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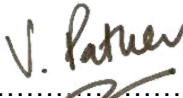

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## 1. INTRODUCTION

This standard establishes control ranges and limits for chemical parameters in open and closed auxiliary cooling water systems. This document is generic in nature and therefore is applicable in all aspects to all of these cooling systems. Specific modes of operation will apply at individual power stations according to the plant, which is installed, and in particular, the type of make-up water used.

All limits and ranges are based on practical experience within Eskom and, in some cases, originate from international research projects.

Where Original Equipment Manufacturers (OEM) requirements are prescribed, documented proof must be available for record purposes. Where the OEM requirements differ to this standard, the more stringent requirement shall be applicable.

## 2. SUPPORTING CLAUSES

### 2.1 SCOPE

This standard outlines the chemical and microbiological limits, inter-related limits and control ranges which must be controlled in order to effectively operate the auxiliary and ancillary cooling systems.

#### 2.1.1 Purpose

The objective of this standard is to provide a framework for the operation of auxiliary and ancillary cooling water systems, focusing on important aspects such as corrosion and the impact of water losses on the receiving environment.

#### 2.1.2 Applicability

This document shall apply throughout Eskom Holdings SOC on all systems that have auxiliary and ancillary cooling systems with water as the cooling medium. This excludes the main condenser cooling water.

### 2.2 REFERENCES

#### 2.2.1 Normative References

- [1] [240-55864764](#) Chemistry Standard for Potable Water
- [2] [240-53113712](#) Demineralised Water Production Using Ion Exchange Resins Chemistry Standard
- [3] [240-56030499](#) Condenser Health Care Guideline
- [4] [240-107677940](#) Specification Standard for High Pressure Water Jetting of Condenser and Heat Exchanger Tubes

#### 2.2.2 Informative

- [5] Corrosion Engineering Handbook 3<sup>rd</sup> Edition, January 1, 1986, Publisher McGraw-Hill, by A. Norbert Greene; Fontana, Mars (Author), ISBN-13. 978-0071003605.
- [6] Corrosion Inhibitors NACE 1973.
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- [17] SANS 893 - 1. Risk management & 2. The Control of Legionella in Water Systems
- [18] Government Gazette No. 44348, OHSACT, 1993 – Regulations for Hazardous Chemical Agents, 2021
- [19] 240-156965709 Biocide and Biodispersant Dosing for Microbiological Control in Cooling Water Scope for a Supply Contract Guideline,

### 2.3 DEFINITIONS

Definition	Description
Algae	Relatively large organisms generally coloured blue-green or green by the presence of chlorophyll. Algae require sunlight for growth.
Ancillary equipment	Ancillary equipment is machines and other technical things which are used with the main items of equipment to create a complete system, eg. coolers, compressor cooling, air conditioners ,etc.
Ancillary Cooling Water	Ancillary cooling water is the water that is used to cool ancillary equipment.
Auxiliary Cooling Water	All water used for cooling purposes, excluding the main condenser cooling water
Bacteria - Planktonic	Bacteria which are found dispersed through the bulk medium.
Bacteria - Sessile	Bacteria that attach themselves to wetted equipment surfaces.
Biodispersants	Compounds that will penetrate and detach microbial deposits while preventing re-attachment.
Biostats	Compounds with broad-spectrum properties that will create adverse conditions that effectively keep the microbial population in the lag phase. Biostats are biocides which do not kill the organism but rather keep it in a non-reproductive state.
Biocide - Non-Oxidising	Compounds used to kill off planktonic micro-organisms.
Biocide - Oxidising	Chemicals that literally "burn up" / oxidise any organic compound they come into direct contact with. Effective against planktonic microbes and the top layer of biofilm.
Cavitation Damage	A special form of erosion corrosion that is caused by the formation and the collapse of vapour bubbles in a liquid near the metal surface.

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Corrosion	The destruction or deterioration of a material because of reaction with its environment.
Corrosion Engineering	The specialist discipline of applying scientific knowledge, natural laws and physical resources in order to design and implement materials, structures, devices, systems and procedures to manage the natural phenomenon known as corrosion. <a href="http://www.corrosionpedia.com">www.corrosionpedia.com</a>
Corrosion Fatigue	The reduction of fatigue resistance due to the presence of a corrosive medium and a cyclic stress.
Erosion Corrosion	The acceleration or increase in the rate of deterioration or attack on a metal because of relative movement between a corrosive fluid and the metal surface.
Fatigue	The tendency of a metal to fracture under repeated cyclic stressing.
Fungi	Microscopic plants larger than bacteria, which could cause wood decay in cooling towers.
Inhibitor	A substance that, when added in small concentrations to an environment, decreases the corrosion rate.
Passivity	The loss of chemical activity experienced by certain metals and alloys under particular environmental conditions.
Selective Leaching	The removal of one element from a solid alloy by corrosion processes. (i.e. dezincification)
Stress Corrosion Cracking	The cracking caused by the simultaneous presence of a tensile stress and a specific corrosive medium.

### 2.3.1 Classification

#### Controlled Disclosure

This document is classified as 'Controlled Disclosure' to external parties (either enforced by law, or discretionary).

### 2.4 ABBREVIATIONS

Abbreviation	Description
ALARA	As low as reasonably achievable
AMP	Aminophosphonates
CCPP	Calcium Carbonate Precipitation Potential
CFU	Colony Forming Units
D	Daily
DBNPA	2,2-dibromo-3-nitrilopropionamide
LSI	Langelier Saturation Index
M	Monthly
Nitrite/Borax	Sodium nitrite / Sodium tetra borate blend

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NTU	Nephelometric Turbidity Units
pH	Activity of the hydrogen ion concentration
TOC	Total organic carbon
TSP	Tri-sodium phosphate
TTA	Tolyltriazole
W	Weekly

## 2.5 ROLES AND RESPONSIBILITIES

- The Chemical Services Manager shall take cognisance of this Standard when compiling site specific surveillance and specification procedures for auxiliary and ancillary systems.
- The Chemical Services Manager shall ensure that approved safe handling procedures for the relevant chemical products are available and adhered to.
- The Senior Manager: Auxiliary Plants Engineering will be responsible for the periodic review of this Standard.
- Chemical Services Manager will ensure compliance with this standard. This includes cases where contractors are used to maintain the systems.
- The System Engineer is responsible for identification of all applicable systems.
- The records shall be periodically reviewed by Chemistry Specialists within Generation Engineering with corrective actions taken as and when required.

## 2.6 PROCESS FOR MONITORING

Excursions beyond the limiting conditions of this Standard shall be monitored, tracked and reasons recorded within the Laboratory Information Management System (LIMS) maintained by each power station laboratory.

The records shall be periodically reviewed by Chemistry Specialists within Generation Engineering with corrective actions taken as and when required.

## 3. CHEMISTRY REQUIREMENTS FOR AUXILIARY COOLING WATER SYSTEMS

### 3.1 MAKE-UP WATER

- Where demineralised water is used as make up water, the quality is governed by the document, Chemistry Standard for the Pre-treatment and Production Processes of Demineralised Water 240-53113712. Logistics often necessitate the tapping of demineralised water at points such as polishing plant outlets, condensate extraction pumps and demineralised water storage tanks.
- Where potable water is used as make up water, the quality is governed by the Chemistry Standard for Potable Water 240-55864764 unless otherwise stated in this standard.

### 3.2 RECIRCULATING AUXILIARY COOLING WATER

Samples should be taken from the re-circulating water in the system. As far as possible, the sample must be taken from low-point drains. It should be noted that the surveillance frequency should increase if the desired level of control cannot be achieved with the recommended frequency of chemical analysis. The chemical specifications for the different systems are as follows:

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**Table 1: Chemistry requirements for closed systems with demineralised water make-up**

Parameter	Units	Limit or range	Surveillance frequency	Note
Turbidity	NTU	<1	Weekly	4.1
pH		In accordance with correct chemical additives concentration	Weekly	4.3
Conductivity	$\mu\text{S.cm}^{-1}$	In accordance with correct chemical additives concentration	Daily	4.2
Inhibitor(s)*	$\text{mg.kg}^{-1}$	In accordance with vendor and or Eskom recommendation	Weekly	4.17 and 4.18
Copper	$\mu\text{g.kg}^{-1}$	< 50	Weekly	4.9
Iron	$\mu\text{g.kg}^{-1}$	< 200	Weekly	4.9
Oil	$\text{mg.kg}^{-1}$	< 5	Weekly	4.13
System water losses	% loss	< 2 % per week	Weekly	4.14
Total hardness as $\text{CaCO}_3$	$\text{mg.kg}^{-1}$	< 5	Weekly	4.6
Dissolved oxygen	$\text{mg.kg}^{-1}$	In accordance with inhibitor requirements	Weekly	4.10

\*Any copper containing system, employing nitrite as an inhibitor, should also be analysed for ammonia on a weekly basis. The concentration should never exceed  $0.5 \text{ mg.kg}^{-1}$ .

**Table 2: Planktonic bacteriological counts for closed systems with demineralised water make-up**

Parameter	Units	Limit or range	Surveillance frequency	Note
Total aerobic bacteria	CFUs/ml	<10 000	Monthly	4.16
Total anaerobic bacteria	CFUs/ml	<1000	Monthly	4.16
$\text{H}_2\text{S}$ producers	CFUs/ml	<10	Monthly	4.16

NOTE: The limits specified are not absolute and the actual equilibrium concentrations must be verified as being acceptable for continuous operation.

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**Table 3: Chemistry requirements for closed systems with potable water make-up**

Parameter	Units	Limit or range	Surveillance frequency	Note
Turbidity	NTU	$\leq 1$	Weekly	4.1
pH		In accordance with chemical additives concentration	Weekly	4.3
Conductivity	$\mu\text{S.cm}^{-1}$	In accordance with chemical additives concentration	Weekly	4.2
Corrosion inhibitors	$\text{mg.kg}^{-1}$	In accordance with vendor and or Eskom recommendations	Weekly	4.17 and 4.18
Copper	$\mu\text{g.kg}^{-1}$	$< 50$	Weekly	4.9
Iron	$\mu\text{g.kg}^{-1}$	$< 200$	Weekly	4.9
Oil	$\text{mg.kg}^{-1}$	Not Detected*	Weekly	4.13
Water losses	% loss	$< 2\%$ per week	Weekly	4.14
Calcium carbonate precipitation potential	$\text{mg.kg}^{-1}$	$> 0$ but $< 5$	Weekly	4.15.1
Total hardness as $\text{CaCO}_3$	$\text{mg.kg}^{-1}$	$< 100$	Weekly	4.6
Chlorides	$\text{mg.kg}^{-1}$	$< 25$	Weekly	4.4
Sulphate	$\text{mg.kg}^{-1}$	$< 45$	Weekly	4.5
Dissolved oxygen	$\text{mg.kg}^{-1}$	In accordance with inhibitor requirements	Weekly	4.10
Legionella	CFU/L	$< 100$	Quarterly	

\*If oil is detected, an investigation should be conducted to identify the source of contamination

If the inhibitor programme is not compatible with residual chlorine, alternatives must be evaluated. Alternatively, continuous monitoring of the chlorine concentration in the make-up water is essential.

Any copper containing system, employing nitrite as an inhibitor should also be analysed for ammonia on a weekly basis. The concentration should never exceed  $0.5 \text{ mg.kg}^{-1}$ .

Thus for closed loop systems with potable water as make-up water (using the zinc polyphosphate), specifications are as follows:

Pre-treatment of the system for one week with  $30 \text{ mg.kg}^{-1}$  zinc polyphosphate.

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**Table 4: Additional specifications for closed loop systems with potable water as make-up water**

Zinc polyphosphate as polyphosphate	10 mg.kg <sup>-1</sup> to 15 mg.kg <sup>-1</sup>
pH	6.5 to 7.5
Calcium as Ca <sup>2+</sup>	> 7.5 mg.kg <sup>-1</sup> and < 40 mg.kg <sup>-1</sup>

**Table 5: Planktonic bacteriological counts for closed systems with potable water make-up**

Parameter	Units	Limit or range	Surveillance frequency	Note
Total aerobic bacteria	CFUs per ml	<10000	Monthly	4.16
Total anaerobic bacteria	CFUs per ml	<1000	Monthly	4.16
H <sub>2</sub> S producers	CFUs per ml	<10	Monthly	4.16
Legionella	CFU/L	<100	Quarterly	

NOTE: The limits specified are not absolute and the actual equilibrium concentrations must be verified as being acceptable for continuous operation.

The biocide application rate should be measured once a week and recorded with all other parameters in the chemistry database. Pump calibration vessels can be employed to accurately determine dose rates.

Table 6 below relates to the secondary cooling of the closed loop cooling system.

**Table 6: Chemistry requirements for open evaporative systems with potable or raw water make-up**

Parameter	Units	Limit or range	Frequency	Note
Turbidity	NTU	< 15	Daily	4.1
pH		8.3 to 8.9	Daily	4.3
Conductivity	μS.cm <sup>-1</sup>	Conforms to the cycles of concentration being used but generally < 4000	Daily	4.2
Corrosion inhibitors	mg.kg <sup>-1</sup>	In accordance with vendor and or Eskom recommendations	Weekly	4.17 and 4.18
Sodium	mg.kg <sup>-1</sup>	< 500	Weekly	4.8
Potassium	mg.kg <sup>-1</sup>	< 500	Weekly	4.8
Oil	mg.kg <sup>-1</sup>	< 5 / Negotiable	Weekly	4.13
Water losses	% loss	In accordance with evaporation and blow down requirements	Weekly	4.14

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M Alkalinity	mg.kg <sup>-1</sup>	<p><b>(Depending on CAPP)</b> 80 to 120 mg.kg<sup>-1</sup> as CaCO<sub>3</sub> without a crystal modifier dosing programme.</p> <p><b>(Depending on CAPP)</b> 120 to 160 mg.kg<sup>-1</sup> as CaCO<sub>3</sub> with a crystal modifier dosing programme.</p>	Daily	
Total hardness as CaCO <sub>3</sub>	mg.kg <sup>-1</sup>	< 500	Daily	4.6
Calcium carbonate precipitation potential Using Stasoft	mg.kg <sup>-1</sup>	<p>&gt;10 but &lt; 30 With scale control program</p> <p>&lt; 5 Without scale control program</p>	Weekly	4.15.1
Copper	mg.kg <sup>-1</sup>	< 500	Weekly	4.9
Iron	mg.kg <sup>-1</sup>	< 500	Weekly	4.9
Chlorides	mg.kg <sup>-1</sup>	< 400	Weekly	4.4
Sulphates	mg.kg <sup>-1</sup>	<p><u>Poor quality concrete – Stations</u></p> <p>&lt;1000 mg.kg<sup>-1</sup> if Na<sup>+</sup> &lt; 250 mg.kg<sup>-1</sup></p> <p>&lt;750 mg.kg<sup>-1</sup> if Na<sup>+</sup> &gt; 250 mg.kg<sup>-1</sup></p> <p><u>High quality concrete – Stations</u></p> <p>&lt; 1500 mg.kg<sup>-1</sup> if Na<sup>+</sup> &lt; 500 mg.kg<sup>-1</sup></p> <p>&lt; 1000 mg.kg<sup>-1</sup> if Na<sup>+</sup> &gt;500 mg.kg<sup>-1</sup></p> <p>Note: Mg<sup>2+</sup> to be &lt;160 mg.kg<sup>-1</sup> as CaCO<sub>3</sub></p>	Weekly	4.5
Magnesium	Mg (as CaCO <sub>3</sub> ) × SiO <sub>2</sub>	Mg (as CaCO <sub>3</sub> ) × SiO <sub>2</sub> < 25 000	Weekly	
Silica	as SiO <sub>2</sub>	< 150 mg.kg <sup>-1</sup> as SiO <sub>2</sub> . While also taking cognisance of Mg × SiO <sub>2</sub> limitation of 25000	Weekly	
TSS	mg.kg <sup>-1</sup>		Weekly	
Langelier Saturation Index (LSI)	-	-0.5 < 0 < 0.5	Weekly	

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**Table 7: Bacteriological counts for open evaporative systems with potable makeup**

Parameter	Units	Limit or range	Surveillance frequency	Note
Total aerobic bacteria	CFUs per ml	< 10 000	Monthly	4.16
Total anaerobic bacteria	CFUs per ml	< 1000	Monthly	4.16
H <sub>2</sub> S producers	CFUs per ml	< 10	Monthly	4.16
Legionella	CFU per litre	<100	Quarterly	

NOTE: The limits specified are not absolute and the actual equilibrium concentrations must be verified as being acceptable for continuous operation.

The biocide application rate should be measured once a week or prior to dosing and recorded with all other parameters in the chemistry database. Pump calibration vessels can be employed to accurately determine dose rates.

**Table 8: Chemistry requirements for open evaporative systems with demineralised water make-up**

Parameter	Units	Limit or range	Surveillance frequency	Note
Turbidity	NTU	< 15	Weekly	4.1
pH		8.5 to 9.0	Weekly	4.3
Conductivity	µS.cm <sup>-1</sup>	< 300	Daily	4.2
Corrosion inhibitors	mg.kg <sup>-1</sup>	In accordance with vendor and or Eskom recommendations	Weekly	4.17 and 4.18
Copper	µg.kg <sup>-1</sup>	< 500	Weekly	4.9
Iron	µg.kg <sup>-1</sup>	< 500	Weekly	4.9
Oil	mg.kg <sup>-1</sup>	< 5	Weekly	4.13
Water losses	% loss	In accordance with evaporation and blow down requirements	Weekly	4.14
Total hardness as CaCO <sub>3</sub>	mg.kg <sup>-1</sup>	< 10	Weekly	4.6

NOTE: Control of the pH should be achieved through the addition of caustic soda.

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**Table 9: Bacteriological counts for open evaporative systems with demineralised water make-up**

Parameter	Units	Limit or range	Surveillance frequency	Note
Total aerobic bacteria	CFUs per ml	<10 000	Monthly	4.16
Total anaerobic bacteria	CFUs per ml	<1000	Monthly	4.16
H <sub>2</sub> S producers	CFUs per ml	<10	Monthly	4.16
Legionella	CFU/l	<100	Quarterly	

NOTE: The limits specified are not absolute and the actual equilibrium concentrations must be verified as being acceptable for continuous operation.

The biocide application rate should be measured once a week and recorded with all other parameters in the chemistry database. Pump calibration vessels can be employed to accurately determine dose rates.

**Table 10: Typical control ranges for Inhibitors dosed in systems with demineralised water make-up**

Inhibitor	Provides protection for	Control range mgkg <sup>-1</sup>	pH Range	Remarks
Nitrite	Fe	250 to 1000	8.5 to 10.5	Will cause pitting at concentrations below 150 mgkg <sup>-1</sup> at pH > 7.5
Molybdate	Fe and Al	200 to 1000	8.5 to 10.5	More effective in combination with nitrite and or dissolved oxygen
Nitrite Molybdate	Fe and Al	250 to 310	8.5 to 10.5	Nitrite susceptible to bacteriological degradation
Hydrazine*	Fe Fe and Cu	5 to 50	8.5 to 10.5 8.5 to 9.5	Ultra low dissolved oxygen concentrations required for copper protection
Carbohydrazide	Fe Fe and Cu	5 to 50	8.5 to 10.5 8.5 to 9.5	Ultra low dissolved oxygen concentrations required for copper protection
TTA and BZT	Cu	5 to 30	8.5 to 10.5	Best results with occasional shock dosing
Phosphates	Fe and Cu	15 to 500	9.0 to 11	Can cause pitting at low concentrations
Silicate	Fe, Cu and Al	20 to 50	8.5 to 10.5	Forms fragile films at pH less than 7
Chromates**	Fe, Cu, Zn, Al and soft solder	150 to 300	8.5 to 10.5	Not approved for use due to environmental impact

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NOTE: These recommendations will provide adequate protection provided that water losses from the system are kept to less than 2 % per week. It can also be reiterated that no system can be protected with inhibitors if the operating and maintenance of the system is such that transient conditions are regularly experienced

\* The OHSACT – Regulations for Hazardous Chemical Agents [18] stipulate that Hydrazine is a hazardous chemical (a carcinogen) and provides the maximum occupational exposure limits permitted for personnel to hydrazine. The Chemical Services Manager is responsible to ensure that there are station specific procedures in place ensuring that this maximum exposure limit is adhered to at all times and that the necessary PPE is available for personnel handling the chemical. Stations utilising hydrazine must evaluate alternative chemicals for dosing and phase out the use of this hazardous chemical in Eskom.

\*\* Stations utilising chromates are required to phase them out of use as they are not approved for use due to their environmental impact during blowdowns or possible release from dams.

## 4. RATIONALE FOR INDIVIDUAL AND RELATED PARAMETERS

### 4.1 TURBIDITY

Suspended matter, such as clays, silt and corrosion products are always present in open recirculating cooling water systems. Particles scrubbed from the air add to the suspended solid loading. These materials are usually soft and non-abrasive. They are capable of depositing in low flow velocity areas, forming a physical barrier, and preventing oxygen from reaching the metal/solution interface. This build up will contribute to the formation of differential aeration cells and will promote localised attack (crevice corrosion). If the turbidity is found to be greater than 1 NTU, further investigation for deposition of solids is warranted.

### 4.2 CONDUCTIVITY AT 25°C

Dissolved constituents in water can have a variety of effects, both individually and through their interactions. The effects include increased corrosion in addition to scale and deposit formation. Increasing the dissolved solid content of waters increases its conductivity. Galvanic effects due to the coupling of dissimilar metals are extended in waters with a higher salinity compared to waters with a low conductivity.

### 4.3 PH AT 25°C

The normal pH range for an open re-circulating cooling water system is 8 to 8.7. Closed systems operate at a pH of 8.5 to 9.0 and even beyond pH 11 depending on the inhibition programme. These pH values are the bulk pH of the water, but the actual pH at the metal surface can be different, depending on the prevailing surface conditions. Oxygen reduction will produce hydroxyl ( $\text{OH}^-$ ) ions, raising the pH, but under deposit corrosion can depress the pH. In the case of orthophosphate inhibition using trisodium phosphate ( $\text{Na}_3\text{PO}_4$ , TSP, TSP dissociates to disodium hydrogen phosphate ( $\text{Na}_2\text{HPO}_4$ ) and sodium hydroxide ( $\text{NaOH}$ ), the latter controlling the bulk solution pH. If the TSP concentration is high enough it can concentrate under deposits to cause caustic gouging.

The corrosion of steel in aerated water decreases within the normal operating pH range of 8,0 to 8,7. The corrosion rates are still too high and chemical additives are used to reduce the rate to manageable levels of less than 0,13 mm/yr (5mls/yr).

Copper alloys are not as sensitive to pH as carbon steel. Acidic pH will accelerate general corrosion. As the pH increases, uniform corrosion decreases significantly. However, general thinning is not as severe a problem as the formation of cupric ions ( $\text{Cu}^{2+}$ ), which can cathodically deposit on steel and create active anodic sites for pitting attack.

Aside from the effect of pH on corrosion, increasing the pH of waters with moderate levels of calcium and alkaline values can result in  $\text{CaCO}_3$  precipitation. The deposition of this alkaline scale can impede the diffusion of oxygen to the metal surface in addition to forming a heat transfer barrier.

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#### 4.4 CHLORIDE

Chlorides and sulphates are known to have a deleterious effect on steel. Much of the antagonistic nature of the chloride ions is due to their ability to be adsorbed onto the metal surface and interfere with the formation of passive films. Pitting is the most common form of attack. The small exposed areas where Cl<sup>-</sup> ions have adsorbed are anodic to the large cathodic passive oxide surface. High current densities are generated at the Cl<sup>-</sup> ion site. Once the corrosion begins, hydrolysis of the metal ions from the anodic reaction causes a decrease in pH, which discourages film repair and accelerates attack. The level of chloride ions needed to initiate attack can be as low as a few milligrams per litre for some stainless steels in high purity waters. The more susceptible an alloy is for general attack, the less effect there is from chlorides. Carbon steel will corrode in waters containing chloride primarily from uniform corrosion rather than localised attack.

Copper alloys are subject to degradation by Cl<sup>-</sup> ions that modify the Cu<sub>2</sub>O structure. The small, negatively charged Cl<sup>-</sup> ion can migrate through the Cu<sub>2</sub>O film to areas of high positive charge density. Substitution of the monovalent charged chloride species for divalent charged oxygen species could occur. To maintain electron neutrality, cuprous ions (Cu<sup>+</sup>) are ejected (dissolved) into the aqueous phase. The loss of Cu<sup>+</sup> ions is, by definition, corrosion.

#### 4.5 SULPHATE

Sulphate ions are somewhat more elusive than chloride ions in their contribution to corrosion. Sulphate ions do not appear to have the film piercing properties of chloride ions. There is even some evidence that SO<sub>4</sub><sup>2-</sup> ions may inhibit corrosion of some stainless steels.

Sulphate, in open evaporative cooling systems with potable water as a make-up water source, originates from the neutralisation of alkalinity with sulphuric acid. Natural concentration depends on the sulphate concentration of the make-up water. Calcium sulphate gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O) is the most common form of calcium sulphate scale in these systems. Due to CaSO<sub>4</sub>·2H<sub>2</sub>O being more soluble than calcium carbonate by a factor of at least 50, it will precipitate only after the latter scale has been formed. This phenomenon provides the basis for H<sub>2</sub>SO<sub>4</sub> addition to control CaCO<sub>3</sub> scale in concentrated cooling water systems. The normal upper limit for calcium and sulphate in the absence of susceptible material such as concrete is expressed by:

$$[\text{Ca}^{2+}] \times [\text{SO}_4^{2-}] = 500000 \text{ (NOTE: Calcium as Ca)}$$

The introduction of low molecular weight polymers (1000 amu to 10000 amu) at 1 mg.kg<sup>-1</sup> to 2 mg.kg<sup>-1</sup> can increase the solubility of calcium sulphate by a factor of 20.

Another chemical that controls CaSO<sub>4</sub> precipitation efficiently is the phosphonate AMP. The family of aminophosphonates has been found to be extremely effective. The level of AMP needed is approximately 0,5 mg.kg<sup>-1</sup>.

#### 4.6 HARDNESS (CALCIUM AND MAGNESIUM)

Hardness ions (Ca and Mg) and HCO<sub>3</sub><sup>-</sup> are inhibitive and will suppress corrosion. There is, however, a fine line separating this suppression from scale formation that will impede heat transfer. Increasing the concentration of the hardness ions can reduce the aggressiveness of water. The overall aggressiveness of water is related to its hardness and alkalinity. Soft waters that are low in calcium are more corrosive than hard waters. Most waters used for cooling water have a pH in the vicinity of neutral or above. This environment is very conducive to the formation of a protective film of CaCO<sub>3</sub> even when the water is below the saturation level of this salt. The actual mechanism that occurs at the water/metal surface interface is

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more involved than simple deposition of deposit. It is quite probable that the  $\text{CaCO}_3$  formation is due to electrochemical changes at the metal surface. The pH at the surface is usually higher than that of the bulk water because of an increase in  $\text{OH}^-$  ion concentration, which is a reaction product of oxygen reduction.

Calcium carbonate formation can be controlled by adding acids or specific chemicals tailored to inhibit its formation or modify the crystal lattice. Sulphuric acid is inexpensive and is often used for this purpose. The sulphate originating from the  $\text{H}_2\text{SO}_4$  will contribute to salt loading, especially in make-up water with high alkalinity.

#### 4.7 TEMPERATURE

Corrosion is an electrochemical phenomenon and an increase in temperature will cause an increase in corrosion rates. Temperature plays a dual role with respect to oxygen corrosion. Increasing the temperature will lower the solubility of oxygen. In open systems where the oxygen can be released, corrosion will increase up to a temperature of  $80^\circ\text{C}$ . Beyond this temperature the reduced oxygen content limits the oxygen reduction reaction, preventing the ion dissolution process. Thus the corrosion rate of carbon steels decreases, and at boiling water conditions the temperature effect is similar to room temperature with a high oxygen content. It is for this reason that the scaling potential be calculated at the maximum measured in the system of the specific station. The parameter should indicate the temperature at which the scaling rate is calculated. If LIMS are programmed to perform the calculation, the correct correlation factors must be used.

#### 4.8 SODIUM AND POTASSIUM

Sodium and potassium ions are considered neutral species and have no discernible effect. These ions, however, contribute to the overall salinity of the cooling water and could impact on galvanic effects in dissimilar couplings.

#### 4.9 CORROSION PRODUCTS

Depending on the materials of construction, iron, copper zinc, aluminium and chromium concentration in circulating cooling waters could be indicative of the corrosion rate. In cases where the corrosion products redeposit or settle, as a result of low flow velocities, a false picture will emerge from the analytical data. Some of these deposits could in turn contribute to other forms of corrosion as result of environmental changes in other areas. It is therefore important to conduct internal or endoscope inspections at regular intervals to establish the reliability of assessing the corrosive tendency of the cooling water through analytical techniques. The application of corrosion coupons and corrosion product surveys are proven techniques in obtaining peace of mind.

#### 4.10 DISSOLVED GASES

Dissolved gases are a major factor contributing to the natural corrosion of steel.

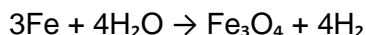
##### 4.10.1 Oxygen

It has been shown that oxygen is part of the overall electrochemical reactions occurring at the interface between the metal surface and the aqueous phase. Steel corrosion is therefore proportional to the oxygen content of the water. Oxygen solubility in water will vary with temperature, pressure and electrolyte concentration. Increasing the temperature decreases the solubility but increasing the partial pressure of oxygen increases its solubility. Concentrated electrolytes decrease oxygen solubility. For open re-circulating cooling water systems, the concentration of dissolved oxygen is approximately  $6 \text{ mgkg}^{-1}$ .

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The presence of oxygen is necessary for the formation of protective oxides on copper ( $\text{Cu}_2\text{O}$ ), aluminium ( $\text{Al}_2\text{O}_3$ ) and steel ( $\text{Fe}_2\text{O}_3$ ). In the absence of dissolved oxygen, the corrosion of steel is greatly reduced. A uniform protective film of magnetite ( $\text{Fe}_3\text{O}_4$ ) is formed according to the following reaction.



This reaction is not likely at low temperatures.

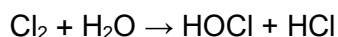
Overall, oxygen can have either a negative or a positive impact on the corrosion of steel. In aerated systems, uneven distribution of corrosion products can form on the metal surface, giving rise to localised corrosion. Under deaerated conditions, the  $\text{Fe}_3\text{O}_4$  film isolates the base metal from the water, drastically reducing corrosion.

#### 4.10.2 Carbon dioxide

Carbon dioxide is more soluble than oxygen in pure water (1.3 gram per litre at 30 °C) and will convert to carbonic acid ( $\text{H}_2\text{CO}_3$ ), producing a solution with a pH of less than 6 which is where acid attack can predominate. Adjusting the pH of the water upward redistributes the ratio of dissolved carbonic species. Carbonic acid will dissociate to form bicarbonate ions ( $\text{HCO}_3^-$ ) and subsequently carbonate ions ( $\text{CO}_3^{2-}$ ). The ratio of the various components can be calculated from the pH of the system. In open recirculating cooling systems the pH is usually controlled within the 8.5 pH to 9.0 range. The mentioned behaviour of carbon dioxide is significant where demineralised water is used as the make-up water.

#### 4.11 CHLORINE

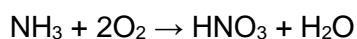
Chlorine is not a natural constituent of cooling waters but is added for biofouling control. When dissolved in water, chlorine will convert to hypochlorous acid ( $\text{HOCl}$ ) and hydrochloric acid ( $\text{HCl}$ ), which will suppress the pH.



Acid attack on steel is a concern when the pH falls below 7. Above this pH the deleterious effects of chlorine are reduced. Adequate biological control can be achieved if the pH is maintained at approximately 7.5. However, chlorine will accelerate the corrosion of copper alloys, even at alkaline pH. It is one of the most aggressive species to copper alloys in cooling waters as it can induce localised attack and degrade the protective  $\text{Cu}_2\text{O}$  film.

#### 4.12 AMMONIA:

Ammonia is not a natural constituent of cooling water but can originate from the breakdown of carbonylhydrazide and/or hydrazine and biocides. The effect of ammonia on ferrous alloys is minimal, it has a drastic impact on copper rich brasses and alloys. These alloys can experience both rapid thinning and stress corrosion cracking. Nitrifying bacteria can oxidize ammonia to nitrate. This is accompanied by a decrease in pH and occurs according to the reaction:



Any copper containing system, employing nitrite, as an inhibitor should also be analysed for ammonia on a weekly basis. The concentration should never exceed 0,5 mgkg<sup>-1</sup>.

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#### 4.13 OIL

Oil ingress from oil coolers is a function of the pressure difference between the two mediums. The presence of oil in the cooling water is indicative of an oil cooler leak and the Operations Department should be alerted when oil is detected. Fouling, microbial activity and corrosion can be aggravated in the presence of oil.

#### 4.14 MECHANICAL PROBLEMS

Mechanical problems can have a significant impact on the chemistry of cooling water systems. Leakage from these systems leads to the addition of untreated water to the system. The make-up water can dilute the system chemistry if an automated dosing system is not installed. The introduction of dissolved oxygen can deplete oxygen scavenging corrosion inhibitors applied in closed loop systems.

Chemical treatment should not be used to compensate for mechanical and operational problems and errors, nor should deficiencies be hidden with extensive treatment programmes. Cascading of the inhibition chemicals to the receiving environment or system could have adverse effects such as:

- Increased microbial activity,
- Additional salt load, and
- Increased effluent volumes
- The elimination of chromates as an inhibitor was necessary because of the impact on the environment from leakage.

Water losses are caused by:

- Cross connections to systems operating at lower pressure,
- Expansion tank discharges,
- Valve, gland packing, fitting, seal and other leaks,
- Manual mode of make-up into the expansion tank, often flushing inhibition chemicals to the drains, and
- Passing seals in the water to water coolers. Other areas of concern regarding the mechanical aspect are:
  - Dissimilar metals in contact with each other that could lead to accelerated corrosion, and
  - Stagnant and low flow areas allowing deposition and poor mixing of the inhibitor.

#### 4.15 SCALE

Water formed deposits, commonly referred to as scale, can be defined as a crystalline growth of adherent layer (barrier) of insoluble salt or oxide on a heat exchanger surface. The rate of formation is a complicated function of many variables, including temperature, concentration of scale forming species, pH, organic contamination and hydrodynamic conditions. The normal solubilities of scales increase with temperature, but few, for example,  $\text{CaCO}_3$  and  $\text{CaSO}_4$ , have the opposite trend. Both these salts are present in Eskom's cooling water systems in significant concentrations. The prevention of scale in the large open evaporative systems is done through the selection of treatment processes and make-up water quality control. The same surveillance intensity and treatment processes cannot be provided for the small systems and chemical additives are the preferred method of threshold control.

##### 4.15.1 Calcium carbonate

Calcium carbonate is the most commonly found scale in concentrated cooling water systems. Calcium and bicarbonate alkalinity is both needed to form this scale. Alkalinity is the concentration of the  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$  and  $\text{OH}^-$  ions present in the water. An increase in temperature and or a change in pH value will cause the  $\text{HCO}_3^-$  to decompose to  $\text{CO}_2$  and  $\text{CaCO}_3$ .



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The highest concentration of calcium carbonate will be experienced at the hottest area. Many methods have been proposed to predict the formation of calcium carbonate scale. However, they are all based on the thermodynamic equilibrium of  $\text{H}_2\text{CO}_3$  and are alkalinity corrected for temperature and dissolved solids (ionic strength). Outputs from these methods relate to the ability of the water to precipitate or dissolve calcium carbonate. These tools are only correct if there is no interfering organic contamination present in the cooling water. The Scaling Index (CCPP or LSI) should be calculated at the maximum temperature applicable to the specific site. If the LIMS is to perform the calculation, temperature should be added as a field on the analysis.

#### 4.15.2 Calcium sulphate

Calcium sulphate can precipitate in various forms in cooling water systems, the most common form being gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ). The hemihydrate ( $\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$ ) and anhydrous ( $\text{CaSO}_4$ ) are much less common. Because  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  is more soluble than  $\text{CaCO}_3$  by at least a factor of 50, it will precipitate only after the latter scale has been formed, within the normal cooling water pH range of 8 to 9. This phenomenon provides the basis for controlled sulphuric acid addition to control  $\text{CaCO}_3$  in recirculating cooling water systems. The normal upper limit for calcium and sulphate concentration in the absence of a scaling inhibitor is expressed by:

$$[\text{Ca}^{2+}] \times [\text{SO}_4^{2-}] = 500\,000$$

Where the values in brackets are the ionic concentrations expressed in  $\text{mg.kg}^{-1}$ . To convert calcium concentrations expressed as  $\text{CaCO}_3$  to Ca apply a 0,40 factor. i.e.  $150 \text{ mg.kg}^{-1}$  as  $\text{CaCO}_3 \times 0,4 = 60 \text{ mg.kg}^{-1}$  as Ca.

#### 4.15.3 Calcium phosphate

Increasing pH and the calcium concentration together with phosphate addition for chemical control have provided the potential for this deposit to form. Other sources of phosphate contamination could be from treated sewage water recovery and spillages from phosphate inhibited cooling water systems.

The solubility of  $\text{Ca}_3(\text{PO}_4)_2$  decreases with an increase in pH. It is essentially unaffected over normal temperature ranges (25 °C to 75 °C). Because of the low solubility of  $\text{Ca}_3(\text{PO}_4)_2$  (about  $10^{-30}$ ) deposits can easily form in waters containing  $5 \text{ mg.kg}^{-1}$   $\text{PO}_4$  and  $300 \text{ mg.kg}^{-1}$  of calcium as Ca. The scale forming tendency of  $\text{Ca}_3(\text{PO}_4)_2$  is a function of pH, calcium hardness,  $\text{PO}_4^{3-}$  concentrations, ionic strength, and temperature.

Rule of thumb relationships between these variables do not exist. Also, in the absence of any phosphate deposit, the  $\text{PO}_4^{3-}$  ions can contribute to the corrosion inhibition of carbon steel.

#### 4.15.4 Silicate scales

Calcium silicate ( $\text{CaSiO}_3$ ) and magnesium silicate ( $\text{MgSiO}_3$ ) scales tend to develop under more alkaline cooling water conditions, in which the pH is approximately 8,5 or greater. These scales are very tenacious, dense, and difficult to remove from the heat transfer surfaces. Although the solubility of silica ( $\text{SiO}_2$ ) increases with pH, the solubility of the alkaline silicates decreases with an increase in pH.

An upper limit for silica ( $\text{SiO}_2$ ) concentration is  $150 \text{ mg.kg}^{-1}$  in recirculating cooling water, although other factors affect this value. Magnesium silicate ( $\text{MgSiO}_3$ ) can precipitate on heat transfer surfaces with magnesium concentrations as low as  $50 \text{ mg.kg}^{-1}$  and  $150 \text{ mg.kg}^{-1}$   $\text{SiO}_2$ . A rule of thumb pseudosolubility product of  $[\text{Mg}^{2+}] \times [\text{SiO}_2] = < 8400$  has been developed (bracket values are in  $\text{mg.kg}^{-1}$  and magnesium as such). The value for this index with magnesium expressed as  $\text{CaCO}_3$  adopted by Eskom for adequate assurance is  $< 25000$ .

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#### 4.15.5 Scale prevention

##### 4.15.5.1 Scaling inhibitors

Inhibitors used in the prevention of  $\text{CaCO}_3$  scale are the polymeric inorganic phosphates. This class of compounds includes the salts of pyrophosphates, tri-polyphosphates and hexametaphosphate. At dosage levels of  $1,0 \text{ mg.kg}^{-1}$  these products inhibit the crystallisation of  $\text{CaCO}_3$  crystallites by suppressing both nucleation and crystal growth.

Disadvantages of the polyphosphates is their ability to hydrolyse or revert back to  $\text{PO}_4^{3-}$  ions, that have no scale inhibition properties and might contribute to the formation of calcium phosphate scale. If drains containing these products are recovered to the main cooling water system, lime softening will be negatively affected depending on the volumes recovered and concentrations.

##### 4.15.5.2 Crystal modifiers

Organic polymers have also been found to have effective calcium carbonate scale prevention properties. These include polycarboxylates, such as polyacrylates, polymethacrylates, polymaleates, and their copolymers. Dose rates are in the order of  $2,0 \text{ mg.kg}^{-1}$  to  $4,0 \text{ mg.kg}^{-1}$ .

The polymers adsorb onto the  $\text{CaCO}_3$  crystal structure, limiting the growth of  $\text{CaCO}_3$  and ultimately limiting scale formation. These polymers are more frequently considered dispersants. They retard  $\text{CaCO}_3$  scale by maintaining small particles of distorted crystalline material in suspension.

##### 4.15.5.3 Scale prevention programmes

###### 4.15.5.3.1 Calcium sulphate

Calcium sulphate scale control can be achieved through the application of  $0,5 \text{ mg.kg}^{-1}$  (AMP) aminophosphonate or by the application of  $1,0 \text{ mg.kg}^{-1}$  to  $2,0 \text{ mg.kg}^{-1}$  of polyacrylates, their copolymers and phosphinocarboxylates.

###### 4.15.5.3.2 Calcium phosphate

Calcium phosphate scale is a scale that is extremely difficult to inhibit. Scale control is achieved through the application of  $10 \text{ mg.kg}^{-1}$  to  $15 \text{ mg.kg}^{-1}$  of products such as acrylic acid hydroxypropylacrylate copolymer, styrene sulfonic acid-maleic and phosphino/acrylic acidorgano-sulfonic acid copolymer. These products function as a dispersant and also modify the morphology and size of the  $\text{Ca}_3(\text{PO}_4)_2$  deposit. The mentioned dose rates will prevent  $\text{Ca}_3(\text{PO}_4)_2$  in waters containing up to  $500 \text{ mg.kg}^{-1}$  calcium as calcium carbonate.

###### 4.15.5.3.3 Magnesium silicate

The addition of chemicals as a preventative measure is essentially non-existent except for external treatment with lime. The most effective method of control is to keep the silica and magnesium concentrations such that the rule of thumb solubility product is not exceeded.

#### 4.16 FOULING

Foulants tend to form deposits in stagnant and low flow velocity areas. These deposits create areas of differential aeration and are normally infested with anaerobic bacteria.

##### 4.16.1 Fouling deposits

Water-borne deposits, commonly known as foulants, are loose, porous insoluble materials suspended in water. They include such diverse substances such as particulate matter scrubbed from the air, migrated corrosion products, silt, sand and ash suspended in the make-up water, organic contaminants (oils),

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biological matter, floc carry-over from clarifiers, and extraneous materials such as leaves, grass and twigs. Fouling interferes with the flow of cooling water as opposed to the reduction of heat transfer caused by barrier scales. Fouling can reduce the heat transfer efficiency when the heat exchangers are plugged with foulants.

High flow velocities in the order of  $1.5 \text{ m.s}^{-1}$  to  $2.5 \text{ m.s}^{-1}$  can sweep away foulants but settling will occur in areas with flow velocities less than  $0.6 \text{ m}^{-1}$ . These areas are generally cooling tower ponds, water boxes and shell side coolers. Tube plates also act as screens and trap large solids on the tube plates. The integrity of strainers is therefore, of paramount importance if the performance of the heat exchanger is to be maintained through the production cycle.

Foulants that cannot be eliminated through the aforementioned techniques can be controlled by the addition of synthetic polymers with dispersal properties. These polymers are applied at low dose rates and maintained as long as the fouling problem exists. The elimination of foulants by changing the make-up water source is more often than not, a more economical solution.

Incompatibility of some antiscalant products with cationic polymers, employed in the clarification of the make-up water, can lead to the fouling of heat exchangers, especially if the polymers are overdosed.

#### 4.16.2 Biological fouling

The presence and growth of living matter is commonly referred to as biofouling. Biofouling can interfere with the flow of water through the heat exchangers and other conduits. This limits heat transfer and contributes to corrosion and the general deterioration of the cooling system.

Recirculating cooling water systems are ideal incubators for promoting the growth and proliferation of micro-organisms. Water saturated with oxygen, and exposed to sunlight, which is maintained at a temperature of  $30^{\circ}\text{C}$  -  $60^{\circ}\text{C}$  and a pH of 7 to 9 ensures abundant nutrients and an appropriate environment for life sustaining growth.

The build-up of a biofilm is initiated by the adhesion of bacteria to the metal surface from the bulk water. Transport of microbial particles to the surface is due to the turbulent flow. The micro-organisms attached to the surface; grow by the assimilation of nutrients from the bulk water. They produce a slimy coating as part of their metabolism. Other suspended solids (sand, clay, bacteria) are trapped in the biological slime which causes the biofilm to expand.

Biofilms can cause losses in heat transfer because of their insulating properties. Kinetic energy is absorbed from the flowing water over the rippled surface.

Three major classes of micro-organisms are associated with recirculating cooling water systems, namely: algae, fungi and bacteria. Fungi are only significant for cooling systems containing wood and are therefore not dealt with in this document.

Algae can range from very simple single cell (unicellular) plants to multicellular species. The latter include diverse forms and shapes, including slimy masses composed of several cells or long strands (filaments) of algae. All algae contain coloured pigments, the most important of which is chlorophyll. Algae usually flourish on wetted surfaces exposed to sunlight and oxygen and will not grow in the absence of sunlight.

Their impact on metal corrosion can be severe. The algal biomass contributes to the formation of favourable environmental conditions for crevice corrosion and pitting. Algal mats can block openings in distribution trays and can also clog screens and block the flow in the pipelines by sloughing off surfaces. The most troublesome algae in cooling water systems are the blue green and green algae, but diatoms and other types have been found in cooling water deposits.

Bacteria are unicellular microscopic organisms that are much smaller than algae and lack chlorophyll. They exist in three basic forms: rod-shaped (bacillus), spherical (coccus), and spiral (spirillum). The nutrients required for growth must be in solution, which necessitates a certain amount of moisture for their environment. Some bacteria require other carbon forms, in addition to  $\text{CO}_2$ , in order to produce

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carbohydrates for food. Therefore, water or wet environments, high in organic content are suitable for the proliferation of bacteria. Heat exchangers provide the ideal environment for this biomass, which can significantly reduce heat transfer efficiency and also aggravate under-deposit corrosion.

Sulphate Reducing Bacteria have been cited as the culprits in Microbiologically Induced Corrosion (MIC). These organisms are anaerobic and convert dissolved sulphur containing compounds, that is,  $\text{SO}_4^{2-}$  to hydrogen sulphide ( $\text{H}_2\text{S}$ ). Carbon steel and stainless steel are severely corroded by  $\text{H}_2\text{S}$ . Acid producing bacteria (*Thiobacillus*, *Nitrobacter* and *Beggiatoa*) have also been implicated as contributors in the MIC process.

*Desulfovibrio desulfuricans* is the most prevalent sulphate-reducing species. It exists mainly under deposits devoid of oxygen. The form of corrosive attack on carbon steel by these bacteria is quite distinctive; it is recognisable by the smooth disc shaped concentric rings formed on the metal surface. The formation of black iron sulphide deposits in conjunction with the rotten egg odour and bright metal under the deposit are also characteristic of sulphate-reducing bacteria attack.

*Thiobacillus* are aerobic sulphur bacteria, which can oxidise sulphur, sulphides or sulphates to sulphuric acid ( $\text{H}_2\text{SO}_4$ ). *Thiobacillus* and *Desulfovibrio* bacteria can both exist simultaneously in close proximity. The anaerobic sulphate-reducers can survive beneath the aerobic sulphur bacteria deposits.

*Nitrobacter agilis* oxidise nitrite base inhibitors as well as ammonia to nitrate. The oxidation of the nitrite in a nitrite - based inhibitor renders the inhibitor ineffective and rapid general thinning of copper based alloys and steel can occur.

Iron depositing bacteria (*Gallionella*) can oxidise water-soluble  $\text{Fe}^{2+}$  ions to insoluble  $\text{Fe}_2\text{O}_3$ , which will subsequently deposit on the inside of piping where it could aggravate crevice corrosion under cooling water chemical conditions.

Slime forming bacteria (*Pseudomonas*) form a dense, sticky biomass that impedes water flow and contributes to fouling by sustaining the growth of other organisms.

#### 4.16.3 Detection of microbiological influenced corrosion

Microbiological influenced corrosion (MIC) is typically complicated with conventional corrosion/scaling deposits or other microbiological problems. The identification and detection of MIC by simple visual inspection is difficult. There is a series of interrelated criteria that can help in recognising the existence of MIC. These are:

- Pitting corrosion rather than lateral surface corrosion
- The presence of microbial-biomass on corroded surfaces,
- The presence of hydrogen sulphide in anaerobic environments and metal sulphide in aerobic environments,
- The presence of ferric (ous) hydroxide in aerobic environments,
- Excessive bacterial populations in the bulk water,
- Corrosion in stagnant or "dead flow "areas,
- Hemispheric tubercles with pits underneath, and
- Corrosion in systems with non-aggressive water chemistry (e.g. high pH, alkalinity and low temperatures)

When several of the above are present, it may indicate that the corrosion is related to the uncontrolled growth of the micro-organisms. The consultation of a specialist microbiologist to confirm the findings is, however, essential.

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#### 4.16.4 Biofouling control

The chemical materials currently in use to control growth of micro-organisms are classified as “biocidal” or “biostatic”. The biocides kill the micro-organisms and the biostats inhibit their growth and reproduction. Ideally, the microbial control programme should keep the population level in the “lag” phase at numbers well below the critical population level. It has been shown to be possible to keep the population at this critical level when the environment contains one or more adverse factors that control the growth and reproduction of the micro-organisms. The adverse factor must be stabilised in a consistent state so that the population does not go through a transition into the “lag” phase.

##### 4.16.4.1 Biostats

A biostat with broad-spectrum properties will create an adverse condition that effectively keeps the population in the “lag” phase. The frequency of addition will depend on the persistence of the biostat in the system and the residual effect that can be maintained in the environment where the microflora exists.

##### 4.16.4.2 Biocides

A broad spectrum-biocide (microbiocide) can also be used to accomplish the same objective. The distinction, however, is that the activity of the biocide may be intermittent and does not require that the concentration of the biocide be maintained on a constant residual. The addition of a biocide to a system is timed so that the re-population never achieves a reproduction rate that exceeds the kill rate. It is necessary to maintain sufficient concentration of the biocide in the system for adequate contact time to kill most viable segments of the microflora without upsetting the biological equilibrium. Dosing of alternating biocides is advisable to minimise the risk of biocidal resistance. Maintaining the “lag” phase condition when using a true biocide can be achieved consistently only when the operating conditions of the system are relatively stable and not subjected to repeated changes.

When selecting a microbial control program the inputs of specialist microbiologists are essential to assist in selecting an effective program.

###### 4.16.4.2.1 Factors determining the choice of microbiocides

Selection of the proper biocide or combination of biocides depends on a number of factors. The primary considerations are:

- a. The type of micro-organisms involved,
- b. The prior operating history of the system,
- c. The type of process cooling water,
- d. The chemicals being used for scale and corrosion control,
- e. The chemical and physical characteristics of the water in the system,
- f. Environmental and safety limitations and restrictions, and
- g. Water losses from the system

###### 4.16.4.2.2 Types of biocides

The chemicals used to control the growth of micro-organisms in industrial process water systems are commonly referred to as biocides, biocides, algacides, fungicides, bactericides and slimicides.

These biocides are usually classified into two groups, i.e., oxidising and non-oxidising.



**Oxidising biocides:**

The following oxidising biocides are found in general use in cooling water systems.

- a. Chlorine and chlorine yielding materials
- b. Hypo-chlorides
- c. Chloro-iso-cyanurates
- d. Chlorine dioxide
- e. Sodium bromide

An effective auxiliary and system biocide and / or biodispersant should conform to the following requirements:

- a. Solid organo-bromine/chlorine compounds
- b. Ozone
- c. Sodium or hydrogen peroxide

**Non-oxidising biocides:**

The following non-oxidising biocides are found in general use in cooling water systems:

- a. Isothiazolone compounds
- b. Dibromonitrilopropionamide
- c. Polymeric quaternary ammonium salts;
- d. Organo-tin compounds;
- e. Organo-sulphur compounds;
- f. Chlorophenate / phenol compounds;
- g. Glutaraldehyde;
- h. Quaternary ammonium salts;
- i. Rosin amines as algaecides;
- j. Organo-bromine;
- k. Organic thiocyano-azole; and
- l. Dodecylguanidine hydrochloride.

Biocides used in industrial process waters will occasionally consist of two or more different types of active ingredients. These synergistic blends are required to broaden the spectrum of the product. It is however recommended that alternating biocide dosing with different biocides is part of the formal treatment regime.

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#### 4.16.4.3 Chemicals used for microbial control

- a. It is effective against sessile and planktonic micro-organisms and particularly effective against the strains of bacteria which contribute to fouling or MIC mechanisms in auxiliary cooling systems;
- b. It is compatible with the corrosion inhibitors, dispersants and other chemicals that may be used in the system;
- c. It is effective at the pH of the cooling water;
- d. It is able to penetrate and disperse biomass;
- e. It will maintain its toxic properties while in the system;
- f. It will degrade to compounds that do not interfere with the system operation; and
- g. It is easy to handle with relative safety to staff.
- h. Cost effective.

##### 4.16.4.3.1 Non oxidising biocides

Glutaraldehyde disrupts the organism by cross-linking cell protein. It is effective against bacteria, yeasts and moulds and is most effective over a pH range of approximately 6 to 9. Above a pH of 9, glutaraldehyde starts to degrade, but can still achieve a rapid kill prior to degradation. Glutaraldehyde is non corrosive to metals, at the recommended application rates of 25 mg.kg<sup>-1</sup> to 100 mg.kg<sup>-1</sup>, as the active ingredient.

##### Advantages:

- a. The residual products emanating from glutaraldehyde dosing are carbon, hydrogen and oxygen and thus it does not contain any residual contaminants,
- b. Glutaraldehyde is compatible with common scale and corrosion inhibitors, and
- c. Active concentrations can be measured with field kits available from the suppliers. Nitrites might, however, interfere in the test.

##### Disadvantages:

Glutaraldehyde decomposes to carbon dioxide and possibly to glutaric acid, which can result in a drop in pH, incompletely decomposed organic products can be nutrients, and Glutaraldehyde increases the TOC level and could lead to foaming.

Isothiazolone is usually supplied as a 1.5 % active solution and is also available as a 6 or 14 % active solution. The product is extremely hazardous and is thus preferably handled as the 1.5 % solution. Eye and skin contact must be avoided. Isothiazolone inhibits macromolecular synthesis and is effective against algae, planktonic and sessile bacteria. It is also effective against anaerobes, including sulphate-reducing bacteria. Isothiazolone is most effective at a pH range of 6 to 9 with 8 being the optimum. The product is not aggressive towards metals unless in very high concentrations.

Residual contaminants from isothiazolone dosing are magnesium, chlorides, sulphate and copper. The application rate varies from 10 mg.kg<sup>-1</sup> to 25 mg.kg<sup>-1</sup> as active ingredient.

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## Advantages:

- a. It is a water based product and does not contain organics,
- b. Isothiazolone acts very rapidly, and
- c. Isothiazolone is very effective against nitrifying and denitrifying bacteria

## Disadvantages:

- a. Sulphate and chloride contribution,
- b. Copper residual contaminant could contribute to galvanic corrosion when precipitating from solution in the absence of a suitable inhibitor,
- c. Copper residual could also deplete tolyltriazole,
- d. Isothiazolone is extremely hazardous and quickly damages skin and eyes and could further trigger allergic reactions, and
- e. Each 1.5 mg.kg<sup>-1</sup> of active biocide applied will contribute 1.3 mg.kg<sup>-1</sup> chloride and 0.7 mg.kg<sup>-1</sup> sulphate to the system water.

Methylene Bis (Thiocyanate) is a methylene ester of thiocyanic acid. The thiocyanate fragment of the molecule blocks the transfer of electrons in the respiratory system of the micro-organisms. Methylene Bis (Thiocyanate) is very effective against bacteria, fungi and algae. At pH values above 7,5 the biocide hydrolyses but can be effective up to pH 8,5. At pH 8,5 the half-life of the biocide is approximately four hours. Methylene Bis (Thiocyanate) is not aggressive to metals at the recommended application rate of 1 mgkg<sup>-1</sup> to 8 mg.kg<sup>-1</sup> as active ingredient.

## Advantages:

- a. Methylene Bis (Thiocyanate) is effective at low application rates, and
- b. Methylene Bis (Thiocyanate) is a broad-spectrum biocide.

## Disadvantages:

- a. Methylene Bis (Thiocyanate) decomposes to less toxic substances.
- b. Repeated applications will increase TOC concentrations in the cooling system.
- c. Methylene Bis (Thiocyanate) is an emulsion.
- d. Contributes 0,75 mg.kg<sup>-1</sup> of sulfates per 1mg.kg<sup>-1</sup> active ingredient applied.
- e. Chloride contamination of the bulk system has not been confirmed.

2,2 dibromo-3-nitrilopropionamide (DBNPA) interacts with enzymes and interferes with cell respiration and metabolism. DBNPA is very effective against bacteria and achieves a significant kill rate in 1 h to 3 h. It is very effective against aerobic and anaerobic bacteria at pH levels below 7.5. Above this pH the compound hydrolyses but can still be effective up to a pH of 8.3. DBNPA is not aggressive to metals at the recommended application rate of 0.5 mgkg<sup>-1</sup> to 10 mgkg<sup>-1</sup>.

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## Advantages:

- a. DBNPA acts very rapidly.
- b. Low dose rates are required.

## Disadvantages:

- a. The glycol solvent adds to the TOC values and could further serve as a nutrient for microbes,
- b. It contributes 0.7 mg.kg<sup>-1</sup> bromine per 1 mg.kg<sup>-1</sup> DBNPA, and
- c. The pH dependent hydrolyses reduces half-life dramatically.

**4.16.4.3.2 Oxidising biocides**

Oxidising biocides are seldom used in closed cooling systems as the nitrite inhibitor will be oxidised to nitrate.

Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) is an aqueous oxidising agent and acts by destroying the protein groups in microbial substances. Hydrogen peroxide is not compatible with nitrite inhibition. Hydrogen peroxide is a potentially explosive mixture in concentrations of 60 % to 100 %. It can be used with molybdate inhibited systems but since it is an oxidising biocide it might increase corrosion rates. Hydrogen peroxide is compatible with all metals but the oxidising effect could increase the corrosion rate of ferrous and copper alloys. Application rate varies from 10 mg.kg<sup>-1</sup> to 100 mg.kg<sup>-1</sup> as H<sub>2</sub>O<sub>2</sub>.

## Advantage:

- a. Hydrogen peroxide does not contribute to any residual contaminants of the cooling water.

## Disadvantage:

- a. Hydrogen peroxide might cause foaming if it reacts with significant biological material.

**4.16.4.3.3 Biocides not compatible with closed systems.**

Dodecylguanidine hydrochloride contributes 3 mg.kg<sup>-1</sup> to 7 mg.kg<sup>-1</sup> chlorine at typical application rates of 25 mg.kg<sup>-1</sup> to 50 mg.kg<sup>-1</sup>.

Carbamates can attack copper alloys and precipitate iron. Carbamates are more applicable to open recirculating cooling water systems.

Quaternary ammonium salts (Quats) contribute to the chloride concentration of the system. No specific contribution can be listed as a result of the extent of formulations available.

Chlorine cannot be applied to close cooling water system (with demineralised water makeup) as result of the chloride contamination. Chlorine, however, remains a good biocide for open evaporative systems provided the system pH is within the most effective range for chlorine. But safety issues have limited its use.

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#### 4.17 CORROSION PROCESSES IN RECIRCULATING WATER SYSTEMS

An understanding of the relationship between cooling water and the build-up of deposits and corrosion of heat transfer surfaces requires an awareness of cooling systems characteristics. There are basically two types of cooling systems employed in Eskom, namely:

##### 4.17.1 Open recirculating systems

Open recirculating cooling system continuously re-uses the water that passes through the heat transfer equipment. Evaporative cooling to the atmosphere expels the unwanted heat transferred to the cooling water. Open recirculating cooling systems are oxygen saturated and may contain a high level of dissolved solids. These factors can significantly affect the build-up of deposits and deterioration of the heat transfer equipment.

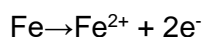
##### 4.17.2 Closed recirculating systems

Closed recirculating systems should have very little water loss and continuously recirculates the same water. The heat absorbed from the heat transfer equipment is dissipated to another heat sink. Because there are no evaporative losses and provided that the system is operated correctly, make-up water is minimal and the mineral content remains essentially constant. However, corrosion by-products can easily accumulate and foul heat transfer equipment.

#### 4.18 THE CORROSION MECHANISM

Corrosion can be defined as the deterioration of the metal caused by the reaction with its surrounding environment. For the corrosion reaction to take place between water and the metal surface, a potential difference must exist between different areas on the surface. This causes the passage of electrical current through the metal from the area of high potential to the area of low potential. Thus the corrosion of metals in contact with water is electrochemical in nature. The basic reaction occurs at the area of lower potential, which is the anode. The dissolution reaction causes metal ions to form and go into solution.

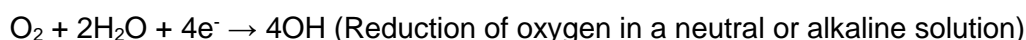
The anodic reaction can be generally represented by:



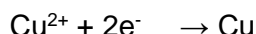
or in the case of copper



The liberated electrons that migrate through the metal to the areas of higher potential are used in the reduction of other ions or oxygen in the water. The following reactions take place at the cathodic site of the metal:



(Hydrogen evolution)



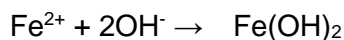
(Metal deposition)



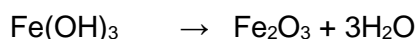
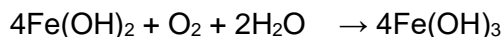
(Reduction of metal ions)

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Interaction between the products of the anodic and cathodic reactions can occur, forming solid corrosion products on the metal surface. For example, ferrous ions ( $\text{Fe}^{2+}$ ) coming from the corrosion of the metallic iron will react with the hydroxyl ions ( $\text{OH}^-$ ) produced from the reduction of dissolved oxygen:



Ferrous hydroxide ( $\text{Fe}(\text{OH})_2$ ) is further oxidized to form ferric hydroxide ( $\text{Fe}(\text{OH})_3$ ), which is unstable and subsequently transformed to hydrated ferric oxide ( $\text{Fe}_2\text{O}_3$ ), also known as red rust.



A build-up of rust ( $\text{Fe}_2\text{O}_3$ ) occurs at the anodic sites, forming mounds known as tubercles. Under these mounds, localised corrosion continues to accelerate.

Not all corrosion products are detrimental. The oxide films of copper  $\text{Cu}_2\text{O}$  and aluminium  $\text{Al}_2\text{O}_3$  actually protect these metals against some forms of corrosion.

The corrosion process between water and metal can take many forms. The more common forms that have been observed in heat transfer equipment have the following characteristics:

#### 4.18.1 Corrosion Types

##### 4.18.1.1 General corrosion

General corrosion, or uniform attack, occurs when the anodic areas on the metal surface keep shifting to different sites. This continual shifting results in relative uniform metal removal. Because this type of corrosion can often be predicted, material loss can be taken into account during the design stage.

##### 4.18.1.2 Galvanic corrosion

Galvanic corrosion occurs when dissimilar metals are in contact in a conducting fluid (water). Accelerated corrosion occurs with the least resistant alloy, while the more resistant alloy is protected. The resistance of alloys can generally be described by the galvanic series. The alloys closer to the active end of the series will behave as the anode and will corrode while the alloys close to the noble end will behave as the cathode and will be protected. The intensity of the attack will depend on the relative surface areas of the metals in electrical contact. Large cathodic areas in contact with relatively small anodic areas will aggravate galvanic corrosion and cause severe dissolution of the more active metal.

Galvanic corrosion should be considered in the design of a system, similar metals or metals close to one another in the galvanic series should be used. Less obvious is the damaging effect that can occur when a dissolved noble metal is transported through the water and is capable of depositing on an active metal. For example, copper ions can plate on to steel surfaces setting up local corrosion cells.

##### 4.18.1.3 Erosion corrosion

Erosion corrosion is normally restricted to copper-based alloys. It occurs in areas where turbulence intensity at the metal surface is high enough to cause mechanical disruption of the protective film. Corrosion occurs at these sites and forms horseshoe-crescent-shaped indentations facing upstream of the water flow. The process is usually accelerated when abrasive solid particles are entrained in the water. Because turbulence increases with velocity, areas having higher water velocities are prone to attack.

For example, turbulence intensity is much higher at tube inlets than some distance down the tube, resulting in the phenomenon of inlet-end corrosion-erosion.

Cavitation is a phenomenon that occurs in moving water when the flow is disturbed so as to create a local pressure drop. Under these conditions a vapour bubble will form and then collapse, applying a momentary stress of up to 414 MPa to the surface. The current theories of cavitation state that this repeated

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mechanical working of the surface creates a local fatigue situation that aids the removal of metal. Cavitation damage will be confined to the area where the bubbles collapse, usually immediately downstream of the low-pressure zone. Cavitation damage can only be eliminated through design or redesign of systems suffering from this form of attack.

#### 4.18.1.4 Crevice corrosion

Crevice corrosion is an electrochemical attack due to a difference in the corrosive environment between a shielded area and its surroundings. Attack usually occurs in areas having a small volume of stagnant solution, such as tube sheet supports, under deposit tubercles and at threaded joints. Corrosion is usually initiated because the oxygen concentration within the crevice is lower than that of the surrounding area. The outside area is higher in oxygen concentration and becomes predominantly cathodic. Anodic dissolution occurs at the stagnant area. Once attack is underway, the area in the crevice or under a deposit becomes increasingly more aggressive because of the pH depression and an increase in electrolyte concentration.

#### 4.18.1.5 Pitting corrosion

Pitting corrosion is one of the most insidious forms of attack. It takes place at small discrete areas where general corrosion is negligible. The pit develops at a localised anodic site on the surface and continues to grow because of a large cathodic area surrounding the anode. High concentrations of metal chlorides often develop within the pit and hydrolyse to produce an acidic pH environment. This solution remains stagnant, with a high salt content and low oxygen concentration. The reactions within the pit become self-sustaining (autocatalytic) with very little tendency for them to be suppressed, ultimately causing penetration through the base metal. Pitting corrosion has also been associated with both crevice and galvanic corrosion. Metal deposition (copper ions plated on a steel surface) can also create sites for pitting corrosion.

#### 4.18.1.6 De-alloying

De-alloying is the selective removal of one element (usually the least noble) from an alloy, by the corrosive environment. This mechanism is also referred to as selective leaching or dezincification, denickelification, etc. thereby designating the element removed from the alloy.

#### 4.18.2 Corrosion control

Corrosion control requires knowledge of the metallurgy of the system, an understanding of the susceptibility of the metals to corrode under the operating conditions encountered, and an understanding of the limitations of the specific corrosion inhibitors applied. Principal economic advantages for the use of corrosion inhibitors in cooling water stem from two sources, namely;

- a. they reduce the frequency of maintenance and inspection shut-downs, and
- b. they permit more extensive use of iron and carbon or low alloy steels.

Aqueous corrosion has been shown to consist of electrochemical processes. The detrimental effects of these processes in cooling water environments can be significantly reduced by various methods, such as

- designing systems with more corrosion resistance materials,
- applying protective coatings which could including anti-fouling properties as has successfully been used in coating of condenser tubing,
- using sacrificial anodes (cathodic protection), and
- effective chemical inhibition programmes.

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For chemical treatment or corrosion inhibition programs to be effective, they:

- must protect all exposed metal from corrosive attack,
- must be effective at low concentration,
- must not cause deposit on the metal surface,
- must remain effective under a broad pH range,
- must remain effective under a broad temperature range,
- must remain effective under a broad water quality range,
- must remain effective under a broad heat flux range,
- must prevent scale formation and disperse deposits, j) must have minimal toxicological effect when drained or discharged,

It must be noted that inhibitors require metal surfaces free of deposits to be effective. Inhibitors can be broadly classified as cathodic, anodic and mixed.

#### **4.18.2.1 Cathodic inhibitors**

Cathodic inhibitors impede the cathodic reaction, for example, oxygen reduction reaction. Cathodic inhibitors are not as effective as the anodic inhibitors.

#### **4.18.2.2 Anodic inhibitors**

Anodic inhibitors suppress anodic reactions; that is, the rate of metal ions being transferred into the aqueous environment is reduced. Anodic inhibitors are often considered to be “pitting prone” because an underfeed of the inhibitor can cause pitting.

#### **4.18.2.3 Mixed inhibitors**

When the anodic and cathodic reactions are both affected by the chemical treatment programme, a mixed mode of inhibition is in effect.

#### **4.18.2.4 Corrosion inhibition programme**

In selecting a corrosion inhibition programme cognisance must be taken of several important aspects. Aspects to be considered are the:

- a. Ease of quantifying the active ingredient,
- b. analytical surveillance required,
- c. complexity of the laboratory test method for the active ingredient(s),
- d. ease of administering the inhibitor (dosing plant),
- e. cost of the programme,
- f. safety of personnel,
- g. suitability of the programme for the lay-up of the system or,
- h. compatibility of the inhibitor with lay-up chemicals, if not the same,
- i. materials of construction of the cooling water system,
- j. type or quality of make-up water,
- k. volume of the cooling water system,

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- l. type of cooling water system i.e. open or closed,
- m. un-controllable water losses from the cooling water system,
- n. impact of the inhibitor on the receiving environment, and
- o. biocides required to protect the inhibitor against biodegradation.

#### 4.18.2.5 Practical use of inhibitors

##### 4.18.2.5.1 Sodium nitrate

NOTE Nitrite oxidises to nitrate in open cooling water systems and can thus only be used in closed loop systems.

The main advantage of nitrite as an inhibitor is the fact that oxygen is not required to form the inhibition film. Sodium nitrite is an anodic inhibitor and requires a critical concentration for the protection of steel. Sodium nitrite is one of the inhibitors used in cooling water. The nitrite concentration should always be at least equal to the chloride concentration of the cooling water and exceed the sulphate concentration by at least 250 mg.kg<sup>-1</sup> to 500 mg.kg<sup>-1</sup> as sodium nitrite. It should therefore be applied at a minimum concentration of >250 mg.kg<sup>-1</sup> in demineralised water cooling systems. The use of chloride containing biocides could alter this dosing requirement. At a pH above 7.5 nitrite may contribute to the pitting of carbon steel if the nitrite concentration falls below this critical level.

Another method of determining the required nitrite level in cooling systems using potable water as make-up water is to apply a treatment level of sodium nitrite to a weight ratio of one with aggressive ion concentrations. i.e.

$$[\text{NO}_2] / ([\text{Cl}] + [\text{SO}_4]) = 1$$

When formulated with borax, nitrites are excellent corrosion inhibitors for closed loop cooling systems. Dosage levels for the borax should be in the order of 1500 mgkg<sup>-1</sup> to 2000 mgkg<sup>-1</sup> with nitrite at the critical level. It should be noted that nitrites are nutrients for some species of bacteria, which can oxidise nitrite ions and render them ineffective for corrosion inhibition. Biocides must thus be used in conjunction with nitrites to ensure the integrity of the programme. Thus, for any close loop cooling system operating with demineralised or good quality potable water make-up the dosing must be as follows:

Sodium nitrite as NaNO<sub>2</sub> > 250 mg.kg<sup>-1</sup> as NaNO<sub>2</sub>

Sodium tetra borate as Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> > 1500 mg.kg<sup>-1</sup> as Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>

Biocide (Glutaraldehyde) 50 mg.kg<sup>-1</sup> as active ingredient

##### 4.18.2.5.2 Molybdates

Molybdates are classified as anodic inhibitors. In waters with moderate Cl<sup>-</sup> concentrations (200 mg.kg<sup>-1</sup>) the level of sodium molybdate (Na<sub>2</sub>MoO<sub>4</sub>) needed for protection is at least 1000 mg.kg<sup>-1</sup>. In systems with demineralised make-up water the level can be reduced to 150 mg.kg<sup>-1</sup> provided no chlorides are introduced through biocide dosing. Normal treatment practices consist of a combination of molybdates with other inhibitors to produce a synergistic affect. This reduces the high level of molybdate ions (MoO<sub>4</sub><sup>2-</sup>) needed when used alone.

Combinations with zinc salts, phosphonates, inorganic phosphates, nitrites and carboxylates such as long chain acrylates and azoles (benzo or tolytriazole), have been proven effective in controlling corrosion in multimetal systems. Sodium molybdate is a non-oxidizing inhibitor and needs a suitable oxidising agent to augment the inhibitor and to impart a protective film. In aerated systems, the most abundant oxidiser is

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oxygen. Any of the mentioned combination inhibitors can be used with molybdate in an open system apart from sodium nitrite.

The use of molybdates in closed systems requires an oxidising salt, such as  $\text{NaNO}_2$ . The optimum composition for the  $\text{Na}_2\text{MoO}_4$  :  $\text{NaNO}_2$  system consists of a 60:40 weight ratio of the two salts. Thus for any closed loop cooling system operating with demineralised or good quality potable water as make-up water the dosing must be as follows:

$\text{Na}_2\text{MoO}_4$  (Sodium Molybdate) 250  $\text{mg.kg}^{-1}$

$\text{NaNO}_2$  (Sodium nitrite) 170  $\text{mg.kg}^{-1}$

Biocide (Glutaraldehyde) 50  $\text{mg.kg}^{-1}$  as active ingredient

Open evaporative cooling water systems operating with potable water make-up at elevated cycles of concentration must be treated as follows:

$\text{Na}_2\text{MoO}_4$  (Sodium Molybdate) 1000  $\text{mg.kg}^{-1}$

Biocide could be any of the above-mentioned or bromochlorohydrone and hypo-chlorides could also be applied with swimming pool applicators.

The precipitation of calcium molybdate ( $\text{CaMoO}_4$ ) is a concern in systems with moderate to high calcium concentrations. This precipitation however is only taking place at relatively high pH values (pH 10+).

#### 4.18.2.5.3 Phosphates

Sodium phosphate  $\text{Na}_3\text{PO}_4$  is an anodic inhibitor and is effective in the presence of oxygen. Its protective properties toward steel are a function of the pH. The use of phosphate as an inhibitor should be relegated to more alkaline environments (pH > 9,0).

In open recirculating systems, phosphate treatment levels should be 15  $\text{mg.kg}^{-1}$  to 20  $\text{mg.kg}^{-1}$  but at lower concentration  $\text{PO}_4^-$  ions could cause pitting attack. Inhibition by  $\text{PO}_4^-$  ions is sensitive to electrolyte concentration:

$\text{Cl}^-$  ions can promote pitting attack. Because the protective oxide film contains voids and other inclusions,  $\text{Cl}^-$  ions are easily adsorbed to soluble complexes. Hydrolysis of these complexes produces acid domains, which leads to localised acidic attack.

With water of high calcium hardness the potential for deposit formation increases and additional factors such as pH and temperature come into effect. The need for a calcium phosphate scale inhibitor becomes exceedingly more important with an increase in cycles of concentration.

Thus for any closed loop cooling system operating with demineralized or good quality potable water as make-up water the dosing must be as follows:

$\text{Na}_3\text{PO}_4$  as  $\text{PO}_4$  100  $\text{mg.kg}^{-1}$

pH > 10

Dissolved oxygen > 2  $\text{mg.kg}^{-1}$

Tolyltriazole >10 $\text{mg.kg}^{-1}$  with occasional shock dosing at 30 $\text{mg.kg}^{-1}$

The use of phosphate in open evaporative cooling water systems is not recommended.

#### 4.18.2.5.4 Chromates

Chromates are highly effective in protecting ferrous and many nonferrous alloys against corrosion. The negative impact of chromates on the environment makes this product not environmentally acceptable and is therefore not approved for use in Eskom.

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#### 4.18.2.5.5 Copper corrosion inhibitors

Benotriazole and tolyltriazole have been found to be superior to mercaptobenthiazole (MBT) as copper corrosion inhibitors. Benzotriazole and tolyltriazole can deactivate dissolved copper and prevent the deposition on other steel structures of the cooling system. Copper deposition on steel could result in corrosion as a result of potential differences. Benzotriazole and tolyltriazole are more resistant to oxidation than MBT, although free chlorine is harmful to their function. They are compatible with glycol antifreeze and are therefore suitable for use in closed systems constructed with copper alloys.

Aromatic azoles produce a corrosion resistant film on copper and copper based alloy surfaces, which does not wipe off and is resistant to the action of water. Azoles are classified as cathodic inhibitors because they adsorb at cathodic sites and interfere with the oxygen reduction action.

Application of azoles requires an initial high concentration ( $30 \text{ mg.kg}^{-1}$ ) treatment to passivate the system against ongoing corrosion with subsequent dosing at a reduced rate ( $10 \text{ mgkg}^{-1}$  to  $15 \text{ mgkg}^{-1}$ ). Best practice however, is to consistently evaluate dose rates against the copper corrosion products in the system and optimise the dosing accordingly.

#### 4.18.2.5.6 Polyphosphates

Sodium salts of the polyphosphates are normally used for corrosion control. The pH of the environment directly affects the protective properties of the phosphates. Normal concentrations are  $15 \text{ mg.kg}^{-1}$  to  $20 \text{ mgkg}^{-1}$  and the pH should be maintained in the pH range of 6.5 to 7.5 if steel and copper alloys are both part of the system metallurgy.

The polyphosphates are relatively insensitive to the electrolyte concentrations, but do require an increase in dosage with an increase in water corrosivity. They are effective inhibitors in controlling galvanic attack between two dissimilar metals, but do not prevent deposition of cathodic species on the more active metal, that is, copper on steel.

Divalent metal ions and  $\text{Ca}^{2+}$  in particular are needed with the polyphosphates for the effective inhibition of steel. The ratio of  $\text{Ca}^{2+}$  ions in solution to polyphosphate should be at least 0.2 and preferably 0.5. The protective film develops through the formation of a positively charged colloidal complex that migrates to the cathode.

The polyphosphates will revert back to  $\text{PO}_4^{3-}$  ions, which have a potential scaling tendency in the presence of sufficient calcium at an elevated pH. It is extremely difficult to inhibit the precipitation of calcium phosphate scale. This tenacious scale can only be inhibited with new generation scaling inhibitors.

Thus, for closed loop systems with good quality potable water as make-up water the specifications are as follows:

Polyphosphate as polyphosphate  $15 \text{ mg.kg}^{-1}$  to  $20 \text{ mg.kg}^{-1}$

pH 6.5 to 7.5

Calcium as  $\text{Ca}^{2+}$   $7.5 \text{ mg.kg}^{-1}$  to  $10 \text{ mg.kg}^{-1}$  ( Times 2.5 for as  $\text{CaCO}_3$ )

Pre-treat the system for one week with  $45 \text{ mg.kg}^{-1}$  polyphosphate

#### 4.18.2.5.7 Zinc polyphosphate

The addition of zinc to the polyphosphate does not appreciably change the general nature of the polyphosphate. This method retains its threshold inhibition of  $\text{CaCO}_3$  and  $\text{CaSO}_4$ , its ability to protect ferrous and non-ferrous metals, and its detergent properties. Zinc polyphosphate inhibitors also enable multivalent metal ions to form positively charged colloidal complexes.

Zinc increases the rate at which the protective film is formed on the metal surface. This rapid protective film formation improves the general protection of the system.

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Maintenance concentrations are generally  $10 \text{ mg.kg}^{-1}$  as polyphosphate. Good practice requires a dosage two to three times the maintenance concentration as a pre-treatment of the system for a short period of time, that is, less than one week. A pH range of 6.8 to 7.2 is required for good control. This limitation in pH is necessary to prevent excessive corrosion of the copper-based alloys while at the same time preventing the precipitation of calcium phosphate.

Thus for closed loop systems with good quality potable water as make-up water the specifications are as follows:

Zinc polyphosphate as polyphosphate  $10 \text{ mg.kg}^{-1}$  to  $15 \text{ mg.kg}^{-1}$ ,

pH 6.5 to 7.5

Calcium as  $\text{Ca}^{2+} > 7.5 \text{ mg.kg}^{-1}$  and generally  $< 40 \text{ mg.kg}^{-1}$  Pre-treatment of the system for one week with  $30 \text{ mg.kg}^{-1}$  zinc polyphosphate

#### 4.18.2.5.8 Phosphonates

Phosphonates differ from polyphosphate in terms of hydrolytic stability, which reduces the problem of reversion to  $\text{PO}_4^-$  common to polyphosphates. Two classes of materials are extensively used, namely: AMP (Aminomethylenephosphonic acid) and HEDP (1 Hydroxyethylidene-1, 1- diphosphonic acid). AMP will degrade in the presence of chlorine and must not be applied to the same system. HEDP resists oxidation to a greater extent and can be used with chlorine.

Phosphonates form very stable complexes with a variety of metal ions and thus accelerate their corrosion. They also react aggressively to copper and its alloys, although this can be rectified by blending zinc polyphosphate and specific copper corrosion inhibitors with phosphonates. The risks of blending these products at a power station are high and proprietary blends should be carefully selected.

Calcium phosphate deposition is a reality in moderate alkalinity and hardness water. An application at  $15 \text{ mg.kg}^{-1}$  to  $20 \text{ mg.kg}^{-1}$  is recommended for all ferrous, closed loop systems operating with potable water as the only source of make-up water.

Thus for all ferrous, closed loop systems, with potable water as the only source of make-up water, the recommendations are as follows:

pH 8.0 to 8.5

Phosphonates  $15 \text{ mg.kg}^{-1}$  to  $20 \text{ mg.kg}^{-1}$

Calcium hardness  $< 100 \text{ mg.kg}^{-1}$  as  $\text{CaCO}_3$

M Alkalinity  $< 100 \text{ mg.kg}^{-1}$  as  $\text{CaCO}_3$

#### 4.18.2.5.9 Zinc phosphonates

The combination of zinc and phosphonates provides significantly improved protection compared to phosphonates alone. The addition of zinc makes the formulation synergistic in its protection to carbon steel while negating the antagonistic effect on the alloys of copper.

Overall treatment level is in the order of  $8 \text{ mg.kg}^{-1}$  to  $10 \text{ mg.kg}^{-1}$  as phosphonate with  $2 \text{ mg.kg}^{-1}$  to  $3 \text{ mg.kg}^{-1}$  zinc. The need for zinc becomes paramount in the presence of copper based alloys. When used alone, the phosphonates are aggressive to copper and form a strong copper-phosphonate complex. Zinc effectively negates this antagonistic effect by forming a stronger and more stable complex. The zinc effectively counteracts the anodic character of the phosphonates through the formation of a phosphonate-zinc complex, which is cathodic compared to the phosphonates alone.

Due to this complex, broad pH application becomes possible. The zinc phosphonate treatment can be used over a pH range of 6.5 to 9. Zinc is held in solution at these more alkaline pH levels, and protection actually improves with the increased alkalinity.

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With zinc phosphonate little sensitivity is shown with increased electrolyte concentration and temperature effects are minimal. Zinc phosphonate systems can be used over a wide range of quality and high temperature of the bulk water. (70 to 75 °C)

Degradation of phosphonates to  $\text{PO}_4^-$  ions by chlorine is significantly reduced with a phosphonate/zinc blend, and the latter can be used in a chlorine environment.

Thus for mixed metallurgy, closed loop systems, with potable water as the only source of make-up water, the recommendations are as follows:

Zinc phosphonate:  $8\text{mg.kg}^{-1}$  to  $10\text{mg.kg}^{-1}$

Zinc:  $2\text{mg.kg}^{-1}$  to  $3\text{mg.kg}^{-1}$

pH: 7.5 to 9.0

Calcium <  $100\text{mg.kg}^{-1}$  as  $\text{CaCO}_3$

Alkalinity <  $100\text{mg.kg}^{-1}$  as  $\text{CaCO}_3$

#### 4.18.2.5.10 Hydrazine

The use of hydrazine, a known carcinogen, should be phased out unless authorisation is granted formally.

Hydrazine reacts with the iron and copper oxides to form protective oxide ("passive") films. Control ranges are in the order of  $5\text{mg.kg}^{-1}$  to  $50\text{mg.kg}^{-1}$  and application rates exceeding  $200\text{mg.kg}^{-1}$  are acceptable for all ferrous systems. Hydrazine is either used without additives or with the addition of morpholine for pH buffering. The pH range for copper containing systems is 8.5 to 9.5 and 8.5 to 10.5 for all ferrous systems. Hydrazine can decompose to ammonia and can thus lead to the corrosion of copper alloys. When using hydrazine as an inhibitor, ammonia concentrations must be verified weekly and should not exceed  $0.5\text{mg.kg}^{-1}$  at any stage. The application of hydrazine is further restricted to systems with little to no oxygen ingress and relatively low operating temperatures ( $<50^\circ\text{C}$ ). Catalytic decomposition of hydrazine is a function of contact with heavy metals such as molybdenum, copper and chromium or their oxides. Rapid decomposition of hydrazine in contact with type 316 stainless steel seems possible but could not be confirmed through laboratory studies. (Type 316 stainless steel contains chromium and significant levels of molybdenum).

NOTE: Hydrazine is a carcinogen and special safety precautions must be followed to ensure staff safety [18].

#### 4.18.2.5.11 Reducing and passivating agents

Diethylhydroxylamine (DEHA), hydroquinone and erythorbic acid are agents that can be applied as inhibitors for closed cooling water systems. All three of these compounds act in the same manner as hydrazine in forming a passive layer on the surface of ferrous alloys and can only be used in all ferrous metallurgy systems. Dosage rates are not well established and these products can be used alone or with amine (e.g. morpholine) for pH control. DEHA can decompose to ammonia and will cause copper corrosion. These products should also only be considered for systems with minimal make-up water requirements.

#### 4.18.2.5.12 Silicates

The most frequently used inhibitors are the glassy amorphous polymeric silicates. The most likely mechanism for corrosion protection is the formation of a negatively charged colloidal particle that migrates to the anodic area. The colloidal particle is possibly the product of the hydrolysis of the silicate in water.

Silicates provide protection for copper, aluminium and ferrous alloys. Dosage range from  $20\text{mg.kg}^{-1}$  to  $50\text{mg.kg}^{-1}$  as  $\text{SiO}_2$  above the normal background, inorganic silica content of the water. Dose rates of up to  $200\text{mg.kg}^{-1}$  can be employed with relative safety.

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Silicates do not perform well at low pH values (below 7.0) however, silicates are effective in low salinity waters with a pH above 7.5 and even as high as 10.5. Polysilicates are in an alkaline medium and increase the pH of the water. Caustic soda can be used for pH control when applying silicates as corrosion inhibitors.

Disadvantages of silicates are the slow formation of the film (days to weeks versus hours) and the fragile nature of the film.

#### 4.18.2.5.13 Diesel generator cooling systems

##### Blended glycol formulations

Glycol antifreeze solutions are normally supplied containing an appropriate proprietary inhibitor or blend of inhibitors. In ordering these products care should be taken in specifying an inhibited ethylene glycol. The corrosion inhibitor concentration for glycol coolants differs considerably from the normal applications.

One of the major corrosion problems in glycol/cooling systems is the slow breakdown of glycol into organic acids at elevated temperature. This breakdown leads to a reduction in buffer capacity with the resulting lower pH values. A sequestering agent such as tolyltriazole must be added to glycol coolants to chemically bond with the copper and iron to minimise their catalytic affect in the breakdown of glycol. To counter the effect of organic acid production, glycol solutions are buffered with high concentrations of tri-sodium phosphate, sometimes fortified with sodium tetraborate and caustic soda to provide a pH of 10 to 10.5 once the inhibited glycol antifreeze concentrate is diluted to a 50 % solution. Potassium phosphate salts are often used as a result of the higher solubility at elevated temperatures.

Typical phosphate concentrations range from 1000 mg.kg<sup>-1</sup> to 2000 mg.kg<sup>-1</sup> as PO<sub>4</sub><sup>-</sup> and at these concentrations phosphate serves as an inhibitor for steel as well. Glycol antifreeze formulations should never be used at concentrations lower than 50 %. The reason for this is that ethylene glycol becomes a nutrient for microbial growth at less than approximately 30 %. This could be serious in diesel generators serving in a standby function as high coolant temperatures are seldom achieved.

Tolyltriazole is generally added to formulations at concentrations of 500 mg.kg<sup>-1</sup> to 3000 mg.kg<sup>-1</sup> as active ingredient. The azole serves several purposes namely:

- a. It sequesters copper and iron corrosion products which catalyses glycol breakdown.

It inhibits copper alloy corrosion and controls the solder corrosion by shutting down the cathodic reaction on the copper solder galvanic couple.

In a closed cooling system, a build-up of corrosion products can deplete tolyltriazole concentrations between extended maintenance intervals. Since the cost of TTA is small in comparison to glycol cost, a high initial tolyltriazole concentration provides insurance against premature azole depletion.

The principal corrosion inhibitor for aluminium and cast iron in antifreeze formulations is silicate. Silicate can also be effective in reducing copper alloy corrosion and in inhibiting the copper/solder galvanic couple should the tolyltriazole become depleted. Silica is added to glycol formulations at 500 mg.kg<sup>-1</sup> to 1000 mg.kg<sup>-1</sup> as SiO<sub>2</sub>. Rapid aluminium corrosion will occur if the silicate concentration falls to below 50 mg.kg<sup>-1</sup> in the system. Sodium nitrite (NaNO<sub>2</sub>) at a concentration of 500 mg.kg<sup>-1</sup> to 1500 mg.kg<sup>-1</sup> (as NO<sub>2</sub>) is used in addition to silicate to control aluminium pitting corrosion.

An antifoam, such as 200 mg.kg<sup>-1</sup> ethylene oxide / propylene oxide copolymer, is generally added to the glycol formulations to prevent foaming that might produce air pockets within the cooling system with subsequent false level indications. Foaming could also lead to the overflow of expansion tanks. Dyes are normally added to glycol formulations to provide a visual indication of the presence or condition of the glycol formulation.

Sodium nitrite is generally not included in light duty automotive engine glycol formulations. This is due to the corrosive effect of nitrite on solder. Soft solders (containing approximately 92 % lead) are very susceptible to corrosion when galvanically coupled to copper alloys. Nitrite generally accelerates the solder corrosion rate, causing high lead phosphate (corrosion product) concentrations that can restrict flow in

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radiator tubes or failure of the solder joint. Sodium nitrite at concentrations of  $50\text{mg.kg}^{-1}$  to  $1000\text{ mg.kg}^{-1}$  as  $\text{NO}_2$ , is often added to glycol formulations to inhibit cavitation induced pitting on cast iron piston sleeve liners of diesel engines. The vibration of the piston can induce cavitation bubble formation on the outside of the sleeve liners, often resulting in intense pitting of the liners. Silicates and additional tolyltriazole can effectively counteract the adverse effects of nitrite on solders.

In selecting a suitable inhibited glycol formulation, the objective should first be to collect all the information regarding the specific system metallurgy. This information, together with information regarding the capacity and operating conditions of these systems, should be used in collaboration with specialist and reputable suppliers of these products, to select a suitable product.

NOTE: No inhibition programme will be effective in preventing corrosion if the losses from coolant systems are not under control.

#### 4.18.2.5.14 Cleaning of fouled (dirty) system

Deposits that cause fouling accumulate in equipment and piping and impede heat transfer or fluid flow. These deposits will prevent effective corrosion inhibition if corrosion inhibitors are applied to a fouled system. Deposits may be organic, inorganic or a mixture of the two. Deposits are of many types of which hardness (calcium and magnesium) and iron oxides are the most common in cooling water systems.

Treatment chemicals, if not properly controlled, can add to the fouling deposits and scale. Silica can form hard, adherent deposits in cooling systems. Corrosion products can add to deposits. Combinations of water treatment chemicals can result in severe fouling: the best example of this is the incompatibility of cationic polymers with antiscalant chemicals.

To select an effective cleaning procedure the deposit must be characterised or identified. Deposit samples for laboratory testing should be representative.

Only once online chemical cleaning is ruled out through efficacy or cost should one resort to mechanical cleaning.

[20] Circulation is the most common method applied to clean columns, heat exchangers and cooling water jackets. If the total volume required filling the system is excessive, circulation and fill and soak methods can be ruled out in terms of cost. In cases like this other means such as high pressure water washing/jetting and acid cleaning are still viable options. Reference [3] provides detailed guidelines with respect to chemical cleaning and water washing. Reference [4] specifies the requirements for high pressure water jetting applicable to shell and tube heat exchangers.

Chemical cleaning of these systems should first be clarified with a specialist.

Cleaning methods more often than not require that the equipment to be removed from service and opened to some degree for the cleaning. In some cases, on-line cleaning is effective and more convenient. On-line cleaning can be chemical and or mechanical. On-line cleaning can save time and labour and can prevent a shut down or trip. Examples of on-line cleaning include:

- Side stream filtration (prevents chemical transients with respect to the inhibitor concentration and should be the preferred option for removing suspended matter from auxiliary and ancillary systems)
- air bumping of heat exchangers
- reverse flow in heat exchangers
- depressing the pH or adding sequestrants and dispersants to cooling water

Not all deposits can be removed through on-line cleaning and each case must be evaluated individually to determine if on-line cleaning will be cost-effective.

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April 2016	0.1	R Govender	Final Draft after SCOT SC review
April 2016	0.2	R Govender	Final Draft for Comments Review Process
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September 2017	1	R Govender	Final Document for Authorisation and Publication
December 2022	1.1	D Lalla	First draft containing the following changes:  Title adjusted to include ancillary systems, phasing out the use of Hydrazine, M-alk and CCPP adjusted to align with main CW standard limits, inclusion of TSS and LSI, removal of biocide dosing in closed loop systems,
February 2023	1.2	D Lalla	First draft updated after CG review:  Conductivity adjusted to align with main CW standard limits, definition of ancillary added, inclusion of Biocide contract guideline as reference.
March 2023	1.3	D Lalla	Final Draft after all updates and Comments Review
March 2023	2	D Lalla	Final Rev 2 Document for Authorisation and Publication

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