Eskom	**Standard**	**Asset Management**

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TABLES

1. INTRODUCTION

This standard establishes the upper and lower bound values, for chemical parameters in open evaporative recirculating condenser cooling water systems. Specific modes of operation will apply at individual power stations according to the plant which is installed and, in particular, the quality of the make-up water supply.

All limits and ranges are based on practical operating experience within Eskom generating plant.

This standard lays down the minimum frequency for sampling and analysis for the relevant parameters.

The objectives of this standard are to detail the agreed chemical conditions which will ensure most cost effective operation of a cooling water system while focusing on important aspects such as overall water management, cost effective treatment and control, the availability, reliability and efficiency of the processes and plant in contact with the cooling water.

The limits and ranges reflect practical achievable chemistry that can be maintained through the application of sound water treatment and water management techniques, whilst taking cognisance of specific limitations. Recommendations from such organisations as EPRI and the VGB with respect to modern power plant practices have also been considered.

2. SUPPORTING CLAUSES

2.1 SCOPE

This standard lays down the chemical and microbiological limits, inter-related limits and control ranges which must be controlled in order to effectively operate an open evaporative recirculating condenser cooling water system.

2.1.1 Purpose

The purpose of this standard is to define the upper and/or lower boundary values for chemical parameters in open evaporative condenser recirculating cooling water systems. This standard excludes auxiliary and ancillary cooling water systems.

2.1.1.1 Rationale for individual and related parameters

An explanation of the background and the development of the targets, upper and lower bound values for each parameter in this standard has been provided.

2.1.1.2 Chemistry control ranges and limits

The ranges and limits together with the suggested analytical frequencies are itemised.

Where a standard Eskom analytical method is not available, users are advised to use published methods or methods developed by themselves provided that this method conforms to generally accepted validated analytical techniques.

2.1.1.3 Supplementary procedures

To supplement this standard, individual Power Plant Chemistry Sections should establish site specific procedures for the operation and maintenance of relevant plant and equipment.

2.1.2 Applicability

This document shall apply throughout Eskom Holdings SOC Limited.

2.2 NORMATIVE/INFORMATIVE REFERENCES

2.2.1 Normative

[1] 240-56030499 Condenser Healthcare Guideline

[2] 240-57127944 Preservation of Power Plant during Outages Guideline

[3] 240-56030508 Cooling Water System Health Care Guideline

[4] 240-106192541 Chemistry Standard for Auxiliary and Ancillary Cooling Water

[5] 240-123919938 Legionella Control and Management in Water Systems

[6] Condenser Tube Failures: Theory and Practice. Volumes 1 & 2, EPRI 1010188

[7] SANS 893 - 1. Risk management & 2. The Control of Legionella in Water Systems

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2.2.2 Informative

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[10] Calcium Carbonate Precipitation Kinetics, Part 2, Water SA 3 (3), L Benjamin, R E Lowenthal, GVR Marais.

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2.3 DEFINITIONS & ABBREVIATIONS

The following definitions and abbreviations are used in this standard.

2.3.1 Definitions

Definition	**Description**
Algae	Relatively large organisms generally coloured blue-green or green by the presence of chlorophyll. Algae require sunlight for growth.
Biodispersants	Compounds that will penetrate and detach microbial deposits while preventing re-attachment.
Biocide - Non-Oxidising	Compounds used to kill off micro-organisms affecting cell construction, composition or metabolic pathways. Normally slower acting than oxidising, e.g. Isothiazalone, DBNPA. Effective against planktonic microbes and the top layer of biofilm. Biocide resistance may be developed.
Biocide - Oxidising	Chemicals that literally “burn up” / oxidise any organic compound they come into contact with e.g. chlorine, bromine compounds, peroxide. Effective against planktonic microbes and the top layer of biofilm. No development of biocidal resistance.
Blow-down	That volume of water that must be permanently removed from a system for it to be within the specified limits of the limiting parameter.
Drift	Cooling water, inclusive of all the appropriate salts that is lost to the atmosphere.
Eddy Current Testing	A non-destructive inspection technique that will reveal the inner and outer condition of heat exchanger tubes.
Fouling	The formation of deposits on equipment surfaces, which significantly decrease equipment performance and/or the useful life of the equipment.
Fungi	Microscopic plants, larger than bacteria, which could cause wood decay in cooling towers.
Evaporation	Water lost into the atmosphere by the conversion of water to water vapour which is free from salts.
Health Care Programme	Maintenance and investigative activities that will control the deterioration of plant components.
Limit	The values representing either an operating range or an absolute “end of the line” condition.
Limiting Parameter	That parameter which will first concentrate to such an extent that the specified limit is reached or exceeded. (Limiting ion has the same meaning).
Local Decision (LD)	The frequency of increasing analysis is left to the discretion of the Chemical Services Manager at the Power Station. The justification and rationale for this decision must be communicated to relevant stakeholders.
Make-up	The volumetric requirement to replenish losses from a system from evaporation, blow-down and drift.
Pre-Treatment	Clarification and/or softening and/or sterilisation of water prior to use as cooling tower make-up.
Scale	Scale is a dense coating of predominantly inorganic material formed from

	the precipitation of water-soluble constituents.
Water Management	Control of the cascading, pollution, supply, use, storage and disposal of water and water containing effluents in accordance with the relevant legislation and standards.

2.3.2 Classification

Controlled Disclosure: Controlled Disclosure to External Parties (either enforced by law, or discretionary).

2.3.3 Abbreviations

Abbreviation	Description
AAS	Atomic Absorption Spectrometry
Alk	Alkalinity
CCPP	Calcium Carbonate Precipitate Potential
CFU	Colony Forming Units
CoC	Cycles of Concentration
COD	Chemical Oxygen Demand
DWS	Department of Water and Sanitation
EPRI	Electric Power Research Institute
FOG	Fats, Oil, and Grease
LIMS	Laboratory Information Management System
NTU	Nephelometric Turbidity Units (sometimes designated as FTU or NTU)
PEI	Production Engineering Integration
PPB	Parts per billion or $\mu g.kg^{-1}$.
PPM	Parts per million or $mg.kg^{-1}$.
PS	Power Station
RT&D	Research, Testing and Development
SANS	South African National Standard
TOC	Total Organic Carbon
TSS	Total Suspended Solids
VGB	Vereinigung Der Grosskraftwerksbetreiber.
WUL	Water Use License
ZLED	Zero Liquid Effluent Discharge

2.4 PROCESS FOR MONITORING

Laboratory Information Management System (LIMS) Database is utilised to store laboratory analysis so that the quality of the condenser cooling water can be monitored. Excursions beyond the limiting conditions of this Standard shall be monitored, tracked and reasons recorded within and maintained by each power station laboratory. The records shall be periodically reviewed by Chemistry Specialists within PEI with corrective actions taken as and when required.

2.5 RELATED/SUPPORTING DOCUMENTS

None

2.6 ROLES AND RESPONSIBILITIES

- The Power Station Chemical Services Manager shall be responsible for the implementation of this Standard and ensuring that the requirements are met.
- The Chemistry Specialist (PEI) will be responsible for review of compliance with the requirements of this Standard.
- The Centre of Excellence Manager (Chemical) within Group Technology Engineering is the custodian of this Standard and shall be responsible for periodic review and updating.

3. MANDATORY LIMITS FOR COOLING WATER SYSTEM PARAMETERS

The mandatory limits for cooling water related parameters, and the testing frequencies are given in the sections below. These represent the auditable criteria of this standard.

3.1 ACTION LEVELS AND RISK ASSESMENT

It is important to note that when parameters are not being adhered to, a thorough risk assessment will be done to determine the effects of operating under these conditions. This risk assessment shall be supported by the CSM and PEI, and shall be authorised by the PSM. The action level is such that if the limit for a particular parameter is exceeded on three (3) consecutive measurements, then the risk assessment described above shall be done. The reader is directed towards the notes of the tables for additional information.

3.2 MAKE-UP WATER

The term "make-up water" refers to all water sources recovered into the cooling water systems or treatment plants. The quality of make-up water is evaluated during the design stage of a power station. Needs such as the use of third party effluents are often not foreseen during the design stage. Decisions to recover effluents as cooling tower make-up is done to maintain the water balance at the Power Station. The effluent should be evaluated against the specified limits and the desalination and/or blow-down needs.

The recommended frequency of analysis for all make-up water streams is as follows:

Table 1: Frequency of Analysis for Make-Up Water

Parameter	**Units of measurement**	**Frequency (make-up waters)**
pH at 25 °C		Daily
Conductivity	$\mu S.cm^{-1}$ at 25 °C	Daily
"P" alkalinity	$mg.kg^{-1}$ as $CaCO_3$	Daily
"M" alkalinity	$mg.kg^{-1}$ as $CaCO_3$	Daily
Turbidity	FTU / NTU	Daily
Total hardness	$mg.kg^{-1}$ as $CaCO_3$	Daily

Calcium hardness (a)	mg.kg^{-1} as $CaCO_3$	Daily
Magnesium hardness	mg.kg^{-1} as $CaCO_3$	Daily
Sodium	mg.kg^{-1} as Na	Weekly
Potassium	mg.kg^{-1} as K	Weekly
Chloride	mg.kg^{-1} as Cl	Weekly
Sulfate	mg.kg^{-1} as SO_4	Weekly
Silica	mg.kg^{-1} as SiO_2	Weekly
Ammonium	mg.kg^{-1} as NH_4	Weekly
Phosphate	mg.kg^{-1} as PO_4	Weekly
TOC	mg.kg-^{1} as C	Weekly
Oxygen absorbed (b)	mg.kg^{-1} as O_2	Weekly
$CaCO_3$ precipitation potential at 25 °C	mg.kg^{-1} as $CaCO_3$.	Weekly
Bacteriological quality (c)	CFU.ml^{-1}	Monthly
Strontium (c)	mg.kg^{-1} as Sr	Quarterly
Manganese (c)	mg.kg^{-1} as Mn	Quarterly
Iron (c)	mg.kg^{-1} as Fe	Quarterly
Fluoride (c)	mg.kg^{-1} as F	Quarterly
Aluminium (c)	mg.kg^{-1} as Al	Quarterly
Barium (a)	mg.kg^{-1} as Ba	Quarterly
Nitrate	mg.kg^{-1} as NO_3	Quarterly
Arsenic	mg.kg^{-1} as As	Quarterly
Chromium	mg.kg^{-1} as Cr	Quarterly
Lead	mg.kg^{-1} as Pb	Quarterly
Cyanide	mg.kg^{-1} as CN	Quarterly
Cadmium	mg.kg^{-1} as Cd	Quarterly
Copper	mg.kg^{-1} as Cu	Quarterly
Zinc	mg.kg^{-1} as Zn	Quarterly
Mercury	mg.kg^{-1} as Hg	Quarterly
Phenolic compounds	mg.kg^{-1} as Phenols	Quarterly
Boron	mg.kg^{-1} as B	Quarterly
Selenium	mg.kg^{-1} as Se	Quarterly
FOG	mg.kg^{-1}	Quarterly for raw water, monthly for recovered streams

NOTES:

a. For make-up water analysis, calcium hardness can either be calculated from the ICP method or the titration method
b. The 4hr OA method must be used when determining OA
c. This is a Local decision depending on problems or observations associated with these parameters; additionally, the frequency can be increased based on increasing trends.

Deviation from this surveillance requirement (Table 1) is acceptable as long as the rationale is based on a risk assessment supported by the CSM and PEI and approved by the PSM. A documented work instruction which includes all deviations must be available.

Trace metal analyses are required in order to trend changes in pollution levels. The requirements for analysis apply equally to all streams recovered to cooling water systems. Thus, it includes ash water, station drain water, sewage effluent and mine water.

Where cooling water is desalinated, trace contaminant analyses becomes more important and the surveillance requirement should be monthly. This statement is specifically true for contaminants that could lead to membrane fouling. Typical membrane fouling constituents that need to be monitored are Si, Ba, Sr, Al, TOC, and FOG.

Samples are to be taken at the hot duct (furthest unit from the cooling tower) of the main condenser on the cooling water circuit. Certain CW parameters, some of which include CCPP, chloride and sulfate, will be used in the indices calculations.

3.3 SPECIFICATIONS AND TEST FREQUENCIES FOR COOLING WATER

The limits and analysis frequencies for cooling water in the cooling water system are given in Table 2 below.

Table 2: Specifications for Cooling Water

Parameter	Limit or range	Frequency of analysis
Turbidity	As low as cost effectively possible but < 100 NTU for continuous operation	Every 8 hours or once per shift
Conductivity	Conforms to the cycles of concentration being used but generally < 4000 μS.cm^{-1}	Daily
Condenser temperatures T1, T2 and Δ T	Must be incorporated in the chemistry data sets.	Daily
pH	Range: 8.1 to 8.6 @ 25 °C. Optimum pH is 8.3	Every 8 hours or once per shift
“P” alkalinity	< 7,5 mg.kg^{-1} as $CaCO_3$	Daily
“M” alkalinity Guideline limits only and will not constitute an out of specification condition provided that the CCPP conforms to the	**(Depending on CCPP)** 80 to 120 mg.kg^{-1} as $CaCO_3$ without a crystal modifier dosing programme. **(Depending on CCPP)** 120 to 160 mg.kg^{-1} as $CaCO_3$ with a crystal	Every 8 hours or once per shift

specified limits	modifier dosing programme.	
Calcium	200 to 500 mg.kg^{-1} as $CaCO_3$	Daily
Parameter	**Limit or range**	**Frequency of analysis**
Reactive Silica	< 150 mg.kg^{-1} as SiO_2. While also taking cognisance of Mg × SiO_2 limitation	Daily Plants with Lime Softening – once per week
Permanent hardness Only when: Tot Hard > M Alk	< 400 mg.kg^{-1} as $CaCO_3$ (Tot Hardness – M Alk = Permanent hardness)	Daily
Calcium carbonate precipitation potential (CCPP) at T2	Calculated with Stasoft Software Without crystal modifier dosing: > 10 but < 30 mg.kg^{-1} as $CaCO_3$ With crystal modifier dosing: > 10 but < 45 mg.kg^{-1} as $CaCO_3$	Daily
Sulfate	Poor quality concrete – Stations <1000 mg.kg^{-1} if Na+ < 250 mg.kg^{-1} <750 mg.kg^{-1} if Na+ > 250 mg.kg^{-1} High quality concrete – Stations < 1500 mg.kg^{-1} if Na+ < 500 mg.kg^{-1} < 1000 mg.kg^{-1} if Na+ >500 mg.kg^{-1} Note: Mg^{2+} to be <160 mg.kg^{-1} as $CaCO_3$	3 times per week
Chloride	< 400 mg.kg^{-1} as Cl	3 times per week
Sodium	< 500 mg.kg^{-1} as Na (See also sulfate)	3 times per week
Phosphate	< 0,5 mg.kg^{-1} as PO_4^{3-}	Weekly
OA	< 20 mg.kg^{-1}	Weekly
COD	< 200 mg.kg^{-1}	Weekly

TOC	As low as economically possible	Weekly, only where desalination plants are installed
Ammonia	< 40 mg.kg^{-1} as NH_4	Weekly
CoC	Calculated using Potassium values	Weekly
Total Suspended Solids	Not specified, Measured as mg.kg^{-1}	Weekly
Nitrate and nitrite	Not specified, Measured as mg.kg^{-1} N	Weekly
Potassium	Not specified, Measured as mg.kg^{-1} as K	Weekly
Iron	Not specified, Measured as mg.kg^{-1} as Fe	Monthly
Copper	Not specified, Measured as mg.kg^{-1} as Cu	Monthly if tube material is brass. Quarterly, if tube material is titanium or stainless steel
Zinc	Not specified, Measured as mg.kg^{-1} as Zn	Monthly if tube material is brass. Quarterly, if tube material is titanium or stainless steel
Barium	Not specified, Measured as mg.kg^{-1} as Ba	Quarterly
Strontium	Not specified, Measured as mg.kg^{-1} as Sr	Quarterly
Manganese	Not specified, Measured as mg.kg^{-1} as Mn	Quarterly
Fluoride	Not specified, Measured as mg.kg^{-1} as F	Quarterly
Aluminium	Not specified, Measured as mg.kg^{-1} as Al	Quarterly
FOG	Not specified, Measured as mg.kg^{-1}	Quarterly As and when required
Bacteriological quality	Measured as CFU.ml^{-1} (refer to Table 3)	Monthly

NOTES:

a. If the specified limit is exceeded on more than 3 consecutive measurements, then the surveillance shall be increased to the extent necessary to manage the risk. The necessary actions to rectify the excursion must be implemented with necessary risk assessments (supported by the CSM and PEI and approved by the PSM) conducted on operating with the parameter in exceedance of its limits.

b. It is critical that the Ca^{2+} be done using titration method for CCPP and NOT the ICP or AA method. However, when calculating the cation/anion balance, use the Ca^{2+} concentration obtained by the ICP method. A calibrated thermometer must be used to obtain the T2 temperature at the time of sampling. The highest temperature must be used for the calculations.
c. It is important to note that if the CW system is operated at higher alkalinities, this far exceeds the CCPP limit of 45 $mg.kg^{-1}$ as $CaCO_3$, hence be careful not to exceed the CCPP limit. If the CCPP limit is exceeded, the scale build in the tubes would be severe.
d. For optimal use of water, it is essential to control the limiting chemical parameter below the target value but not too low. A lower limit is not specified but a norm should be not lower than 90% of the target value.
e. If a desalination plant is installed, FOG must be measured more frequently than quarterly as stated in Table 2. It should be kept as low as possible. The frequency is local detection.
f. TSS, i.e. silts, sediments and pieces of scale, is currently not measured or calculated. Additional research work to be carried out before this parameter is included in the standard
g. For details regarding the parameters refer to Appendix A: “RATIONALE FOR INDIVIDUAL AND RELATED PARAMETERS”

3.4 BACTERIOLOGICAL QUALITY

According to the SANS Legionella Standard (893-1 and 2), every site must develop a formal microbiological treatment program for cooling water. The total bacteria results of the treatment efficacy must be recorded so that the biocide is proven to be effective. Where no limit is specified, the requirement is that trends are closely observed to detect deviations from the norm.

Table 3: Bacteriological quality (planktonic)

Parameter	Target	Limit	Frequency of analysis
Total aerobic bacteria	$<10^5$ CFU/ml	$<10^5$ CFU/ml	Minimum Monthly
Total anaerobic bacteria	$<10^4$ CFU/ml	$<10^4$ CFU/ml	Minimum Monthly
Total Coliforms (TC) When treated sewage is recovered to the condenser cooling water system(s)	Not specified TC per 100 ml but should be in line with the PS WUL and final sewage effluent specifications	Not specified TC per 100 ml	Minimum Monthly
Faecal Coliforms (FC) When treated sewage is recovered to the condenser cooling water systems	Not specified FC per 100 ml but should be in line with sewage specifications	Not specified TC per 100 ml	Minimum Monthly
Faecal streptococci (FS) When treated sewage is recovered to the condenser cooling water system	Not specified FS per 100 ml but should be in line with sewage specifications	Not specified TC per 100 ml	Minimum Monthly

Legionella	<100CFU/L	<10 000 CFU/L	Quarterly
H_2S producers	< 50 CFUs/ml	< 50 CFUs/ml	Minimum Monthly
Chlorophyll A	Not specified $\mu g.kg^{-1}$	< 25 µg.kg^{-1}	Not necessary unless there is an algal bloom.

NOTES:

a. Surveillance of the microbial quality of the cooling water must be such as to provide sufficient information with respect to the application and optimisation of control programmes but not less than monthly.

b. The interaction between biofouling and heat transfer was not considered in the limits given above however, this is currently being researched by Eskom.

Table 4: Bacteriological quality (sessile)

Parameter	**Target**	**Recommended frequency of analysis**
Total aerobic bacteria	< 10^6 CFU/cm^2	Minimum of Quarterly
Total anaerobic bacteria	< 10^5 CFU/cm^2	Minimum of Quarterly
H_2S producers	< 100 CFU/cm^2	Minimum of Quarterly

3.5 BYPASS CLARIFICATION AND PRE-TREATMENT

Table 5: Clarification clarifier outlet

Parameter	**Target**	**Limit**	**Frequency of analysis**
Turbidity	5 NTU	< 15 NTU	6 × Daily

3.6 LIME SOFTENING

Table 6: Lime Softening Clarifier Outlet

Parameter	Target	Limit	Frequency of analysis
pH	Optimal pH to achieve maximum removal of: "M" alkalinity, or Ca Hardness, or Mg Hardness, or Non-carbonate hardness (during soda ash application)	Optimal pH to achieve maximum removal of: "M" alkalinity, or Ca Hardness, or Mg Hardness, or Non-carbonate hardness (during soda ash application)	6 × Daily
FOG	Non detectable in Reverse Osmosis feed	Non detectable in RO Feed water	Daily
Turbidity	5 NTU	15 NTU	6 × Daily
Clarifier Outlet "M" Alkalinity	> 50% reduction across the process*		6 × Daily
Clarifier reaction zone "M" Alkalinity	2P=M		6 x Daily

NOTES:

The sludge volume and pH in the mixing zone needs to be monitored by taking a sample in the mixing zone of the clarifier. The minimum shall be 6 samples daily.

3.7 DRAINS, ASH, MINE OR WASTE WATER RECOVERY TO THE COOLING WATER SYSTEMS

The recovery of any drains/waste water must only be through a clarifier together with suitable treatment to comply with cooling water standards. The recovery of any drains/waste water must only be allowed if a concentration factor of greater than 2 can be achieved. The effect on the water mass balance and effluent blowdown volumes will need to be evaluated.

Refer to section 3.2 to 3.4 for parameters.

Appendix B represents a method of assessing the suitability of waste water for recovery to the cooling water system without desalination.

4. FURTHER CONSIDERATIONS REGARDING COOLING WATER SYSTEMS

4.1 INTERPRETATION OF WATER ANALYSIS

In order to understand a water analysis, a thorough understanding of the general terms used is necessary. These general terms are almost always expressed as calcium carbonate. However, it is important to always state the units of analysis.

4.1.1 General terms

Table 7: The meaning of general terms used on the analytical report

Symbol	**Stands for**	**Represents**
Tot H	Total hardness	Total calcium and magnesium hardness
CaH	Calcium	Total calcium hardness
M Alk	Methyl-orange alkalinity	Bicarbonates and carbonates or carbonates and hydroxides
P Alk	Phenolphthalein alkalinity	½ Carbonates and all hydroxides.
Hydroxides = 2P Alk–M Alk	Hydroxides	Calcium, magnesium or sodium hydroxides
Na Alk = M Alk – Tot H	Sodium alkalinity	Sodium hydroxide, carbonate and phosphate
Carbonates	Total carbonates	Calcium, magnesium and sodium carbonate
Na_2CO_3 = Na Alk – Hydroxides	Sodium carbonate	Sodium carbonate
HCO_3^- = M Alk – 2P Alk	Bicarbonates	Calcium, magnesium and sodium bicarbonate
Perm Hard = Tot H – M Alk	Sulfate hardness	Calcium and magnesium sulfate
$Ca(OH)_2$=Hydroxides – Na Alk	Free lime	Calcium hydroxide
FMA	Free Mineral Acid	Free acids such as sulphuric and hydrochloric (does not include CO_2)

4.1.2 Speciation of hardness and alkalinity

4.1.2.1 Water with no hydroxide alkalinity (2xP Alkalinity < M Alkalinity)

General terms expressed as $CaCO_3$

Table 8: When M alkalinity > total hardness

Symbol	**Represents**
M Alk – Tot Hardness	Sodium bicarbonate
Tot H – Ca Hardness	Magnesium bicarbonate
Ca Hardness	Calcium bicarbonate

Table 9: When Total hardness > M alkalinity (and CaH is also > M alkalinity)

Symbol	Represents
Tot H – Ca Hardness	Magnesium sulfate
Ca Hardness – M Alk	Calcium sulfate
M Alkalinity	Calcium bicarbonate

Table 10: When Total hardness > M alkalinity (but CaH <M alkalinity)

Symbol	Represents
Tot H – M Alk	Magnesium sulfate
M Alk – Ca Hardness	Magnesium bicarbonate
Ca Hardness	Calcium bicarbonate

4.1.2.2 Waters with hydroxide alkalinity present (2xP Alkalinity > M Alkalinity)

Table 11: Where sodium alkalinity > hydroxide alkalinity

Symbol	Represents
Tot Hard –Ca Hardness	Magnesium carbonate
Ca Hardness	Calcium carbonate
Hydroxides (2 x "P" Alk –"M" Alk)	Sodium hydroxide
Sodium Carbonate ("M" Alk – Tot H)	Sodium carbonate

Table 12: When sodium alkalinity < hydroxide alkalinity (Typical ash water)

Symbol	Represents
Tot Hard – $Ca(OH)_2$ (Tot H – (2 x "P" Alk – "M" Alk))	Calcium carbonate
Na Alkalinity ("M" Alk – Tot Hardness)	Sodium hydroxide
Free lime ((2 x "P" Alk – "M" Alk) – ("M" Alk – Tot H))	Calcium hydroxide
Perm Hardness (Tot H – "M" Alk)	Sulfate hardness
Hydroxides (2 x "P" Alk – "M" Alk)	Calcium and sodium hydroxide

4.2 LIME SOFTENING

The objectives of bypass treatment are two-fold. The first objective is the controlled removal of alkalinity and hardness salts by precipitation of calcium carbonate and magnesium hydroxide using lime or lime plus soda-ash. The second objective is to control the cooling water turbidity using a sedimentation process either in isolation or in conjunction with a softening process.

The reactions in the lime/soda process are given in the equations below.

Softening reactions and alkalinity relationships

$$Ca(HCO_3)_2 + Ca(OH)_2 \Rightarrow 2CaCO_3\downarrow + 2H_2O\text{.........}(1)$$

$Mg(HCO_3)_2 + 2Ca(OH)_2 \Rightarrow Mg(OH)_2 \downarrow + 2CaCO_3 \downarrow + 2H_2O$…..(2)

$MgSO_4 + Ca(OH)_2 \Rightarrow Mg(OH)_2 \downarrow + CaSO_4$………..(3)

$2NaHCO_3 + Ca(OH)_2 \Rightarrow Na_2CO_3 + CaCO_3 \downarrow + 2H_2O$……(4)

$CaSO_4 + Na_2CO_3 \Rightarrow CaCO_3 \downarrow + Na_2SO_4$…….(5)

$CaCl_2 + Na_2CO_3 \Rightarrow CaCO_3 \downarrow + 2NaCl$……. (6)

Note: When ↓ follows a compound it indicates that, that compound will precipitate during the reaction.

The quantity of cooling water which is required to be treated is a function of the incoming make-up water alkalinity, the load being generated, the efficiency of alkalinity and hardness salts removal process.

It is of vital importance to adjust or regulate treatment flows when the above parameters change. Either under-treatment or over-treatment is to be avoided. Over-treatment will result in an over reduction in cooling water alkalinity and a gradual conversion of the bicarbonate species to the carbonate species. The net result will be an increase in pH and precipitation of calcium carbonate. Over treatment has a cost implication. Also important to note that if the M-Alkalinity is depressed too far, it can also promote dezincification of condenser tubes plates.

When sulphuric acid is utilised for alkalinity and pH control, it is essential that the acid is dosed on a continuous basis. Slug dosing of acid which causes major drops in alkalinity followed by equivalent increases in alkalinity must be avoided. Such operations result in alternate corrosive conditions followed by scale forming conditions. The amount of acid required can be calculated from the incoming make-up water(s) alkalinity, the make-up water flow (load) and the cooling water alkalinity together with the cycles of concentration.

Sulphuric acid dosing for alkalinity control will impact on the blow-down requirement as the sulfate ion will become the limiting ion in terms of concentrations. The benefits of lime treatment include lower water consumption and an improved water balance.

See Appendix C for more details on alkalinity control with sulphuric acid.

Using lime as opposed to ash water incurs costs though the sulfate problem associated with ash water is avoided. As with ash water sufficient lime (ash water alkalinity) (2 x 'P" Alk = "M" Alk) has to be added to react with the bicarbonate alkalinity of the cooling water. Some incidental precipitation of magnesium hydroxide occurs:

$$Ca(OH)_2 + MgSO_4 \Rightarrow CaSO_4 + Mg(OH)_2\downarrow \text{…………(7)}$$

Hence the amount of lime (and ash water) required to react with bicarbonate ions is always in excess of the stoichiometric requirement for bicarbonate. The permanent hardness produced by the reaction with magnesium salts will have to be controlled by the reaction with sodium carbonate:

$$CaSO_4 + Na_2CO_3 \Rightarrow CaCO_3\downarrow + Na_2SO_4 \text{…….. (8)}$$

Again, costs are incurred when using soda-ash. Soda-ash treatment is used to control the calcium concentration within the prescribed limits. Rapid reduction in calcium levels is possible because as long as the added soda-ash is stoichiometrically less than the permanent calcium hardness, then calcium is precipitated without excessive carry-over of carbonate species.

4.3 FOULING OF HEAT EXCHANGER SURFACES

Corrosion is one of the costly results of fouling in addition to energy losses resulting from increased heat transfer resistance and frictional resistance. In the plant, biofouling frequently occurs in conjunction with other types of fouling including crystalline or precipitation fouling and particulate fouling.

4.3.1 Types of fouling deposits

4.3.1.1 Biological fouling

Biological fouling is the attachment of macro and/or micro-organisms and their subsequent metabolic by-products, onto the surfaces of the system.

4.3.1.2 Chemical reaction fouling

Deposits formed by chemical reaction in which the surface material (e.g. condenser tube) is not a reactant. Polymerisation of petroleum products is an important example of this type of fouling.

4.3.1.3 Corrosion fouling

The surface material itself reacts with compounds in the liquid phase to produce a deposit or degrade the surface material.

4.3.1.4 Particulate fouling

Particulate fouling is the accumulation on the equipment surface of finely divided solids suspended in the process fluid (cooling water). Sedimentation fouling is an appropriate term if gravity is the primary mechanism for deposition. Particulate fouling can also contribute to erosion / corrosion in heat exchangers.

4.3.1.5 Precipitation fouling

The precipitation of dissolved substances on the equipment surface is called precipitation fouling. This process is termed scaling and takes place once the solubility threshold is exceeded. Calcium carbonate has inverse temperature solubility characteristics and precipitation may take place on surfaces subjected to elevated temperatures. Scaling contributes to corrosion mechanisms taking place as it acts as a contributor to under deposit corrosion. Pitting and dezincification are direct results of scaling in heat exchangers.

4.3.2 Fouling control

4.3.2.1 Biological fouling

Successful mitigation of micro-biologically influenced corrosion (MIC) is achievable. The cost however must be considered against the benefit of improved heat transfer. In order to achieve the most cost effective microbial control programme, it is essential to regularly quantify the performance of the dosing regimen and the maintenance of the effect. The use of biodispersants in conjunction with biocides has been proven, according to several case studies from suppliers, to be successful. The control of the microbial population in the planktonic phase is essential due to the possible safety risks due to Legionella bacteria but it is however complicated by high make-up rates and favourable temperatures for microbiological growth within the cooling water system. The reattachment of slime forming bacteria, on surfaces, takes place soon after batch additions of biocides. The continuous dosing of an effective bio-dispersant with regular, effective biocide additions is, according to several case studies from suppliers, regarded as the most cost effective solution. In terms of the Legionella standard, records have to be maintained proving biocide treatment efficacy.

Certain small areas in cooling water systems are more prone to corrosion than others (low or no flow areas). Treatment of the bulk system to achieve results in these small areas should be evaluated against the application of other means, such as sacrificial coatings, epoxy coatings and induced current protection.

4.3.2.2 Chemical reaction fouling

Fouling of heat exchanger surfaces through polymerisation of petroleum products can be best catered for by prevention. Oil in particular will cause additional problems of particulate agglomeration, interference with corrosion inhibition and increased micro-biological populations. The application of oil dispersants during disastrous conditions is essential and the best advice can be obtained from a reputable vendor. If oil dispersants are used, always ensure that anti-foam is available.

4.3.2.3 Corrosion fouling

The water chemistry is of importance in controlling corrosion fouling. A prominent problem encountered is dezincification. Dezincification is the selective leaching of zinc from brass when the protective alkalinity of the cooling water is affected by contaminants such as organics. This theory was never proved through analytical work and the only evidence to substantiate this theory stems from observations during plant inspections. It has been proven that exceeding certain levels of chlorides and sulfates will cause dezincification. The combined effect of both species is however lower than that for the individual species but certain levels should not be exceeded.

4.3.2.4 Particulate fouling

The control of turbidity in the cooling water and maintaining the design velocities are of importance in controlling this type of fouling. The removal of settled silt from cooling tower ponds annually has proved to improve the biological quality of cooling water. Suspended solids usually accumulate in low flow areas or in locations where an abrupt change of flow velocity occurs.

Particulate matter that accumulates as sludge in the cooling water ducts or cooling tower sprayer distribution piping reduces the overall operation of the cooling system and drastically reduced the thermal efficiency of the plant.

The removal of any accumulated particulate matter during off-load periods is essential in minimising plant damage during storage, especially the cleaning of condensers.

4.3.2.5 Precipitation fouling

This form of fouling will not occur when conforming to the thresholds specified in this guideline. Emergency conditions such as failure of plant, drought and sudden changes in water quality can result in situations where the threshold limits are exceeded.

It must be noted that once scale has formed on a heat exchanging surface the scaling process becomes almost self-propagating as the seed has been established. When the CCPP is maintained over 30 for a long period of time the use of crystal modifiers is essential. Crystal modifiers modify the crystal structure creating a bulky, transportable sludge instead of a hard deposit. Crystal modifiers will not interfere with the operation of a lime softening process. Scaling inhibitors however, will interfere with the softening process as threshold inhibition will prevent the precipitation of calcium carbonate in the softening process. Crystal modifiers are lignins, tannins and polymeric compounds.

4.3.2.6 Corrosion and coatings

Guidelines for corrosion and coatings relating to CW systems can be found in [1 and 4].

Eskom has extensive knowledge and expertise in conducting condenser failure investigations and root cause analysis of condenser deterioration. Extensive literature sources are consulted during investigations including but not limited to the references provided in EPRI reports [5].

Eskom has a long history of condenser tube failure mechanism investigation and confirmation with the aim of determining the root cause of condenser deterioration. Failure investigations and evaluations for all condenser investigations across the Eskom condenser fleet are stored on a database on Hyperwave [20].

The major mechanisms responsible for degradation in brass based tubing in Eskom are water touched mechanisms (erosion-corrosion). The root causes of these mechanisms are directly related to cooling water quality. Although steam-side mechanisms are prevalent, the contribution is far less than that of the water touched tube failures and leaks.

The following are examples of the most prevalent or typical waterside failure/degradation mechanisms experienced in Eskom condensers – specifically for brass based tubing [20]:

- General tube wall thinning due to erosion-corrosion.
- General tube wall thinning due to dezincification.
- Inlet end erosion
- Pitting (off-load, mothballed) tube damage progressed by erosion-corrosion.
- General tube wall thinning due to abrasion from ring-coated Taprogge balls (only experienced to date on Lethabo main condenser).

Typical damage mechanisms experienced on the steam-side of brass based Eskom condensers includes [20]:

- Ammonia grooving
- Support plate wear
- Erosion (steam impingement)

Eskom has experienced pitting corrosion in the air extraction zone of the condenser at Hendrina, which employs 304 stainless steel tubes.

Titanium tubing in Eskom's fossil fleet is only susceptible to vibration and steam impingement damage. Titanium is immune to corrosion mechanisms in Eskom fossil condensers [1, 5 and 20]. Eskom has experienced extremely reliable service from titanium tubing at sites where this material is installed. Very few failures have been experienced due to normal operation. However, all the limits prescribed in this standard still apply to stations that have titanium or stainless steel condenser tubes. The scaling aspects for these condensers as well as the corrosion aspects of all other plant materials such as CW duct steel lining, CW valves (austenitic stainless steel materials), condenser waterboxes and tubesheets still need to be considered.

4.4 CONDENSER HEALTH CARE

Comprehensive information relating to a condenser health care programme is available in [1].

4.5 COOLING TOWERS AND CW SYSTEM

Comprehensive information relating to cooling tower and CW ducting health care is available in [3].

As mentioned, the method of measuring TSS (including silt, sediments and pieces of scale) for cooling water and the extent of its effect on CW systems is still to be researched. Experience on our power stations has however proven that uncontrolled quantities of sediment and scale fragments in the cooing water have a (sometimes extreme) detrimental effect on condenser and, in particular, cooling tower performance. Until such a time as the results are available, it is recommended that the TSS be kept as low as feasibly possible.

4.6 MATERIALS OF CONSTRUCTION

Comprehensive information on material selection is available in [1].

5. AUTHORISATION

This document has been seen and accepted by:

Name & Surname	Designation
Cooling Water Care Group Members	
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Water Science and Technology Study Committee Members	
[redacted]	

Name & Surname	Designation
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7. DEVELOPMENT TEAM

The following people were involved in the development of this document:

- [redacted]
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APPENDIX A: RATIONALE FOR INDIVIDUAL AND RELATED PARAMETERS

1. Turbidity

Turbidity in cooling water is usually a function of the presence of silt, clay, sand, pulverised fuel ash, coal dust, precipitated salts and algae. The source of these suspended particles is the make-up water(s), internal micro-biological growth or dust particles scrubbed from the air being supplied to the tower.

Suspended matter is responsible for a number of problems:

- Fouling of pipe-work, heat exchanger surfaces, cooling water packing’s and drift eliminators, particularly where velocities are low or have been reduced intentionally. Fouling of heat exchange surfaces not only results in inefficient heat transfer and hence increased costs, but in addition, micro-biologically induced corrosion (generally anaerobic) is enhanced.
- Siliceous suspended matter can also give rise to erosion / corrosion of pump internals, volutes, heat exchanger tubing and pipe-work. The most abrasive particles are sand and grit.
- Suspended materials can also co-precipitate with calcium carbonate and calcium sulfate.
- Algae, fungi and bacterial growths flourish in the cooling tower environment and conditions such as the presence of sunlight or absence of sunlight and an adequate food supply sustain such growths.
- The limit for turbidity has been specified as < 100 NTU in the cooling water. However, this must not be taken as a mandate to operate at the maximum levels. Generally, the turbidity should be controlled as low as is cost effectively possible. During flood conditions the turbidity of raw water supplies can rise dramatically over a period of a few days. During these periods, stations may well depend on their reservoirs to supply water until the turbidity subsides. Extended operation of condensers above the 100 NTU threshold has proven to be detrimental to condenser tubes. Severe thinning of condenser tubes has been experienced where the threshold was regularly exceeded.

2. Conductivity at 25 °C

The conductivity at 25 °C is a function of the total dissolved ionic solids. With the raw waters currently being supplied to Eskom’s fossil fired plant, the limit for the concentrated cooling water system has been set at $< 4000\ \mu S.cm^{-1}$ ($< 400\ mS.m^{-1}$) at 25 °C. This is an arbitrary limit and has been set for the following reasons:

- To minimise galvanic corrosion in highly saline / oxygenated water,
- To prevent damage to adjacent vegetation by salts released by the cooling tower drift, and
- To allow sufficiently high cycles of concentration to be obtained in order to obtain “zero liquid effluent discharge”.

It must be clearly understood that the conductivity limit must not be viewed in isolation as some ions are definitely more corrosive than others, e.g. chloride ions are more corrosive than sulfate with respect to metallic components.

3. Alkalinity, pH, calcium hardness, conductivity, calcium carbonate, precipitation potential and the sulfate concentration

All five parameters are inter-related and as such, the limits specified must be viewed in conjunction with one another.

- The objective in controlling this group of parameters is:
- To minimise corrosion (dezincification) by maintaining adequate protective alkalinity,
- To prevent / minimise the leaching of calcium from asbestos cement drift eliminators and or cooling tower packing's,
- To avoid precipitation of calcium carbonate scale on heat exchanger surfaces and on the cooling tower packing,
- To allow effective removal of alkalinity by precipitation processes, and
- To minimise the use of sulphuric acid as a neutralisation agent for alkalinity.

The chemistry of the carbonate species in cooling water is in fact quite complex. Calcium carbonate precipitation results primarily from localised heating of calcium bicarbonate solutions.

$Ca(HCO_3)_2$ (heat) $\Rightarrow CaCO_3 + H_2O + CO_2$………………………………. (1)

Carbonate could be added to the cooling water from bypass treatment plants when using lime. When 2 x “P” alkalinity > “M” alkalinity hydroxides are carried over from the lime clarifier to the cooling water. This will lead to the formation and possible precipitation of calcium carbonate in the cooling system. The end state of the calcium carbonate however, is calcium bicarbonate.

$CaCO_3 \quad + \quad CO_2 \quad + \quad H_2O \quad \Rightarrow \quad Ca(HCO_3)_2$………………… (2)

Various computer programs have been developed to calculate the calcium carbonate precipitation potential. Care must be taken in applying such programs as there are limitations. Some programs do not compute the correct effect of ionic strength on the values of equilibrium constants and most do not take into account complex formation such as that which occurs with fulvic and humic acids. Some programs are in fact based on outdated data for the solubility product of calcium carbonate and incorrect values for the second dissociation constant of carbonic acid.

Natural organic matter (NOM) in cooling water forms metal organic complexes (metal-NOM), rendering the metals unavailable for scale formation (RES/RR/04/25222, RES/RR/08/30118, RES/RR/09/31035, RES/RR/10/32724, Thesis-Modelling studies of interactions between natural organic matter and metals: Effects on cooling water precipitation potentials in power generation plants). Hence the concentration of the “free” or unbound metal, example Ca^{2+} is relatively lower, which results in less scale formation.

Ca^{2+} (aq) + CO_3^{2-} (aq) $\Rightarrow$ $Ca(CO)_3$ (s)

For the correct calculation using either CCPP or LSI, it is essential to analyse the Ca^{2+} concentration by the titration method (Standard Methods for the Examination of Water and Wastewater 20th Edition, Edited by Lenore S. Clesceri et.al (Pg. 3-64 and Pg. 2-37) and not by the inductively coupled plasma (ICP) or the atomic absorption (AA) method. The reason being that with the ICP method, the total Ca^{2+} concentration is determined i.e. the bound Ca as well as the "free" Ca^{2+} whereas with the titration method, only the "free" and hence active Ca^{2+} is determined.

Stasoft version 4 however, is recommended program to calculate the calcium carbonate precipitation potential. Care should be taken when low alkalinity removal efficiencies are experienced across the lime softening process

A problem which started to surface more frequent is low calcium concentrations of the cooling water in the so-called bottom-end problems. This is primarily as a result of sodium alkalinity in the make-up water. Water contains sodium alkalinity when the "M" Alkalinity > Total Hardness. This sodium alkalinity convert to soda ash during the lime treatment process and precipitate the calcium associated with sulfate as calcium carbonate. The chemical process is best explained by the following equation:

$$2NaHCO_3 + Ca(OH)_2 + CaSO_4 \Rightarrow 2CaCO_3\downarrow + Na_2SO_4 + 2H_2O \ldots\ldots\ldots\ldots\ldots (3)$$

4. Sulfate

Sulfate is controlled for two reasons in cooling water:

- To minimise sulfate corrosion of exposed concrete and asbestos cement, and
- To avoid precipitation of calcium sulfate on heat transfer surfaces.

Reinforcing steel in concrete is protected by the alkaline properties of the cement. This alkalinity is as result of the calcium hydroxide content of the cement. The permeability or porosity of the concrete dictates the rate at which the concrete would carbonise and also the extent to which chemical species would diffuse into the concrete. The reaction of the free lime in the concrete with different forms of sulfate generally depletes the alkalinity of the concrete, the larger ettringite molecule precipitate within the concrete resulting in a mechanical stress. This volume change eventually leads to spalling which normally exposes sections of the steel reinforcing. Magnesium sulfate is the most aggressive sulfate species for cement corrosion.

Annual visual examination by trained personnel is required to assess sulfate attack. Where such attack is found the "Eskom Research, Testing & Development : Corrosion Department" should be consulted to advise on the appropriate procedure for provision of an appropriate protective coating.

Compressive strength and permeability are important properties of concrete with reference to corrosion resistance to sulfate. High compressive strength and lower permeability are conducive to high corrosion resistance.

Core samples below or at the water line are generally taken from the cooling tower pond wall or from the basin to assess compressive strength and permeability.

It is important to note that the physical properties of concrete vary considerably throughout Eskom's cooling towers and no single sulfate limit is entirely applicable.

At Tutuka, the compressive strength is very high and the permeability is very low. Sulfate attack is not likely and coating of exposed concrete is not required.

At Matla, the physical properties are poor and protective coating is recommended.

At Duvha, the compressive strength is variable and protective coating is recommended if sulfate levels consistently exceed 2000 mg.kg-1 for a period in excess of two years.

At Arnot and Hendrina, high permeability has been found and sulfate levels should be controlled below 1000 mg.kg-1 provided that magnesium levels are below (<160 mg.kg-1 as CaCO3) and sodium levels are below 250 mg.kg-1. The basis for this specification is supported by the fact that the sulfates of magnesium and sodium are the most prominent forms of sulfate in concrete corrosion. Calcium sulfate has very low impact on concrete.

The corrosion mechanism proceeds in accordance with the following chemical reactions with the free lime in the cement:

$Ca(OH)_2 + Na_2SO_4 + 2H_2O \Rightarrow CaSO_4.2H_2O + 2NaOH$……………..(4)

This reaction is followed by the transformation of aluminates in the cement into highly expansive ettringite. (Factor 2 to 2.5)

$3CaO.Al_2O_3.12H_2O + CaSO_4.2H_2O + 13H_2O \Rightarrow 3CaAl_2O_3.3CaSO_4.27H_2O$…… (5)

When magnesium sulfate is present the magnesium hydroxide precipitate as primary reaction which, is then followed by precipitation of ettringite. The absence of caustic in this reaction reduces the solubility of aluminium and thus the rate of ettringite formation. However, the formation of brucite (Mg(OH)2) enhances the solubilisation of the lime, which leads to the depletion of the alkaline properties of the concrete.

$MgSO_4 + Ca(OH)_2$ (lime in cement) $\Rightarrow Mg(OH)_2 + CaSO_4$…………..(6)

Calcium sulfate can also be precipitated on heat transfer surfaces when the solubility of gypsum is exceeded. The direct application of the solubility product is complicated by the presence of an un-ionised complex ($CaSO_4°$) in concentrations governed by the equilibrium constant.

5. Silica and magnesium

Silica is generally found in water supplies in three different forms: reactive, colloidal and suspended particles (e.g., sand). The reactive portion of the total dissolved silica reacts readily with the molybdate reagent as applied in the colorimetric test. The colloidal silica will not react with the ammonium molybdate reagent.

The reactive form is silicon dioxide and when it is dissolved in water, it forms the monosilicic acid (H_4SiO_4) as shown below:

$SiO_2 + 2H_2O \rightarrow H_4SiO_4$……………………… (7)

The mere fact that silica is present as monosilicic acid means its inclusion in the cation-anion balance is not correct.

The empirical limit for silica is 150 mg.kg-1. This limitation is based on experience and because the complex precipitation mechanisms for silicates are not well understood. The magnesium (as $CaCO_3$) times the silica (as SiO2) product is set at 25 000 so as to avoid precipitation of magnesium silicate complexes. Where precipitation has occurred, hard highly insoluble deposits are formed which often resist even chemical cleaning. The higher the pH of the cooling water the bigger is the risk of precipitating silicates.

Magnesium can be controlled through precipitation in the lime softening process. Magnesium hydroxide floc particles are highly charged and silica is attracted to and adsorbed onto the highly charged magnesium hydroxide precipitate, magnesium removal therefore serves a dual function. At a pH of 10,2 about 10 % magnesium removal is obtained whilst rapid reduction in magnesium is obtained at pH 10,4.

6. Calcium phosphate

The ortho-phosphate is highly reactive with calcium and the limits is set at 0.5 $mg.kg^{-1}$ as PO_4 so as to avoid precipitation of calcium phosphate, particularly at elevated cooling water temperatures experienced at the outlet of the condensers and coolers. It is recommended that treated sewage water be introduced via the cold lime softening clarifiers. This will prevent the accumulation of phosphate in the cooling water system

7. OA, COD

Organic matter must be controlled as fulvic and humic acids are known complexing agents which prevent the precipitation of calcium carbonate in the lime softening process. Though on the other hand, the same substances will also restrict calcium carbonate precipitation in the cooling water system.

A major symptom of organic interference is high outlet alkalinity's (> 60 mg.kg-1 as CaCO3) measured on bypass softening plants. A guide value for OA (0,5 h boiling test) of < 25 mg.kg-1 as O2 is recommended. Major sources of OA and COD are recovered sewage. Sewage effluent should not be recovered direct to cooling water circuits. Chlorination and treatment through a clarifier with the emphasis on organic reduction is advisable.

Some power stations have high level TOC analysers and are recording organic contamination by this means. It must be noted that organic contamination, low cooling water calcium concentrations and the presence of high concentrations of sodium alkalinity (mine water) will restrict the efficiency of the cold lime softening process to remove alkalinity.

8. Chloride, sodium and potassium

The major use of the chloride, sodium and potassium concentrations is to calculate the cycles of concentration of the cooling water circuits.

It is also confirmed that high chloride concentrations will leach the alkaline properties from concrete. This will lead to the corrosion of the reinforcing steel with detrimental impact on the structures.

9. Nitrate and nitrite

Whilst no limit is specified as yet for nitrate and nitrite it is necessary for these parameters to be measured as discharge of blow-down to the environment may be required.

Nitrate and nitrite are indicators of both industrial and domestic pollution of water supplies principally from sewage and sewage effluents.

10. Trace elements

Trace elements are measured as they constitute restraints to discharging blow-down to the environment. These parameters should be compared to their concentration in the raw water or make-up streams together with the cycles of concentration calculated from the chloride, sodium and potassium results.

The absence or presence of zinc in the cooling water is not indicative of the extent of dezincification of the brass components in the cooling water system. Indicative of dezincification of condenser tubes is the reddish brown discoloration (uniformly or randomly) of the inner surface of the tube. Examination of particularly leaded brass tube plates may exhibit even white nodules of zinc/zinc oxides which can easily be confused as being calcium carbonate.

11. Ammonia, sulphide

Ammonium contained in water can contribute to the destruction of concrete in two ways:

- By developing acidifying nitrification which can only take place in aerobic media such as cooling towers.
- By releasing the ammonia displaced by the alkaline conditions in the cement which then speeds up the solubilisation of the lime in the cement to deplete the alkaline properties.

Ammonia and sulphide are aggressive corrosion agents even in alkaline waters. Almost no data exist on the concentration of both these species. Sulphide is responsible for corrosion of non-ferrous and ferrous materials, particularly when it is formed by reduction of sulfate through bacterial action.

Ammonia in small concentrations is a known stress corrodant of non-ferrous materials. Sources of ammonia are generally polluted make-up water streams or sewage effluent.

12. Algae

Algae, are relatively large organisms. They are normally green or blue green in colour, caused by the presence of chlorophyll in the cell structure; sunlight is necessary for growth and the most effective control method is the exclusion of sunlight. Deposits of dead algae provide food for bacteria and fungi, since they act as a filter and catch other organisms. Algae are not known to cause corrosion directly, except for occasional occurrences under algae deposits. Algal growth is mainly responsible for the blockage of cooling tower screens and massive build-up in the clarifier launders.

13. Bacteria

Excessive biofilm can be seen with the naked eye when large concentrations of bacteria are present. Species identification is difficult and bacteria are normally controlled in total. Each bacterial species has a specific action and often is referred to by its effect on materials (e.g. Sulfate Reducing bacteria). Some classes of bacteria cause slime, corrosion and /or gas production. One bacterial species common in cooling-water systems, are the slime-formers (eg Pseudomonas), they produce a slimy, gelatinous deposit that can clog heat exchange tubes, increase friction losses and shield heat exchanger surfaces from inhibitors and the cooling medium.

Sulphide-producing bacteria anerobically produce chemicals that result directly in corrosion of metals. These bacteria convert water soluble sulphur compounds to hydrogen sulphide. This conversion usually starts with sulfates that either occur naturally or come from the addition of sulphuric acid for alkalinity control.

Hydrogen sulphide is acidic and aggressively attacks metals, principally mild steel, but also stainless steel and copper alloys. However, most metals are subjected to corrosion under low pH, reducing conditions and the presence of sulphides.

In a recirculating cooling-water system corrosion, due to these organisms, can occur at a rapid rate and perforation of a 16 mm mild steel coupon within 60 days has been recorded.

Special toxicants are necessary to control these bacteria; the favourable temperature and high make-up rates further complicate control. The application of biocides is essential but care must be taken to ensure that the system conditions do not affect the action of the biocide. Biodispersants capable of controlling the attachment of slime producing bacteria have provided the most cost effective although limited control programme for these bacteria. Biodispersants can only provide sufficient protection in areas where the water flow conditions are such that the dispersant can function, in areas of stagnant, low flow and areas under deposits may still be subjected to microbial corrosion.

14. Sodium alkalinity

The presence of sodium alkalinity in mine and raw water is creating problems with respect to the lower end of the specified calcium thresholds. This phenomenon is generally not well understood. If the M alkalinity is higher than the total hardness the water contains sodium alkalinity. When the ingress of sodium alkalinity stoichiometrically exceeds the permanent hardness ingress, calcium concentrations will be reduced through precipitation and cooling tower blow downs. This will lead to bottom end limitations with respect to the specified thresholds for calcium of the concentrated cooling water.

In the absence of permanent hardness, sodium alkalinity will react with lime in accordance with the equation below.

$2NaHCO_3 + Ca(OH)_2 \Rightarrow CaCO_3\downarrow + Na2CO_3 + 2H_2O$………… (8)

While in the presence of sufficient permanent hardness, sodium alkalinity will react with lime in accordance with the reaction below:

$CaSO_4 + 2NaHCO_3 + Ca(OH)_2 \Rightarrow 2CaCO_3\downarrow + Na_2SO_4 + 2H_2O$…(9)

From the two equations above it can be concluded that any significant ingress of sodium alkalinity ingress will always deplete the calcium in the cooling water. Problems that can be encountered as result of the depletion of calcium is metal corrosion and leaching of calcium from asbestos cement drift eliminators. This will lead to the failure (breakage) of the drift eliminators. Where this phenomenon is not acute the matter could be rectified through partial de-carbonation of the cooling water with sulphuric acid. Where the phenomenon is acute, recirculation of lime softening sludge following a sulphuric acid dissolving stage are regarded as the only economic viable solution.

The extent of sodium alkalinity ingress can be quantified from an accurate analytical report, as follows:

If M Alkalinity is greater than Total Hardness the water contains sodium alkalinity, while if the M Alkalinity is smaller than the Total Hardness the water contains Permanent Hardness.

Therefore: M Alkalinity – Total Hardness = Sodium Alkalinity

15. Permanent hardness

Permanent hardness can be regarded as directly the “opposite” of sodium alkalinity as the one could be used to control the impact of the other. (See Table 10).

Water with permanent hardness normally enters the cooling water system with the raw water or during the recovery of mine water. Permanent hardness in moderately polluted raw water is normally present as magnesium sulfate. The reactivity of species dictates that sodium alkalinity will be first neutralised during acid ingress, followed by magnesium bicarbonate prior to reacting with the calcium bicarbonate. It is for this reason that unpolluted raw water normally contains sodium alkalinity. Moderately polluted raw water will contain magnesium sulfate (See Table 11) and badly polluted water will contain both magnesium and calcium sulfate The leaching of sodium alkalinity from strata such as in some mine waters is most probably due to the biological reduction of sulfate by sulfate reducing bacteria over the ages.

Magnesium sulfate converts to calcium sulfate during the cold lime softening process.

$MgSO_4 + Ca(OH)_2 \rightarrow CaSO_4 + Mg(OH)_2\downarrow$……. (10)

16. Legionella

Legionella bacteria are naturally present in all surface waters. They cause a pneumonia-like disease which may be fatal. This risk is increased in the elderly and immunocompromised.

Legionnaires disease can ONLY be contracted when the bacteria is inhaled into the lungs in aerosol sized water droplets. There is no risk from bathing, swimming or drinking the water.

The water spray cooling zone of cooling towers is an area of increased risk due to the forced minimisation of water droplet size to facilitate maximum cooling. The region around the tower where windage and spray come into contact with personnel are the main areas of concern.

The development of biofilms in the cooling water system protects the Legionella bacteria and allows them to multiply unheeded. The problem arises when biofilms slough off releasing a small amount of the biofilm into the water for dispersal. Proper regular, effective dosing of the cooling water system is thus essential to ensure minimal Legionella contamination.

The SANS standard for Legionella specifies the need for a risk assessment per plant and proof of a formal, routine, documented chemical treatment regime that proves continued reduction of the Legionella counts. This standard is used as the basis for the Eskom Legionella standard (240-123919938)

APPENDIX B: ASSESSING RECOVERY OF WASTE WATER

The following technique could be used to assess the recovery of waste water to the cooling water system using only lime softening as preliminary treatment.

Example 1

Parameter	**Units**	**CONDENSOR COOLING WATER Specification**	**Concentration in waste water**	**Comments**
Calcium	mg.kg^{-1} as $CaCO_3$	< 500	96	
Magnesium	mg.kg^{-1} as $CaCO_3$	< 170	21	
Total hardness	mg.kg^{-1} as $CaCO_3$	< 670	117	
M Alkalinity	mg.kg^{-1} as $CaCO_3$	< 120	537	Controlled introduction into CONDENSOR COOLING WATER system with upper end calcium problems. See comments on sodium alkalinity and sulfate below
Permanent hardness	mg.kg^{-1} as $CaCO_3$	< 380	Nil	M Alkalinity > Total hardness
Sodium alkalinity	mg.kg^{-1} as $CaCO_3$	Nil	420	537 – 117 = 420
Sodium	mg.kg^{-1} as Na	< 500	487	This water will not be suitable for cooling water systems where the system is already operating close to the specified threshold for sodium.
Potassium	mg.kg^{-1} as K	< 500	9.3	
Chloride	mg.kg^{-1} as Cl	< 400	81	
Sulfate	mg.kg^{-1} as SO_4	< 750 or < 1000	661	Should it be possible to overcome the sodium limitation a 34% only volume reduction is possible through tower evaporation when operating at a 1000 mg.kg^{-1} sulfate specification.
Silica	mg.kg^{-1} as SiO_2	< 150	0.31	

This water could only be used as a source of soda ash without desalination. It is also worth noticing that this water is particularly very low in calcium and magnesium due to the presence of sodium alkalinity. This water is ideal for desalination as high water recovery rates will be attained. Please note that the microbiology of this water should also be checked before reuse.

Example 2

Parameter	**Units**	**CONDENSOR COOLING WATER Specification**	**Concentration in waste water**	**Comments**
Calcium	mg.kg^{-1} as $CaCO_3$	< 500	159	
Magnesium	mg.kg^{-1} as $CaCO_3$	< 170	89	
Total hardness	mg.kg^{-1} as $CaCO_3$	< 670	248	
M Alkalinity	mg.kg^{-1} as $CaCO_3$	< 120	315	
Permanent hardness	mg.kg^{-1} as $CaCO_3$	< 380	Nil	M Alkalinity > Tot hardness
Sodium alkalinity	mg.kg^{-1} as $CaCO_3$	Nil	67	315 – 248 = 67
Sodium	mg.kg^{-1} as Na	< 500	242	Should it be possible to overcome the sodium limitation a 52% volume reduction is possible through tower evaporation.
Potassium	mg.kg^{-1} as K	< 500	3.5	
Chloride	mg.kg^{-1} as Cl	< 400	65	
Sulfate	mg.kg^{-1} as SO_4	< 750 or 1000	371	
Silica	mg.kg^{-1} as SiO_2	< 150	5.5	

This water could be used as a source of soda ash without desalination. It is also worth noticing that this water is particularly very low calcium and magnesium due to the presence of sodium alkalinity. Recovery of this water through the cooling towers following lime softening reduces the desalination requirement by 52%. Thus, when recovering 10 Ml per day the additional desalination requirement or blow down will be 4.8Ml per day to remove the additional salt load as introduced by the mine water.

Example 3

Parameter	Units	CONDENSOR COOLING WATER Specification	Concentration in waste water	Comments
Calcium	mg.kg^{-1} as $CaCO_3$	< 500	250	
Magnesium	mg.kg^{-1} as $CaCO_3$	< 170	250	The magnesium will all be present as $MgSO_4$ and will convert to $CaSO_4$ during lime softening. Thus 250 × 1.133 = 283
Total hardness	mg.kg^{-1} as $CaCO_3$	< 670	500	
M Alkalinity	mg.kg^{-1} as $CaCO_3$	< 120	69	
Permanent hardness	mg.kg^{-1} as $CaCO_3$	< 380	431	500 – 69 = 431 Following lime treatment the permanent hardness will be 464 mg.kg^{-1} as $CaCO_3$ 431 + (283 – 250) = 464
Sodium alkalinity	mg.kg^{-1} as $CaCO_3$	Nil	Nil	
Sodium	mg.kg^{-1} as Na	< 500	32	
Potassium	mg.kg^{-1} as K	< 500	6.1	
Chloride	mg.kg^{-1} as Cl	< 400	9.5	
Sulfate	mg.kg^{-1} as SO_4	< 750 or 1000	466	
Silica	mg.kg^{-1} as SiO_2	< 150	6.0	

Following lime softening this water will have a permanent hardness concentration of 464 mg.kg^{-1} as $CaCO_3$. This implies that this water will pollute the CONDENSOR COOLING WATER with calcium. This water however, will be excellent make-up for the ash water system as it contains low levels of soluble salts.

APPENDIX C : WATER MANAGEMENT AND PROCESS SELECTION

The object of water management is to maintain a zero liquid effluent discharge (ZLED) philosophy.

Water is used for seven main purposes in electrical power generation. These are:

- Make-up to the closed circuit evaporative cooling water systems,
- Potable water production,
- Demineralised water production,
- A transport medium for both bottom and fly ash,
- Dust suppression on ash and coal in transit and storage,
- Irrigation on rehabilitated ash disposal site, and
- Housekeeping and maintenance.

1. Aspects of water management

a. Flow metering

Sufficient and accurate on terrace flow meters are essential in water management as no deficiencies in the water balance can be identified without flow metering. On terrace flow meters can also assist in highlighting bulk raw water metering errors. The accuracy of flow meters for potable water supply to 3rd Parties is paramount in accounting for the power stations water consumption. The correct application of chemicals such as flocculants is also not possible without the flow recordings.

b. Cascading

The cascading of water which is no longer suitable for the original process, to another process, is an important aspect in reducing effluent volumes. Examples are:

- Sand-filter backwash water recovery to the cooling water clarifiers
- Raw water sludge recovery to the cooling water clarifiers
- The recovery of low salinity regeneration effluents
- Desalination plant, first stage permeate to demineralised water production

c. Treatment process efficiency

The efficiency of the cold lime softening process and more specific the ability of the process to precipitate calcium carbonate is of utmost importance in achieving the objective treating the smallest volume of cooling water. It is possible to treat large volumes of cooling water inefficiently and still be within specified limits. The addition of chemicals to facilitate the treatment contributes to the salt loading of the water; it is therefore essential that the maximum benefit of the treatment is realised. Using R/GW hour as performance indicator for cooling water treatment instead of R/Ml treated will highlight deficiencies in the treatment process provided that the make-up water quality remains constant.

Poor softening efficiency manifests as incomplete calcium carbonate precipitation, as highlighted by the poor reduction of M Alkalinity across the process. Reduced lime softening efficiency could only be as result of:

1. Incomplete reaction time for crystal growth as a result of flow short circuiting. This is normally due to blockages of the circulation zone with sludge / mud banks / walls. These banks of mud / sludge normally come about following a loss of agitation such as when the flow is stopped without prior removal of the sludge or when the impellors are stopped. The Hendrina, Arnot and Kriel clarifiers, which employ hydraulic sludge circulation, are specifically susceptible to flow stoppage when operating with a sludge blanket. The clarifiers at stations other than Kriel Power Station not susceptible to flow stoppage but power failures and a sort of “wild cat” dropping of the sludge blanket cause problems that could only be ascribed to flow short circuiting. These conditions can only be

rectified by removing all the sludge from the clarifiers. This implies shutting down the Arnot, Hendrina and Kriel clarifiers for high pressure hose washing while the later designs could be mediated through blow-downs. The impellor type design clarifiers, however, must be taken off line when not effective in precipitating calcium carbonate. It is therefore recommended that blow-downs, to recover the efficiency of the process, are done offline in order to minimise the inefficient operation period.

2. Contamination of the cooling water with organics. Though not fully understood, it is believed that the anaerobic digestion of sludge produces organic compounds that could inhibit the precipitation of calcium carbonate. Current research on cooling waters indicates that significant concentrations of calcium could be present associated with an organic compound as anion. This implies that calcium in this form will most probably not partake in the normal dynamics of calcium carbonate precipitation. The interference of these compounds is best nullified through the addition of flocculants such as aluminium sulfate or ferric chloride.
3. Polymers, depending on their molecular weight, can act as either dispersants or flocculants. In general anionic and non-ionic polymers with a molecular weight < 20 000 are excellent dispersants. The molecular weight of flocculants is generally in excess of 1 000 000.
4. The precipitation of calcium carbonate is totally dependent on the calcium and carbonate concentration, the depletion of calcium through sodium alkalinity ingress will reduce the chemical driving force, thus leading to poor alkalinity reduction across the softening process. Controlled addition of sulphuric acid to form permanent hardness through the neutralisation of bicarbonates or the circulation of lime softening sludge following neutralisation with sulphuric acid is the only viable option to counter this. Alternatively, acid mine drainage, when available, could be introduced into the process.

The uncontrolled pollution of the cooling water systems with inefficient lime softening processes cannot be allowed unabated. Thus should the softening process become inefficient through any of the means as described above, the clarifier must be taken off line and the condition rectified prior to returning the clarifier to service.

d. Treatment process selection

The optimum process for cooling water alkalinity control will be the process that effectively controls the cooling water chemistry and allow cycles of concentration that will ensure ZLED can be maintained with any quality of raw water that could be fed to the power station.

The type of cooling water treatment employed and the raw water quality determines the water consumption as poor process choices will lead to excessive blow-down volumes. The cooling water treatment process will also dictate the recoverability of the ash water from a wet ashing system.

e. Cooling water alkalinity control with sulphuric acid

Cooling water alkalinity control with sulphuric acid is a neutralisation process and a salt is added (SO_4) during the treatment. It should be noted that continuous controlled continuous dosing is preferred over slug dosing. The effect is best illustrated by the following chemical equations.

$$Ca(HCO_3)_2 + H_2SO_4 \Rightarrow CaSO_4 + 2CO_2 + 2H_2O \ldots\ldots\ldots\ldots\ldots(1)$$

$$Mg(HCO_3)_2 + H_2SO_4 \Rightarrow MgSO_4 + 2CO_2 + 2H_2O \ldots\ldots\ldots\ldots\ldots(2)$$

The magnesium sulfate ($MgSO_4$) that forms in the second reaction will react with the lime (OH^-) in the ash water to convert to calcium sulfate. ($CaSO_4$)

$$MgSO_4 + Ca(OH)_2 \Rightarrow CaSO_4 + Mg(OH)_2\downarrow \ldots\ldots\ldots\ldots\ldots\ldots(3)$$

As can be seen from the above reaction the hydroxide content of the ash water is depleted while producing the calcium sulfate. The calcium sulfate generated in the process determines the recoverability of the ash water. Permanent hardness (calcium sulfate) can only be removed from the water cycle through absorption on the ash or through precipitation when the overall calcium concentration and pH of the ash water provides for sufficient driving force. Precipitation of calcium when not at the saturation point can be facilitated through the application of soda ash. The disadvantage of the lime soda process is the gain of sodium while sulfate remains in solution as an even more mobile salt.

$$CaSO_4 + Na_2CO_3 \Rightarrow Na_2SO_4 + CaCO_3\downarrow \text{……………….……}(4)$$

f. Cooling water alkalinity control with lime and or ash water

Cooling water alkalinity control with lime is a precipitation process and the hardness species removed during this process remain insoluble in the ash water and are therefore permanently removed from the water cycle. This is best explained by the following chemical equations.

$$Ca(HCO_3)_2 + Ca(OH)_2 \Rightarrow 2CaCO_3\downarrow + H_2O\text{……………………}(5)$$

$$Mg(HCO_3)_2 + 2Ca(OH)_2 \Rightarrow Mg(OH)_2\downarrow + 2CaCO_3\downarrow + 2H_2O\text{………..}(6)$$

If any sodium bicarbonate alkalinity is present in the make-up water the reaction with lime will be as follows.

$$2NaHCO_3 + Ca(OH)_2 \Rightarrow Na_2CO_3 + CaCO_3\downarrow + 2H_2O\text{…….…....}(7)$$

Any permanent hardness that might enter or be formed during the treatment process will then react as follows with the sodium carbonate.

$$CaSO_4 + Na_2CO_3 \Rightarrow CaCO_3\downarrow + Na_2SO_4\text{……………………..…..}(8)$$

When the raw water contains sodium alkalinity and the cooling water is treated with lime bottom end (below specification) calcium hardness concentration problems could be experienced in the cooling water. This phenomenon, however, is simpler to contend with than the excess effluents produced by acid treatment. Only minor quantities of salts are added during the softening process if flocculants are employed.

g. Natural ettringite process in ash water

A small portion of the salts in pulverised fuel ash (PFA) is soluble in water, the solution being alkaline due to the hydrolysis of the calcium oxide.

$$CaO + H_2O \Rightarrow Ca(OH)_2\text{……………………………….……..}(9)$$

The lime that forms in this reaction provides the alkaline conditions that dissolve aluminium as $Al(OH)_3$. In contrast with other metals the solubility of the Aluminium hydroxide increases with increase in pH and at a pH of 11.6 to 12.0 conditions are favourable for the precipitation of ettringite. Basic chemical reactions that enhance sulfate removal through the ettringite process are:

$$Ca(HCO_3)_2 + H_2SO_4 \Rightarrow CaSO_4 + 2CO_2 + 2H_2O\text{……………}(10)$$

$$Mg(HCO_3)_2 + H_2SO_4 \Rightarrow MgSO_4 + 2CO_2 + 2H_2O\text{……………}(11)$$

$$MgSO_4 + Ca(OH)_2 \Rightarrow Mg(OH)_2\downarrow + CaSO_4\text{…………………..}(12)$$

Note: The magnesium sulfate originates from the neutralisation of the cooling water alkalinity with sulphuric acid.

This reaction (conversion of magnesium sulfate) further benefits the precipitation of ettringite and calcium sulfate as can be seen by the following:

$$6Ca^{2+} + 3SO_4^{2-} + 2Al(OH)_3 + 37H_2O \rightarrow 3CaO.3CaSO_4.Al_2O_3.31H_2O\downarrow + 6H_3O^{+}\text{……}(13)$$

h. Solubility of calcium sulfate in ash water

The normal upper limit for calcium and sulfate concentration in the absence of an inhibitor is expressed by:

$$[Ca^{2+}] \text{ X } [SO_4^{2-}] = 500\ 000 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (14)$$

This upper limit will be exceeded constantly and calcium sulfate will also precipitate (as $CaSO_4$) within the ash both calcium sulfate and ettringite will remain sparingly soluble within the ash. Ettringite will dissolve incongruently to gypsum and aluminium hydroxide below pH 10.3.

The stability / solubility of these two precipitates beyond closure of the ash dump will be ensured by the pozzalanic properties of the ash and the low water penetration of the ash following rehabilitation (topsoil and vegetation) of the ash dam (dump). The alkaline properties of the ash will be maintained by a reducing release of calcium oxide from the glass spheres.

The completeness of the sulfate precipitation is dependent on the sodium sulfate concentration of the ash water and sulfate concentrations as low as 250 $mg.kg^{-1}$as SO_4 is possible. However, the disposal of spent regenerants with the ash increases the sodium sulfate concentration which implies that the sulfate precipitation will not be complete.

The ettringite process thus precipitates the sulfate associated with calcium and allows for the reuse of the ash water.

i. Cooling water contamination

The recovery of the station drains to the cooling water system is quite often a source of contamination of the cooling water. Contaminants that typically find their way into the cooling water systems along this route are:

- organic solvents
- dispersed or dissolved lubricants or as free oil
- ash particles
- spent regenerants (NaOH + H_2SO_4)
- soaps and detergents
- chemical inhibitors from auxiliary cooling systems

These products could play havoc with treatment processes and condenser performance. They are also excellent nutrients for microbes. Spent regenerants will dramatically increase the blow-down requirements and could also damage concrete drain systems.

j. Effluent concentration and disposal

If the effluent volume exceeds the effluent sink capacity. ZLED will be compromised as effluents will have to be discharged to a public stream (resource). Concentration plants are then employed to concentrate blow-downs and effluents in order to reduce the volume of effluents. Typical concentration techniques employed by Eskom are:

- reverse osmosis
- thermal distillation using evaporators

It is important to note that when blow-downs are opened to control a specific ion (limiting parameter) concentration, it should not be done to such an extent that the concentration is reduced too far below the specified limit. This practice significantly increases the blow-down volume in comparison to a controlled blow-down where the concentration of the specific ion is controlled close to or on the specified limit.

k. Storm water management

The harvesting of storm water is permitted where the storm-water is polluted. It is further a requirement that clean water yielding areas within a large dirty area be separated from the dirty stream.

The regular cleaning of silt traps and correct maintenance and operation of the oil spill clean-up equipment is of paramount importance in the management of the storm water drains system. Where cut-off drains exist, the drains must be kept clean from silt sand and plant growth to ensure unhindered runoff. Overflows from large clean areas as a result of blocked cut off drains could lead to volumetric constraints within the Power Station drains system. Regular removal of silt from drains dams to maintain their design capacity is also essential if the ability to contain flood water is to be maintained. The correct maintenance of channels and dams is a requirement of Government Notice 704 (GN 704).