No corrosion observed
B 12 Brass	1 week	A B		Black colour coating
B 18 Brass	2 weeks	A B		Black adherent coating
B 11 Brass	3 weeks	A B		Black coating developed, no corrosion observed
B 22 Brass	4 weeks	A B		Black colouring adherent coat

B 14	8 weeks	A B		Uniform adherent corrosion product
B 17 Brass	12 weeks	A B		Brown corrosion product

From the results it can be observed that mild steel coupons showed signs of corrosion early in the experiment. The mild steel in the D tower showed the localized type of corrosion while one exposed to K501 had uniform corrosion. Visually inspecting the mild steel from K501 showed pitting and localized corrosion in the first week of the experiment. More severe pitting corrosion is shown in K501 mild steel than in the mild steel in D tower. The pretreated mild steel coupons from D tower and K501 experienced different corrosion types and the corrosion product in D tower was adherent while in K501 was loose.

Brass in K501 had a thick black coat on the first week of exposure compared to brass in D tower. Brass in the D tower had a thin black coating after the first three weeks of exposure and there was no corrosion observed in the coupons while those exposed to the K501 displayed a black coloured coating thicker than that from the D tower environment, for the first four weeks of exposure. Corrosion was observed on the coupons in the following weeks.

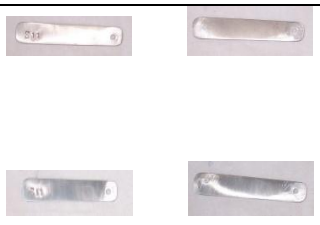
The coatings have different colours, brass exposed to K501 exhibited a green-black coating in the first week of exposure and after a month it had a yellowish colour. After the third month the colour of brass in K501 had changed to reddish brown. For

brass exposed in D tower it had a thin greenish-black colour for the first three weeks and there was no colour observed for the remaining experimental period. According to Bastos et al. (2008) the reddish colour which is significant in brass coupons can be due to cuprite while the gold orange colour may be attributed to the presence of tolbacite, $CuCl_2$. The corrosion products of blue colour may be copper hydroxide, and copper chlorides, while the green colour is related to copper sulphates (Bastos et al., 2008). According to Uhlig (1963) and Revie and Uhlig (2008) brass does experience dezincification and the alloy so corroded retains its shape and may appear undamaged except for surface tarnish which explains the colour observed in brass coupons.

The stainless steel corrosion coupons exposed in D tower and K501 did not show any sign of corrosion throughout the experimental period. Wang et al. (2003) found that stainless steel forms a passive film which helps prevents corrosion. They concluded that the main passivating element in stainless steel is chromium.

The trend shows that the coupons exposed to K501 showed early signs of corrosion, and they are more susceptible to corrosion compared to that exposed under D tower conditions. This is because the quality of water in the two environments is not the same since the D tower is from the river while the K501 is plant wastewater and has a heavy chemical load. This is shown by Strittmatter et al. (1992) in their research whereby they concluded that the water chemistry has a greater effect on corrosion rate than whether or not ozone is used.

Table 4.3: Visual examination results for corrosion coupons exposed for three months to different environments of D tower

Metal	Environment		Picture	Visual Examination
M 14 Mild steel	Chemically treated water	A B		Localized pitting corrosion. The corrosion product not easily removed
M 44 Mild steel	Ozone treated water	A B		Localized pitting corrosion
B 19 Brass	Chemically treated water	A B		No corrosion observed
B 34 Brass	Ozone treated water	A B		Non-localized corrosion was observed and corrosion product is adherent to the coupon
S 11 Stainless steel	Chemically treated water	A B		No corrosion was observed

S 34 Stainless steel	Ozone treated water	A B		No corrosion was observed

Results in Table 4.3 above show that mild steel is the most corroded metal followed by brass and lastly stainless steel in both ozone treated water and chemically treated water. Brass did not exhibit corrosion when exposed to chemically treated water but it did in D tower which is ozone treated. It is evident that coupons exposed to ozone treated water experienced corrosion compared to those exposed to chemically treated water.

4.1.2 Corrosion rates measurements

The corrosion rates obtained by using the measured surface areas exhibited the same graphical trend as corrosion rates derived using the calculated surface areas, refer to the appendix B. The results are also supported by the calculations of the deviation as depicted in Table C1 and as such there was no significant difference in the corrosion rates from the two methods and the graph of corrosion rate obtained by using measured surface area was used to show the results. Mild steel showed high corrosion rates followed by brass and lastly stainless steel. The corrosion rate results are presented in Figure 4.1 below.

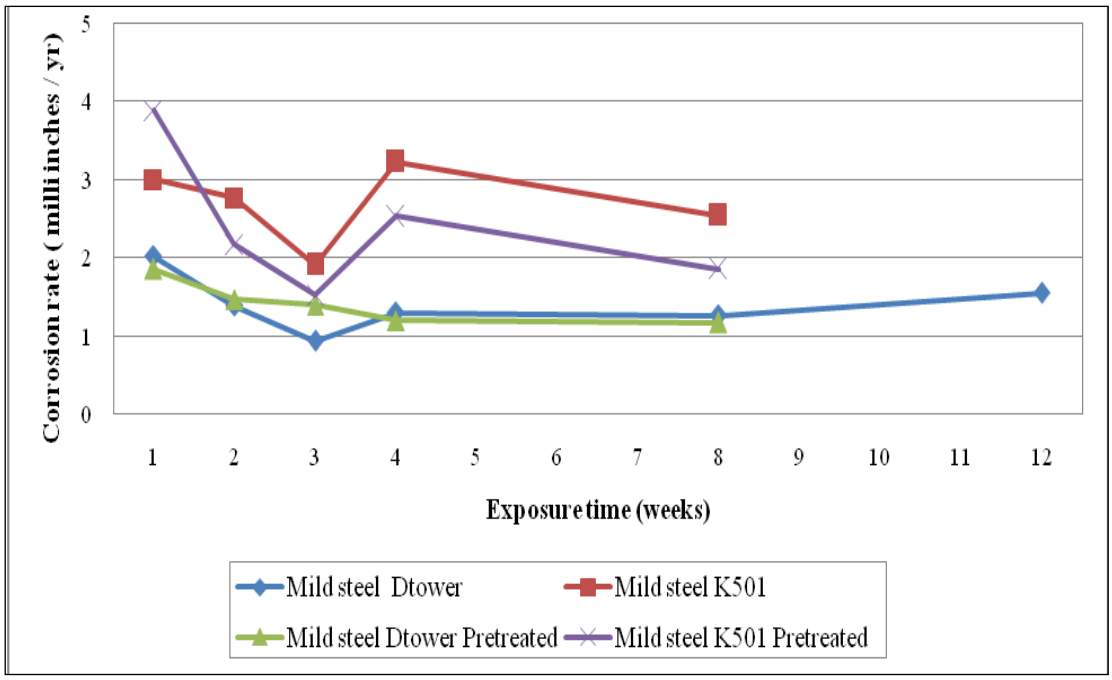


Figure 4.1 Corrosion rates of mild steel exposed to chemically treated water (D tower) and ozone treated water (K501) using measured surface areas

From Figure 4.1 above, there was a decrease in corrosion rate for the first three weeks and after wards there was a peak in the fourth week. Results for mild steel K501, mild steel K501 pretreated and mild steel in D tower for the twelveth week are not included because the coupons could not be retrieved. Mild steel in K501 exhibited highest corrosion rates followed by pretreated mild steel also in K501 and the lowest corrosion rates were observed for pretreated and untreated mild steel in D tower. The pretreated mild steel, which was coated with zinc phosphate as a corrosion inhibitor, in both K501 and in D tower had lower corrosion rate compared to the untreated mild steel in K501 and D tower respectively which implies that the treatment does reduce the corrosion rate.

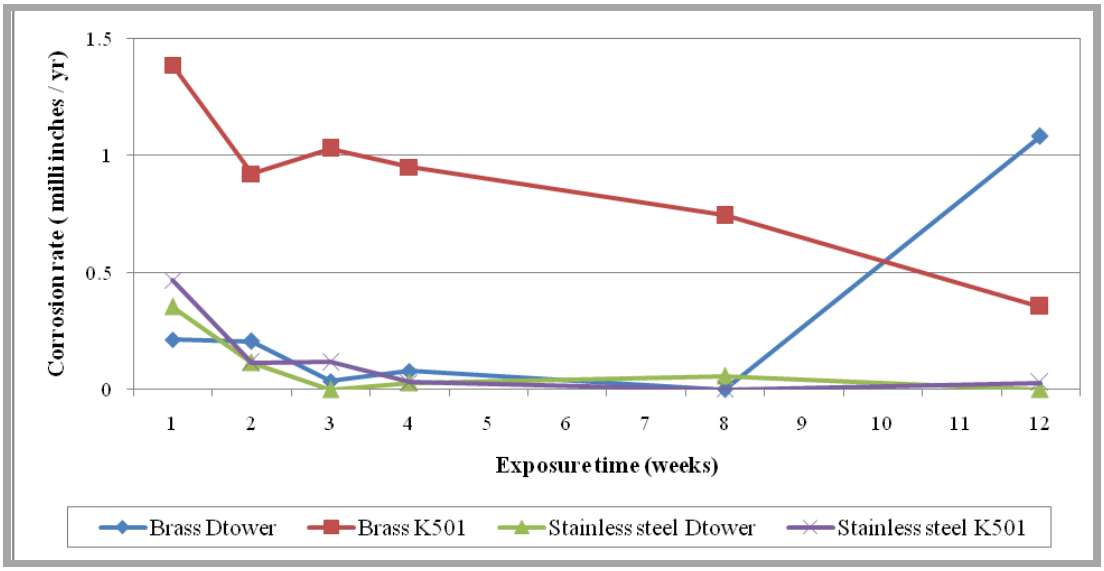


Figure 4.2: Corrosion rates of brass and stainless steel coupons using measured surface areas exposed to both chemically and ozone treated water

Due to the corrosion rates for brass and stainless steel being about an order of magnitude lower than those for pretreated and untreated mild steel, the results for brass and stainless steel have been plotted on a separate graph with appropriate scale. Brass in K501 showed high corrosion rates compared to the brass in D tower except for the twelfth week. The brass coupons in K501 had a black adherent coating from the first week and those in D tower had a much thinner coat of the same black film, but there was no visible corrosion observed. The coating started to reduce in intensity during the fourth week and a brownish adherent corrosion product started forming.

According to Marshakov (2005) and Uhlig (1963) brass loses its zinc to corrosive media and copper appears on the brass surface in the form of a fine grained porous

layer. This dezincing is reported to occur throughout the coupon surface or it can be localized at some areas forming plugs, which was what was exhibited by the brass coupons after week four. Brass may consist of copper and zinc containing minerals which may be responsible for the passivity of brass during short exposures and when this passivity breaks down there will be an increase in weight loss which gives a high corrosion rate (Bastos et al., 2008). This could be an explanation for the increase in the corrosion rate of the brass exposed in D tower during the last period of experiment.

Generally there was no detectable corrosion on stainless steel throughout the experimental period. According to Figure 4.2 above, stainless steel in K501 exhibited high corrosion rates as compared to stainless steel in D tower.

According to Polo et al. (2002) stainless steel forms a passive film which Bastidas et al. (2002) found to be a mixture of iron and chromium oxides, with hydroxide and water containing compounds concentrated in the outer region of the film and the metal film interface is chromium oxide. According to Bastidas et al. (2002) and Stellwag (1998), this film protects the stainless steel from corrosion. Furthermore, in order to improve the resistance of the metal to pitting corrosion, the stainless steel forms a film which is less susceptible to penetration by aggressive anions. Rading (2007) report that stainless steels are resistant to corrosion as they contain at least 12 % chromium which on contact with air forms a thin impervious layer of chromium oxide. He states that the oxide protects the stainless steel from further attack and since austenitic stainless steel contains nickel, it increases its corrosion resistance.

Table 4.4: Corrosion rates of different metal coupons exposed to different environments of D tower for three months

Metal	**Corrosion rate (milli inches / year)**	
	Ozone treated water	**Chemically treated water**
Brass	1.531	1.079
Mild steel	2.098	1.550
Stainless steel	0.000	0.000

From Table 4.4 above mild steel experienced a higher corrosion rate in ozonated water than in chemically treated water, the same trend was also observed with brass (see appendix B, figure B3). Stainless steel did not show any signs of corrosion in either environment. The results reveal that mild steel is the most vulnerable metal to corrosion followed by brass and lastly stainless steel under both conditions. Comparing the corrosion rates for two different environments in D tower, ozone exposed coupons had higher corrosion rates compared to chemically treated water.

4.2 Scale characterization

The scales were qualitatively analysed using the XRD and TGA and AAS was attempted to analyse the scale quantitatively. The results obtained from the experiments are shown and discussed in this section.

4.2.1 Scale from air- side of heat exchanger

The purpose of characterizing this scale was to obtain a base case for the nature of corrosion scale in the absence of either chemically treated or ozone treated water.

The scale from the air side of heat exchanger is independent of cooling water and it consists of iron compounds. The scale is not influenced by chemicals nor ozone treated water and iron is indicative of presence of corrosion from the metal as discussed by Shakkthivel et al. (2004).

4.2.1.1 XRD results for the scale from the air side of a heat exchanger

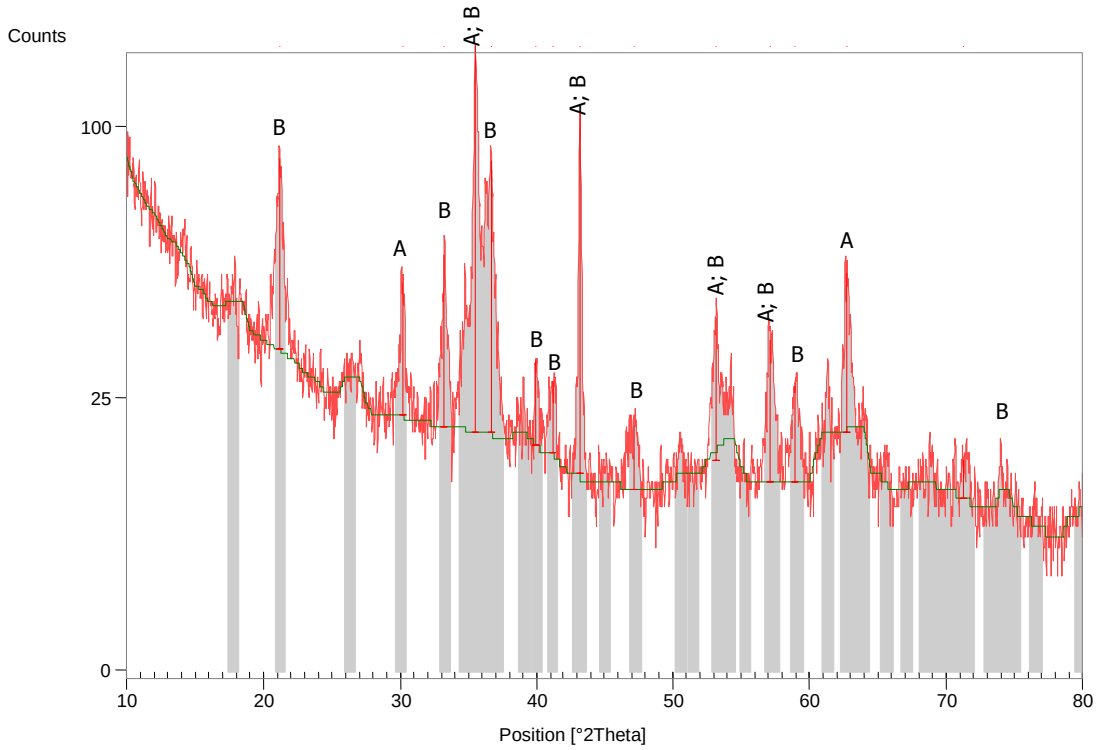


Figure 4.3: Graph showing the components of scale from the air side of a heat exchanger; A zinc iron oxide, B goethite

The scale from the heat exchanger was reddish brown in colour which could be attributed to the presence of iron. The figure above (Figure 4.3), shows that the scale from the heat exchanger consisted of A, (zinc iron oxide, $ZnFe_2O_4$), and B, (goethite, Fe + 3O (OH). According to Valenzuela et al. (2002) the XRD pattern for the samples of $ZnFe_2O_4$ has a pattern similar to the one depicted in Figure 4.3.

According to Revie and Uhlig (2008) zinc in copper-zinc alloys dissolve from the alloy through a surface diffusion mechanism and can be detected in solutions. According to Betancur et al. (2004) goethite is one the most common products of corrosion of iron and steel and therefore its presence in the scale indicates that corrosion occurred.

4.2.1.2 TGA results for the scale from the air side of a heat exchanger

Since the TGA curves were difficult to interpret, the data from the proximate analysis was used to draw averaged derivative graphs (see data appendix D). The thermograms have inverse peaks since the gradients of the TGA curves are negative, which means the change in y is negative. In some areas the graph is steeper and this is because there is higher mass loss occurring within a small temperature change. At the peak, the gradient is zero which indicates that there was no or insignificant mass loss.

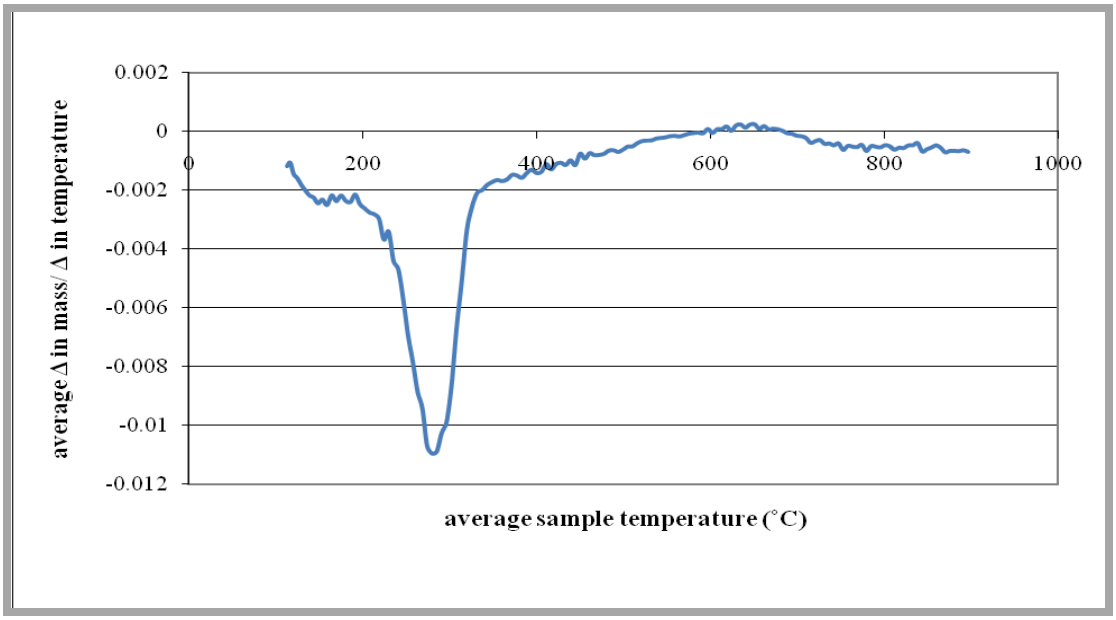


Figure 4.4: Derivative graph for scale sample from the air side of the heat exchanger

According to the thermogram, which is endothermic, there are distinct peaks at 158 °C and 280 °C which is the highest. The first peak at about 158°C is attributed to the removal of adsorbed water. The second peak at 280°C according to Prasad et al. (2006) and Laskou (2006) is due to the dehydration of goethite which starts at 200°C and ends at 360°C. This is in agreement with the XRD results depicted in Figure 4.3 where goethite was detected.

4.2.2 Scale from the chemically treated cooling water

The scale was collected from the cooling tower packing and the backwash from the sand filter and the water in these two environments was chemically treated.

4.2.2.1 XRD scale results from cooling tower packing

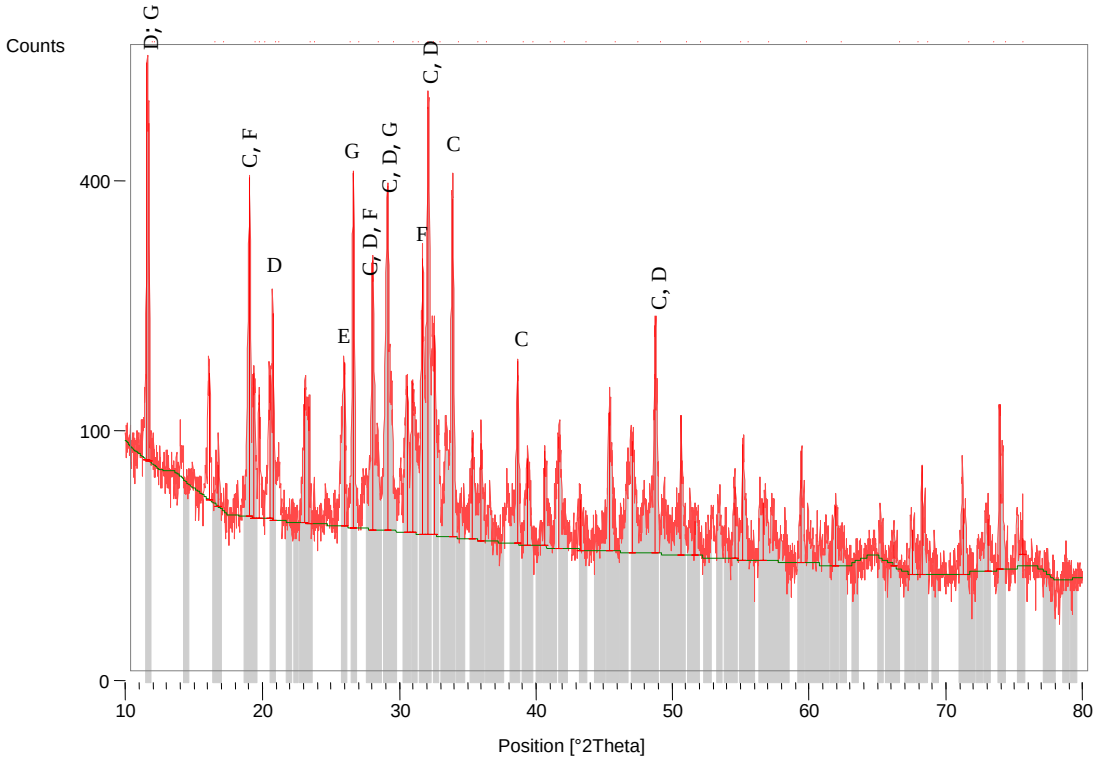


Figure 4.5: Scale components from the cooling tower packing (chemically treated water)

Figure 4.5 above shows that the scale from cooling tower packing had lots of compounds since it is chemically treated. The scale was whitish in colour. The analysis revealed that among the compounds are C, (thernadite, Na_2SO_4), D, (gypsum, $CaSO_4\,2H_2O$), E, (sodium phosphate, $(Na\,PO_3)_6$), F, (potassium iron oxide, $KFeO_2$) and G, (purpurin hydrate, $C_{14}H_8O_5H_2O$).The highest peaks are for the gypsum and purpurin hydrate and the second highest is for thernadite and gypsum. Purpurin hydrate may be indicative of presence of biomass in the sample.

4.2.2.2 TGA scale results from the cooling tower packing

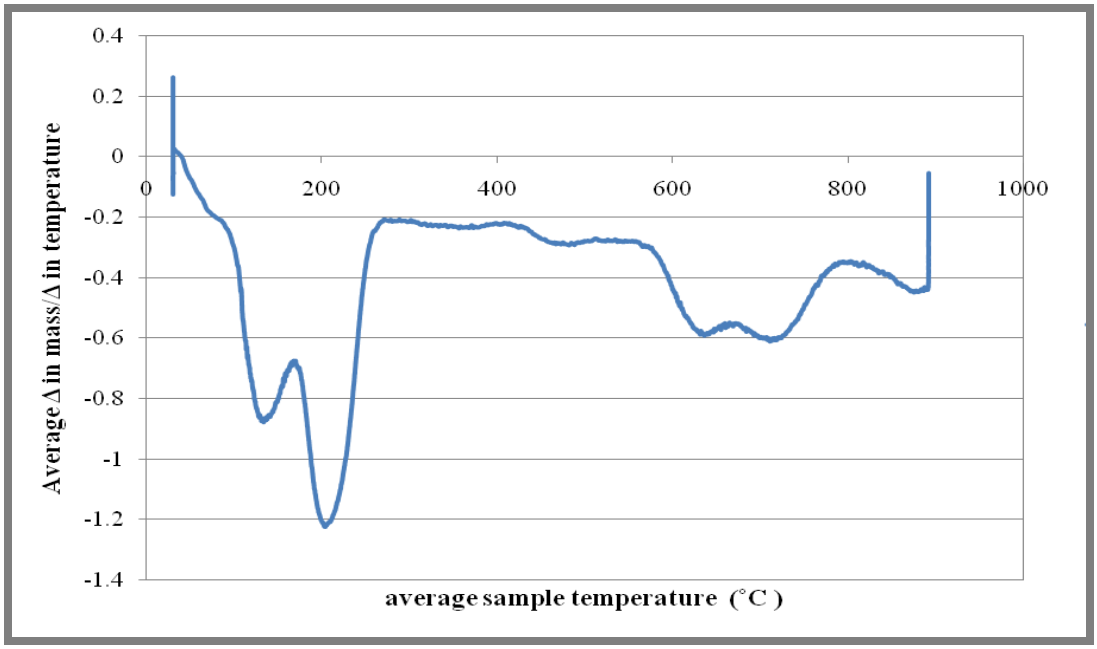


Figure 4.6: Derivative graph for scale sample from the cooling tower packing

The results from the thermogram shows peaks at 126 °C, 197 °C, 472 °C, 622 °C, 703 °C and lastly at 876 °C. According to Adams et al. (1992) hygroscopic water

and hemihydrate water from gypsum is lost between 60 °C and 200 °C which account for the peaks at 126 °C and 197 °C respectively. According to Plante et al. (2009) dehydration of gypsum occurs at 115 °C. Peaks for the release of water, carbon dioxide and SO_x from the compounds are observed at 450 °C according to Warne and Bubrawski (1989) which explains the peak at 472 °C. The peaks above 600 °C may be due to oxidation of the biomass.

4.2.2.3 XRD scale results from sand filter backwash

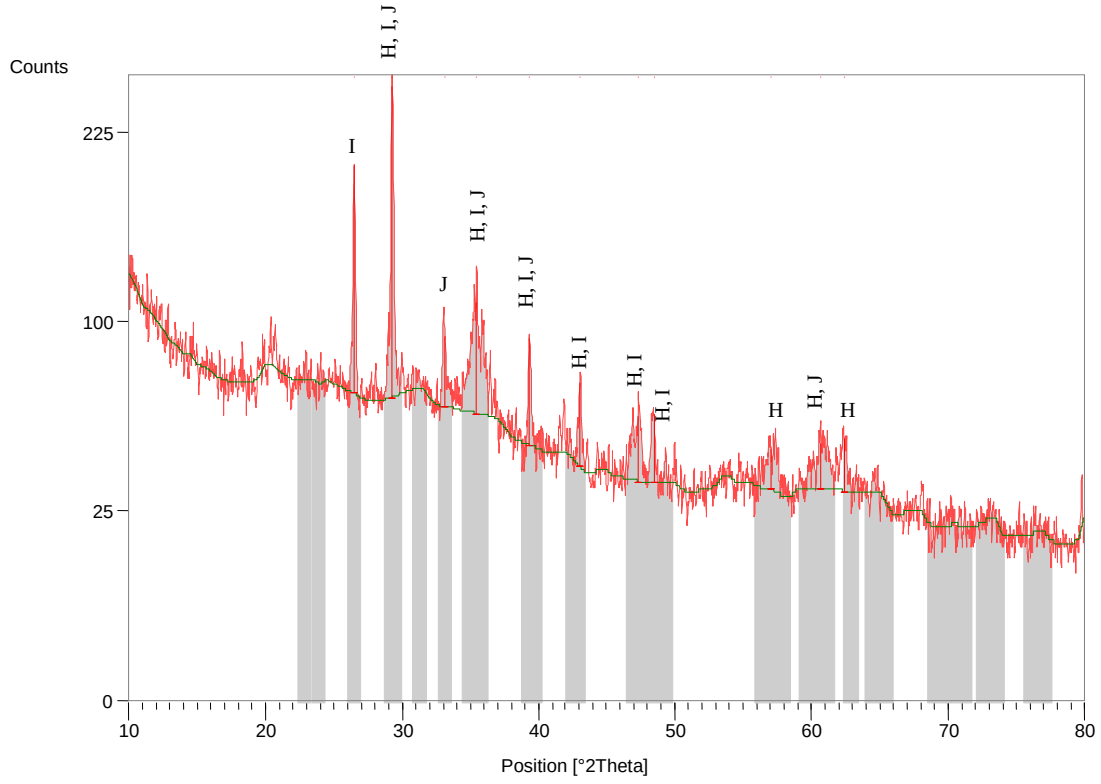


Figure 4.7: X - ray diffraction pattern showing components of the sand filter backwash scale (chemically treated water)

From the x - ray diffraction pattern, Figure 4.7, it is indicated that the sand filter backwash scale is composed of H, (calcite, $CaCO_3$), I, (calcium oxide, CaO) and J,

(calcium iron oxide, CaOFeO2). According to Rice and Wilkes (1994) carbon dioxide occurs naturally in water and it reacts to produce carbonates and carbonic acid. During ozonation, the solution is stripped of carbon dioxide and the pH of the solution increases which in turn increases the concentration of carbonate ions. As a result of the evaporation of water, calcium ions are concentrated up in the recirculating cooling water (Rice and Wilkes, 1994; Xyla et al., 1992) so that calcium carbonate precipitates (Brandt et al., 2006; Rice and Wilkes, 1994). According to Shakkthivel et al. (2004) iron ions found in the scale are due to corrosion and they are leached out into the solution that will undergo precipitation.

4.2.2.4 TGA scale results from the sand filter backwash

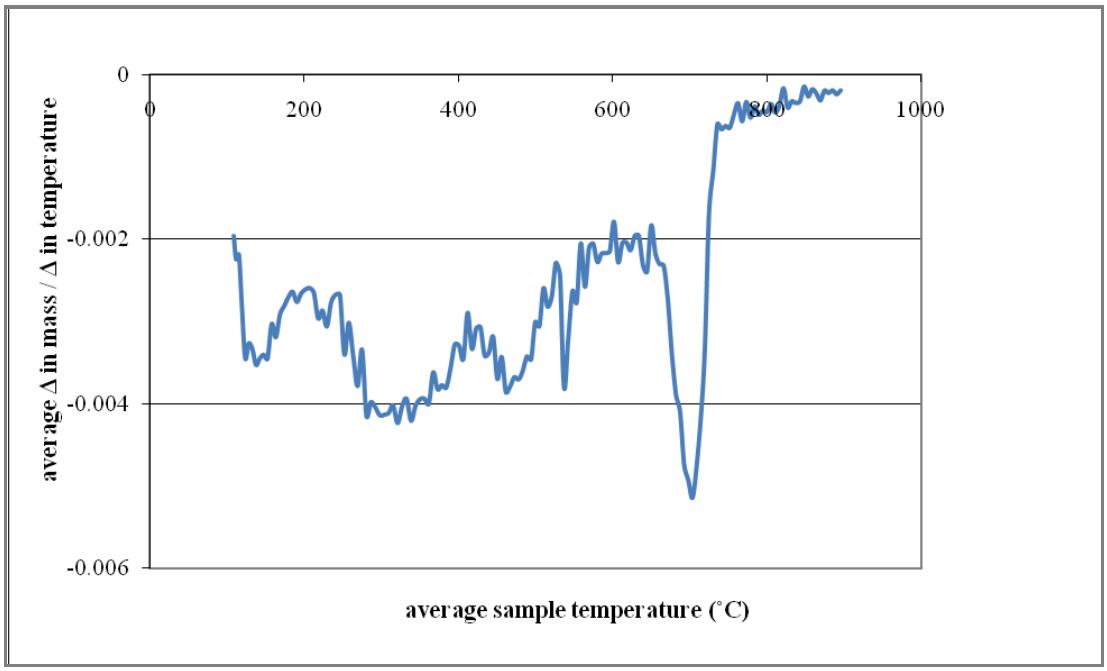


Figure 4.8: Derivative graph for scale sample from the sand filter backwash

The data was averaged and the graph is depicted in Figure 4.8 above. All of the peaks in this graph are an order of magnitude smaller than the peaks in the other TGA graphs. This is why the derivative curve is so noisy. According to the graph, there are extremely small peaks at 138 °C, 330 °C, 461 °C, 537 °C and the highest peak was observed at 753 °C. According to Plante et al. (2009) and Sørensen et al. (2000) calcite decomposes in the temperature range from 750 °C to 990 °C.

4.2.3 Scale from ozone treated cooling water

The scale was collected from two different points; the chiller heat exchanger and the cooling tower packing which were ozone treated environments.

4.2.3.1 XRD scale results from the chiller heat exchanger

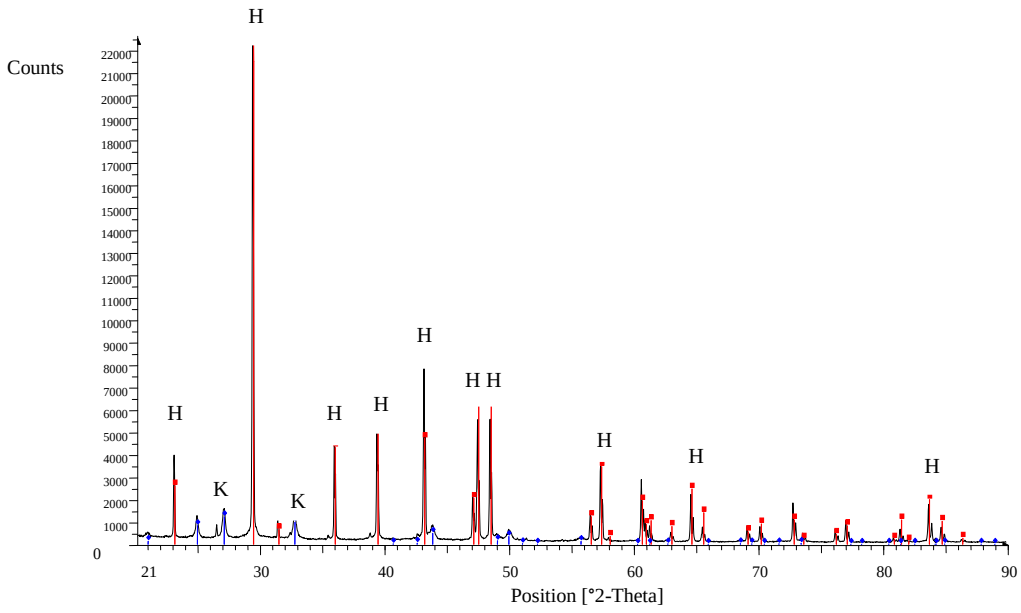


Figure 4.9: X - ray diffraction pattern showing components of the chiller heat exchanger

The x-ray diffraction pattern from the chiller heat exchanger shows that the scale is composed of calcite ($CaCO_{3,}$) denoted H in figure 4.9 and vaterite, K, ($CaCO_3$). The highest peak is identified to be calcite and vaterite is mainly small peaks. According to Rao, (1973) and Falini et al. (1998) calcium carbonate can be precipitated as three crystalline phases: calcite, aragonite and vaterite. Calcite is the most stable while the vaterite is the least stable of the polymorphs and it is formed at temperatures below 30 °C (Rao, 1973; Turnbull, 1973; Chen and Xiang, 2009; Ogino et al., 1987). This is confirmed by the results since this is a chiller unit which operates at lower temperatures. Ogino et al. (1987) and Kralj et al. (1990) state that vaterite is the most soluble and it transforms easily and irreversibly into calcite at 40 °C when in contact with water and it is the first solid phase of calcium carbonate scale formation. This explains the results in Figure 4.9 above as calcite is the predominant component.

4.2.3.2 TGA scale results from the chiller heat exchanger

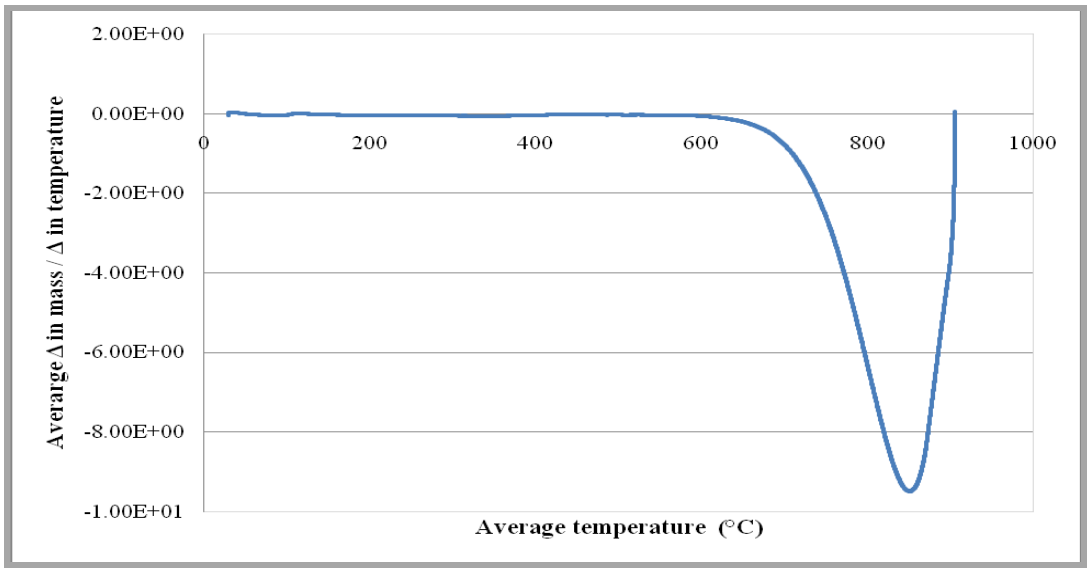


Figure 4.10: Derivative graph for scale sample from the chiller heat exchanger

The results shows that there is only one large peak at 855 °C. According to XRD results, the chiller unit scale is composed of calcite and vaterite. According to Turnbull (1973) vaterite is converted to calcite at 490 °C with no mass loss, while calcite decomposes at temperatures between 750 °C and 990 °C (Plante et al., 2009 and Sørensen et al., 2000). In this curve no mass loss is observed until the single peak at 855 °C. Thus the vaterite is converted to calcite at 490 °C (no mass loss) and then the calcite decomposes at 855 °C .

4.2.3.3 XRD scale results from the cooling tower packing

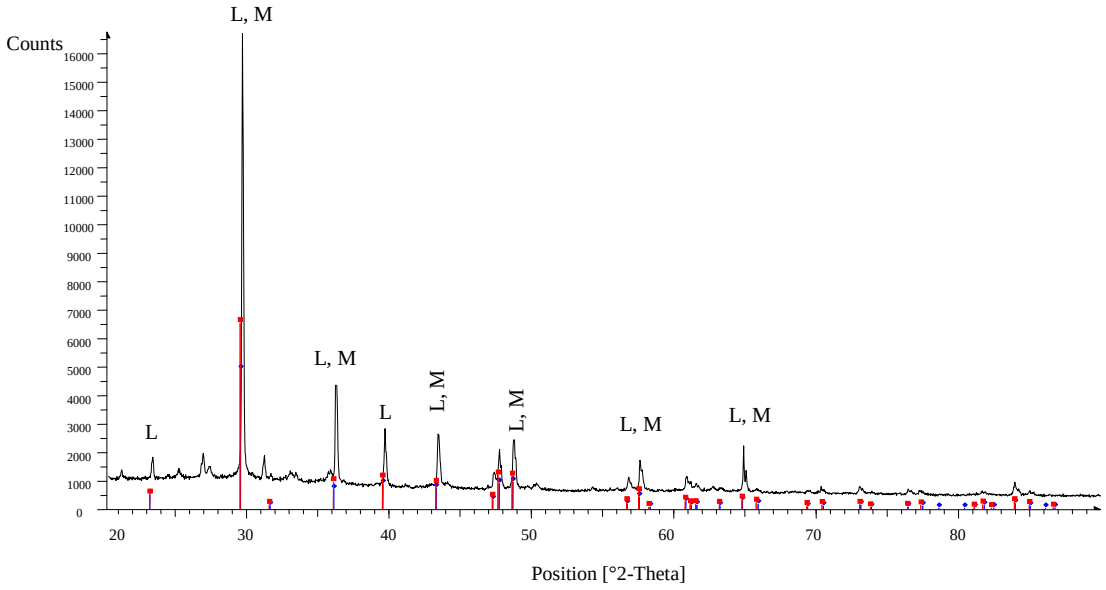


Figure 4.11: X - ray diffraction pattern showing components of the cooling tower packing scale

The x- ray diffraction pattern shows that the D tower scale is composed of mainly calcium carbonate, L, and magnesium calcite, M. The highest peak is the calcium carbonate and the magnesium calcite is identified in small peaks. Magnesium which is used as a corrosion inhibitor can react with carbon dioxide, normally as hydrogen carbonate, which causes carbonate hardness of the water (Brandt et al., 2006). Rice and Wilkes (1994) in their literature reported that even though magnesium ions cannot be oxidized by ozone, the secondary products of ozone treatment can result in insoluble calcium salts which could be the reason for the presence of calcium carbonate in the scale. Further, Nancollas et al. (1982) stated that the presence of magnesium ions tends to inhibit the formation of calcite, preferentially forming magnesium calcite, which is in accordance with the XRD results.

In their study, Nancollas et al. (1982) reported that most surface water, which in this study is water from the Vaal River, contains high concentrations of calcium ions. In addition, calcium carbonate is one of the more important scale forming minerals and this is supported by the results as most of the scale analysed contains the same.

4.2.3.4 TGA results for the scale from the cooling tower packing

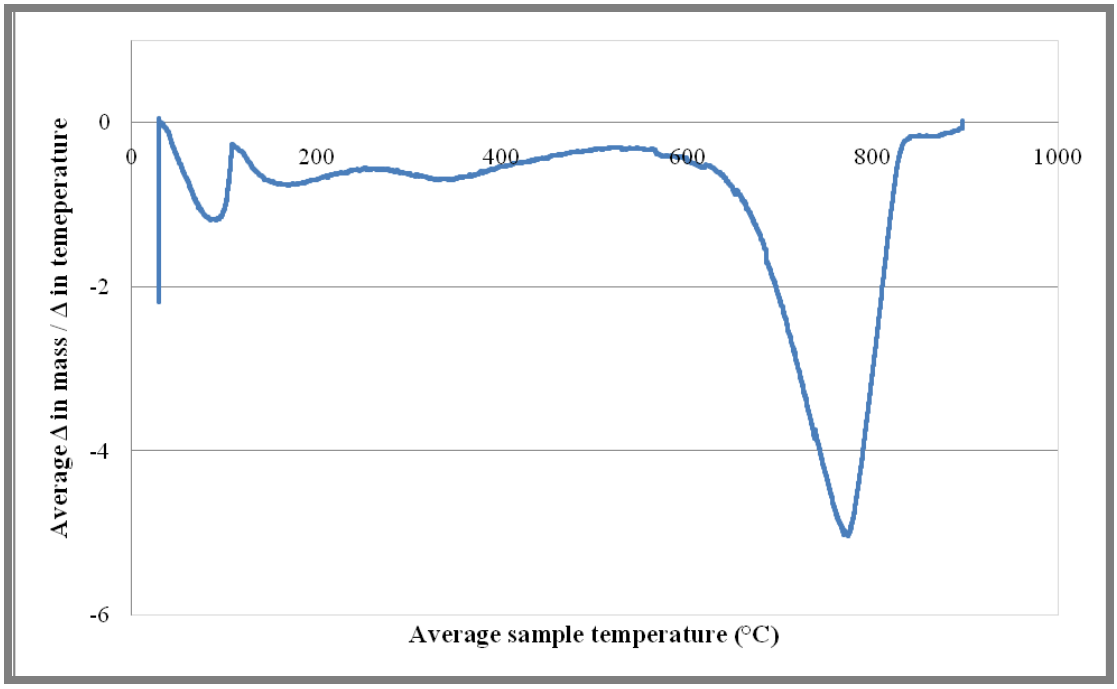


Figure 4.12: Derivative graph for scale sample from the cooling tower packing

The D tower scale is composed of calcium carbonate and magnesium calcite. There are small peaks at 85 °C, 158 °C, 320 °C and a large peak at 765 °C. Adsorbed water is lost at temperatures below 120 °C (Biscontin et al., 2002) explaining the peak at 85 °C. We are not certain what the peaks at 158 °C and 350 °C are due to. According to Pope and Judd (1977) the decomposition of calcium carbonate occurs at 700 °C in air and Biscontin et al. (2002) reported that the loss of carbon dioxide from carbonate occurs at 792 °C.

4.2.4 Atomic Absorption Spectrophotometry

The scale cannot be quantitatively verified using AAS and discussed, as the scale did not dissolve completely in the presence of acid possibly due to the presence of biomass fragments. However after filtering the solutions, the presence of some of the metals detected by XRD were confirmed. According to the XRD results the scale from the heat exchanger is made up of zinc iron oxide and goethite. The cooling tower scale was made up of thernadite, gypsum, sodium phosphate, potassium iron oxide and purpurin hydrate. According to the results from the AAS, see appendix E, the scale from the heat exchanger had high concentrations of zinc followed by sodium, iron and lastly potassium, and for the cooling tower packing scale, the results revealed that sodium, potassium and iron are present in the scale. There was no zinc detected in this sample. The results are in agreement with the XRD results which indicated that the scale was made up of mainly sodium compounds. For the sand filter backwash scale sample, the results confirmed the presence of iron. AAS cannot be used to determine calcium ions.

In summary, the scale from the sand filter backwash, which is chemically treated, is composed of calcium compounds and iron ions while the scale from the heat exchanger which is ozone treated water, consists of calcite and vaterite. The calcium is naturally found in water while the iron ions from the chemically treated sand filter backwash are due to corrosion and they are leached out into the solution. The scale from the cooling tower packing which is chemically treated is composed of a range of compounds, namely; thernadite, gypsum, sodium phosphate, potassium iron oxide and purpurin hydrate. The sodium, potassium, sulphate and phosphate ions are from the chemicals dosed into the plant cooling system. It is evident that there is corrosion as the scale contains iron ions.

The scale from the same cooling tower packing, with same water quality but treated with ozone, comprises of calcium carbonate and magnesium calcite alone which are contributed by the water quality. No iron ions were detected.

5.0 CHAPTER 5: CONCLUSION

Corrosion rates of different metals exposed to cooling water of different qualities were researched in this report. The following conclusions can be made from the research work:

5.1 Corrosion rates

From the visual inspection, it is evident that

- Mild steel is susceptible to corrosion followed by brass and lastly stainless steel in both water systems as it showed pitting corrosion in the K501 environment throughout the entire experiment.

- Water quality influences the rate of the corrosion of metals. The water quality in the two cooling water circuits is different, K501 is effluent from another plant while D tower is from the river and the corrosion observed from these is different, especially for brass.

- Corrosion rates observed in the D tower, ozone treated environment, exhibited higher corrosion rates for different metal coupons, brass has a corrosion rate of 1.531 g/milliinches/yr in ozone treated water while that of mild steel is 2.098 g/milliinches/yr and in chemically treated water the corrosion rate is 1.079 g/milliinches/yr and 1.550 g/milliinches/yr respectively, than for the same system when the water was chemically treated and it can be concluded that ozone does not suppress corrosion in water with heavy chemical load.

- Lower corrosion rates were measured for pretreated mild steel (1.829 g/milliinches/yr in K501 at two months) compared to untreated mild steel (2.486

g/milliinches/yr in K501 at two months of exposure time) in all conditions which implies that pretreating mild steel improves the corrosion resistance of the material.

- When calculating the corrosion rate, the use of either a measured surface area of the corrosion coupon or a calculated surface area gave similar results.

5.2 Scale identification

Scale was collected from various points in the cooling system (as shut downs permitted) under different operating conditions and the XRD was used to identify them. As water is being cooled in the cooling towers, the dissolved solids become concentrated and when they reach the solubility limit they precipitate out of solution and consequently form scale deposits in the components. These are the observations;

- Scale from the heat exchanger was reddish in colour and it consists of zinc iron oxide and goethite. The iron in these compounds could be a contributory factor to the colour of the scale. Literature shows that the presence of goethite confirms the occurrence of corrosion. This sample was from the air side of a heat exchanger which shows normal corrosion without any influence from ozone or chemicals in treated water.

- From the cooling tower scale, thernadite, gypsum, sodium phosphate, potassium iron oxide and purpurin hydrate were identified. Purpurin hydrate indicates the presence of biomass. The diverse range of cations and anions are an indication of the chemicals dosed into the water during chemical treatment.

- The scale from the sand filter backwash is composed of calcite, calcium oxide, and calcium iron oxide.

- Scale from the chiller unit and D tower, which are ozone treated, had calcium carbonate as the main components which according to literature is the main salt dissolved in natural water (Rice and Wilkes, 1994).

- Results from the TGA are in support of those found using the XRD.

- The conclusion of the research is that ozone treated water does not contribute directly to scaling while chemical treatment does.

6.0 CHAPTER 6: RECOMMENDATIONS AND FUTURE WORK

The corrosion rates of metals used in the experiment revealed that stainless steel is not susceptible to corrosion and therefore it can be recommended for use in the construction of cooling water systems.

For future work, it is recommended that same water quality be used, that is either water from the Vaal River or water from the main treatment plant can be used to compare ozone and chemical treatment of the water. ICP can be used in quantitative analysis of the scale samples in order to determine wider range of elements. Instead of using visual inspection alone to characterise the type of corrosion other techniques like optical microscopy can be used.

7.0 CHAPTER 7: REFERENCES

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APPENDIX A: CORROSION RATE CALCULATIONS

1 m = 1000 mm

1 mm = 0.0254 m

1 inch = 1000 minches

g/milliinches/yr: $V_{u\ X}$ (1 kg/1000g) x (1000mm/m)^2 x (1000minches/1 inch) x (1 inch/ 0.0254m)

Metal and place of exposure	**Exposure period, (weeks)**	**Change in mass (g)**	**Calculated surface area (mm^2)**	**Calculated corrosion rate (g/mm^2)**	**Calculated corrosion rate ($g/mm^2/wk$)**	**Calculated corrosion rate (g/milli inches/yr)**
B, D tower	1	0.002	2265	8.829E-07	8.829E-07	0.211
B, K 501	1	0.013	2337	5.562E-06	5.562E-06	1.329
B, D tower	2	0.004	2305	1.735E-06	8.675E-07	0.207
B, K 501	2	0.017	2233	7.612E-06	3.806E-06	0.910
B, D tower	3	0.001	2244	4.456E-07	1.485E-07	0.036
B, K 501	3	0.029	2351	1.234E-05	4.112E-06	0.983
B, K 501	4	0.036	2311	1.558E-05	3.895E-06	0.931

B, D tower	4	0.003	2268	1.323E-06	3.307E-07	0.079
B, K 501	8	0.056	2327	2.407E-05	3.008E-06	0.719
B, D tower	8	0	2239	0	0	0
B, K 501	12	0.04	2324	1.721E-05	1.434E-06	0.343
B, D tower	12	0.122	2252	5.417E-05	4.515E-06	1.079

Table A1 Corrosion rates of brass (B) using calculated surface areas

Metal and place of exposure	**Exposure period, (weeks)**	**Change in mass (g)**	**Measured surface area (mm^2)**	**Calculated corrosion rate (g/mm^2)**	**Calculated corrosion rate ($g/mm^2/wk$)**	**Calculated corrosion rate (g/milli inches/yr)**
B, D tower	1	0.002	2232	8.962E-07	8.962E-07	0.214
B, K 501	1	0.013	2243	5.796E-06	5.796E-06	1.385
B, D tower	2	0.004	2321	1.724E-06	8.618E-07	0.206
B, K 501	2	0.017	2207	7.704E-06	3.852E-06	0.921

B, D tower	3	0.001	2227	4.491E-07	1.497E-07	0.036
B, K 501	3	0.029	2248	1.290E-05	4.300E-06	1.028
B, K 501	4	0.036	2264	1.590E-05	3.975E-06	0.950
B, D tower	4	0.003	2264	1.325E-06	3.313E-07	0.079
B, K 501	8	0.056	2253	2.486E-05	3.107E-06	0.743
B, D tower	8	0	2244	0	0	0
B, K 501	12	0.04	2244	1.782E-05	1.485E-06	0.355
B, D tower	12	0.122	2250	5.423E-05	4.520E-06	1.080

Table A2 Corrosion rates of brass (B) using measured surface areas

Metal and place of exposure	**Exposure period, (weeks)**	**Change in mass (g)**	**Calculated surface area (mm^2)**	**Calculated corrosion rate (g/mm^2)**	**Calculated corrosion rate ($g/mm^2/wk$)**	**Calculated corrosion rate (g/milli inches/yr)**
M, K 501	1	0.026	2323.5	1.119E-05	1.12E-05	2.918
MP, D tower	1	0.016	2238.64	7.1472E-06	7.15E-06	1.864
M, D tower	1	0.018	2268.02	7.9364E-06	7.94E-06	2.070
MP, K 501	1	0.033	2246.65	1.4689E-05	1.47E-05	3.831
M, K 501	2	0.047	2257.34	2.0821E-05	1.04E-05	2.715
M, D tower	2	0.024	2270.69	1.0569E-05	5.28E-06	1.378
MP, D tower	2	0.027	2257.34	1.1961E-05	5.98E-06	1.560
MP, K 501	2	0.038	2284.05	1.6637E-05	8.32E-06	2.169
MP, K 501	3	0.039	2230.62	1.7484E-05	5.83E-06	1.520
M, K 501	3	0.051	2278.7	2.2381E-05	7.46E-06	1.946
M, D tower	3	0.024	2254.66	1.0645E-05	3.55E-06	0.925

MP, D tower	3	0.035	2219.94	1.5766E-05	5.26E-06	1.371
M, K 501	4	0.111	2292.06	4.8428E-05	1.21E-05	3.157
MP, K 501	4	0.089	2366.85	3.7603E-05	9.4E-06	2.452
M, D tower	4	0.045	2308.09	1.9497E-05	4.87E-06	1.271
MP, D tower	4	0.042	2324.11	1.8071E-05	4.52E-06	1.178
MP, K 501	8	0.124	2209.56	5.612E-05	7.01E-06	1.829
M, K 501	8	0.165	2163.85	7.6253E-05	9.53E-06	2.486
MP, D tower	8	0.08	2249.32	3.5566E-05	4.45E-06	1.159
M, D tower	8	0.088	2276.03	3.8664E-05	4.83E-06	1.260
M, D tower	12	0.16	2243.98	7.1302E-05	5.94E-06	1.550

Table A3 Corrosion rates of mildsteel (M) and pretreated mildsteel (MP) using calculated surface areas

Metal and place of exposure	**Exposure period, (weeks)**	**Change in mass (g)**	**Measured surface area (mm^2)**	**Calculated corrosion rate (g/mm^2)**	**Calculated corrosion rate ($g/mm^2/wk$)**	**Calculated corrosion rate (g/milli inches/yr)**
M, K 501	1	0.026	2262.14	1.1494E-05	1.15E-05	2.997
MP, D tower	1	0.016	2249.59	7.1124E-06	7.11E-06	1.855
M, D tower	1	0.018	2330.23	7.7246E-06	7.72E-06	2.015
MP, K 501	1	0.033	2215.52	1.4895E-05	1.49E-05	3.885
M, K 501	2	0.047	2218.8	2.1183E-05	1.06E-05	2.762
M, D tower	2	0.024	2263.07	1.0605E-05	5.3E-06	1.383
MP, D tower	2	0.027	2223.11	1.2145E-05	6.07E-06	1.584
MP, K 501	2	0.038	2289.01	1.6601E-05	8.3E-06	2.165
MP, K 501	3	0.039	2236.33	1.7439E-05	5.81E-06	1.516
M, K 501	3	0.051	2330.99	2.1879E-05	7.29E-06	1.902

M, D tower	3	0.024	2235.41	1.0736E-05	3.58E-06	0.933
MP, D tower	3	0.035	2182.53	1.6036E-05	5.35E-06	1.394
M, K 501	4	0.111	2244.85	4.9447E-05	1.24E-05	3.224
MP, K 501	4	0.089	2298.47	3.8721E-05	9.68E-06	2.525
M, D tower	4	0.045	2266.07	1.9858E-05	4.96E-06	1.295
MP, D tower	4	0.042	2298.48	1.8273E-05	4.57E-06	1.191
MP, K 501	8	0.124	2185.62	5.6734E-05	7.09E-06	1.850
M, K 501	8	0.165	2116.48	7.796E-05	9.74E-06	2.541
MP, D tower	8	0.08	2235.4	3.5788E-05	4.47E-06	1.167
M, D tower	8	0.088	2287.49	3.847E-05	4.81E-06	1.254
M, D tower	12	0.16	2254.08	7.0982E-05	5.92E-06	1.543

Table A4 Corrosion rates of mildsteel (M) and pretreated mildsteel (MP) using measured surface areas

Metal and place of exposure	Exposure period, (weeks)	Change in mass (g)	Calculated surface area (mm^2)	Calculated corrosion rate (g/mm^2)	Calculated corrosion rate ($g/mm^2/wk$)	Calculated corrosion rate (g/milli inches/yr)
SS, D tower	1	0.003	2214.6	1.35465E-06	1.355E-06	0.347
SS, K 501	1	0.004	2260.01	1.7699E-06	1.770E-06	0.453
SS, D tower	2	0.002	2318.77	8.62526E-07	4.313E-07	0.110
SS, K 501	2	0.002	2305.42	8.67521E-07	4.338E-07	0.111
SS, D tower	3	0	2398.9	0	0	0
SS, K 501	3	0.003	2318.77	1.29379E-06	4.313E-07	0.110
SS, D tower	4	0.001	2377.54	4.20603E-07	1.052E-07	0.027
SS, K 501	4	0.001	2174.54	4.59867E-07	1.150E-07	0.029
SS, D tower	8	0.004	2348.15	1.70347E-06	2.129E-07	0.054
SS, K 501	8	0	2294.73	0	0	0

SS, D tower	12	0	2209.26	0	0	0
SS, K 501	12	0.003	2345.48	1.27906E-06	1.066E-07	0.027

Table A5 Corrosion rates of stainless steel (SS) using calculated surface areas

Metal and place of exposure	**Exposure period, (weeks)**	**Change in mass (g)**	**Measured surface area (mm^2)**	**Calculated corrosion rate (g/mm^2)**	**Calculated corrosion rate ($g/mm^2/wk$)**	**Calculated corrosion rate (g/milli inches/yr)**
SS, D tower	1	0.003	2159.35	1.38931E-06	1.389E-06	0.356
SS, K 501	1	0.004	2194.85	1.82245E-06	1.822E-06	0.466
SS, D tower	2	0.002	2222.51	8.99883E-07	4.499E-07	0.115
SS, K 501	2	0.002	2232.02	8.96049E-07	4.480E-07	0.115
SS, D tower	3	0	2279.56	0	0	0
SS, K 501	3	0.003	2206.49	1.35963E-06	4.532E-07	0.116
SS, D tower	4	0.001	2267.93	4.40931E-07	1.102E-07	0.028

SS, K 501	4	0.001	2091.26	4.78181E-07	1.195E-07	0.031
SS, D tower	8	0.004	2260.45	1.76956E-06	2.212E-07	0.057
SS, K 501	8	0	2246.64	0	0	0
SS, D tower	12	0	2144.58	0	0	0
SS, K 501	12	0.003	2294.5	1.30747E-06	1.090E-07	0.028

Table A6 Corrosion rates of stainless steel (SS) using measured surface areas

APPENDIX B: CORROSION RATE GRAPHS

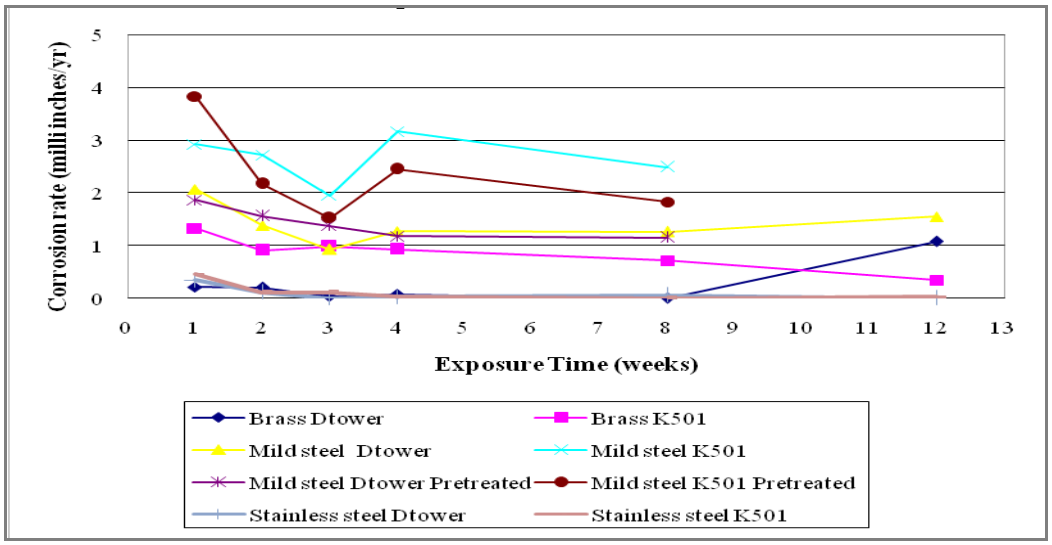


Figure B1 Graph of corrosion rates using calculated surface area for coupons exposed to both ozone and chemical treated cooling water system

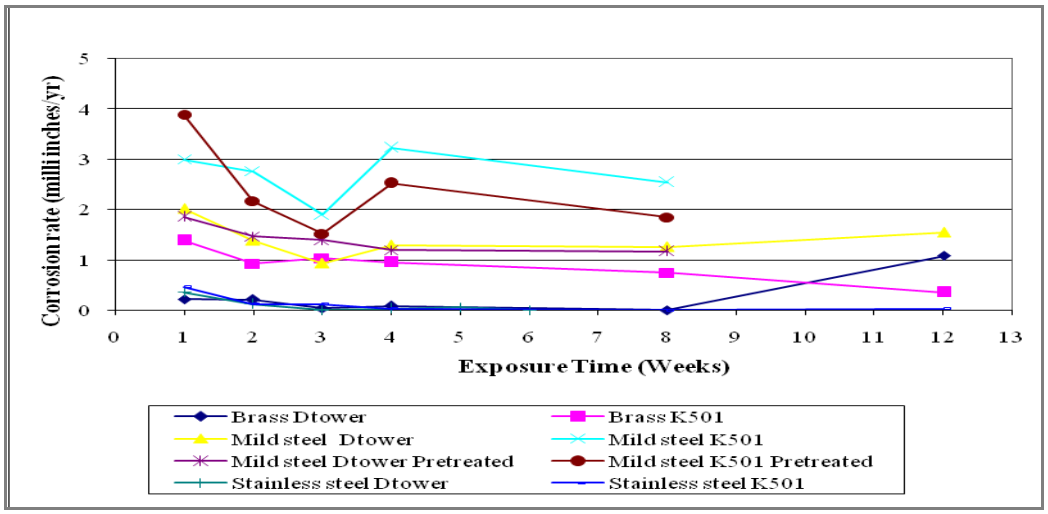


Figure B2 Graph showing corrosion rates using measured surface area

The graphs in appendix B shows that mild steel (both pretreated and untreated) in K501 experienced the highest corrosion rate for the whole period of study in both the measured and calculated surface area graphs followed by brass in K501, then brass in D tower and lastly stainless steel. The brass in D tower had higher corrosion rates for 2, 4 and 12 weeks. There was a drop in corrosion rate for brass in K501 at the end of the study period while the corrosion rate of brass coupon in the D tower loop decreased steadily except for the rate measured after 12 weeks which was higher than all the other readings.

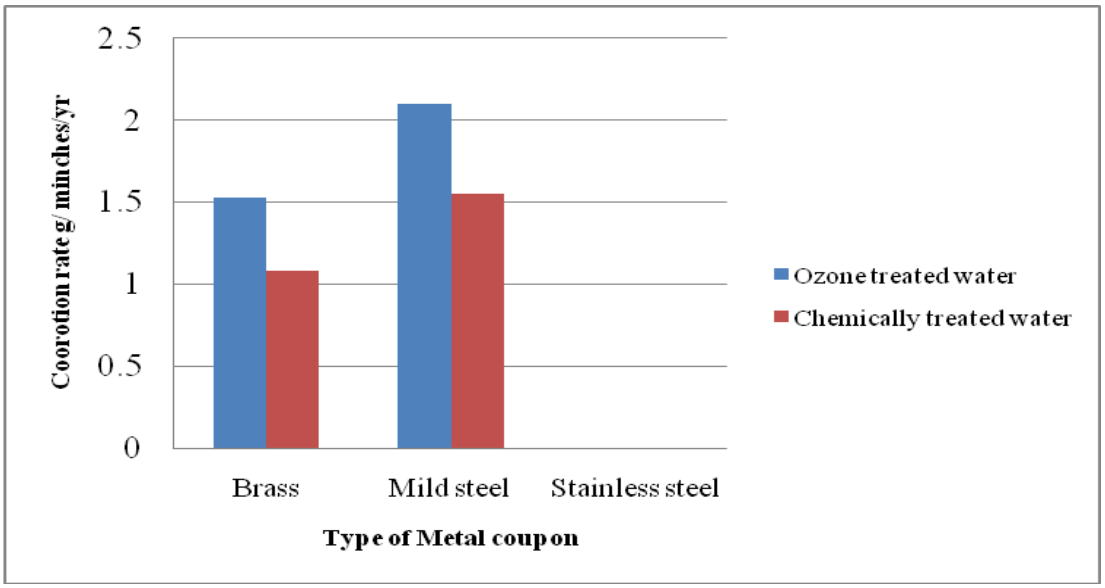


Figure B3: Graph showing corrosion rates of different metal coupons exposed to chemically and ozone treated water in D tower for three months

From figure B3 above, brass experienced higher corrosion rates followed by mildsteel and then lastly stainless steel in all D tower environments.

APPENDIX C: CORROSION RATES DEVIATIONS

Table C1 calculation of deviations using corrosion rates

Metal, exposure period (weeks)	**Corrosion rate using measured surface area (milli inches/ yr)**	**Corrosion rate using calculated surface area (milli inches/yr)**	**Average**	**Deviation**
Brass D tower week 1	0.214	0.211	0.2125	0.00096
Brass D tower week 2	0.206	0.207	0.2065	0.00032
Brass D tower week 3	0.036	0.035	0.0355	0.00032
Brass D tower week 4	0.079	0.079	0.079	0
Brass D tower week 8	0	0	0	0
Brass D tower week 12	1.08	1.079	1.0795	0.00032
Brass K 501 week 1	1.385	1.329	1.357	0.01792
Brass K 501 week 2	0.921	0.91	0.9155	0.00352
Brass K 501 week 3	1.028	0.983	1.0055	0.0144
Brass K 501 week 4	0.95	0.931	0.9405	0.00608
Brass K 501 week 8	0.743	0.719	0.731	0.00768
Brass K 501 week 12	0.355	0.343	0.349	0.00384
Mildsteel D tower week 1	2.014	2.07	2.042	0.01792
Mildsteel D tower week 2	1.384	1.378	1.381	0.00192
Mildsteel D tower week 3	0.934	0.925	0.9295	0.00288
Mildsteel D tower week 4	1.295	1.271	1.283	0.00768
Mildsteel D tower week 8	1.254	1.26	1.257	0.00192
Mildsteel D tower week 12	1.543	1.55	1.5465	0.00224
Mildsteel K 501 week 1	2.997	2.918	2.9575	0.02528
Mildsteel K 501 week 2	2.762	2.715	2.7385	0.01504

Mildsteel K 501 week 3	1.902	1.946	1.924	0.01408
Mildsteel K 501 week 4	3.224	3.158	3.191	0.02112
Mild steel K 501 week 8	2.541	2.486	2.5135	0.0176
Mildsteel D tower Pretreated week 1	1.855	1.864	1.8595	0.00288
Mildsteel D tower Pretreated week 2	1.467	1.56	1.5135	0.02976
Mildsteel D tower Pretreated week 3	1.394	1.371	1.3825	0.00736
Mildsteel D tower Pretreated week 4	1.191	1.178	1.1845	0.00416
Mildsteel D tower Pretreated week 8	1.167	1.153	1.16	0.00448
Mildsteel K501 Pretreated week 1	3.883	3.831	3.857	0.01664
Mildsteel K501 Pretreated week 2	2.165	2.17	2.1675	0.0016
Mildsteel K501 Pretreated week 3	1.516	1.52	1.518	0.00128
Mild steel K501 Pretreated week 4	2.524	2.451	2.4875	0.02336
Mild steel K501 Pretreated week 8	1.849	1.829	1.839	0.0064
Stainless steel D tower week 1	0.355	0.346	0.3505	0.00288
Stainless steel D tower week 2	0.115	0.11	0.1125	0.0016
Stainless steel D tower week 3	0	0	0	0
Stainless steel D tower week 4	0.028	0.027	0.0275	0.00032
Stainless steel D tower week 8	0.057	0.054	0.0555	0.00096
Stainless steel D tower week 12	0	0	0	0
Stainless steel K501 week 1	0.466	0.453	0.4595	0.00416
Stainless steel K501 week 2	0.115	0.111	0.113	0.00128
Stainless steel K501 week 3	0.116	0.11	0.113	0.00192
Stainless steel K501 week 4	0.031	0.029	0.03	0.00064
Stainless steel K501 week 8	0	0	0	0
Stainless steel K501 week 12	0.028	0.027	0.0275	0.00032

APPENDIX D: THERMOGRAVIMETRIC ANALYSIS GRAPHS

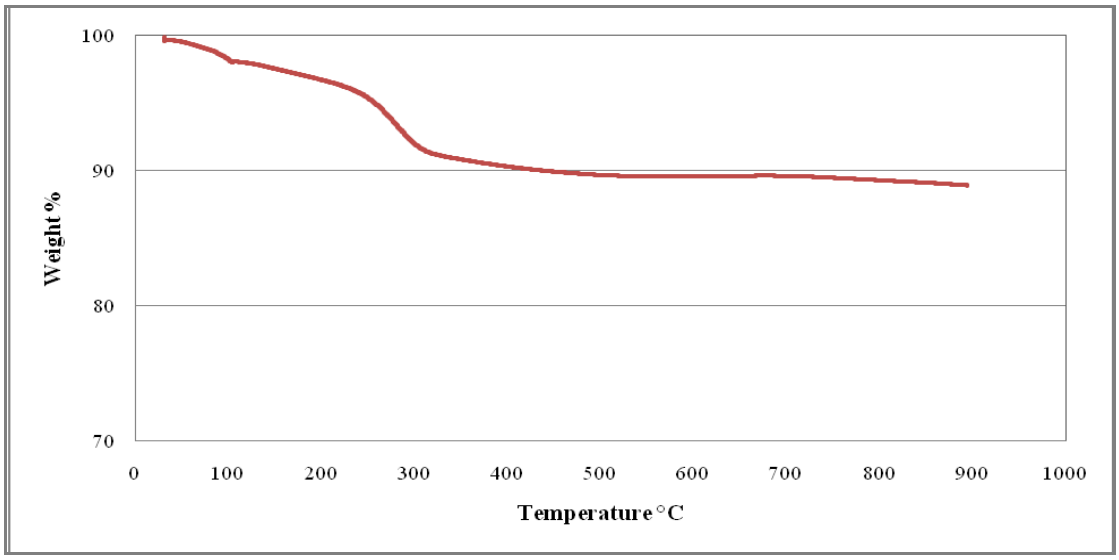


Figure D1 Thermographimetric analysis of scale from heat exchanger

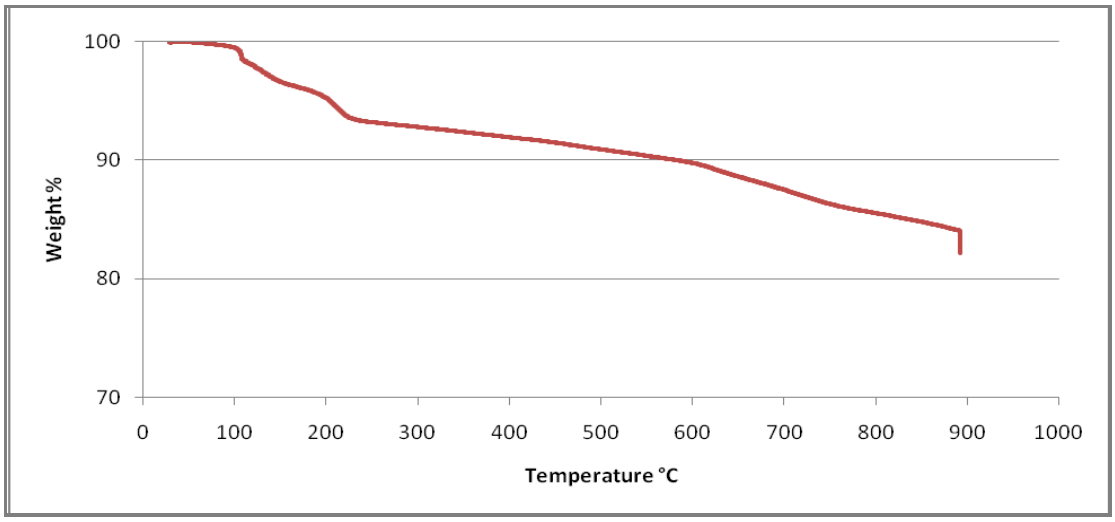


Figure D2 Thermogravimetric analysis of scale from cooling tower packing

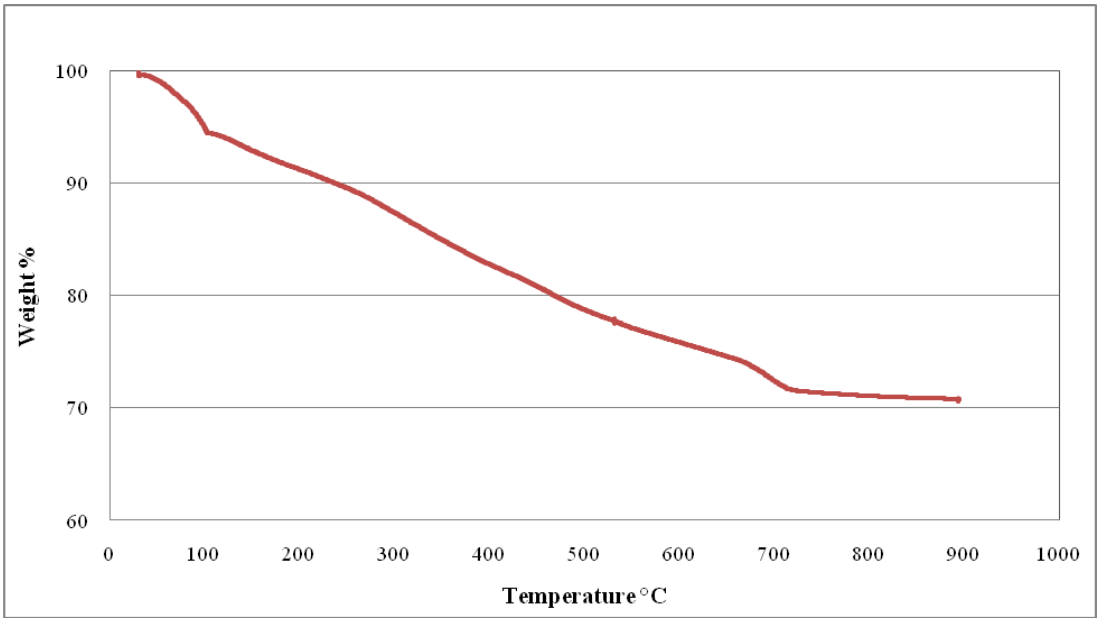


Figure D3 Thermogravimetric analysis of scale from sand filter backwash

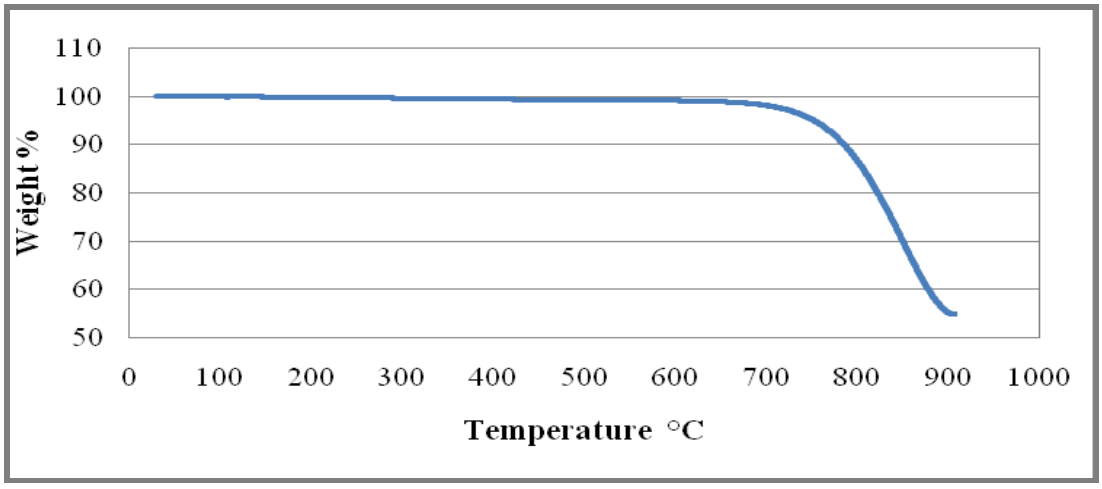


Figure D4 Thermogravimetric analysis of scale from the chiller unit

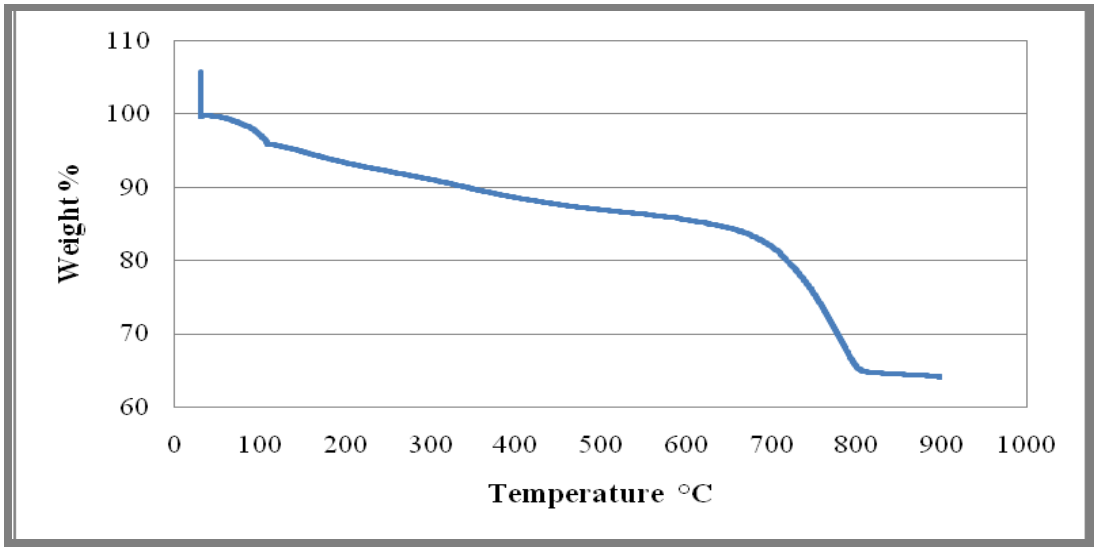


Figure D5 Thermogravimetric analysis of scale from chill tower

APPENDIX E: AAS RESULTS

	Sampling point		
Element	**Heat exchanger unit**	**Sand filter backwash**	**Cooling tower packing**
Sodium	1.724 µg/ ml	0.0 µg/ml	151.167 µg/ml
Iron	0.5 µg/ml	60.5 µg/ml	0.0 µg/ml
Potassium	0.0 µg/ml	0.0 µg/ml	16.1 µg/ml
Zinc	114.7 µg/ml	0.5 µg/ml	0.267 µg/ml

Table E1 showing AAS results of scales from different sections of the cooling tower

From the table above, heat exchanger unit is composed of mainly zinc followed by sodium and lastly iron.In sand filter scale sample, iron and zinc were detected and for the scale sample from cooling tower packing, sodium was the most abundant followed by potassium and lastly zinc, there was no iron detected in the sample. These results are in agreement with the XRD results but due to the fact that the samples could not dissolve completely the results were not quantitatively verified.