Eskom	JUSTIFICATION FOR KOEBERG NPS CHEMISTRY OPERATING SPECIFICATIONS	Allocation Centre 38A	REFERENCE NUMBER KBA0022CHEMJUSTIF2	REV 2a CCJ-080

JUSTIFICATION FOR THE KOEBERG NPS CHEMISTRY OPERATING SPECIFICATIONS

Page

1 of 111

COMPILED	REVIEWED	AUTHORISED
	Pretorius	
N VAN EEDEN	CATE PRETORIUS	B MAPUMULO
CHIEF SCIENTIST NUCLEAR SUPPORT	SENIOR ENGINEER SAFETY CASE GROUP	MANAGER (acting) SAFETY CASE GROUP
DATE: 2019-05-06	DATE: 2019-05-06	DATE: 2019-05-06

PAGE STATUS INDEX

PAGE	REVISION								
	0	0a CCJ -059	1 CCJ -062	2 CCJ -074	2a CCJ -080				
1	X		x	X					
2	X		x	X	X				
3	X		x	X	X				
4	X	X							
5	X			X					
6	X								
7	X								
8	X			X					
9	X								
10	X				X				
11	X			X	X				
12	X		x	X					
13	X			X					
14	X			X					
15	X		X						
16	X		X	X					
17	X		x	X					
18	X			X					
19	X			X					
20	X								
21	X		x	X	x				
22	X		x	X	X				
23	X		x	X	X				
24	X		X						
25	X		x						
26	X								
27	X		X						
28	X		X						
29	X		X						
30	X		x	X					
31	X								
32	X		x	X					
33	X		x	X					
34	X			X					
35	X								
36	X		x	X					
37	X		x	X					
38	X		X	X					
39	X								
40	X			X					
41	X		X	X					
42	X	X	X						
43	X	X	X						
44	X	X	X	X					
45	X		x	X					
46	X								
47	X								
48	X								
49	X								
50	X								
51	X		x						
52	X		X	X					
53	X		X						
54	X		X						
55	X		X						
56	X		x						
57	X		X	X					
58	X								
59	X								
60	X								
61	X								
62	X		X	X	X				
63	X		X	X	X				
64	X		X						
65	X		X						
66	X		X						
67	X		X						
68	X								
69	X								
70	X								
71	X			X	X				
72	X		X	X	X				
73	X		x	X					
74	X		x	X					

PAGE	REVISION								
	0	0a CCJ -059	1 CCJ -062	2 CCJ -074	2a CCJ -080				
75	X			X					
76	X			X					
77	X		x	X					
78	X		X						
79	X		x						
80	X		x		X				
81	X		X	X	X				
82	X		X		X				
83	X		X						
84	X		X	X					
85	X								
86	X		x	X					
87	X		X						
88	X				X				
89	X			X					
90	X			X					
91	X		X	X					
92	X			X					
93	X	X		X	X				
94				X					
95				X					
96				X					
97				X					
98				X					
99				X					
100				X					
101				X					
102				X					
103				X					
104				X					
105				X					
106				X					
107									
108									
109									
110									
111					X				
End									

PAGE	REVISION								
	0	0a CCJ -059	1 CCJ -062	2 CCJ -074	2a CCJ -080				

Lower-case “x” indicates editorial change only.

TABLE OF CONTENTS

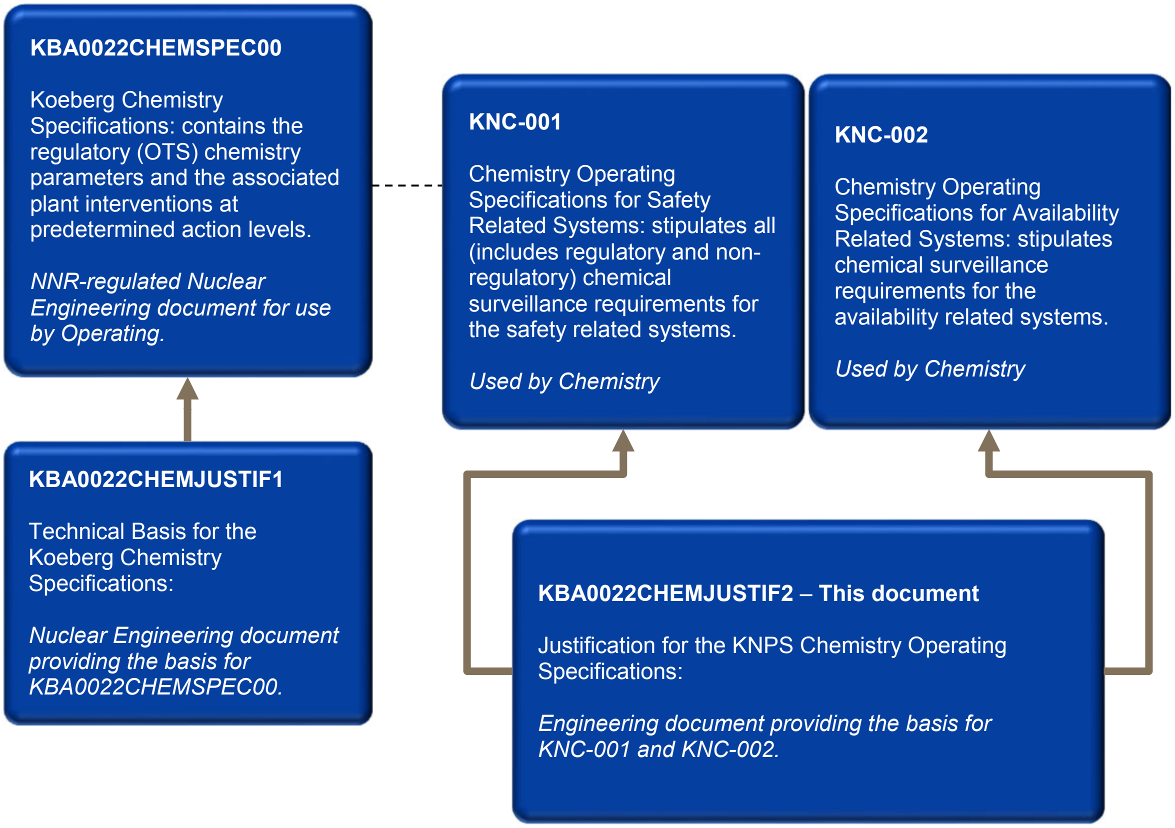
TABLE OF ATTACHMENTS

1.0 INTRODUCTION

Day-to-day operation of a PWR and its long-term plant health relies on effective chemical control of the various plant systems. The chemistry operating specifications are contained in KNC-001 for the safety related systems and in KNC-002 for the availability related systems.

Chemistry parameters with safety significance are reflected in the licence binding document, KBA0022CHEMSPEC00 (*Koeberg Chemistry Specifications (OTS-KCS)*), along with associated plant interventions at predefined action levels. The basis for these OTS-KCS action levels, limit values, and analysis frequencies are documented in KBA0022CHEMJUSTIF1 (*Technical Bases for Koeberg Chemistry Specifications*).

This document, (KBA0022CHEMJUSTIF2), is the justification for KNC-001 and KNC-002 (I.e. the *Chemistry Operating Specifications*).



KBA0022CHEMSPEC00

Koeberg Chemistry Specifications: contains the regulatory (OTS) chemistry parameters and the associated plant interventions at predetermined action levels.

NNR-regulated Nuclear Engineering document for use by Operating.

KNC-001

Chemistry Operating Specifications for Safety Related Systems: stipulates all (includes regulatory and non-regulatory) chemical surveillance requirements for the safety related systems.

Used by Chemistry

KNC-002

Chemistry Operating Specifications for Availability Related Systems: stipulates chemical surveillance requirements for the availability related systems.

Used by Chemistry

KBA0022CHEMJUSTIF1

Technical Basis for the Koeberg Chemistry Specifications:

Nuclear Engineering document providing the basis for KBA0022CHEMSPEC00.

KBA0022CHEMJUSTIF2 – This document

Justification for the KNPS Chemistry Operating Specifications:

Engineering document providing the basis for KNC-001 and KNC-002.

Figure 1: Interrelationship of the chemistry specifications and basis / justification documents

The content in this document includes explanations for:

- controlling each chemical parameter;
- the limiting values, target values, and the analysis frequencies (in as far as clarification is required for each) for chemical additives and impurities;
- radiochemistry specifications;
- the risks associated with each parameter (where this is applicable); and
- chemistry strategies.

For each parameter the following is discussed:

- general principles defining the objective, strategy, and risks of the parameter; and
- the desired operating envelope for each system that is affected by the parameter. The detail may vary according to the importance of the parameter and the extent of information available.

***NOTE 1**: The references do not always agree on every aspect regarding limit values and analysis frequencies. The bases stated for the parameters can thus be considered to be informed by all the reference documents, but in certain cases the actual limit values and analysis frequencies applied in the KNPS chemistry specifications are not necessarily identical to any one specific reference. The bases for the actual limit values and analysis frequencies take into account all references and plant operating experience. This document therefore clarifies these differences and defines the position taken for KNPS.*

***NOTE 2**: This document is a living document and the detailed clarification of the basis and strategies contained in Attachment A and Attachment B will continue to evolve with time. Currently, some of the details are not yet developed, and some are completed for specific aspects only. These attachments will continue to be developed and reviewed periodically based on operational requirements and operating experience.*

2.0 SCOPE

2.1 PURPOSE

To provide the technical bases for KNC-001 and KNC-002 (*Chemistry Operating Specifications*) and to explain the rationale for the various plant chemistry strategies applied at Koeberg Power Station.

2.2 APPLICABILITY

The document is applicable to Chemistry Control Programme at Koeberg Power Station.

3.0 NORMATIVE / INFORMATIVE REFERENCES

3.1 NORMATIVE

[1] KSC-003 The Chemistry Programme

[2] 238-8 Nuclear Safety and Quality Manual

3.2 INFORMATIVE

[3] KBA 0022 OTS 0000001 Operating Technical Specifications (OTS)

[4] Koeberg Safety Analysis Report (SAR)

[5] KBA-0022-SRSM-000-00 Safety Related Surveillance Manual (SRSM)

[6] KBA 0022 CHEMSPEC 00 Koeberg Chemistry Specifications (OTS-KCS)

[7] Electricité de France Chemistry and Radiochemistry Specifications

[8] Electric Power Research Institute Chemistry Guidelines

[9] Westinghouse Chemistry Guidelines

[10] AREVA Chemistry Guidelines

[11] Turbine Vendor Guidelines

[12] ANT PWR Primary Side Coolant Chemistry

[13] ANT PWR Secondary System Chemistry

[14] OEM Specifications, Guidelines and Procedures

[15] WANO Data Elements Manual

[16] Eskom Corporate Chemistry Standards

[17] Eskom Design Documents (DSE)

[18] Optimisation of Ethanolamine Treatment of a PWR Secondary System

[19] KNC-001 Chemistry Operating Specifications for Safety Related Systems

[20] KNC-002 Chemistry Operating Specifications for Availability Related Systems

[21] IAEA Safe Long Term Operation of NPPs and SALTO Peer Review Guidelines

The above are generally consulted references. Specific references are cited in the detailed clarifications in Attachment A and Attachment B.

4.0 DEFINITIONS AND ABBREVIATIONS

4.1 DEFINITIONS

4.1.1 Action Levels

For the OTS chemistry parameters listed in OTS-KCS, action levels prescribe threshold values of a parameter beyond which system reliability may be at risk.

The intent of the action levels is to protect the plant, in particular steam generators and fuel cladding, from exposure to detrimental conditions that may result in serious and/or extensive damage. Exposure may be considered as the product of the magnitude of the excursion and the duration in which the condition persists. Action levels therefore emphasise the direct increasing threat to the steam generator and/or the fuel cladding as the control parameter value deteriorates during operation, and therefore imposing increasing levels of urgency to correct the situation.

4.1.2 Dose Equivalent I-131

The dose equivalent iodine-131 (I-131) relates to the internal contamination of the thyroid gland. The dose equivalent I-131 is estimated from the combined activities of the different isotopes of iodine according to the formula:

$$A(equivalent) = A(I-131) + \frac{A(I-132)}{30} + \frac{A(I-133)}{4} + \frac{A(I-134)}{50} + \frac{A(I-135)}{10}$$

where the weighting coefficients are derived from the maximum permissible water dissolved isotopic concentration for workers.

4.1.3 Equilibrium Activity

Equilibrium activity is activity values normalised for letdown flow and make-up (not applicable for noble gas activities). Activity values shall be measured while the reactor is operating at stable power; the reactor is considered to be stable after operation at a specific power level for a period of 48 to 72 hours.

4.1.4 I-134 Activity (A1)

The I-134 activity (A1) represents the theoretical change in I-134 activity coming from contamination from previous cycles. A1 is calculated by RFE.

4.1.5 Operating Domains

RCD	Reactor Completely Defueled
RSD	Refuelling Shutdown
MCSD	Maintenance Cold Shutdown
SD / RRA	Shutdown on RRA
SD / SG	Shutdown on Steam Generators

- RP Reactor at Power

4.1.6 Peak I-131 Equivalent Activity

Peak I-131 equivalent activity is the instantaneous activity measured during a transient (not normalised for letdown flow or make-up).

4.1.7 Limit Value (Specification Limit)

Limit values indicate the minimum and/or maximum boundary limits for a parameter.

4.1.8 Ammonia Regime

The feedwater is conditioned with ammonia solution for pH control (ETA dosing is out-of-service).

4.1.9 Ethanolamine Regime

The feedwater is conditioned with ETA (and ammonia) for pH control (ammonia dosing may be in-service or out-of-service).

4.1.10 Analysis Frequency

The analysis frequency for a parameter that must be adhered to.

4.1.11 Total Noble Gas

Total noble gas activity is used for limit values in operating technical specifications and is calculated according to the formula:

$$A(Total\ Noble\ Gas) = A(Kr\text{-}85m) + A(Kr\text{-}87) + A(Kr\text{-}88) + A(Xe\text{-}133m) + A(Xe\text{-}133) + A(Xe\text{-}135) + A(Xe\text{-}138)$$

4.1.12 Target Value

Station administrative value(s) indicating the optimum conditions or conditions being strived to achieve based on the strategic objective for the specific parameter and to serve as a margin from the action levels and limit values.

4.2 ABBREVIATIONS

Abbreviation	Description
AL	Action level
ALARA	As low as reasonably achievable
BOC	Beginning of cycle
CC	Cation conductivity
CEI	Chemistry effectiveness indicator
CILC	Crud-induced localised corrosion
CIPS	Crud-induced power shift
CPI	Chemistry performance indicator

Abbreviation	Description
EOC	End of cycle
ETA	Ethanolamine
FAC	Flow-accelerated corrosion
IGA	Intergranular Attack
KNPS	Koeberg Nuclear Power Station
LIMS	Laboratory information management system
LOCA	Loss of Coolant Accident
NTU	Nephelometric Turbidity Units
OEM	Original Equipment Manufacturer
OTS	Operating Technical Specifications
OTS-KCS	Koeberg Chemistry Specifications
pH_T	pH at operating temperature
PbSCC	Lead-induced Stress Corrosion Cracking
PWSCC	Primary Water Stress Corrosion Cracking
RFE	Reactor Fuel Engineering
SALTO	Safety Assessment for Long-Term Operation
SCC	Stress Corrosion Cracking
SDO	Short-duration Outage
SFP	Spent Fuel Pool
SG	Steam Generator
STP	Standard Temperature and Pressure
TRC	Technical Review Committee
VCT	Volume Control Tank
2 × M	Twice per month
3 × W	Three times per week

5.0 OBJECTIVES AND OVERVIEW OF THE CHEMISTRY PROGRAMME

The main objectives of primary water chemistry control are to:

- Ensure primary system pressure boundary integrity,
- Ensure fuel cladding integrity and achievement of fuel design performance,
- Minimise out-of-core radiation fields, and
- Ensuring plant condition for long-term-operation.

Control of the primary plant chemistry at KNPS is based on a modified elevated pH programme aligned to the EPRI Pressurised Water Reactor Primary Water Guidelines [8]. The current pH programme has been implemented since 2010 (cycles 119 and 218) and is aimed at a target pH of 7,25 (at operating temperature, pH_T) while also respecting the fuel vendor limit on lithium concentration at the beginning of a cycle. The target pH_T is maintained by adjusting the lithium concentration in co-ordination with the boron (boric acid) concentration as it changes throughout the fuel cycle by dilution (and boration). This regime supports long-term operation since elevated pH_T reduces corrosion and corrosion product transport, and hence minimises the activation of corrosion products. Corrosion initiating impurities / contaminants (e.g. chloride, fluoride, sulphate) are maintained as low as achievable in the reactor coolant, the spent fuel pool system, and the make-up water systems. Hydrogen overpressure is maintained on the primary system to ensure that oxygenated radicals formed by radiolysis of water molecules recombine in order to prevent the production of oxygen during power operation which would lead to accelerated corrosion of the system materials.

Activated corrosion products (e.g. cobalt-58) and other species which could lead to source term accumulation are routinely trended. Since 2014 / 2015 (fuel cycles 121 / 221), depleted zinc acetate has been added to the reactor coolant to reduce out-of-core radiation fields and dissolved zinc is also mitigation for the initiation of stress corrosion cracking of the system components. Fuel cladding integrity is confirmed by monitoring fission products (e.g. iodine isotopes and noble gas) in the primary coolant and primary to secondary leak rate is determined by radionuclide comparative analysis with activity present in the steam generator blowdown. The technical operating specification chemistry control parameters are listed in the Koeberg Chemistry Specifications (OTS-KCS) along with action levels, limit values, and surveillance frequencies. OTS-KCS also contains the actions to take when a parameter limit value is exceeded. The diagnostic parameters with limit values, target values, and analysis frequencies are included in KNC-001.

The main objectives of secondary water chemistry control are to:

- Protect the steam generators from degradation,
- Minimise flow accelerated corrosion,
- Minimise corrosion product transport,
- Minimise the introduction of impurities and
- Ensuring plant condition for long-term-operation.

Secondary plant chemistry is controlled by adding volatile alkalising agents (all volatile treatment) to prevent general corrosion of the mainly carbon steel feed-train (all ferrous) and by maintaining low dissolved oxygen to protect the steam generator nickel-alloy tubing material. Hydrazine is continuously added to the feedwater to maintain reducing conditions. During 2000 / 2001, both units commenced advanced amine treatment by injecting ethanolamine (ETA) into the feedwater to limit flow-accelerated corrosion (FAC) in the two-phase (steam/water) regions such as the moisture separator reheaters and the bled steam lines. In 2013, this regime was optimised according to Koeberg operating experience and international practices [18]. Steam generator secondary chemistry technical specification controls include monitoring of pH, cation conductivity and sodium.

Actions to take when these limit values are exceeded are stated in OTS-KCS. Diagnostic parameters are listed in KNC-001 and KNC-002. The condensate polishing plant is bypassed under normal plant operation and is available to be placed in-service to clean up the secondary water and to protect the SGs from impurity ingress, should this occur.

Chemistry monitoring is performed on a routine schedule and trends are analysed to ensure that target values are achieved. Chemistry performance is assessed using the WANO chemistry performance indicator (CPI) and the INPO chemistry effectiveness indicator (CEI) as a tool to support long-term operation [15].

Plant chemistry is controlled during all operating domains including start-up and shutdown of units, unit transients and for periods of non-operation (e.g. outage). These operational control procedures are:

- KWC-CH-001 (*Chemistry Control of a Unit during Start-up from Normal Cold Shutdown to Full Power Operation*);
- KWC-CH-002 (*Preparation of the Feedwater Plant for Starting Up a Unit after Shutdown*);
- KWC-CH-003 (*Steam Generator Hide-Out Return Sampling and Analysis*);
- KWC-CH-004 (*Chemical Control of a Unit during Shutdown*);
- KWC-CH-005 (*Secondary System and Steam Generator Conservation*);
- KWC-CH-006 (*Chemistry Procedure for Degassing and Oxygenation of the Primary Circuit*);
- KWC-CH-007 (*Feedwater Pump Flushing*);
- KWC-CH-008 (*Chemistry Control from Hot Shutdown Conditions to Full Power Operation*);
- KWC-OP-SDA-002 (*Chemistry Procedure for Operating the Water Production Plant*); and
- KWC-ATE-003 (*Chemistry Procedure for Operating the Condensate Polishing Plant*).

Producing high purity process water at the Water Production Plant is essential for the Chemistry operational effectiveness.

The quality of plant process chemicals is assured by analysis prior to acceptance and all chemical products must comply with KAA 751 (*Chemical Restrictions and Control at Koeberg*).

Transformer insulation oil, turbine and pump lubrication oil, hydraulic fluid and diesel fuel systems are included in the Chemistry Operating Specifications and microbiological surveillance is also performed on various systems.

Effluent discharge is monitored by implementing surveillance criteria and adhering to the environmental release limits based on legislative requirements (Department of Environmental Affairs and KNPS Radiation Protection Standards) and waste minimisation good practice. The Environmental Survey Programme monitors the area surrounding the plant for radionuclides that are potentially produced by KNPS as is required by the National Nuclear Regulator (NNR).

Worker health aspects and safely regulations are taken into account in development of specifications (Hazardous Chemical Regulations).

Chemistry operating specifications of plant systems are documented and deviation is managed in accordance with KAA-688 (*The Corrective Action Process*). Chemistry results from plant-installed on-line analysers and laboratory grab sampling are recorded in the laboratory information management system (LIMS) database. The LIMS provides alarms for out-of-trend and out-of-specification parameters. Analysis methods are validated and results are reported subsequent to quality control (QC) samples passing statistical process control criteria. QC processes are documented in KSC-001 (*Radiochemistry*) and KSC-004 (*Analytical Chemistry*).

The basis for each chemistry parameter is given in Section 7.1 and detailed in Attachment A. The strategies that support this overview are shown in Section 7.2 and detailed in Attachment B. Attachment C is a review of the Chemistry Programme to demonstrate alignment to the IAEA – SALTO attributes for ageing management.

6.0 RELATIONSHIP BETWEEN CHEMISTRY AND THE MAIN TYPES OF CORROSION

The table below describes the relationship between main plant/component and the type of corrosion that the material is susceptible to, and list the associated chemical mitigation measures.

System	Materials	Type of corrosion	Chemical Cause	Chemical Mitigation
Primary Side	All	General (dose rates)	pH acidic or too alkaline	Optimum pH control
	Zirconium alloy	General corrosion	pH very alkaline	Limit lithium and sodium
		Various localised	Oxygen, fluoride, zeolite deposits	Add hydrogen, limit oxygen, fluoride, calcium, magnesium, aluminium, silica
	Nickel alloy	Stress corrosion (cracking)	(under stress) Sodium, chloride, oxygen	Limit sodium, chloride, oxygen
Primary and Auxiliary	Austenitic stainless steel	Stress corrosion (cracking)	Oxygen at high temperature, chloride, fluoride, sulphurous compounds	Add hydrogen to RCP, limit chloride, fluoride, sulphate
Cooling Auxiliaries (RRI, SRI)	Carbon steel	General corrosion	pH too low	Add inhibitor trisodium phosphate and pH > 11
Secondary Side Water/Steam	Carbon steel	General corrosion	pH too low	Add pH conditioning chemicals, ammonia, ethanolamine
		Flow accelerated corrosion	pH in liquid phase too low	Ethanolamine
	Copper alloy	Copper dissolution	Ammonia too high	Optimise pH control agents ammonia and ethanolamine
	Various	Various	Oxygen	Reduce air, add hydrazine
Secondary Side Steam Generator	Carbon steel plates	General corrosion (denting)	Acids (chloride), oxygen, copper, oxidants	Reduce sea water, air ingress, add hydrazine
			Iron, grit	Eliminate debris
	Nickel alloy	Intergranular attack/stress corrosion cracking	Sodium hydroxide, oxidants, sulphate, sulphur, lead, resins, carbon dioxide, copper	Reduce alkaline pollutants, air ingress, make-up water contamination, SRI in-leakage
		Pitting corrosion	Chloride, oxygen, copper, resins	Limit pollution, preservation at shutdown
		Thinning	Acidic pollutants	Add alkaline conditioning agents, avoid acid conditions, prevent sulphate and chloride ingress

7.0 REQUIREMENTS

7.1 BASIS FOR CHEMISTRY SPECIFICATIONS

The table below provides a brief basis/justification for each chemical parameter that is monitored at KNPS and provides a reference to a more detailed clarification in Attachment A.

Parameter	Justification for monitoring	Details in Attachment A
Aluminium	• Impurity. Oxides and silicates form insoluble deposits on fuel and on the surfaces of plant systems.	A.12
Ammonia	• pH chemical conditioning agent for secondary plant corrosion control. • Used in secondary plant conservation. • Potential impurity in primary system.	A.16
Boron	• Reactivity control element in primary system (chemical shim). • Potentially toxic to the environment.	A.1
Calcium	• Impurity. Oxides and silicates form insoluble deposits on fuel and on the surfaces of plant systems.	A.12
Cation Conductivity	• Determines low-level anionic impurities in the secondary system. • A non-specific measure of aqueous dissolved anionic chemical species / impurities	A.18
Chloride	• Known harmful impurity species in primary and secondary systems.	A.2
Chlorine	• Inhibits marine growth in heat exchangers. • Disinfectant for water treatment to inhibit biofouling. • May lead to / result in elevated chloride levels. • Harmful to the environment.	A.23
Chromium	• Corrosion product from mechanical wear of stainless steel components. • Activation to Cr-51 resulting in out-of-core radiation fields.	A.14
Cobalt	• Corrosion product from mechanical wear of high cobalt alloys is activated to Co-60 resulting in out-of-core radiation fields. • Nickel is activated to Co-58 resulting in out-of-core radiation fields.	A.14
Conductivity	• A non-specific measure of aqueous dissolved ionic chemical species for primary and secondary systems.	A.8
Copper	• Corrosion product from plant system material, the dissolution of which is accelerated in/by high pH environments. • Has been shown to accelerate corrosion of Nickel alloy.	A.1
Ethanolamine (ETA)	• Chemical conditioning agent for secondary plant corrosion control. • Mitigates flow-accelerated corrosion (FAC). • Potentially toxic to the environment.	A.16

Parameter	Justification for monitoring	Details in Attachment A
Fluoride	• Known harmful impurity species in primary and secondary systems.	A.2
Gamma spectrum	• Identification and quantification of gamma emitting radionuclides. • Indication of total activity of all radionuclides present. • Calculated total activity is proportional to dose to personnel, public and environment.	A.1A.22
Hydrazine	• Chemical conditioning agent to maintain a reducing environment in secondary system by scavenging oxygen. • Used in conservation of secondary plant. • Scavenges oxygen in primary plant during start-up prior to introduction of hydrogen. • Is highly toxic to the environment.	A.17
Hydrogen	• Added to primary circuit to maintain reducing conditions to minimise corrosion by counteracting the production of oxygen by radiolysis. • Used for generator cooling.	A.6
Iodine	• Fission products that indicate fuel defects. • Iodine isotopes are fission products and these have significant contribution to radioactive dose. • The dose equivalent I-131 is estimated from the combined activities of the isotopes.	A.22
Iron	• Corrosion product from plant system material. Accumulates in SGs creating areas for impurities to concentrate. • Activation to Fe-55 and Fe-59 resulting in out-of-core radiation fields.	A.1
Lead	• Implicated in accelerating stress corrosion cracking in the secondary system. • Toxic to the environment.	A.24
Lithium	• Chemical conditioning agent added as lithium hydroxide for pH control of the primary circuit.	A.5
Magnesium	• Impurity. Oxides and silicates form insoluble deposits on fuel and on the surfaces of plant systems.	A.12
Manganese	• Potentially toxic to the environment.	A.24
Nickel	• Corrosion product from SG tubing becomes activated to Co-58 and Ni-63 resulting in out-of-core radiation fields.	A.14
Noble gas	• Fission product gases that indicate fuel defects.	A.22
Oxygen	• Involved in forming metal oxide passive layers. • Involved in corrosion mechanisms.	A.4
pH	• Optimised pH programmes are implemented to minimise corrosion of metals in primary and secondary plant. • Affects corrosion product transport and radiation fields. • High and low pH effluent can adversely affect the marine environment.	A.7
Silica	• Deposit forming impurity species, potentially harmful in primary and secondary plant.	A.9

Parameter	Justification for monitoring	Details in Attachment A
Sodium	• Known harmful impurity species in secondary plant causing caustic SG crevice environments. • Influences general corrosion in primary. • Na-24 arises from neutron activation.	A.11
Sulphate	• Known harmful impurity species in primary and secondary systems.	A.3
Suspended solids	• Can be harmful and accumulate as deposits in primary and secondary plant. • Can be harmful to marine life.	A.1
Total Organic Carbon	• Potentially harmful contaminant especially the organohalide compounds in secondary plant.	A.20
Trisodium Phosphate	• Corrosion inhibitor in carbon steel closed cooling water systems. • Radioactive iodine scrubbing agent and pH adjustment for primary system spray during LOCA. • Potentially harmful to the environment.	A.21
Tritium	• Tritium is a beta emitter generated from hydrogen activation and can displace natural hydrogen in the environment, therefore releases must be quantified. • Potential dose to personnel, public and environment.	A.22
Turbidity	• Turbidity and total suspended solids measurements provide an indication of the optical clarity of the water.	A.19
Zinc	• Can form oxide and silicate insoluble deposits on fuel and on the surfaces of plant systems. • Added to reactor coolant to mitigate out-of-core radiation field development. • Mitigates primary water stress corrosion cracking.	A.15

7.2 CHEMISTRY STRATEGIES

The table below provides a list of the various chemical control strategies employed at KNPS and provides a reference to an explanation in Attachment B.

Strategy	Brief explanation of strategy	Details in Attachment B
Primary Water Management	Explanation of how the primary water chemistry strategy is designed to meet the objectives of the Chemistry Programme.	B.1
Secondary Water Management	Explanation of the how the secondary water chemistry strategy is designed to meet the objectives of the Chemistry Programme.	B.2

8.0 ACCEPTANCE AND AUTHORISATION

As a minimum, this document is reviewed by Chemistry, Reactor Fuel Engineering, Steam Generator Engineering Programme, and Flow-Accelerated Corrosion Engineering Programme.

This document has been seen and accepted by:

Name	Designation
M Stwayi	Chemistry Manager
I Greeff	Reactor Fuel Engineering
I Naidoo	Corrosion Engineering Programme
L Salie	Steam Generator Engineering Programme
D Jeannes	Nuclear Environmental Manager
I Malgas	Nuclear Analysis
N Mahlangu	OPG
S Pietersen	Radiation protection
H Bosman	DPSA Group
H Nicolson	Corporate Specialist, Nuclear Engineering
U Louw	Specifications Engineering

See also 11.0 Review Information

9.0 REVISION INFORMATION

Date	Rev.	Compiler	Remarks
August 2016	0	N van Eeden	Original release. This document is compiled to provide the bases for and to explain the chemistry operating specifications and chemical strategies applied at Koeberg Power Station. The following attachments are included in this original release: • A.1: Boron • A.2: Chloride and fluoride • A.3: Sulphate • A.4: Oxygen, for RCP, RCV, REA, AHP and ASG only • A.5: Lithium • A.6: Hydrogen, for RCP, RCV, TEP, and RPE only • A.7: pH, for APG and SEK only • A.8: Conductivity, for REA only • A.9: Silica, for RCP and PTR only • A.11: Sodium, for APG only • A.17: Hydrazine, for AHP only • A.18: Cation Conductivity, for APG only • A.21: Trisodium Phosphate, for EAS only • A.22: Radiochemistry, for Gamma Spec, Iodine and Noble Gas This is intended to be a living document and the detailed bases will continue to be reviewed, developed, and updated.
January 2017	0a	N van Eeden	An alternate lithium control strategy has been added to enable management of steam generator leak rate.
March 2018	1	N van Eeden	A.1: Boron updated for KER and SEK A.4: Oxygen updated for CEX, RRI, SRI, DEG, DEL and GST A.7: pH updated for RCP, AHP, RRI, SRI, SES, DEG, DEL, SEU, KER and SEK A.11: Sodium updated for CEX, VVP and RCP/RRA A.12: Aluminium, Calcium, Magnesium added A.8: Conductivity updated for SEU A.21: Trisodium Phosphate updated for RRI, SRI, SES, DEG and DEL A.23: Chlorine completed B.1: Primary Power Operation strategy added B.5: Secondary Plant Power Operation strategy added
May 2019	2	N van Eeden	A.8: Conductivity in SEU updated A.15: Zinc added A.16: Ethanolamine and ammonia added B.1: Primary Water Chemistry Management added B.2: Secondary Water Chemistry Management added Attachment C added, for the Chemistry Programme alignment to the SALTO Attributes for ageing management

Date	Rev.	Compiler	Remarks
November 2019	2a	N van Eeden	A.10: Suspended solids added A.13: Iron and Copper added for AHP A.14: Nickel, Cobalt and Chromium added A.19: Turbidity in AHP / ASG added A.20: Total Organic Carbon added A.22: Tritium in CEX added A.24: Lead and Manganese added

ATTACHMENT A
CHEMISTRY PARAMETERS BASIS DETAILS

This is a living document and the detailed clarifications of the bases contained in this attachment will continue to be developed. Some of the attachments are not yet developed, and some are currently completed for specific aspects only which are given in the Status column in the table below. The attachments will continue to be developed and be reviewed periodically.

Attachment	Parameter	Status
A.1	Boron	Complete
A.2	Chloride and Fluoride	Complete
A.3	Sulphate	Complete
A.4	Oxygen	Complete
A.5	Lithium	Complete
A.6	Hydrogen	Complete for RCP, RCV, TEP, and RPE
A.7	pH	Complete
A.8	Conductivity	Complete for REA and SEU
A.9	Silica	Complete for RCP and PTR
A.10	Suspended Solids	Complete
A.11	Sodium	Complete for APG, CEX, VVP, and RCP / RRA
A.12	Aluminium, Magnesium, Calcium	Complete
A.13	Iron, Copper	Complete for AHP
A.14	Nickel, Cobalt, Chromium	Complete
A.15	Zinc	Complete
A.16	Ethanolamine, Ammonia	Complete
A.17	Hydrazine	Complete for AHP
A.18	Cation Conductivity	Complete for APG
A.19	Turbidity	Complete for AHP and ASG
A.20	Total Organic Carbon	Complete
A.21	Trisodium Phosphate	Complete
A.22	Radiochemistry	Complete
A.23	Chlorine	Complete
A.24	Lead, Manganese	Complete

A.1 Boron

A.1.1 Objective and Strategy

Boron is used in the reactor coolant to limit and control reactivity by the absorption of neutrons. Purified natural boric acid is dissolved in the reactor coolant water, which decreases the thermal utilisation factor resulting in decreased reactivity. Therefore, by varying the concentration of boric acid in RCP, the reactivity of the core can be accurately controlled. Boration creates negative reactivity and if the boron concentration is reduced by dilution, positive reactivity is added. Varying the boron concentration primarily compensates for fuel burn-up, manual control rod movement, or poison build-up. The variation in boron concentration minimises control rod usage, which results in a more uniform flux profile over the core than can be achieved by control rod manipulation.

Boron has two naturally occurring isotopes, ^{10}B (19,9%) and ^{11}B (80,1%). The reactivity control mechanism of soluble boron is primarily due to the large thermal neutron absorption cross-section of ^{10}B. After absorbing a neutron, the excited nucleus decays by alpha emission and is transformed into a lithium nucleus.

$$^{10}B + {}^{1}n_{(t)} \rightarrow {}^{7}Li + {}^{4}He$$

A.1.2 Physical Characteristics of Boric Acid

Some of the physical characteristics of boron are:

- low acidity;
- high solubility;
- significant neutron capture; and
- good physical and chemical stability.

A.1.3 Concentration

Boron concentration limits are imposed for reactivity control and not for chemistry reasons. Due to its nuclear safety implications, the surveillance and concentrations in the primary systems are OTS requirements.

The boron meter shall be operable for monitoring changes in RCP boron concentration to avoid reactivity excursions due to uncontrolled dilution and to verify that authorised limits are respected.

A.1.4 Corrosiveness

Boric acid is a weak acid, especially at high temperatures, and is not excessively corrosive with regards to the materials of the primary system with which it comes into contact during normal operating conditions of the RCP. The acidic environment is neutralised by addition of lithium hydroxide to minimise potential general corrosion of the RCP materials.

There is risk of corrosion to the stainless steels if very high concentrations of boron and pollutants, such as chloride, are present in an oxidising environment.

A.1.5 Basis for Limit Values and Analysis Frequencies

A.1.5.1 Reactor Coolant System/Residual Heat Removal System (RCP / RRA)

A.1.5.1.1 Reactor at Power (RP)

The initial dilution to criticality (after core configuration changes) is managed in accordance with operating procedures. The decrease in boron concentration throughout the cycle follows the burn-up of the fuel. The specific concentrations of boron may vary according to characteristics of the fuel and thus these values relate back to OTS and fuel management.

The maximum allowed concentration is imposed to minimise the risk of boron crystallisation in the core during accident conditions.

The limit values are determined by the plant operational requirements for reactivity management [1].

The boron meter shall be operable for monitoring changes in primary coolant boron concentration to avoid reactivity excursions due to uncontrolled dilution and to verify that authorised limits are respected.

The analysis frequency for a manual chemical analysis is weekly to verify the accuracy of the boron meter. This frequency has been established as sufficient by plant operational experience. The same analysis frequency is employed by EDF [2].

If the boron meter is inoperable, approach and dilution to criticality is prohibited and it is required to verify the boron concentration by sampling every 24 hours. ([3], Event REN 1).

The boron concentration in the pressuriser (RCP 001 BA) must be maintained as close as practical to boron concentration in the loops. The concentration in the pressuriser must not be > 50 mg $B.kg^{-1}$ less than the concentration in the loop. Maintaining a low differential boron concentration between the pressuriser and the primary circuit ensures that no significant reactivity excursion will occur during a pressuriser out-surge.

The pressuriser must be analysed weekly and when the RCP loop boron concentration changes by > 100 mg $B.kg^{-1}$ in any 6-hour period ([3], Event RCP 2).

Boron isotopic analysis is established to enable RFE to provide accurate core measurement data and to determine critical boron concentrations. $^{10}B/^{11}B$ in the reactor coolant is determined monthly and during zero-power fuel physics tests as well as during flux maps.

A.1.5.1.2 Normal Shutdown – SG (SD / SG)

After reload, the lower limit value boron concentration of the primary circuit shall be greater than the minimum value at the start of zero-power core physics tests. This minimum value, provided by RFE, assures a $k_{eff} \leq 0{,}95$ and sufficient time for the operator to react in the event of a dilution accident [1].

For all other cases, where the primary temperature is greater than or equal to 284°C (P12) and/or the primary pressure is greater than 13,8 MPa(g) (P11), the concentration shall be greater than or equal to that required at hot shutdown. A curve of the required boron concentration versus burn-up at hot shutdown is provided in the Physics Data Book.

By respecting the required concentration limit, the assurance is provided that the required hot shutdown sub-criticality margin is respected.

For the other cases, where the primary temperature is less than 284°C (P12) and/or the primary pressure is less than 13,8 MPa(g) (P11), the concentration shall be greater than or equal to that required at normal cold shutdown (CSD). A curve of the required boron concentration versus burn-up at cold shutdown is provided in the Physics Data Book. By respecting the required concentration limit, assurance is provided that the required cold shutdown sub-criticality margin is respected.

The upper limit value of 2700 mg $B.kg^{-1}$ for the primary coolant corresponds to the maximum boron concentration of the PTR tank. This value ensures that boron precipitation will not occur before the start of hot leg injection following a LOCA, where the primary coolant reaches saturation temperature [1].

If the boron meter is inhibited, it is required to verify the boron concentration by sampling every eight hours ([3], Event REN 1).

A.1.5.1.3 Normal Shutdown – RRA (SD / RRA)

After fuel handling, the lower limit value boron concentration of the primary circuit shall be greater than the initial value for zero-power core physics tests. This value, provided by RFE, assures a $k_{eff} \leq 0,95$ and sufficient time for the operator to react in the event of a dilution accident. For all other cases, the lower limit value is greater than or equal to that required in normal cold shutdown or greater than the value ensuring $k_{eff} < 0,95$ after reload and before rods have been qualified. This provides assurance that the required cold shutdown sub-criticality margin is respected [1].

The upper limit value is the same as for SD / SG.

The analysis frequency is every 48 hours to verify the operability of the boron meter. More frequent analysis may be required by Operating. Event REN 1 is still applicable.

A.1.5.1.4 Maintenance Cold Shutdown – MCSD

The lower limit value ensures a shutdown margin of 5263 pcm ($k_{eff} \leq 0,95$) when all control rods are inserted. This value for each fuel cycle is determined during core reload safety analysis checks and provided to Operating by RFE before core reload. When the primary coolant is at vessel flange level, there is an additional requirement that the minimum boron concentration be > 2440 mg $B.kg^{-1}$. It allows sufficient time for the operator to react in the event of a dilution accident. A curve of the required boron concentration versus burn-up at cold shutdown is provided in the Physics Data Book.

The upper limit value of 2700 mg $B.kg^{-1}$ corresponds to the maximum concentration of the PTR tank [1].

The boron meter shall be lined up to the RRA circuit whilst the RRA is homogenising the primary circuit to ensure prompt detection of an unexpected dilution of the primary circuit. The analysis frequency is every 48 hours to verify the operability of the boron meter. More frequent analysis may be required by Operating. Event REN 1 is still applicable.

A.1.5.1.5 Refuelling Shutdown – RSD

The lower limit value is 2440 mg B.kg^{-1} and upper limit value is 2700 mg B.kg^{-1}. The lower value corresponds to the minimum boron concentration for the SFP, and prevents dilution of the SFP when the fuel transfer tube is opened and the SFP is connected to the reactor cavity [1]. This limit is also a requirement for the uncontrolled boron dilution accident to ensure that the operator has sufficient time to stop the cause of the dilution.

A.1.5.2 Reactor and Spent Fuel System (PTR)

A.1.5.2.1 PTR 001 BA (while the contents are not in the reactor cavity)

The lower limit value is 2500 mg B.kg^{-1} and upper limit value is 2700 mg B.kg^{-1}. This value is compatible with the accident study criteria for a design basis LOCA. The lower limit value provides assurance that core sub-criticality requirements are met during the accident. The upper limit value ensures that boron precipitation will not occur before the start of hot leg injection following a LOCA, where the primary coolant reaches saturation temperature [1].

The analysis frequency is monthly.

A.1.5.2.2 Spent Fuel Pool (SFP) and Reactor Cavity

The lower limit value is 2440 mg B.kg^{-1} and upper limit value is 2700 mg B.kg^{-1}. The lower limit is derived for fuel storage in Region II of the SFP, ensuring an initial boron concentration for reactivity addition events. These include boron dilution of the SFP and the beyond-design-basis accidental misplacement of a fuel assembly. In practice, a limit of 2500 mg B.kg^{-1} is applied to prevent the lower limit on the PTR Tank being challenged.

The upper limit provides a margin to boron crystallisation [1].

The analysis frequency is weekly. More frequent analysis may be requested by Operating. The SFP is analysed after make-up. Analysis is upon request during fuel movement.

A.1.5.2.3 Heat Exchangers PTR 001, 002, and 004 RF

The analysis frequency is upon request from Operating to identify potential RRI leakage into the heat exchangers and to prevent subsequent dilution of the SFP boron with high-density fuel racks [4].

The lower limit value is 440 mg B.kg^{-1}.

A.1.5.3 Reactor Make-Up System (REA)

A.1.5.3.1 Unit 1, 2 REA 004 BA and 9 REA 003 BA

Approximately 45 m^3 of 7300 mg B.kg^{-1} boric acid solution is required to meet cold shutdown conditions based on nominal conditions of temperature and pressure for fuel enriched up to 4,4% [1].

The lower limit value is 7300 mg $B.kg^{-1}$ and upper limit value is 7700 $mg.kg^{-1}$. The boric acid solution shall not exceed 7700 mg $B.kg^{-1}$ to avoid any risk of crystallisation in the piping or tanks [1].

The analysis frequency is monthly. Additional analysis is required when any changes are made to the concentration, such as batching of the tank.

A.1.5.4 Reactor Safety Injection System (RIS)

A.1.5.4.1 Accumulators RIS 001, 002, and 003 BA

The lower limit value is 2500 mg $B.kg^{-1}$ and upper limit value is 2700 $mg.kg^{-1}$.

The minimum boron concentration value is used in the post-LOCA boron concentration calculation. The concentration is calculated to assure reactor sub-criticality in a post-LOCA environment.

The maximum boron concentration is used in the determination of the cold leg to hot leg recirculation injection switch-over time and minimum sump pH [1].

A.1.5.4.2 Boron Injection Tank – RIS 004, 021 BA

The lower limit value is 2000 mg $B.kg^{-1}$ and upper limit value is 5600 $mg.kg^{-1}$.

The lower limit ensures adequate neutron absorption during a safety injection. The upper limit is imposed to prevent boron crystallisation. For practical reasons, the actual concentration in the tank ranges between 2440 mg $B.kg^{-1}$ and 2700 mg $B.kg^{-1}$ (which is the required concentration in PTR 001 BA).

The analysis frequency is monthly. Additional analysis is required when any changes are made to the concentration, such as batching of the tank.

A.1.5.5 Boron Recovery System (TEP)

Boron from RCV letdown is received into TEP and either released to KER or concentrated for topping-up the PTR SFP. Boron recovery to RCP is not practised at KNPS due to accumulation of tritium and silica and depletion of ^{10}B.

A.1.5.6 Liquid Waste Treatment System (TEU)

The limitation on boron concentration is determined by the solubility of the concentrated waste solution in the evaporator. This is set at 50000 mg $B.kg^{-1}$ as a maximum. For this to remain in solution at operating temperature, the sodium:boron molar ratio must be maintained so that the borate species will remain soluble and thus avoid precipitation in the evaporator. EDF has determined the effective molar ratio experimentally by testing the solubility of concentrated salts at various temperatures simulating operating conditions. The CEA tests are published in the SCECF.304 Report (May 1993) [5]. Na/B × 0,47 (to convert to molar ratio from mg) must be $\geq 0,20$ and $\leq 0,25$ at the end of an evaporator campaign.

The boron concentrations in the TEU tanks are controlled in order to prevent precipitation when treated by the evaporators and to prevent being out of specification when transferred to KER.

A.1.5.7 Liquid Effluent Monitoring System (KER and SEK)

Boron is potentially toxic to the environment and as such the boron concentration needs to be meet environmental criteria.

Limit Value: 2700 mg $B.kg^{-1}$ as a maximum for KER tanks and SEK bypass. The maximum boron limit is based on the maximum expected boron concentration is aligned to the PTR maximum boron limit. Boron at 2700 $mg.kg^{-1}$, after dilution in CRF (dilution factor of 4916) gives a concentration of 0,55 mg $B.kg^{-1}$. This meets the maximum limit in the water permit of 1 $mg.kg^{-1}$. [6] After adding the background concentration of 4,5 mg $B.kg^{-1}$ in sea water ≈ 5,5 $mg.kg^{-1}$ is below the ecological limit of 7 $mg.kg^{-1}$ assumed in the Coastal Water Discharge Permit (CWDP) submission. Thus it meets the maximum boron ecological criteria. [7]

470 mg $B.kg^{-1}$ as a maximum for discharge from SEK tanks (001 and 002 BA). Discharge from the SEK tanks is usually made using SEK 001/2 PO. These are relatively large pumps and the dilution factor in CRF is much lower than for KER. As a result, the maximum boron concentration allowable is 470 $mg.kg^{-1}$ in order to meet the water permit limit of < 1 $mg.kg^{-1}$ after dilution in CRF. The CWDP submission on the other hand allows a much higher ecological limit. [7] A special case can therefore be made to exceed this limit if SEK 006/7 PO is used to discharge the tank.

Analysis Frequency: Prior to release.

A.1.6 References

[1] KBA0022OTSJUSTIF2 Operating Technical Specification Justification Chapter 2

[2] EDF Electricité de France Chemistry and Radiochemistry Specifications, (*Document Standard des Specifications Chimiques Du Palier 900 MWE CP-CP2*), EDEAPC050251, February 2008

[3] KBA0022OTS0000001 Operating Technical Specifications (OTS)

[4] 868972R Nuc. Sys. Eng. Letter Ref. NSE-4206/03, Sampling of a PTR Heat Exchanger Volume, Kobus Mostert, September 2003

[5] SECA-93/425 (*Risques de precipitation au cours de la consentration de mélanges de borates*), SCECF.304, May 1993

[6] Water Permit Water permit and exemption (1133B) issued in 1985 in terms of the Water Act of 1956

[7] NSC-022-17 Environmental Effluent Release Requirements for Boron and pH for SEK, TEU and KER, Deon Jeannes, November 2017.

[8]

A.2 Chloride and Fluoride

A.2.1 Objective and Strategy

Chlorine and fluorine are the two halogens most frequently encountered in the plant systems in the form of the aqueous dissolved anions, chloride, and fluoride.

Chloride and fluoride are known to be harmful impurity species and the strategic objective of parameter control is to maintain their concentrations ALARA.

A.2.2 Source

Chloride is abundant in nature and can enter the water systems as pollution from contaminated demineralised water, condenser tube leaks, process chemicals, and maintenance activities. Chloride contamination from sea air ingress is a known issue at KNPS.

Fluoride is also present in nature but less abundant than chloride. The most typically found origin is welding slag (residues from electrode coatings).

A.2.3 Risks

Chloride-induced stress corrosion cracking occurs when stainless steel is exposed to chloride ions in the presence of oxygen and high-temperature water. Studies show that nickel alloy is susceptible to chloride pitting under acid oxidising conditions. Accelerated corrosion of zirconium-based alloys occurs in high-temperature water containing high levels of fluoride [1].

A.2.3.1 Impact of Halogen-Induced Corrosion

Material Affected	Impact/Corrosion	Location
Nickel alloy	Chloride pitting under acid oxidising conditions. Fluoride IGA.	Primary and secondary
Austenitic stainless steel	Chloride-induced SCC in the presence of oxygen at high temperatures.	Primary and secondary
Zirconium based alloys	Fluoride-induced accelerated corrosion effects at high temperatures.	Primary
Carbon steel	Pitting of the SG tubes and denting of the SG tubes caused by general corrosion.	Primary and secondary

A.2.4 Basis for the Limit Values and Analysis Frequencies

The bases for the limit values, target values, and analysis frequencies for the systems are provided in the subsections that follow.

A.2.4.1 Reactor Coolant System/Residual Heat Removal System (RCP / RRA)

The values are applicable to operating domains: RP, SD / SG, SD / RRA, MCSD and RSD.

Limit Value: 150 µg.kg^{-1} maximum. This value corresponds to the condition that represents the threshold value beyond which plant or research data or engineering judgement indicates significant damage could be done to the system in the short term, thereby warranting a prompt correction of the abnormal condition [1]. EDF specifications also recognise this value [4].

Action Levels: AL1 is entered at > 50 µg.kg^{-1}.

AL2 is entered at > 150 µg.kg^{-1}.

AL3 is entered at > 1500 µg.kg^{-1}.

The actions to take are provided in OTS-KCS (§ 3.2 [6])

Target Value: < 50 µg.kg^{-1}. The concentration may be ≥ 50 µg.kg^{-1} for 24 hours after reactor criticality. There is no firm corrosion basis for this value; rather, it is based on a margin to the limit value and the lack of long-term experience with operation at > 50 µg.kg^{-1} [1].

Analysis Frequency: 3 × W. This frequency is established practice and has been proven sufficient for adequate control at KNPS. EPRI guidelines suggest 3 × W and EDF specifications require one analysis per week.

Normal Operation: Values at KNPS are typically < 20 µg.kg^{-1}, which is within the target value. The surveillance is normally met by performing the analysis on Mondays, Wednesdays, and Fridays. If a surveillance falls on a public holiday, the surveillance may be performed on the preceding or subsequent day.

A.2.4.2 Chemical and Volume Control System (RCV)

RCV chloride and fluoride are analysed downstream of the demineralisers to monitor the performance of the demineraliser. Increasing trends are indicative of resin exhaustion.

Limit Value: 150 µg.kg^{-1} maximum; refer to basis of RCP.

Target Value: < 20 µg.kg^{-1}. There is no firm corrosion basis for this value; rather, it is based on what has been historically achievable and to provide a substantial margin to the limit value.

Analysis Frequency: 2 × M. This frequency is established practice and has been proven sufficient for adequate control at KNPS.

Normal operational values at KNPS are typically well within the target value.

A.2.4.3 Reactor Spent Fuel System (PTR)

Limit Value: 150 µg.kg^{-1} maximum; due to the movement of water between PTR and RCP. This provides assurance that these pollutants are below limit value in these circuits; refer to basis of RCP. This is also a fuel vendor guideline value [3].

Target Value: < 50 µge.kg^{-1}. Same basis as for RCP.

Analysis Frequency: For PTR 001 BA (while tank contents are not in the reactor cavity), the analysis frequency is monthly, which is recommended by the fuel vendor guidelines.
For the SFP, the analysis frequency is 2 × M.
It is recommended that the reactor cavity and SFP be sampled weekly during fuel movement [3].

A.2.4.4 Reactor Make-Up System (REA)

Limit Value: 150 µg.kg^{-1} maximum. REA supplies boric acid solution and dilution water to RCP. This value provides assurance that these pollutants are below limit value in RCP.

For the water tanks, 9 REA 001 and 002 BA, a KNPS limit value of 20 µg.kg^{-1} maximum is imposed. This represents adequate quality of the water supplying REA.

Target Value: < 10 µg.kg^{-1}. Normally achievable operational values for KNPS.

Analysis Frequency: Weekly for the boron tanks (9 REA 003 BA and 1, 2 REA 004 BA) according to the fuel vendor guideline [3].

Monthly for the water tanks, which corresponds to international guidelines and established KNPS practice.

A.2.4.5 Reactor Safety Injection System (RIS)

Limit Value: 300 µg.kg^{-1} maximum – for the boron injection tank (BIT) (RIS 004, 021 BA).

150 µg.kg^{-1} maximum – for the accumulators (RIS 001, 002, 003 BA).

RIS tanks are at low temperature and therefore the corrosion risk is low. For the accumulators, the basis is the same as for RCP because RIS water will enter the RCP in a LOCA. For the BIT, the boron concentration may be slightly higher and therefore there is a possibility of higher chloride as contamination. Since the volume is lower, a higher concentration may be tolerated because of the dilution that will occur in RCP.

Target Values: Target values are KNPS administrative values that have historically been easily achieved under normal conditions. There is no firm technical basis; rather, these provide sufficient margin to the limit values.

Analysis Frequency: Monthly, which is in line with the OTS boron analysis frequency.

A.2.4.6 Component Cooling System (RRI)

Limit Value: 150 µg.kg^{-1} maximum, in order to prevent system material corrosion and to prevent contamination of the primary systems.

Below this limit value, there is low risk of exceeding limit values in the primary systems due to contamination from an RRI inleakage. Similar to EDF [4].**Target Value**: KNPS administrative value. There is no firm technical basis; rather, these provide sufficient margin to the limit values.

Analysis Frequency: Each train must be analysed monthly. Similar to EDF [4].

A.2.4.7 Steam Generator Blowdown (APG)

Limit Value: 10 µg Cl.kg^{-1} maximum to prevent denting, pitting, and formation of acidic crevice conditions in the SGs [4]. Maintains cation conductivity in the Admissible Operating Zone.

Target Value: < 5 µg Cl.kg^{-1} to maintain ALARA and a margin to limit value. Similar to EDF [4].

Normal operational values at KNPS are typically < 1,6 µg Cl.kg^{-1}, which is well within the target value and within the Chemistry Performance Indicator limiting value [8].

For wet lay-up (conservation), the limit value is 250 µg Cl.kg^{-1} maximum [7].

After sludge lancing, flushing water limit value is 250 µg Cl.kg^{-1} maximum.

Analysis Frequency: 3 × W, established KNPS practice that has proven to be practical and sufficient for good control.

A.2.4.8 Auxiliary Feedwater (ASG)

Limit Value: 3 µg Cl.kg^{-1} maximum; to prevent contamination of the SGs. KNPS administrative limit.

Target Value: < 1 µg Cl.kg^{-1}; to respect ALARA strategy.

A.2.4.9 Main Steam (VVP)

Limit Value: 1 µg Cl.kg^{-1} maximum. An established norm at KNPS which is within the turbine vendor recommendation of ≤ 3 µg Cl.kg^{-1} [6].

Analysis Frequency: This parameter is analysed when the cation conductivity the target value is exceeded. This is to determine the source of contamination.

A.2.4.10 Component Cooling System (SRI)

Target Value: < 150 µg Cl.kg^{-1}. To ensure material integrity. KNPS administrative limit.

Analysis Frequency: Once every 3 months and more frequently if a seawater leak is suspected. KNPS administrative surveillance.

A.2.4.11 Liquid Waste Treatment System (TEU)

Limit Value: 2000 mg Cl.kg^{-1} maximum for end-of-evaporator campaign. Chloride must be limited to prevent chloride-induced cracking of stainless steel components at high temperatures and oxidising conditions. The components in contact with evaporator concentrate are austenitic stainless steel 316L, which is highly resistant to chemical products and scaling and decontamination solutions [7]. The basis is possibly from an OEM recommendation and experimental data. To date there is no specific evidence of SCC related damage resulting from KNPS practice.

In the tanks, the maximum limit value is 50 mg Cl.kg^{-1} for transfer to the evaporator, concentration factors taken into account. The limit value may be exceeded for a maximum of 15 days in the TEU tanks; thereafter, action must be taken to reach a value of < 10 mg Cl.kg^{-1}. This practice has been established for KNPS based on material studies and operating experience [5].

A.2.4.12 Liquid Effluent Monitoring Systems (SEK and KER)

Limit Value: 50 mg Cl.kg^{-1}. To limit chlorides to protect tanks and systems from corrosive species. The limit value may be exceeded for a maximum of 15 days; thereafter, action must be taken to reach a value of < 10 mg Cl.kg^{-1}. This practice has been established for KNPS based on material studies and operating experience [5].

A.2.4.13 Demineralised Water (SED and SER)

Limit Value: 3 µg.kg^{-1} maximum. Acceptable quality demineralised water storage based on KNPS operating experience.

Target Value: < 1 µg.kg^{-1}, KNPS administrative limit set based on operating experience. This is within the Eskom corporate standard [9] of 2 µg Cl.kg^{-1} as measured at the outlet of the mixed-bed demineraliser.

Analysis Frequency: Weekly. In line with Eskom corporate standard and international guidelines [9].

A.2.4.14 Emergency Diesel Generators (LHP / LHQ / LHS) Water Cooling Circuits

Limit Value: OEM recommendation.

Target Value: KNPS administrative limit set based on operating experience.

Analysis Frequency: KNPS administrative surveillance found suitable for good control.

A.2.5 References

[1] EPRI Pressurised Water Reactor Primary Water Chemistry Guidelines, Volume 1, Revision 7, TR 3002000505, April 2014

[2] Pressurised Water Reactor Secondary Water Chemistry Guidelines, Revision 7 TR 1016555, February 2009

[3] WEC Westinghouse Supplemental Primary Water Chemistry Guidelines, Revision 5, MTLS-06-131, March 2015

[4] EDF (Electricité de France) Chemistry and Radiochemistry Specifications, (Document Standard des Specifications Chimiques Du Palier 900 MWE CP-CP2), EDEAPC050251, February 2008

[5] KBA 0928 CDFE 17: Test Report on Effluents Wastes on TEU-KER-SEK Systems and Auxiliary System (SRE-RPE).

[6] Alstom Turbine Vendor Recommendations

[7] DSE Eskom Design Documents

[8] WANO Data Elements Manual

[9] 240-53113742 Eskom Chemistry Standard for Demineralised Water Production

A.3 Sulphate

A.3.1 Objective and Strategy

Sulphate is an anionic derivative from sulphur which is a highly reactive element that combines readily with many compounds. In water, sulphuric acid is formed which is corrosive and degrading to metals.

Sulphate is a known harmful impurity species and the objective is to maintain the concentration ALARA.

A.3.2 Source

Sulphur compounds and sulphate are fairly abundant and can enter the water systems as pollution from contaminated demineralised water, condenser tube leaks, process chemicals, and maintenance activities. Cation ion exchange resins have sulphonate functional groups and therefore resin intrusion into systems is a major potential source of sulphates in power plants.

A.3.3 Risks

High sulphate concentrations at high temperature in the presence of oxidising species may accelerate stress corrosion cracking of austenitic stainless steels on primary system components [1].

Reduced species of sulphur in the secondary system appear to interfere with formation of passive films on nickel surfaces and can cause intergranular attack and cracking of high nickel alloy and stainless steel because of chromium depletion at the grain boundaries.

A.3.4 Basis for the Limit Values and Analysis Frequencies

The basis for the limit values, target values, and analysis frequencies for the systems are provided in the subsections that follow.

A.3.4.1 Reactor Coolant System / Residual Heat Removal System (RCP / RRA)

The values are applicable to operating domains: RP and SD / SG.

Limit Value: 150 µg SO_4.kg^{-1} maximum. This value corresponds to the condition that represents the threshold value beyond which plant or research data or engineering judgement indicates significant damage could be done to the system in the short term, thereby warranting a prompt correction of the abnormal condition [1]. EDF specifications also recognise this value [4].

Action Levels: AL1 is entered at > 50 µg.kg^{-1}.

AL2 is entered at > 150 µg.kg^{-1}.

AL3 is entered at > 1500 µg.kg^{-1}.

The actions to take are provided in OTS-KCS (§ 3.2 [6])

Target Value: $< 50\ \mu g\ SO_4.kg^{-1}$. The concentration may be $\geq 50\ \mu g.kg^{-1}$ for 24 hours after reactor criticality. There is no firm corrosion basis for this value; rather, it is based on a margin to the limit the value and the lack of long-term experience with operation at $> 50\ \mu g.kg^{-1}$ [1].

Analysis Frequency: Weekly. This frequency is established practice and has been proven sufficient for adequate control at KNPS. EPRI guidelines suggest 3 × W and EDF specifications require one analysis per month.

Normal Operation: Values at KNPS are typically $< 20\ \mu g.kg^{-1}$, which is within the target value.

A.3.4.2 Reactor Spent Fuel System (PTR)

Limit Value: $150\ \mu g\ SO_4.kg^{-1}$ maximum. Due to the movement of water between PTR and RCP. This provides assurance that these pollutants are below limit value in RCP in these circuits. Refer to basis of RCP. This is also a fuel vendor guideline value.

Target Value: $< 50\ \mu g\ SO_4.kg^{-1}$. Same basis as for RCP.

Analysis Frequency: For PTR 001 BA (while tank contents are not in the reactor cavity), monthly, which is recommended by the fuel vendor guidelines.

For the SFP, 2 × M. It is recommended that the reactor cavity and SFP be sampled weekly during fuel movement [3].

A.3.4.3 Reactor Make-Up System (REA)

Limit Value: $150\ \mu g\ SO_4.kg^{-1}$ maximum. REA supplies boric acid solution and dilution water to RCP. This value provides assurance that these pollutants are below limit value in RCP. For water tanks 9 REA 001 and 002 BA, a KNPS limit value of $20\ \mu g\ SO_4.kg^{-1}$ maximum is imposed. This represents adequate quality of the water supplying RCV.

Target Value: $< 10\ \mu g\ SO_4.kg^{-1}$. Normally achievable operational values for KNPS.

Analysis Frequency: Weekly for the boron tanks (9 REA 003 BA and 1, 2 REA 004 BA) in accordance with the fuel vendor guideline [3]. For the water tanks, the frequency is monthly in accordance with international guidelines and established KNPS practice.

A.3.4.4 Reactor Safety Injection System (RIS)

Limit Value: For the boron injection tanks RIS 004, 021 BA, $300\ \mu g\ SO_4.kg^{-1}$ maximum.

For the accumulators RIS 001, 002, and 003 BA, $150\ \mu g\ SO_4.kg^{-1}$ maximum. RIS tanks are at a low temperature and therefore the corrosion risk is low.

For the accumulators, the basis is the same as for RCP because RIS water will enter the RCP in a LOCA. For the BIT, the boron concentration may be slightly higher and therefore there is a possibility of higher chloride as contamination. Since the volume is lower, a higher concentration may be tolerated because of the dilution in RCP.

Target Values: Target values are KNPS administrative values that have historically been easily achieved under normal conditions. There is no firm technical basis; rather, these provide sufficient margin to the limit values.

Analysis Frequency: Monthly. In line with the OTS boron analysis frequency.

A.3.4.5 Steam Generator Blowdown (APG)

Limit Value: 10 μg $SO_4.kg^{-1}$ maximum. To prevent denting, pitting, and formation of acidic crevice conditions in the SGs [1]. Helps to maintain cation conductivity in the Admissible Operation Zone.

Normal operational values at KNPS are typically < 1,7 μg $SO_4.kg^{-1}$, which is well within the target value and within the CPI limiting value [7].

For wet lay-up (conservation), the limit value is 250 μg $SO_4.kg^{-1}$ maximum [6].

After sludge lancing, flushing water limit value is 250 μg $SO_4.kg^{-1}$ maximum.

Target Value: < 5 μg $SO_4.kg^{-1}$. To maintain ALARA and a margin to limit value. Similar to EDF [4].

Analysis Frequency: 3 × W. Established KNPS practice that has proven to be practical and sufficient for good control.

A.3.4.6 Auxiliary Feedwater (ASG)

Limit Value: 3 μg $SO_4.kg^{-1}$ maximum. To prevent contamination of the SGs. KNPS administrative limit.

Target Value: < 1 μg $SO_4.kg^{-1}$. To respect ALARA strategy.

A.3.4.7 Main Steam (VVP)

Limit Value: 1 μg $SO_4.kg^{-1}$ maximum. An established norm at KNPS, which is within the turbine vendor recommendation of ≤ 3 μg $SO_4.kg^{-1}$ [5].

Analysis Frequency: This parameter is analysed when the cation conductivity the target value. This is to determine the source of contamination.

A.3.4.8 Demineralised Water (SED and SER)

Limit Value: 3 μg $SO_4.kg^{-1}$ maximum. Acceptable quality demineralised water storage based on KNPS operating experience.

Target Value: < 1 μg $SO_4.kg^{-1}$. KNPS administrative limit set based on operating experience. Within the Eskom corporate guideline [8] of 2 μg $SO_4.kg^{-1}$ as measured at the outlet of the mixed-bed demineraliser.

Analysis Frequency: Weekly. In accordance with Eskom corporate standard [8] and international guidelines [1].

A.3.5 References

[1] EPRI Pressurised Water Reactor Primary Water Chemistry Guidelines, Volume 1, Revision 7, TR 3002000505, April 2014

[2] Pressurised Water Reactor Secondary Water Chemistry Guidelines, Revision 7 TR 1016555, February 2009

[3] WEC Westinghouse Supplemental Primary Water Chemistry Guidelines, Revision 5, MTLS-06-131, March 2015

[4] EDF Electricité de France Chemistry and Radiochemistry Specifications, (Document Standard des Specifications Chimiques Du Palier 900 MWE CP-CP2), EDEAPC050251, February 2008

[5] Alstom Turbine Vendor Recommendations

[6] DSE Eskom Design Documents

[7] WANO Data Elements Manual

[8] 240-53113742 Eskom Chemistry Standard for Demineralised Water Production

A.4 Oxygen

A.4.1 Objective and Strategy

Oxygen reacts readily with metals and creates a passive layer on the surface of the base metal as the metal oxide. Passivation is essential and beneficial as the oxide layer protects the base metal from further chemical attack; therefore plant materials are passivated as part of the manufacturing processes. The properties and stability of the oxide film is controlled by the water chemistry variables such a pH, electrochemical potential, chemical species present, as well as the base material composition and thermo-mechanical treatment history.

In the primary system; dissolved oxygen levels in the RCP must be minimised to mitigate primary water stress corrosion cracking (PWSCC) of the nickel alloy steam generator tubes and high-temperature general corrosion of stainless steel. Nickel alloy is susceptible to chloride pitting under acid oxidising conditions and chloride-induced SCC occurs when austenitic stainless steels are exposed to chloride ions in the presence of high concentration of dissolved oxygen in high-temperature water.

In the secondary system, the presence of oxygen can drastically reduce the flow-accelerated corrosion rate (FAC) of carbon steels, as it is known from the fossil-fired plant experience. This is due to the formation of the more oxidised iron oxide, hematite, as a passive layer under oxygenated conditions. Hematite is much less soluble than magnetite which is formed under the reducing conditions of a PWR feedwater system.

Although oxygen could be a very powerful mitigation for FAC, it cannot be applied at PWR plants due to SG tube materials which are susceptible to pitting and SCC under oxidising conditions. When impurities such as chloride occur simultaneously with high dissolved oxygen and low pH, it results in accelerated appearance of various types of corrosion in the steam generator, i.e. pitting of the SG tubes and denting of the SG tubes caused by general corrosion of the carbon steel tube support plates.

For these reasons, the strategic objective for dissolved oxygen control is to maintain the concentration ALARA for both primary and secondary plant during power operation.

A.4.2 Source

Oxygen is an oxidising gas and is naturally abundant as a major component in air at approximately 20,9% (nitrogen is the other major component of air at ± 78,1%).

A.4.3 Risks

Dissolved oxygen plays a major role in corrosion mechanisms in both primary and secondary plants. It reacts with metals; stainless steels at high temperature, carbon steel at all temperatures, and with copper alloys in alkaline medium to form associated corrosion products in each case.

- In RCP, dissolved oxygen increases activated corrosion products, leading to deposition on and corrosion of the fuel cladding.

- Dissolved oxygen allows propagation of halogen-induced stress corrosion cracking of austenitic stainless steel components at high temperature.
- In AHP and ASG, dissolved oxygen increases the quantity of sludge transported towards the steam generators.
- In SGs, an oxidising environment causes corrosion of the secondary side of SG tubes.

Gaseous oxygen supports combustion and can form explosive mixtures with hydrogen.

A.4.4 Basis for the Limit Values and Analysis Frequencies

The basis for the limit values, target values, and analysis frequencies for the systems are provided below.

A.4.4.1 Reactor Coolant System (RCP) – Applicable Domains RP, SD / SG, SD / RRA

Limit Value: 100 µg $O_2.kg^{-1}$ maximum. A concentration of > 100 µg $O_2.kg^{-1}$ corresponds to the EPRI Action Level 2 condition that represents the threshold value beyond which plant or research data or engineering judgement indicates significant damage could be done to the system in the short term, thereby warranting a prompt correction of the abnormal condition [1]. EDF specifications have the same limiting value [4].

Action Levels: AL1 is entered at > 5 µg $O_2.kg^{-1}$.

AL2 is entered at > 100 µg $O_2.kg^{-1}$

AL3 is entered at > 1000 µg $O_2.kg^{-1}$.

The actions to take are provided in OTS-KCS (§ 3.2 [6])

Target Value: < 5 µg $O_2.kg^{-1}$. At > 5 µg $O_2.kg^{-1}$ corresponds to EPRI Action Level 1.

Analysis Frequency: 3 × W. EPRI guidelines only require monitoring when the dissolved hydrogen is < 15 ml $H_2.kg^{-1}$ [1].

Normal Operation: Operating experience demonstrates dissolved oxygen concentrations have been maintained below the target value and the surveillance is augmented by taking a reading of the on-line analyser during each shift.

A.4.4.2 Chemical and Volume Control System (RCV) – Volume Control Tank Gas Space

Limit Value: 5% O_2 in RCV 002 BA gas space. To prevent the risk of an explosive gas mixture with hydrogen. Refer also to § A.6 for more information on explosive mixtures.

Analysis Frequency: 3-monthly. Administrative frequency; operating experience demonstrates that this frequency is sufficient.

Normal Operation: Operating experience demonstrates excellent control of this parameter.

A.4.4.3 Reactor Make-up System (REA)

A.4.4.3.1 Water Tanks – 9 REA 001 and 002 BA

Limit Value: 100 µg O_2.kg^{-1} maximum. A fuel vendor requirement [3]. To maintain low oxygen levels in the RCP from dilution water during the operating cycle.

Target Value: < 20 µg O_2.kg^{-1}. An administrative value that provides a margin to the limit value which has been successfully applied over several years.

Analysis Frequency: Weekly. A fuel vendor requirement [3].

Normal Operation: Operating experience shows compliance with the target value and analysis frequency.

A.4.4.3.2 Boron Tanks – 1 and 2 REA 004 and 9 REA 003 BA

Target Value: < 100 µg O_2.kg^{-1}. The boron tanks are not degassed since boration usually only occurs at shutdown of a unit or a power reduction transient where the volume added is sufficiently low that there is no risk of exceeding the RCP dissolved oxygen limit value.

Analysis Frequency: 3-monthly. Administrative frequency; operating experience demonstrates that this frequency is sufficient for control of this parameter.

A.4.4.4 Condenser Extraction System (CEX)

A.4.4.4.1 Reactor at Power (RP)

Target Value: < 10 µg O_2.kg^{-1}. There is appropriate oxygen monitoring on the feedwater (AHP / ASG), and there are no copper tubes in the condenser, therefore a target value is acceptable for CEX provided that the feedwater oxygen specification is maintained [2].

If the oxygen concentration exceeds 10 µg O_2.kg^{-1}, the reason for the elevated concentration should be determined, negative effects on the secondary cycle components should be assessed and possible corrective actions should be identified.

Analysis Frequency: Once per shift.

Normal Operation: Operating experience shows compliance with the target value and analysis frequency.

A.4.4.5 Steam Generator Feedwater (AHP / ASG)

A.4.4.5.1 Reactor at Power (RP), Reactor Power > 25%

Limit Value:	5 µg $O_2.kg^{-1}$ maximum. > 5 µg $O_2.kg^{-1}$ is an EPRI action level that represents the threshold value beyond which engineering judgement indicates that long-term reliability of a secondary system component may be threatened and corrective actions shall be implemented as soon as possible [1].
Action Levels:	AL1 is entered at > 5 µg $O_2.kg^{-1}$. AL2 is entered at > 100 µg $O_2.kg^{-1}$ The actions to take are provided in OTS-KCS (§ 3.2 [6])
Target Value:	< 1 µg $O_2.kg^{-1}$. An administrative value that provides a margin to the limit value which has been successfully applied over several years.
Analysis Frequency:	Once per shift.
Normal Operation:	Operating experience shows compliance with the target value and analysis frequency.

A.4.4.5.2 Reactor at Power (RP), Reactor Power ≤ 25%

Limit Value:	50 µg $O_2.kg^{-1}$ maximum. It is recognised in EPRI guidelines that it may not be possible to achieve the limit value at the start-up of a unit before the turbine and pump seals are established. For this reason, this limit may be exceeded during start-up of a unit [2].
Action Levels:	AL1 is entered at > 50 µg $O_2.kg^{-1}$. AL2 is entered at > 100 µg $O_2.kg^{-1}$ The actions to take are provided in OTS-KCS (§ 3.2 [6])
Target Value:	< 1 µg $O_2.kg^{-1}$. The value should be achieved as soon as possible.
Analysis Frequency:	Once per shift.

A.4.4.5.3 Shutdown on Steam Generators (SD / SG) and ASG 001 BA not in service

Limit Value:	100 µg $O_2.kg^{-1}$ maximum.
Analysis Frequency:	Weekly.

A.4.4.6 Component Cooling (RRI and SRI) and Chilled Water (DEG and DEL) Systems

Limit Value:	> 4 mg $O_2.kg^{-1}$. This is sufficient based on KNPS operating experience to maintain the adhesive impermeable ferric phosphate layer on the metal surface protecting it from corrosion.
Target Value:	6 mg $O_2.kg^{-1}$.
Analysis Frequency:	Monthly has proven to be sufficient.

A.4.4.7 Stator Cooling Water System (GST)

Target Value: 4 mg $O_2.kg^{-1}$ minimum and 6 mg $O_2.kg^{-1}$ Maximum. High dissolved oxygen is applied for the early detection of hydrogen in leakage. Low dissolved oxygen has no known chemistry effect for stainless steel hollow conductors [5].

Analysis Frequency: 2 × Weekly minimum.

Normal Operation: On-line analyser.

A.4.5 References

[1] EPRI Pressurised Water Reactor Primary Water Chemistry Guidelines, Volume 1, Revision 7, TR 3002000505, April 2014

[2] Pressurised Water Reactor Secondary Water Chemistry Guidelines, Revision 7 TR 1016555, February 2009

[3] WEC Westinghouse Supplemental Primary Water Chemistry Guidelines, Revision 5, MTLS-06-131, March 2015

[4] EDF Electricité de France Chemistry and Radiochemistry Specifications, (Document Standard des Specifications Chimiques Du Palier 900 MWE CP-CP2), EDEAPC050251, February 2008

[5] Eskom Chemistry Standard for Water Cooled Generator Windings, 240-55864795, March 2015

A.5 Lithium

A.5.1 Objective and Strategy

Lithium hydroxide is a strong alkaline compound added to the primary system water to neutralise the weak acidic effect of the boric acid and to achieve an optimum pH at operating temperature (pH_T; i.e. pH @ 296°C for KNPS). A slightly alkaline pH_T decreases corrosion of the structural materials and reduces transport of corrosion products to the core where they deposit on the fuel cladding. Deposits on the fuel increase the risk of crud-induced power shifts (CIPS) and crud-induced localised corrosion (CILC). Activated deposits released into the coolant can be deposited on out-of-core surfaces creating radiation fields and hot spots.

Corrosion rates and corrosion release rates are expected to decrease with increasing pH_T from 6,9 to 7,4 for primary system structural materials and therefore operation at higher pH is beneficial in minimising corrosion product transport to the core [1].

The strategic objective is to accurately control lithium concentration in co-ordination with the boron concentration to achieve a pH_T of 7,25 during the fuel cycle. During the beginning of cycle (BOC), the pH_T achieved is approximately 6,90 due to the maximum lithium limit imposed by the fuel vendors (I.e. high boric acid concentration at BOC and maximum lithium ≈ pH_T 6,90). At KNPS, a modified elevated pH programme is implemented to minimise corrosion and reduce out-of-core radiation fields resulting from corrosion product deposition.

An Alternate Strategy is permissible for operational reasons, such as the management and stabilisation of primary to secondary leak-rate. Operating experience from EDF demonstrates that lower pH generally has the effect of reducing primary to secondary leak-rate which is attributed to steam generator cracks being blocked by the build-up of corrosion products within the crack [6] [7]. To allow this phenomenon to occur, lithium may be controlled at a value which targets a pH_T lower than 7,25. This can be achieved by holding the pH_T constant at a selected pH_T < 7,25, or the pH_T may be decreased by up to 0,1 (of a pH_T unit) and then held constant for 7 days at a time. Successive pH_T decreases may follow, but not to lower than a target pH_T of 6,90.

A.5.2 Source

Lithium hydroxide is the selected alkaline conditioning chemical for PWRs worldwide mainly because it is produced in-core by the neutron reaction with the boron-10 in RCP: ^{10}B (n, a) ^{7}Li. 500 $mg.kg^{-1}$ boron produces approximately 60 $µg.kg^{-1}$ of lithium-7 per 24 hours for a unit at full power. Enriched lithium-7 is injected at BOC to initially achieve the desired pH_T. Enriched lithium-7 (to 99,9%) is used because lithium-6 (6,9% isotope in natural lithium) produces tritium: $^{6}Li + ^{1}n \rightarrow ^{4}He + ^{3}H$.

A.5.3 Risks

Fuel cladding material is susceptible to accelerated corrosion in high concentrations of lithium. Zircalloy corrosion has been observed at concentrations of 7 mg $Li.kg^{-1}$ in laboratory tests. In the presence of boric acid (1000 mg B.kg^{-1}) however, tests show insignificant corrosion from lithium concentrations up to 100 mg Li.kg^{-1} [1].

Operation at low pH_T promotes corrosion, corrosion product transport and corrosion product deposition. Plant dose rates and fuel crud-loading increases may occur. Excessive fuel crud may lead to operational constraints due to fuel integrity being compromised. Therefore the Alternate Strategy may be applied only when it is required for operational reasons after a cycle specific approval is obtained from Reactor Fuel Engineering (RFE).

A.5.4 Basis for the Limit Values and Analysis Frequencies

The basis for the limit values, target values, and analysis frequencies for the systems are provided in the subsections that follow.

A.5.4.1 Reactor Coolant System (RCP)

Limit Value: 3,68 mg Li.kg^{-1} – This is the general maximum limit set by fuel vendors. Lithium may be > 3,68 mg Li.kg^{-1} during zero power critical conditions, but not > 5 mg Li.kg^{-1}.

The general limit value set by the fuel manufacturers is 3,68 mg Li.kg^{-1} (3,5 + 5%) as described in the EPRI guidelines. KNPS has received support from both fuel vendors to operate according to this limit [2] [3]. Higher lithium concentrations may be applied after approval from the fuel manufacturers [1].

Lithium should be controlled within the target band following a plant start-up or transient within 24 hours after achieving xenon equilibrium.

Action Level: In domain RP, AL1 is entered at > 3,68 mg Li.kg^{-1} or when outside of the control band. The action to take is to return the lithium to within the control band as soon as possible (§ 3.2 [6]).

Target Value: 3,5 mg Li.kg^{-1}. Until pH_T of 7,25, and thereafter co-ordinated with boron concentration towards a constant pH_T of 7,25.

For lithium concentrations > 3 mg Li.kg^{-1}, the lithium shall be maintained at the target value within ± 5% of the target concentration until the lithium reaches 3,0 mg Li.kg^{-1}, and then at ± 0,15 mg Li.kg^{-1} until the lithium concentration decreases to 1,25 mg Li.kg^{-1}.

For lithium concentrations < 1,25 mg Li.kg^{-1} until end of cycle (EOC), the lithium must be maintained within ± 12% of the target concentration [1].

Alternate Target: For operational reasons, the target lithium may be co-ordinated with boron concentration towards a constant pH_T between < 7,25 and = 6,90 (i.e. $6,90 \le pH_T < 7,25$). The selected target pH_T and its implementation shall be cycle specific, and only be applied after approval by RFE.

Analysis Frequency: 3 × W. Based on EPRI guidelines and accepted by the fuel vendors.

KNPS Operational Controls: Lithium is analysed daily for optimised primary pH control.

A.5.5 References

[1] EPRI Pressurised Water Reactor Primary Chemistry Guidelines, Volume 1, Revision 7, TR 3002000505, April 2014

[2] WEC Westinghouse Supplemental Primary Water Chemistry Guidelines, Revision 5, MTLS-06-131, March 2015

[3] AREVA Position Letter on Koeberg Lithium Control, Ref. No. FCF1403407 – CPK5227, December 2014

[4] Safety Screening S2016-0072, April 2016

[5] SAR Change Notice 258, May 2016

[6] Coordination bore/lithium: retour d'expérience des tranches utilisant la zone 1 bis pour la gestion des fuites primaire/secondaire, EDEECH070270, August 2007

[7] Correspondence Letters; EDF Plant Chemistry Recommendations for Reducing Primary to Secondary Leak Rate at Koeberg, Eskom ref. NCS-027-16, EDF ref. D455016074280, November 2016

[8] Safety Screening S2016-0574, December 2016

A.6 Hydrogen

A.6.1 Objective and Strategy

Hydrogen is added to the reactor coolant to maintain reducing conditions to minimise general corrosion of the primary system surfaces, fuel cladding, and risks of stress corrosion cracking of susceptible stainless steels and nickel-based alloys [2]. The presence of excess hydrogen ensures that oxygenated radicals formed by radiolysis recombine in order to prevent the production of oxygen. The presence of 10 ml $H_2.kg^{-1}{}_{STP}$ dissolved hydrogen in the coolant is more than sufficient to maintain the equilibrium in favour of reducing conditions and thus prevent radiolysis [1].

RCP dissolved hydrogen in the range of 35 to 50 ml $H_2.kg^{-1}{}_{STP}$ provides a best estimate steam generator crack growth rate reduction of 20 % for Alloy 600 (in the 290 – 243°C temperature range). Below 35 ml $H_2.kg^{-1}{}_{STP}$ increases crack growth rate, and lower values are considered detrimental from a primary water stress corrosion cracking (PWSCC) perspective [2].

The strategy therefore includes suppression of radiolysis of water and elevated levels for mitigation of PWSCC while also preventing the formation of zirconium hydrides in the fuel cladding material by maintaining the dissolved hydrogen ≥ 50 ml $H_2.kg^{-1}{}_{STP}$.

Hydrogen is also used for cooling of the alternator.

A.6.2 Source

Hydrogen is the most abundant chemical element in the universe and in diatomic form is the lightest and lowest density gas. Since hydrogen readily forms covalent compounds with most non-metallic elements, most of the hydrogen on Earth exists in molecular form such as water and organic compounds. Hydrogen gas is a colourless, odourless, tasteless, non-toxic, and highly combustible gas with the molecular formula H_2. It is slightly soluble in water and its solubility is increased proportional to increased pressure on the hydrogenated gas space in contact with the water.

A.6.3 Risks

Hydrogen gas is highly flammable and will burn in concentrations between 4% and 75% by volume. Hydrogen gas forms explosive mixtures with air and oxygen. The mixtures may be ignited by spark or heat. The temperature of spontaneous ignition in air is 500°C.

	Hydrogen (%)	
	In Air	**In Oxygen**
Flammable mixture	4 to 75	5 to 94
Explosive mixture	18 to 59	15 to 90

When changing of gas spaces from hydrogen to air or oxygen, the hydrogen must first be displaced by an inert gas and similarly when changing from air or oxygen to hydrogen.

Elevated levels of dissolved hydrogen in RCP may result in corrosion of the zirconium based fuel assembly materials leading to the formation of zirconium hydrides which causes degradation of the mechanical properties. Nickel metal deposition on zirconium based alloys prior to establishing a protective oxide layer may lead to accelerated hydriding [2].

Also under high dissolved hydrogen conditions, corrosion product solubility changes and the system stable oxide species may be altered leading to uncertainty in fuel crud deposition and composition.

Low levels of dissolved hydrogen, less than 5 ml $H_2.kg^{-1}$ STP, increases the possibility of migrating towards oxidising conditions in RCP, and thereby increasing the risk of the associated corrosion mechanisms on the susceptible system materials.

A.6.4 Basis for the Limit Values and Analysis Frequencies

The basis for the limit values, target values, and analysis frequencies for the systems are provided below.

A.6.4.1 Reactor Coolant System (RCP)

A.6.4.1.1 Reactor Critical and Power Operations

Limit Values: 20 ml $H_2.kg^{-1}$ STP minimum and 50 ml $H_2.kg^{-1}$ STP maximum station-imposed limit values.

Operation below 20 ml $H_2.kg^{-1}$ STP is limited to 24 hours.

The maximum value is selected to minimise the risk of formation of zirconium hydrides in the fuel cladding material, which is of concern for the fuel vendors [3]. KNPS limit values are the same as the EDF limit values [4]. EPRI guidelines Action Level 1 is < 25 ml $H_2.kg^{-1}$ STP and > 50 ml $H_2.kg^{-1}$ STP, the minimum being higher than the KNPS resulting in a narrower range [2]. However, EPRI guidelines only require oxygen monitoring on the reactor coolant when dissolved hydrogen levels drop to < 15 ml $H_2.kg^{-1}$ STP (action level 2). KNPS requires 3 × W dissolved oxygen analysis and the normal practice is a continuous on-line measurement for both hydrogen and oxygen; therefore, this broader band is acceptable practice since it meets the strategic objective.

Action Levels: AL1 is entered at < 20 ml $H_2.kg^{-1}$ STP and > 50 ml $H_2.kg^{-1}$ STP.

AL2 is entered at < 15 ml $H_2.kg^{-1}$ STP.

AL3 is entered at < 5 ml $H_2.kg^{-1}$ STP

The actions to take are provided in OTS-KCS (§ 3.2 [6])

Target Values: ≥ 35 ml $H_2.kg^{-1}$, ≤ 40 ml $H_2.kg^{-1}$.

This target range takes into account two main factors: (i) higher dissolved hydrogen concentrations are preferable for mitigation of PWSCC crack growth rate [2], and (ii) Fuel vendor recommends that the reactor coolant hydrogen operation be limited to a timeweighted cycle average hydrogen concentration of ≤ 40 ml $H_2.kg^{-1}$ STP [3]. This target accommodates these factors and also allows a practical range considering analytical uncertainty and the limited plant operational ability to adjust the dissolved hydrogen concentrations (i.e. pressure regulation on VCT) within this range.

Analysis Frequency: 3 × W minimum. 3 × W is consistent with EPRI guidelines. For KNPS, the analysis is continuous by on-line analyser and a reading is recorded on each shift.

A.6.4.1.2 Load Reductions

Before the shutdown of the reactor, the hydrogen concentration must be reduced:

- early enough not to delay the shutdown; and
- sufficiently late in order not to operate at power with a too low hydrogen concentration, risking altering the water radiolysis equilibrium.

Reduction of hydrogen concentration into the range 20 - 5 ml $H_2.kg^{-1}$ STP is admissible 24 hours before the start of load reduction.

A.6.4.1.3 Shutdown with Oxygenation

During shutdowns with oxygenation, hydrogen must be removed by displacement with nitrogen to avoid the possibility an explosive mixture of hydrogen and oxygen. Prior to oxygenation the RCP dissolved hydrogen must be < 3 ml $H_2.kg^{-1}$ STP. Oxygenation shall be initiated at RCP temperature of ≤ 80°C.

A.6.4.1.4 Shutdown without Oxygenation

There is no need to reduce the hydrogen concentration during the load reduction if there is no intention to breach the primary system during an intermediate shutdown.

A.6.4.1.5 Start-Up

During start-up, it is important to reach the targeted range as soon as possible; however, a minimum value of 5 $ml.kg^{-1}$ must be obtained prior to criticality.

A.6.4.1.6 Action to Take in Case of Exiting the Authorised Range

Taking into consideration the risks and the limits, if > 50 $ml.kg^{-1}$ and < 5 $ml.kg^{-1}$, load reduction to SD / SG within 8 hours is mandatory. Operation at power is authorised for 24 hours between 5 $ml.kg^{-1}$ and 20 $ml.kg^{-1}$. If not back within the control band, load reduction to SD / SG within 1 hour thereafter is mandatory.

A.6.4.2 Volume Control Tank (RCV 002 BA)

A.6.4.2.1 Reactor Critical and Power Operations

Target Value: > 95% H_2 by volume.

The volume control tank (VCT) contains hydrogen and provides the overpressure to attain the dissolved hydrogen control band in RCP. The hydrogen depletes slowly due to the build-up of helium from the neutron reaction with boron: $^{10}B + {}^{1}n_{(t)} \rightarrow {}^{7}Li + {}^{4}He$. The VCT must be purged periodically with pure hydrogen by Operating to ensure the target range is maintained.

A.6.4.2.2 Shutdown with Oxygenation

To prevent the risk of a flammable H_2:O_2 mixture, the VCT is placed on nitrogen and purged to < 2% H_2 by volume prior to oxygenation. [5]

A.6.4.2.3 Gas Spaces/Tanks – RCP 002 BA, TEP 001, 008 BA, RPE 001 BA

Similar to RCV, to prevent the formation of a flammable mixture, the other primary system gas spaces and tanks must be confirmed to be < 2% hydrogen by volume prior to oxygenation. [5]

A.6.5 References

[1] Radiolysis Studies at Belleville (PWR 1300), Water Chemistry with Low Hydrogen Concentration, SFEN, International Reactor Water Chemistry Conference, Nice, April 1994

[2] EPRI Pressurised Water Reactor Primary Chemistry Guidelines, Volume 1, Revision 7, TR 3002000505, April 2014

[3] WEC Westinghouse Supplemental Primary Water Chemistry Guidelines, Revision 5, MTLS-06-131, March 2015

[4] EDF Electricité de France Chemistry and Radiochemistry Specifications, (Document Standard des Specifications Chimiques Du Palier 900 MWE CP-CP2), EDEAPC050251, February 2008

[5] Chemical Dehydrogenation DT309 EDF document EDECME100396, July 2010

A.7 pH

A.7.1 Objective and Strategy

In the primary system, a slightly alkaline pH_T decreases corrosion of the structural materials and reduces transport of corrosion products to the core where they deposit on the fuel cladding. Deposits on the fuel increase the risk of crud-induced power shifts (CIPS) and crud-induced localised corrosion (CILC). Activated deposits released into the coolant can be deposited on out-of-core surfaces creating radiation fields and hot spots. Corrosion rates and corrosion release rates are expected to decrease with increasing pH_T from 6,9 to 7,4 for primary system structural materials and therefore operation at elevated pH is beneficial in minimising corrosion product transport to the core [1]. Addition of the chemical agent lithium hydroxide is used to optimise the pH of the primary system.

In the secondary system, corrosion of several different types, including IGA / SCC and pitting, are strongly affected by the local pH. High pH (caustic conditions) and low pH (acidic conditions) accelerate the rates of IGA / SCC [1]. As with the majority of metallic materials in power plants, an alkaline pH is favourable to mitigate the various forms of corrosion. Acidic environments promote corrosion mechanisms and have a dissolution effect on metal oxide passive layers. The main factors that control the rates of general corrosion and FAC are pH and oxygen concentration. Oxygen concentrations are maintained ALARA because SG tube materials are susceptible to pitting and SCC under oxidising conditions and therefore pH is the main control variable. Chemical treatment agents are added to achieve the optimised pH conditions throughout the systems to reduce corrosion and corrosion product transport. The secondary feedwater is treated with alkaline chemical agents, ethanolamine, and ammonium hydroxide and hydrazine is added to the feedwater to reduce dissolved oxygen.

Effluents that are released to the environment can adversely affect the marine ecology, for this reason, effluents release are maintained within acceptable limits.

A.7.2 Source

pH is a physical variable representing the hydrogen ion concentration (-log $[H^+]$). At 25°C, the pH value indicating a neutral aqueous solution is 7. A higher pH value indicates an alkaline solution while a lower pH value indicates an acidic solution.

Chemical additives used in the plant systems are the source of pH variations.

A.7.3 Risks

Continued operation outside of optimised pH conditions will lead to accelerated corrosion and component failure.

Liquid effluent releases with too high or too low pH may be harmful to the receiving environment.

A.7.4 Basis for the Limit Values and Analysis Frequencies

The basis for the limit values, target values and analysis frequencies for the systems are provided in the sections that follow.

A.7.4.1 Reactor Coolant System (RCP) – Applicable Domain RP

Target Value: 7,25 at average operating temperature (pH_T) as calculated by EPRI ChemWorks® Software. This target is not achievable at the beginning of cycle (BOC) because of high boron concentration and the maximum lithium concentration imposed by the fuel vendors. Therefore, from the BOC the pH_T should be maintained as high as reasonably achievable while respecting the maximum lithium concentration until the boron concentration corresponds to the lithium such that the target value is reached. From this point onwards, the target value is maintained (see the lithium basis described in this document: § A.5).

The above strategy is a modified elevated programme as described in the EPRI Guidelines [1].

Alternate Target: For operational reasons, the target pH_T may be maintained at a specific value selected from 6,90 to 7,25. The selected target pH_T and its implementation shall be cycle specific, and only be applied after approval by RFE ([8] see the lithium basis described in this document: § A.5).

A.7.4.2 Steam Generator Blowdown (APG) – Applicable Domains RP, SD / SG, SD / RRA

Limit Value: 8,0 minimum, 10,5 maximum at 25°C. This range ensures the required environment, since low pH results in the accelerated appearance of various types of corrosion in the steam generator (§ 3.2 [5]).

Target Values: (At 25°C) 9,0-9,4 for ammonia regime, 9,6-9,8 for ETA regime. ETA regime is slightly higher because ETA is less volatile than ammonia; therefore, it is expected that ETA concentrates in the SG bulk water more than ammonia which is more volatile and therefore ammonia is more concentrated in the steam. These administrative limits have been established by operating experience.

Analysis Frequency: Minimum once every shift (§ 3.2 [5]).

KNPS Operational Controls: pH is monitored continuously and the on-line reading is verified with a weekly manual analysis. This is consistent with EPRI guideline recommendations [2].

A.7.4.3 Steam Generator Feedwater System (AHP / ASG) – Applicable Domain RP

Limit Values: 9,0 minimum, 10,0 maximum at 25°C. This range allows protection of the secondary water and steam. These limits are in-line with industry practice for units similar to KNPS [2].

Target Value: 9,65 at 25°C for AHP is the administrative target established by operating experience to provide optimised corrosion protection in the secondary water / steam cycle during power operation.

Analysis Frequency: Minimum once every shift.

KNPS Operational Controls: Normal monitoring is continuous which corresponds to industry best practice.

A.7.4.4 Liquid Effluent Monitoring System (KER and SEK)

Limit Value: 5,0 minimum, 11,5 maximum at 25°C. The minimum value is aligned to the lowest expected pH related to neutralisation of acid in SDX after regeneration of ATE resins and that of boron should it be released at 2700 $mg.kg^{-1}$ via the SEK bypass route. Tests conducted prove that the pH after mixing in CRF will meet the Water Permit requirements. The maximum value is aligned to the maximum pH expected from any system being discharged into SEK (which is SRI). The maximum and minimum values ensure that the environmental receiving water quality objectives [3] and the water permit / exemption limits [4] are met and that the discharge is minimised. This takes into account the worst case dilution factor [5].

Target Values: There are no target values due to the unavailability of pH correction measures in SEK.

Analysis Frequency: Minimum once per week (grab) of SEK bypass and prior to every SEK tank release.

KNPS Operational Controls: pH of the various systems discharging to SEK is monitored regularly and in some cases prior to release (SDX). The risk of a release outside of the receiving water quality guideline is extremely low given the high dilution and buffering capacity of CRF [7]. There have been instances where pH of various systems discharging to SEK have historically exceeded system limits but the new criteria are aligned to maximum expected values of any system discharging to SEK / KER. [5]

A.7.4.5 Nuclear Island Component Cooling System (RRI)

Limit Values: 10,8 minimum and 11,5 Maximum at 25°C. In line with the EDF Specification [10] and to and also intended to limit the impact of high pH and phosphate on the environment.

Target Values: 11,0 minimum and 11,4 Maximum at 25°C.

Analysis Frequency: Weekly for the train in service and at least monthly per train.

A.7.4.6 Conventional Island Component Cooling System (SRI)

Limit Values: 10,8 minimum and 11,5 Maximum at 25°C. In line with the EDF Specification [10] and to and also intended to limit the impact of high pH and phosphate on the environment.

Target Values: 11,0 minimum and 11,4 Maximum at 25°C.

Analysis Frequency: Weekly.

A.7.4.7 Hot Water System (SES)

Target Values: 10,8 minimum and 11,3 maximum at 25°C. Based on KNPS operating experience. The maximum value also intended to limit the impact of high pH and phosphate on the environment.

Analysis Frequency: Weekly.

A.7.4.8 Nuclear Island Chilled Water System (DEG)

Limit Values: 10,8 minimum and 11,7 Maximum at 25°C. In line with the EDF Specification [10]. The maximum value also intended to limit the impact of high pH and phosphate on the environment.

Target Values: 11,0 minimum and 11,5 Maximum at 25°C.

Analysis Frequency: Weekly.

A.7.4.9 Conventional Island Chilled Water System (DEL)

Target Values: 10,8 minimum and 11,7 Maximum at 25°C. Based on KNPS operating experience. The maximum value also intended to limit the impact of high pH and phosphate on the environment.

Analysis Frequency: Weekly.

A.7.4.10 Sewage Treatment Plant (SEU)

Limit Values: 6,0 minimum, 10,5 maximum at 25°C. This value ensures limited erosion of concrete SEO piping, Effective biological processes and margin for chemical dosing for pH control. These values ensure that the water permit / exemption and the national guidelines are met [9].

Target Values: 7,0 minimum, 8,5 maximum at 25°C. To ensure effective denitrification and biological processes.

Analysis Frequency: 2 x M. This frequency is aligned to the General Standard.

A.7.5 References

[1] EPRI Pressurised Water Reactor Primary Water Chemistry Guidelines, Volume 1, Revision 7, TR 3002000505, April 2014

[2] Pressurised Water Reactor Secondary Water Chemistry Guidelines, Revision 7 TR 1016555, February 2009

[3] Department of Water Affairs and Forestry, South African Water Quality Guidelines for Marine Waters, First Edition, 1995

[4] Permit 853N and Exemption 1133B issued in terms of The Water Act 54 of 1956

[5] NSC-022-17 Environmental Effluent Release Requirements for Boron and pH for SEK, TEU and KER, Deon Jeannes, November 2017

[6] Department of Environmental Affairs, National Guideline for the Discharge of Effluent From Land-based Sources into the Coastal Environment, 2014

[7] Internal investigation by KNPS Chemistry Group on the influence of various plant effluents on the pH of sea water, 2016

[8] Safety Screening S2016-0574, December 2016

[9] Chemistry Specification Basis: SEU, NCS-003-17, Deon Jeannes, March 2017 and the references sited therein

[10] Document Standard des Spécifications Chimiques Du Palier 900 MWE CP-CP2), EDEAPC050251, February 2008

A.8 Conductivity

A.8.1 Objective and Strategy

Conductivity provides non-specific indication of ionic species present in water solutions. Ultra-pure water has low conductivity based on the presence of only [H_3O^+] and [OH^-] ions (≈ 0,055 $\mu S.cm^{-1}$ at 25°C). Ion-forming chemical conditioning agents used in the power station systems such as boric acid, lithium hydroxide, ammonium hydroxide, ethanolamine, trisodium phosphate, sodium hydroxide, and sulphuric acid when added to water in solution will increase the conductivity in proportion to the concentration of the chemical agent. Therefore, it is useful to establish the relationship between the expected conductivity values relative to the desired concentrations of the chemical conditioning agents because conductivity is more easily monitored continuously by on-line analysers than is possible for specific ion analysis. Conductivity measurement therefore provides early indications of changes in the chemical characteristics of a system such as the change in the concentration of the chemical agent or ingress of ionic impurities.

A.8.2 Source

The conductivity values for a system are established based on the operationally required or target concentrations of the chemical control agents. An increase in conductivity may either be related to an increase in the chemical conditioning agent concentration or ingress from an unknown source into the system. Although conductivity provides early indication of a potential problem, further investigation must be performed to verify the root cause of significant deviation because it is a non-specific determination. Similarly, a decrease in the system conductivity may be attributed to a dilution of the chemical conditioning agent for operational requirements (i.e. intentionally diluted such as boron in the RCP) or inadvertent ingress from a lower conductivity source (e.g. demineralised water). An unexpected change in conductivity requires further investigation.

A.8.3 Risks

Unexplained conductivity values may be either as a result of an unknown chemical contaminant being present or incorrect chemical conditioning agent concentrations. Both conditions are potentially harmful to system integrity.

A.8.4 Basis for the Limit Values and Analysis Frequencies

The basis for the limit values, target values, and analysis frequencies for the systems are provided in the sections that follow.

A.8.4.1 Reactor Make-Up System (REA), Water Tanks 9 REA 001 and 002 BA

Limit Value: 2,00 $\mu S.cm^{-1}$ (at 25°C) maximum. This value is aligned to the limit is the DSE [1], SAR [2], and EDF [3]. One fuel vendor does not consider conductivity a key parameter for reactor make-up water, but recommends that each plant establish its own operational limits [4]. Another fuel vendor suggests a value of ≤ 1,00 $\mu S.cm^{-1}$ at 25°C for the normal value, but stipulates that this is the expected value measured at the outlet of the water treatment plant [5] (and is not the storage tank criteria).

Target Value: ≤ 1,00 µS.cm^{-1} at 25°C, in order to maintain the water as impurity-free as reasonably achievable (ALARA). This value is in line with the EDF expected value [3] and the value expected at the water treatment plant outlet [5].

Analysis Frequency: Weekly. This is an administrative frequency based on operating experience and is within industry norms. The tank should also be analysed after each make-up to the tank.

KNPS Operational Controls: Analysis is performed weekly on the conductivity and a monthly analysis frequency is required on the associated impurities and also when the tank is filled or topped-up. This is to detect any increasing trend in impurities that may be detrimental to the primary system or the fuel.

A.8.4.2 Sewage Treatment Plant (SEU)

Limit Value: ≤ 5000 µS.cm^{-1} in line with many municipalities maximum allowed conductivity to reduce corrosion of a sewage system and City of Cape Town's sewage effluent bylaws [6] [7].

Target Value: N/A, the conductivity is a function of the pH control and influent.

Analysis Frequency: 2 × M. This frequency is aligned to the General Standard.

A.8.5 References

[1] System Design Manual (DSE), Chapter 3, page 10

[2] Safety Analysis Report (SAR), Part 2, Chapter 7, page 5 (2CHP07-05)

[3] EDF Electricité de France Chemistry and Radiochemistry Specifications, (Document Standard des Specifications Chimiques Du Palier 900 MWE CP-CP2), EDEAPC050251, February 2008

[4] AREVA PWR Fuel Reactor Coolant Chemistry Supplemental Guidelines Revision 7, November 2014

[5] WEC Westinghouse Supplemental Primary Water Chemistry Guidelines, Revision 5, MTLS-06-131, March 2015

[6] Chemistry Specification Basis: SEU, NSC-003-17, Deon Jeannes, March 2017 and the references sited therein

[7] Koeberg Nuclear Power Station: Chemistry Specification Basis for Conductivity in SEU, NSC-002-19, Deon Jeans, February 2019

A.9 Silica

A.9.1 Objective and Strategy

Silica (SiO_2) is a concern for the primary circuit when the reactor is at power. Control of silica along with zeolite-forming elements such as aluminium, calcium, and magnesium is important because precipitation of these species as silicate minerals and the possible incorporation into fuel crud could cause densification of the crud [2]. This would result in diminished heat transfer and underdeposit corrosion of the fuel cladding. For plants injecting zinc, such as at KNPS, strict controls on silica are imposed by the fuel vendor guidelines because of possible precipitation and deposition of zinc silicates on the fuel in addition to the more commonly noted zeolite formers mentioned previously.

Silica is therefore considered an undesired impurity; the strategic objective is to maintain the concentration ALARA.

A.9.2 Source

Silica is abundant in nature as one of the most important constituents of the Earth's crust. Sand and glass are predominantly silica and silicate compounds. In PWRs, decomposition of Boraflex, a neutron absorbing material used in spent fuel racks, has been confirmed as a major source of silica; however, KNPS has not used Boraflex in spent fuel racks in recent years. Other potential sources are from make-up water and as a chemical impurity in plant chemicals such as in the boric acid and lithium hydroxide used for primary system pH control. Maintenance products, gaskets, and packing materials often contain silica as part of the structural composition. Breakdown and leaching of fibreglass filter media has been noted in industry as a suspected silica contributor in the primary systems.

A.9.3 Risks

Deposition of insoluble silicate materials on the fuel elements increases the risk of crud-induced power shifts (CIPS) of the reactor and crud induced localised corrosion (CILC) on the fuel elements. Transfer of PTR water to the reactor cavity during refuelling operations is a pathway by which higher levels of silica can mix with the reactor coolant and increase the average RCP silica concentration for the subsequent start-up.

A.9.4 Basis for the Limit Values and Analysis Frequencies

The basis for the limit values, target values, and analysis frequencies for the systems are provided in the sections that follow.

A.9.4.1 Reactor Coolant System (RCP)

Limit Value: 1500 µg $SiO_2.kg^{-1}$ maximum.

This limit value is half the fuel vendor's recommended operational limit. Zinc injection units with low boiling duty cores may operate with levels up to 3000 µg $SiO_2.kg^{-1}$ prior to injecting zinc, and may commence zinc injection once silica is ≤ 2000 µg $SiO_2.kg^{-1}$. Plants with high boiling duty cores may operate for up to 60 days at the beginning of the cycle with silica levels in the reactor coolant up to 3000 µg $SiO_2.kg^{-1}$, after which the silica level should be reduced to ≤ 1000 µg $SiO_2.kg^{-1}$ prior to injecting zinc [2]. EPRI guidelines list silica only as a diagnostic parameter and refer to fuel vendor requirements for specific limits [1]. EDF also has 1500 µg $SiO_2.kg^{-1}$ as the limit value for reactive silica [3].

Operating experience demonstrates silica concentrations have been below the imposed maximum limit. If circumstances change, there is margin to increase this value (up to the threshold limit of 3000 µg $SiO_2.kg^{-1}$), as the current limit is conservative and the target values have been kept lower in support of the ALARA objective.

Target Value: < 1000 µg $SiO_2.kg^{-1}$. This is the station-imposed administrative target, which is applicable to reactive silica in the domain RP.

This target value is based on operating experience and it provides a practical and applicable margin from the limit value, which also achieves the fuel vendor's recommendation which is to strive to < 1000 µg $SiO_2.kg^{-1}$ as early in the cycle as possible for zinc injecting plants [2].

Analysis Frequency: Weekly. In accordance with fuel vendor's guideline surveillance for zinc injection units.

A.9.4.2 Reactor and Spent Fuel System (PTR)

Limit Value: 3000 µg $SiO_2.kg^{-1}$ maximum. This is the station-imposed maximum limit for KNPS, which is applicable to all operating domains.

Fuel vendors and EPRI guidelines include silica only as a diagnostic parameter in the refuelling water storage tank and the spent fuel pool and do not specify limit values [1] [2]. EDF also has 3000 µg $SiO_2.kg^{-1}$ as the limit value for silica [3].

Target Value: < 2000 µg $SiO_2.kg^{-1}$. This is the station-imposed administrative target.

This is based on KNPS operating experience and provides a practical and applicable margin from the limit value. For practical reasons, the PTR target value is more relaxed than that of the RCP system because the PTR system does not involve the high heat flux associated with reactor power operations which causes silicate materials to deposit on the fuel. Dilution from domain MSCD to domain RP reduces the shutdown concentration immediately by approximately 35% and then further dilution continues during the remainder of the fuel cycle. This allows the RCP silica limit value to be achieved from the beginning of cycle and the target to be achieved from early in the cycle.

Operating experience demonstrates silica concentrations have been maintained below the target value.

Analysis Frequency: Monthly. In accordance with fuel vendor's guideline surveillance.

A.9.5 References

[1] EPRI Pressurised Water Reactor Primary Chemistry Guidelines, Volume 1, Revision 7, TR 3002000505, April 2014

[2] WEC Westinghouse Supplemental Primary Water Chemistry Guidelines, Revision 5, MTLS-06-131, March 2015

[3] EDF Electricité de France Chemistry and Radiochemistry Specifications, (Document Standard des Specifications Chimiques Du Palier 900 MWE CP-CP2), EDEAPC050251, February 2008

[4] Safety Screening S2016-0072, April 2016

[5] SAR Change Notice 258, May 2016

A.10 Suspended Solids

A.10.1 Objective and Strategy

The amount of materials in suspension corresponds to an overall measurement of insoluble material present and can be deposited in various areas throughout the power plant. Deposited material causes problems such as a change in the heat transfer characteristics of systems thereby influencing the efficiency of components such as heat exchangers. Suspended solids, generally present as particles, cause blockages of narrow diameter pipes, high back-pressure on filters, high radioactivity areas and fouling of demineralisers and membranes.

In the primary system, deposits on the fuel can lead to core axial offset effects and fuel damage by crud induced localised corrosion (CILC). In the secondary system, deposits in the steam generators lead to the formation of occluded areas that allow for the concentration of harmful impurities (often referred to as hideout) which leads to underdeposit corrosion.

Suspended solids as particulates typically constitute one of the parameters reflecting the efficiency of the chemical treatment of the systems. The objective is to maintain the suspended solids ALARA.

A.10.2 Source

The sources of suspended solids are generally corrosion products, as metal oxides, and foreign material. Corrosion product levels are elevated when the chemistry regimes are not effective or optimised, or when there are chemical, mechanical or physical transients effecting the plant. E.g. pH fluctuation, power transitions, flow excursions, unit trips, unit startup etc.

Precipitates of silicates from solutions containing high concentrations of silica and zeolite-forming metal cations are also known sources of suspended solids.

A.10.3 Risks

Fuel damage is the highest risk related to deposition of solid materials, causing localised high temperatures on the cladding which could lead to CILC. The amount of suspended solids should be maintained ALARA to minimise the inventory of particulate material that could deposit on fuel cladding, contribute to power shifting (CIPS) effects, and lead to an increase in the radioactivity level of the coolant as activated corrosion products [1].

A.10.4 Basis for the Limit Values and Analysis Frequencies

The basis for the limit values, target values, and analysis frequencies for the systems are provided in the sub-sections that follow.

A.10.4.1 Reactor Coolant System (RCP) in domain RP, Reactor at Power

Limit Value: ≤ 50 $\mu g.kg^{-1}$. Fuel vendor requirement [1]. Maintaining suspended solids at or below 50 ppb minimises the risk of CILC and CIPS. Sustained operation above the limit must be investigated.

Analysis Frequency: Weekly. In accordance with fuel vendors' guideline surveillance.

A.10.4.2 Spent Fuel System (PTR), PTR001BA

Limit Value: ≤ 350 µg.kg^{-1}. Fuel vendors' requirement [1].

Analysis Frequency: Monthly. In accordance with fuel vendor's guideline surveillance.

A.10.4.3 Reactor Make-up System (REA), Water and Boron Tanks

Limit Value: ≤ 50 µg.kg^{-1}. Similar to RCP.

Analysis Frequency: Monthly. In accordance with fuel vendors' guideline surveillance.

A.10.4.4 Component Cooling System (RRI and SRI)

Limit Value: ≤ 5000 µg.kg^{-1}. In-line with EDF specifications [2]. If target value is exceeded, analyse for total iron and total copper.

Target Value: < 1000 µg.kg^{-1}. In line with EDF specifications.

Analysis Frequency: Monthly. In line with EDF Specifications.

A.10.4.5 Steam Generator Feedwater (AHP / ASG)

Target Value: < 10 µg.kg^{-1}. KNPS administrative limit based on operating experience. Sustained operations above the target value must be investigated. During startup, up to 30% Pn, the target is < 200 µg.kg^{-1} because of higher iron transport during this phase.

Analysis Frequency: Monthly. KNPS administrative limit based on best practice.

A.10.4.6 Steam Generator Blowdown (APG)

Target Value: < 1000 µg.kg^{-1}. KNPS administrative limit based on operating experience. In line with EDF specifications [2].

Analysis Frequency: Monthly. KNPS administrative limit based on best practice.

A.10.5 References

[1] WEC Westinghouse Supplemental Primary Water Chemistry Guidelines, Revision 5, MTLS-06-131, March 2015

[2] EDF Document Standard des Spécifications Chimiques du Palier 900 MWe CP1-CP2, 28 April 2017

A.11 Sodium

A.11.1 Objective and Strategy

Sodium is the principal alkaline cation which may occur in concentrated form and which can be present as an impurity in the various plant systems.

In the primary system, the presence of significant levels of sodium will influence the pH of RCP water. Excessive sodium concentrations could increase corrosion products (dose rates), accelerate general corrosion of Zircalloy (fuel cladding), cause cracking in stainless steel and, on the primary side, of the SG tubing material (nickel alloy).

In the secondary system, sodium, in the form of alkaline compound, is one of the main potential causes of caustic intergranular stress corrosion of nickel alloy steam generator tubing. Nickel alloy can crack when exposed to high concentrations.

Since sodium has the ability to induce various corrosion mechanisms, the strategic objective of sodium control is to maintain the concentration ALARA within the plant systems.

A.11.2 Source

Sodium, an alkali metal element, is abundant in nature as salt compounds in seawater and raw water. Sodium compounds are also used in plant applications such as trisodium phosphate chemical conditioning of closed cooling water systems (RRI and SRI). Sodium hydroxide is used for regeneration of SDA and ATE anion exchange resin and sodium chloride is used to perform a brine squeeze to remove organics from anion exchange resin. Sodium hydroxide is used to correct the sodium:boron ratio in the TEU system. Chemical products containing sodium could be used on the plant for test and maintenance activities. All these uses have the potential to contaminate the plant system water and therefore sodium as a contaminant impurity is monitored. Sodium is also present as an impurity in primary and secondary plant conditioning chemicals such as boric acid, lithium hydroxide, hydrazine, ammonia, and ethanolamine.

A.11.3 Risks

High sodium concentrations in the plant systems will lead to accelerated corrosion and component failure.

The major risk is seawater entry into the secondary system in the event of condenser damage.

A.11.4 Basis for the Limit Values and Analysis Frequencies

The basis for the limit values, target values, and analysis frequencies for the systems are provided in the sections that follow.

A.11.4.1 Steam Generator Blowdown (APG)

Limit Value: 5 µg $Na.kg^{-1}$ maximum for the Admissible Operation Zone. > 5 µg $Na.kg^{-1}$ corresponds to EPRI Action Level 1 condition that represents the threshold value beyond which data or engineering judgement indicates that long-term reliability of a secondary system component may be threatened, thereby warranting an improvement of operating practices [1]. EDF specifications also recognise this limiting value [4].

Target Value: < 0,8 µg $Na.kg^{-1}$. This is the limiting value for the WANO chemistry performance indicator (CPI) [5] and the chronic contamination limit condition in the INPO chemistry effectiveness indicator (CEI) [6].

Analysis Frequency: Minimum of once every shift (§ 3.2 [5]).

KNPS Operational Controls: Sodium is monitored continuously and the on-line reading is verified with a weekly manual analysis. This is consistent with EPRI guideline recommendations.

Continuous control of sodium, together with cation conductivity in the SG blowdown, provides the main indication of the concentration of pollutants in the SGs.

A.11.4.2 Condenser Extraction System (CEX)

Limit Value: 5 µg $Na.kg^{-1}$ maximum, based on the EDF specification [4] and in-line with international practice.

Target Value: < 1 µg $Na.kg^{-1}$; based on KNPS experience and international best practice.

Analysis Frequency: Shiftly minimum, the normal analysis is by on-line analyser.

A.11.4.3 Main Steam (VVP)

Limit Value: 1 µg $Na.kg^{-1}$ maximum; within steam purity requirements for turbine operation [7] and international best practice.

Target Value: < 1 µg $Na.kg^{-1}$; based on KNPS experience and international best practice.

Analysis Frequency: When required for operational reasons.

A.11.4.4 Reactor Coolant System Residual Heat Removal System (RCP / RRA)

Limit Value: 200 µg $Na.kg^{-1}$ maximum; aligned to EDF Specifications [4].

Target Value: < 100 µg $Na.kg^{-1}$; aligned to EDF Specifications [4].

Analysis Frequency: Monthly, aligned to EDF Specifications [4].

A.11.5 References

[1] EPRI Pressurised Water Reactor Primary Water Chemistry Guidelines, Volume 1, Revision 7, TR 3002000505, April 2014

[2] Pressurised Water Reactor Secondary Water Chemistry Guidelines, Revision 7 TR 1016555, February 2009

[3] WEC Westinghouse Supplemental Primary Water Chemistry Guidelines, Revision 5, MTLS 06 131, March 2015

[4] EDF Electricité de France Chemistry and Radiochemistry Specifications (Document Standard des Specifications Chimiques Du Palier 900 MWE CP-CP2), EDEAPC050251, February 2008

[5] WANO CPI – Data Elements Manual

[6] INPO CEI – Data Elements Manual

[7] ALSTOM Steam Purity Requirements for Turbine Operation, HDTG 90486, April 2004

A.12 Aluminium, Magnesium, Calcium

A.12.1 Objective and Strategy

Calcium and magnesium are alkaline-earth metals and aluminium is a light metal in the boron group (group 13) in the periodic table. None of these elements on their own have a significant corrosion effect on the plant materials, however the hydroxides, oxides and silicates of calcium, magnesium and aluminium are weakly soluble and can form deposits on the fuel rods which could potentially result in underdeposit corrosion. In the primary system, the concentrations of these elements are limited to avoid formation of hard deposits (zeolites composed essentially on the basis of magnesium, calcium, aluminium, silica) on the fuel cladding, reducing heat transfer and that can lead to clad damage by the resulting increase in temperature [1].

Aluminium, magnesium and calcium are therefore undesirable impurities and the strategic objective is to maintain these ALARA within the plant systems.

A.12.2 Source

Aluminium, magnesium and calcium impurities are introduced as a result of makeup water, refuelling water or boric acid contaminants. Alum is used as a flocculent in the water treatment at KNPS, which could be the source of trace aluminium in the makeup water systems.

A.12.3 Risks

Silica together with zeolite-forming cations (such as aluminium, calcium, and magnesium) are generally thought to promote deposit formation and consolidation, and the eventual formation of hard deposits (i.e., deposits that are not readily dislodged by physical and / or chemical processes), impairing heat transfer. Many oxides and silicates of aluminium, calcium, and magnesium have negative temperature coefficients of solubility, and if present in sufficient concentrations, the mineral(s) will precipitate, preferentially on the fuel. The zeolite-forming minerals may cause densification of porous crud deposits, especially in plants where boiling occurs. This could lead to accelerated cladding corrosion and failure [2].

A.12.4 Basis for the Limit Values and Analysis Frequencies

The basis for the limit values, target values, and analysis frequencies for the systems are provided in the sections that follow.

A.12.4.1 Reactor Coolant System / Residual Heat Removal System (RCP / RRA)

A.12.4.1.1 During power operation, Domain RP

Limit Values: 50 µg Al.kg^{-1} maximum.

50 µg.kg^{-1} (calcium + magnesium) maximum.

25 µg Mg.kg^{-1} maximum.

These limit values are the guidelines recommended by the fuel manufacturer [3].

Analysis Frequency Monthly minimum frequency, as per the fuel manufacturer requirement [3].

KNPS Operational Controls: Analysis is performed weekly so that an increasing trend can be detected early.

A.12.4.1.2 During Startup (Reactor Subcritical and >120°C), Domain SD / RRA, SD / SG

Limit Values: 80 µg Al.kg^{-1} maximum.

80 µg.kg^{-1} (calcium + magnesium) maximum.

40 µg Mg.kg^{-1} maximum.

These limit values are the guidelines recommended by the fuel manufacturer [3].

Analysis Frequency Al, Ca and Mg should be monitored prior to exceeding 120°C, and once again prior to criticality. Any abnormal increase in the concentrations of these elements above typical levels or an upward trend during heat-up should be investigated [3].

A.12.4.2 Reactor and Spent Fuel System (PTR)

A.12.4.2.1 Refuelling Water Storage Tank (PTR 001 BA)

Limit Values: 80 µg Al.kg^{-1} maximum.

80 µg.kg^{-1} (calcium + magnesium) maximum.

40 µg Mg.kg^{-1} maximum.

These limit values are the guidelines recommended by the fuel manufacturer [3] to meet the startup requirements.

Analysis Frequency: Monthly is recommended and in-line with international practice.

A.12.4.2.2 Spent Fuel Pool

Limit Values: 500 µg Al.kg^{-1} maximum.

500 µg.kg^{-1} (calcium + magnesium) maximum.

250 µg Mg.kg^{-1} maximum.

These limit values are the guidelines recommended by the fuel manufacturer [3].

Analysis Frequency: Monthly is recommended and in-line with international practice.

A.12.4.3 Reactor Make-up System (REA)

A.12.4.3.1 Water Tanks (9 REA 001 BA and 9 REA 002BA)

Limit Values: 20 µg Al.kg^{-1} maximum.

5 µg Ca.kg^{-1} maximum.

5 µg Mg.kg^{-1} maximum.

These limit values are the guidelines recommended by the fuel manufacturer [3].

Analysis Frequency: Monthly is recommended and in-line with international practice. The tank must also be sampled after filling an when a significant increase in conductivity is noted.

A.12.4.3.2 Boron Tanks (1 / 2 REA 004 BA and 9 REA 003 BA)

Limit Values: 200 µg Al.kg^{-1} maximum.

200 µg.kg^{-1} (calcium + magnesium) maximum.

100 µg Mg.kg^{-1} maximum.

These limit values are the guidelines recommended by the fuel manufacturer [3]. Elevated silica and hardness elements in boric acid storage tanks can result from impurities in makeup water, virgin boric acid additions and recycled boric acid. Attempts should be made to minimise these contaminants.

Analysis Frequency: Monthly is the minimum and in-line with international practice. The tank must also be sampled after filling an when a significant increase in conductivity is noted.

A.12.4.4 Demineralised Water Storage (SED and SER)

Limit Values: 10 µg Al.kg^{-1} maximum.

10 µg Ca.kg^{-1} maximum.

10 µg Mg.kg^{-1} maximum.

These limits are in-line with international practice.

Target Values: 5 µg Al.kg^{-1} maximum.

5 µg Ca.kg^{-1} maximum.

5 µg Mg.kg^{-1} maximum.

These limits are in-line with KNPS experience.

Analysis Frequency: Monthly is the minimum and in-line with international practice.

A.12.5 References

[1] EPRI Pressurised Water Reactor Primary Water Chemistry Guidelines, Volume 1, Revision 7, TR 3002000505, April 2014

[2] AREVA PWR Fuel Reactor Coolant Chemistry Supplemental Guidelines − Revision 7, 51-9231514-000, November 2014

[3] Westinghouse Supplemental Primary Water Chemistry Guidelines, Revision 5, MTLS-06-131, March 2015

A.13 Iron, Copper

A.13.1 Objective and Strategy

The measurement of iron and copper content allows verification of the effectiveness of the chemical treatment with respect to the materials present and operating conditions of the system. The amount of iron and copper in the secondary circuit is related to the amount of feedtrain material being removed and transported towards the steam generators (SGs). Copper, when present as copper oxide, has been shown by tests in AVT water to accelerate SCC of alloy 600MA. Iron (as iron oxide) causes sludge piles on the tube support plates in the SGs thereby fouling the SGs and reducing the efficiency. Sludge piles create areas for the accumulation and concertation of corrosion accelerating impurities (often referred to as hideout).

The KNPS secondary system is generally all-ferrous, but some copper containing alloy components are also present. The chemical treatment strategy is to minimise corrosion, therefore maintaining the corrosion products as low as possible is the main objective.

A.13.2 Source

Iron and copper are corrosion products from the system materials.

A.13.3 Risks

Copper oxides accelerate SCC of the SG tubing material. Iron oxides form sludge piles which foul the SGs.

A.13.4 Basis for the Limit Values and Analysis Frequencies

The basis for the limit values, target values, and analysis frequencies for the systems are provided in the sub-section that follows.

A.13.4.1 Steam Generator Feedwater (AHP)

Limit Values:	$\leq 5\ \mu g\ Fe.kg^{-1}$.
Target Values:	$< 3\ \mu g\ Fe.kg^{-1}$ and $< 0{,}2\ \mu g\ Cu.kg^{-1}$. These limits are in-line with KNPS experience and within international guidance limits [1].
Analysis Frequency:	Weekly, in-line with international practice.
KNPS Practice:	Sample is collected continuously by integrated corrosion product samplers. The filters are collected and analysed weekly.

A.13.5 References

[1] EPRI Pressurized Water Reactor Secondary Water Chemistry Guidelines, Revision 8, TR 3002010645, Final Report, September 2017

A.14 Nickel, Cobalt, Chromium

A.14.1 Objective and Strategy

Activated corrosion products, such as cobalt-58, cobalt-60, nickel-58, chromium-51 (and iron-59) get incorporated into the oxide layer thereby creating out-of-core radiation fields. Zinc displaces cobalt and also other metal cations like nickel, chromium (and iron) from oxide layers and build up more stable protective oxide layers on the surfaces because zinc has a higher site preference energy than the competing cations and therefore zinc is preferentially taken up into the oxide. This eventually results in radiation field reduction and less corrosion product in the reactor coolant [1].

Nickel, cobalt and chromium are monitored in the reactor coolant after zinc injection.

A.14.2 Source

Corrosion products from the system materials. Co-58 (from Ni-58, SG tube material), Co-60 (from Co-59, cobalt containing materials), Cr-51 (and Fe-59 (from steels)).

A.14.3 Risks

The significance of these species is that they may be insoluble in reaction with other species (such as silica and borate) present in the primary system and deposit onto the fuel cladding, posing a risk of core axial-offset effects and crud-induced localised corrosion.

A.14.4 Basis for the Limit Values and Analysis Frequencies

The basis for the limit values, target values, and analysis frequencies for the systems are provided in the sub-section that follows.

A.14.4.1 Reactor Coolant System (RCP)

Limit Value: ≤ 6 µg $Ni.kg^{-1}$. Fuel vendor guidance value [1]

Analysis Frequency: Weekly for Ni for the 1st month after starting zinc addition, and after that monthly – KNPS Administrative surveillance based on fuel vendor guidance and KNPS operating experience.

Monthly for Co and Cr, KNPS Administrative surveillance.

A.14.5 References

[1] Westinghouse PWR Zinc Addition Guidelines, PE-07-42, Revision 2, April 2012

A.15 Zinc

A.15.1 Objective and Strategy

Zinc is added into the primary system as a solution of zinc acetate, the objective is to reduce plant dose rates, and zinc has also been proven as an effective agent to mitigate primary water stress corrosion cracking (PWSCC) [1].

The primary system materials develop a stable protective oxide layer on the surfaces which have a spinel structure of metal cations in a stable crystal lattice, surrounded by oxygen atoms completing the metal oxide. Activated corrosion products, such as Co-58 (from Ni-58, SG tube material), Co-60 (from Co-59, cobalt containing materials), Cr-51 and Fe-59 (from steels) get incorporated into the oxide layer thereby creating out-of-core radiation fields.

It is understood that zinc can displace cobalt and also other cations like nickel, chromium and iron from oxide layers and build more stable protective oxide layers on the surfaces because zinc has a higher site preference energy than the competing cations. Also, if the zinc concentration is higher compared to the competing metal cations of similar size and charge, then zinc is preferentially taken up into the oxide. This results in radiation field reduction and improvement of corrosion performance of the materials and decreases the amount of activity and corrosion product in the reactor coolant [2].

A.15.2 Source

Zinc is the 24th most abundant element in Earth's crust and has five stable isotopes. Zinc acetate is a salt with the formula $Zn(CH_3CO_2)_2$, which commonly occurs as the dihydrate $Zn(O_2CCH_3)2(H_2O)_2$. Both the hydrate and the anhydrous forms are colourless solids that are commonly used in chemical synthesis and as dietary supplements. Zinc acetates are prepared by the action of acetic acid on zinc carbonate or zinc metal.

A.15.3 Risks

In the presence of a neutron flux, Zn-64 can absorb a neutron to become Zn-65, which is radioactive (1,1 MeV gamma) with a 243,8 day half-life, therefore plants adding natural zinc experience a smaller radiation dose benefit because of the production of Zn-65 [2].

Zeolite-formers like calcium, magnesium, and aluminium can precipitate as silicates under PWR conditions. The potential also exists for the precipitation of various zinc silicates and hydrates. These do not have a direct effect on zirconium alloy (fuel cladding) corrosion, however many oxides and silicates of Al, Ca and Mg have a negative coefficient of solubility and thus may deposit preferentially on fuel rods thereby increasing the risk of under-deposit corrosion because of elevated cladding temperature. Industry experience with Crud Induced Power Shift (CIPS), in high-duty cores indicates that concentration factors approaching 1000 are possible [2]. Zinc acetate injection may only commence once the RCP silica is < 1000 µg $SiO_2.kg^{-1}$.

A.15.4 Basis for the Limit Values and Analysis Frequencies

The basis for the limit values, target values, and analysis frequencies for the systems are provided in the sections that follow.

Limit Value:	40 μg $Zn.kg^{-1}$ maximum, based on the envelope of operating experience from plants injecting zinc [2] [3].
Target Value:	5 μg $Zn.kg^{-1}$, based on the design intent [3]. This may be changed with agreement from RFE and support from the fuel vendor.
Analysis Frequency:	Daily until stabilisation and thereafter a 3 × W, similar to the EDF approach [4].

A.15.5 References

[1] EPRI Pressurised Water Reactor Primary Chemistry Guidelines, Volume 1, Revision 7, TR 3002000505, April 2014

[2] Westinghouse PWR Zinc Addition Guidelines, PE-07-42, Revision 2, April 2012

[3] KNPS Detailed design package 09025, Johannes van Dyk, October 2012

[4] EDF Document Standard des Specifications Chimiques du Palier 900 MWE CP1-CP2, EDEAPC090465, April 2017

A.16 Ethanolamine, Ammonia

A.16.1 Objective and Strategy

Ethanolamine (ETA) and ammonia are both volatile alkaline conditioning agents for the secondary system. Ammonia is used in power plants world-wide to adjust the pH to protect the mainly carbon steel feed-train materials from general corrosion and flow accelerated corrosion (FAC). A slightly alkaline pH of (neutral pH + 1 pH unit at system temperature) supports a favourable environment to minimise corrosion. ETA and ammonia are volatile, so the entire secondary circuit is conditioned, whereas a dissolved solid chemical inhibitor would concentrate in the steam generators leaving the steam phase without adequate conditioning.

Both ETA and ammonia are injected into the feedwater to condition the feedwater and this establishes the pH of the water / steam circuit. The advantage of ETA is that it has a lower portioning coefficient than ammonia and therefore is beneficial in the two-phase regions (where both steam and water coexist) ensuring that both the water and steam can achieve the required pH thereby mitigating FAC. The disadvantage of ETA is that if the concentration is too high, this leads to early saturation of the steam generator blowdown demineralisers which allows leakage of impurities towards the condenser [1].

Under certain conditions it is allowed to inject only ETA or only ammonia:

Normally ETA is the primary conditioning agent being injected into the feedwater (AHP) to provide ≈ 3 mg ETA.kg^{-1} in AHP and this is supplemented by ammonia to give ≈ 1 mg NH_3.kg^{-1} in AHP which achieves the target AHP pH_{25} ≈ 9,65. This regime achieves the required pH throughout the water / steam circuit. When ETA is being injected (with or without ammonia), the regime is termed the 'Ethanolamine Regime'.

Under certain conditions ETA is intentionally not injected and the secondary conditioning is achieved by injecting ammonia alone at higher concentrations to give ≈ 3,5 mg NH_3.kg^{-1} in AHP. This is termed the 'Ammonia Regime'.

The Ammonia Regime is typically applied during start-up of a unit and when the condensate polishing plant (ATE) is in-service. This is to limit exposing the ATE resins to ETA. Furthermore, when steam generator leak rates are high at the beginning of cycle, then it is preferable to apply the Ammonia Regime, because ammonia allows longer steam generator blowdown (APG) resin run-time before breakthrough which is being aggravated by the effect of borate from the primary system in-leakage [2].

The concentrations of ETA and ammonia are controlled to optimise the pH conditions in the secondary circuit.

A.16.2 Source

Ammonia is purchased as ≈ 25% ammonium hydroxide solution and ETA as monoethanolamine 98% w/w. These are commercially available chemical products used in various industrial applications. The chemicals are prepared and batched into the dosing stations from where they are injected into the plant by the chemical dosing system.

A.16.3 Risks

The chemicals must be of good quality and have low impurity levels otherwise they could be a source of system contamination.

Concentrated ammonia solution must be handled with care and is harmful if the fumes are inhaled so appropriate protective equipment is required by the dosing procedure. High ammonia is not compatible with copper, so since the plant does contain some copper components, the allowable concentration of ammonia is limited.

ETA is flammable. ETA must be stored under nitrogen to prevent deterioration / breakdown of the chemical. ETA is detrimental to ion exchange resins, so exposing these resins to high concentrations must be avoided as far as possible.

A.16.4 Basis for the Limit Values and Analysis Frequencies

The basis for the limit values, target values, and analysis frequencies for the systems are provided in the sections that follow.

A.16.4.1 Steam Generator Feedwater (AHP)

Limit Value for ETA:	2 mg ETA.kg^{-1} (minimum). This is applicable from 24 hours after transitioning from Ammonia Regime to the Ethanolamine Regime. The minimum limit is imposed to ensure presence of ETA to combat FAC and is based on operating experience [1] and industry benchmarking [3]. There is no maximum Limit Value but it is recommended to maintain < 4 mg ETA.kg^{-1} based on operating experience [1] which shows that too high concentration leads to impurities entering the condenser when the APG resin is saturated.
Target Values for ETA:	2,5 – 3,5 mg ETA.kg^{-1}. Based on operating experience, this provides the target AHP pH when supplemented with ≈ 1,5 mg NH_3.kg^{-1}.
Target Values for NH_3	There are no limit values, the AHP pH limit values must be respected. Target Values for Ethanolamine Regime: 1 to 2 mg NH_3.kg^{-1} based on operating experience [1]. Target Value for Ammonia Regime: 2,2 to 2,3 mg NH_3.kg^{-1} based on operating experience and industry benchmark [3].
Analysis Frequency:	Weekly for both ETA and ammonia. This is consistent with industry guidance (EPRI) [4] and utility benchmark [3] for secondary conditioning agents.

A.16.5 References

[1] Experience and Optimisation of Ethanolamine Treatment for a PWR Secondary System, Proceedings from the Nuclear Plant Chemistry Conference. Van Eeden, N, Matthee, FWR, Montshiwagae, M, Paris 2012
[2] Unit 1 APG Supressed pH due to Elevated Primary to Secondary Leak rates Chemistry Report, Lotz, PF, Williams, J, January 2017
[3] EDF Document Standard des Specifications Chimiques du Palier 900 MWE CP1-CP2, EDEAPC090465, April 2017
[4] EPRI Pressurized Water Reactor Secondary Water Chemistry Guidelines Revision 8, September 2017

A.17 Hydrazine

A.17.1 Objective and Strategy

Hydrazine is a reducing agent and inhibits general and localised corrosion of ferrous metals by reacting with any available oxygen. Hydrazine also aids in minimising pitting susceptibility in nickel alloy. A hydrazine : oxygen ratio of > 3 is important to maintain reducing conditions on the surface of the SG materials [1].

Hydrazine is also added to the primary system at the start-up of a unit to scavenge the dissolved oxygen.

Hydrazine is toxic to the marine environment and hence its release as effluent must be controlled.

A.17.2 Source

Hydrazine is an inorganic compound with the chemical formula N_2H_4. It is a colourless flammable liquid with an ammonia-like odour. Hydrazine is highly toxic and dangerously unstable unless handled in solution.

A.17.3 Risks

Hydrazine is toxic to the environment and a suspected carcinogen.

A.17.4 Basis for the Limit Values and Analysis Frequencies

The basis for the limit values, target values, and analysis frequencies for the systems are provided in the sections that follow.

A.17.4.1 Steam Generator Feedwater (AHP)

Limit Value: 20 µg $N_2H_4.kg^{-1}$ (minimum) or 8 × the dissolved oxygen concentration, whichever number is the larger [1]. 200 µg $N_2H_4.kg^{-1}$ (maximum) is for limiting the environmental impact.

Action Levels: AL1 is entered at <20 µg $N_2H_4.kg^{-1}$.

AL2 is entered when the N_2H_4:O_2 ratio is < 2.

The actions to take are provided in OTS-KCS (§ 3.2 [6])

Target Values: 70-100 µg $N_2H_4.kg^{-1}$ is the administrative target value established at KNPS, which has been proven to provide good control and sufficient margin to the limits.

Analysis Frequency: Once per shift.

KNPS Operational Controls: Continuous measurement by online analyser; the frequency is met by taking a reading per shift.

A.17.5 REFERENCES

[1] Pressurised Water Reactor Secondary Water Chemistry Guidelines, Revision 7

A.18 Cation Conductivity

A.18.1 Objective and Strategy

Cation conductivity (CC) is the conductivity of an aqueous solution eluting from a cation resin (in the H^+ form) column. CC is a very sensitive non-specific analytical method for detecting low levels of anionic pollutants in the power plant steam/water cycle. For KNPS, the early detection of seawater ingress into the secondary system via a condenser tube leak is of the highest importance. Impurities entering the condenser will be transported via the feed-train to the SGs, where these harmful impurities concentrate up to levels that are a high risk for corrosion damage to the materials in the short term.

Continuous control of CC, together with sodium in the SG blowdown, provides the main indication of the concentration of pollutants in the SGs.

A.18.2 Source

Most sources of impurity ingress will result in an elevated cation conductivity (CC) measurement.

A.18.3 Risks

High CC indicates impurities which could be harmful to the plant components.

A.18.4 Basis for the Limit Values and Analysis Frequencies

The basis for the limit values, target values, and analysis frequencies for the systems are provided in the sections that follow.

A.18.4.1 Steam Generator Blowdown (APG)

A.18.4.1.1 Reactor at Power (RP)

Limit Value: The Limit Value is 1 $\mu S.cm^{-1}$ (at 25°C) which corresponds to the EDF admissible operation zone limit. 1 $\mu S.cm^{-1}$ also corresponds to a maximum chloride concentration of 80 $\mu g\ Cl.kg^{-1}$ or a maximum sulphate concentration of 110 $\mu g\ SO_4.kg^{-1}$. [1] Organic acid breakdown products from Ethanolamine (ETA) contribute to the cation conductivity (CC) value in the SG blowdown. 1$\mu S.cm^{-1}$ is the Admissible Operation Zone per § 3.2 [6], Koeberg Chemistry Specifications.

Target Value: < 0,5 $\mu S.cm^{-1}$

Analysis Frequency: Once per shift.

KNPS Operational Controls: CC is monitored continuously and the on-line reading is verified with a weekly manual analysis. This is consistent with EPRI guideline recommendations.

A.18.4.1.2 SD / RRA (Primary Pressure ≥ 2,3 MPa(g)) to RP

Sampling and analysis can be terminated once the sampling system (REN) is shut down for unit outage.

A.18.5 References

[1] Experience and Optimisation of Ethanolamine Treatment for a PWR Secondary System, Proceedings from the Nuclear Plant Chemistry Conference. Van Eeden, N, Matthee, FWR, Montshiwagae, M, Paris 2012

A.19 Turbidity

A.19.1 Objective and Strategy

A.19.2 Cause

Turbidity is a measure of the degree to which the water loses its transparency due to the presence of suspended particulates. The more total suspended solids in the water, the murkier it seems and the higher the turbidity. Turbidity is considered as a good general measure of the quality of water. Turbidity is an optical determination of water clarity by the scattering of incident light as it encounters particles in the path of the light beam, and therefore is a more sensitive technique than determination of suspended solids by weight. Turbidity is used as an indicator of water clarity in conjunction with the suspended solids measurement in the high purity water systems.

In water treatment, turbidity can come from suspended sediment such as silt or clay, inorganic materials, or organic matter such as algae, plankton and decaying material. In addition to these suspended solids, turbidity can also include coloured dissolved organic matter, fluorescent dissolved organic matter and other dyes.

Humic stain refers to the tea colour produced from decaying plants and leaves underwater due to the release of tannins and other molecules [1].

Corrosion product particles and colloidal silica are also common sources of turbidity in power plant.

A.19.3 Risks

Similar to suspended solids, the main risk is deposits that may form in the plant systems that could lead to underdeposit corrosion. Blocking of filters and fouling of demineralisers is also a concern.

A.19.4 Basis for the Limit Values and Analysis Frequencies

The basis for the limit values, target values, and analysis frequencies for the systems are provided in the sub-section that follows.

A.19.4.1 Steam Generator Feedwater (AHP / ASG)

Limit Value:	≤ 0,3 NTU. KNPS Administrative limit based on operating experience. Turbidity above the limit value must be investigated.
Target Value:	< 0,2 NTU. KNPS Administrative target based on operating experience.
Analysis Frequency:	Weekly. KNPS Administrative surveillance when feeding the Steam Generators.

A.19.5 References

[1] Fondriest Environmental, Inc. Turbidity, Total Suspended Solids and Water Clarity, Fundamentals of Environmental Measurements. 13 Jun. 2014.

A.20 Total Organic Carbon

A.20.1 Objective and Strategy

It is important to minimise the amount of Total Organic Carbon (TOC) in the water production process. Halogenated organic compounds are not readily retained by the demineralisation plant and are able to enter the water makeup supply to the power station. Chlorinated organics break down under the plant thermo-hydraulic conditions resulting in the increase of the chloride ion concentration in the water / steam cycle [1].

A.20.2 Source

Make-up water, chemical additives and ion exchange resin leachates are the usual sources of organics entering the system during normal power operation. Other sources include cleaning agents, lubricants, bacteria and condenser inleakage that can enter the steam / water cycle by contamination during outages or damaged plant during operation. The main source of TOC is the additive ethanolamine (ETA) which is added to the feedwater as a conditioning agent.

A.20.3 Risks

Chloride in contact with metal surfaces has a detrimental effect on the structural integrity for power plants. See risks for chloride in A.2.

A.20.4 Basis for the Limit Values and Analysis Frequencies

The basis for the limit values, target values, and analysis frequencies for the systems are provided in the sub-sections that follow.

A.20.4.1 Demineralised Water Storage (SED)

Limit Value: ≤ 100 µg $C.kg^{-1}$. Based on fuel vendor guidance [2].

Analysis Frequency: Monthly. KNPS administrative surveillance.

A.20.4.2 Potable Water Distribution (SEP)

Limit Value: The are no limits because of the changing nature of the raw water.

Analysis Frequency: Monthly in line with the Corporate Standard [3].

A.20.4.3 Water Production Plant (SDA)

Limit Value: ≤ 250 µg $C.kg^{-1}$ downstream of the mixed bed demineralisers during water production. In-line with the Corporate Standard [3].

Target Value: 45% of TOC reduction across the charcoal bed. KNPS administrative target and in-line with corporate guidance [3].

Analysis Frequency: Monthly analysis upstream and downstream of the charcoal filters while water production is in progress.

Monthly downstream of the anion bed and mixed-bed demineralisers while water production is in progress.

A.20.5 References

[1] An Organic Profile of a Pressurised Water Reactor Secondary Plant, Power Plant Chemistry 2012 14(7), Van Eeden, N, Stwayi, M and Gericke, G, 2012

[2] WEC Westinghouse Supplemental Primary Water Chemistry Guidelines, Revision 5, MTLS-06-131, March 2015

[3] 240-53113712 Demineralised Water Production Using Ion Exchange Resins Chemistry Standard, November 2017

A.21 Trisodium Phosphate (TSP)

A.21.1 Objective and Strategy

Trisodium phosphate dodecahydrate (TSP) is added as a solid crystalline material to the EAS baskets located at the – 3,5 m level in the containment. Upon activation of the containment post-LOCA spray system (EAS), the water-soluble TSP will dissolve in the spray water and elevate the pH of the boric acid spray solution as it is recirculated with the EAS system [1].

The spray system is designed to scrub the elemental iodine from the containment atmosphere post-LOCA and retain radioactive iodine in solution. The addition of TSP to the boric acid spray provides the alkaline pH for dissolution of the gaseous iodine and thus promotes the retention of the iodine in solution as the iodate species. This effect will minimise the release of gaseous radioactive iodine into the environment in the case of containment leakage and thereby ensure that the off-site dose limits are complied with.

TSP is also a corrosion inhibitor for carbon steel and is used as treatment for the closed cooling water circuits, i.e. RRI, SRI, SES, DEG, and DEL. These systems are dosed with trisodium phosphate and a high concentration of dissolved oxygen is maintained in them. This ensures the formation of an adhesive impermeable ferric phosphate layer on the metal surface.

A.21.2 Source

TSP is an inorganic compound with the chemical formula Na_3PO_4. The hydrated form, dodecahydrate, $Na_3PO_4 \bullet 12\ H_2O$, is purchased commercially. TSP is produced by neutralisation of phosphoric acid using sodium hydroxide.

A.21.3 Risks

TSP is not toxic. There is a risk to plant because of possible contamination from thermal barrier leaks between cooling the water circuits and main plant systems on both primary and secondary sides. Operating experience shows that the risk is high when pumps that have been depressurised are returned to service. The concern is largely because sodium is known to be a major deleterious species for both primary and secondary systems and is therefore monitored as a chemistry performance indicator parameter.

A.21.4 Basis for the Limit Values and Analysis Frequencies

The basis for the limit values, target values, and analysis frequencies for the systems are provided below.

A.21.4.1 Containment Spray System (EAS)

The requirement is to determine:

1. the dissolution time of the TSP in the EAS baskets;
2. the resultant pH of a solution of the TSP in boric acid; and
3. TSP levels in the baskets.

Limit Value: The limit values for dissolution time is < 4 hours and the pH of the resultant solution must be > 7,02 at 25°C. The level must not be less than the low level as indication [1].

Analysis Frequency: The analysis frequency is during every refuelling outage.

A.21.4.2 Nuclear Island Component Cooling System (RRI)

Limit Values: 100 mg $PO_4.kg^{-1}$ minimum, 550 mg $PO_4.kg^{-1}$ maximum. This is based on the EDF Specification [2] and Koeberg Operating Experience and therefore the higher maximum level is acceptable. The maximum value is also to limit environmental impact.

Analysis Frequency: Weekly for the train in service and at least monthly per train.

A.21.4.3 Conventional Island Component Cooling System (SRI)

Limit Values: 100 mg $PO_4.kg^{-1}$ minimum, 550 mg $PO_4.kg^{-1}$ maximum. This is based on the EDF Specification [2] and Koeberg Operating Experience and therefore the higher maximum level is acceptable. The maximum value is also to limit environmental impact.

Analysis Frequency: At least monthly and when the pH is out of specification.

A.21.4.4 Hot Water System (SES)

Limit Values: 50 mg $PO_4.kg^{-1}$ minimum, 300 mg $PO_4.kg^{-1}$ maximum. This is based on the EDF Specification [2] and Koeberg Operating Experience and therefore the higher maximum level is acceptable. The maximum value is also to limit environmental impact.

Analysis Frequency: At least monthly and when the pH is out of specification.

A.21.4.5 Nuclear Island Chilled Water System (DEG)

Limit Values: 100 mg $PO_4.kg^{-1}$ minimum, 1250 mg $PO_4.kg^{-1}$ maximum. This is based on the EDF Specification [2] and Koeberg Operating Experience and therefore the higher maximum level is acceptable. The maximum value is also to limit environmental impact.

Analysis Frequency: At least monthly and when the pH is out of specification.

A.21.4.6 Conventional Island Chilled Water System (DEL)

Limit Values: 100 mg $PO_4.kg^{-1}$ minimum, 1250 mg $PO_4.kg^{-1}$ maximum. This is based on the EDF Specification [2] and Koeberg Operating Experience and therefore the higher maximum level is acceptable. The maximum value is also to limit environmental impact.

Analysis Frequency: At least monthly and when the pH is out of specification.

A.21.5 REFERENCES

[1] EAS Soda Tank Removal Detailed Design 02279 Revision 0123c, November 2007

[2] Document Standard des Specifications Chimiques Du Palier 900 MWE CP-CP2), EDEAPC050251, February 2008

A.22 Radiochemistry

A.22.1 Objective and Strategy

Gamma spectrometry is performed to obtain a representation of total activity of all radionuclides present in a sample. Tritium is a beta emitter generated from hydrogen activation and can displace natural hydrogen in the environment; therefore, releases must be quantified. Iodine isotopes are fission products and contribute significantly to radioactive dose. The dose equivalent I-131 is estimated from the combined activities of the iodine isotopes. Fission product gases can indicate fuel defects and therefore, together with iodine, are indicators of fuel integrity.

A.22.2 Basis for I-131 Equivalent and Noble Gas Limiting Values

A.22.2.1 Accident Conditions

Fission products can escape into the space between the fuel and the cladding by a diffusion-type process, and from there, they can be released to the coolant if defects are present in the fuel cladding. The distribution and build-up of these fission products in the reactor coolant and auxiliary systems are considered in determining the possible consequences associated with an accidental release of fission products. In preparation for accident analyses, the maximum fuel activities obtained during a typical equilibrium cycle is determined. In subsequent accident analyses, small cladding defects in 1% of the fuel rods present in the core is assumed. This 1% cladding failure equates to about $1{,}5 \times 10^{11}$ $Bq.m^{-3}$ dose equivalent I-131 (I-131 eq.) (under equilibrium conditions) present in the reactor coolant. From the released activity, due to a range of accidents, the off-site doses are calculated at a number of distances. The calculated doses include thyroid dose, gamma-body dose, and beta-skin dose. In these accident analyses, it is assumed that a maximum value of about $1{,}5 \times 10^{11}$ $Bq.m^{-3}$ I-131 eq. is present in the reactor coolant.

A.22.2.1.1 Limiting the Iodine Peak

The SAR study of the transfer of activity from the primary circuit to the environment, in the event of a steam generator tube rupture together with a steam loss, indicates that, in order to remain below the calculated dose limits, the activity in the primary circuit should always remain below predetermined limits. In taking the results from this study into account and the assumptions made in the study, it is necessary to limit the activity due to I-131 eq. to $1{,}5 \times 10^{11}$ $Bq.m^{-3}$ under transient conditions.

To ensure that this requirement is adhered to under equilibrium conditions, a power transient is induced to measure the I-131 eq. when the Σgas reaches a value of $1{,}5 \times 10^{11}$ $Bq.m^{-3}$.

> ***NOTE 1****: The rate of ≥ 30 MW/min is necessary to release the iodine during the transient period.*

***NOTE 2**: The 10-day period before the planned load reduction is a compromise between equilibrium activity and the operation with possible significant defects (which must be as short as possible).*

The reason for this is that operating experience shows that the activity of I-131 eq. during a power transient is normally lower than the Σgas during equilibrium operation. The I-131 eq. during a transient may be 50 to 100 times larger compared to the stable I-131 equivalent.

A peak I-131 eq. activity larger than $1,5 \times 10^{11}$ $Bq.m^{-3}$ indicates such a degradation of fuel that start-up of the reactor after the transient will not be allowed. In fact, the study mentioned above shows that the dose to the environment will only be respected if the limit value of $1,5 \times 10^{11}$ $Bq.m^{-3}$ I-131 eq. activity is respected at all times (also during transient conditions).

A.22.2.2 Steady State Conditions

The distribution and build-up of fission products in the reactor coolant and auxiliary systems are considered in determining the requirements for biological shielding and for the design of radioactive effluent and waste systems (§ 3.2 [4]).

To evaluate the radiation source needed as input for the design of these systems, the maximum fuel activities obtained during a typical equilibrium cycle is determined. It is then assumed that small cladding defects are present in 1% of the fuel rods in the core. This 1% cladding failure equates to approximately $1,5 \times 10^{11}$ $Bq.m^{-3}$ I-131 equivalent, and to approximately 1×10^{13} $Bq.m^{-3}$ Σgas present in the reactor coolant. This coolant activity was used as design basis for the systems mentioned above.

***NOTE 1**: Due to additional restrictions imposed by the NNR, the effective allowable source term (I-131 eq. for biological shielding and the effluent and waste systems is based on fuel cladding defects being present in 0,14% of the fuel pins). This equates to about $1,85 \times 10^{10}$ $Bq.m^{-3}$ I-131 eq. present in the reactor coolant.*

To prevent exceeding the design limits for biological shielding and the effluent and waste systems, action thresholds were established for steady-state operation.

The limit value of $1,85 \times 10^{10}$ $Bq.m^{-3}$ I-131 eq. is the same as the limit imposed by the NNR. This threshold is considered to represent cladding failure that is sufficiently serious to require reactor shutdown in the short term. The corresponding Σgas limit value is 5×10^{11} $Bq.m^{-3}$. A tolerance of two days allows the operator to confirm the measurement.

Reaching the threshold of $3,7 \times 10^{10}$ $Bq.m^{-3}$ I-131 equivalent, or 1×10^{12} $Bq.m^{-3}$ Σgas indicates fuel cladding failure that is sufficiently serious to require almost immediate shutdown of the reactor. A tolerance of eight hours allows the operator to confirm the measurement. (It should be noted that the activities allowed are substantially lower than the maximum admissible 1% cladding failure allowed by the SAR. The 1% cladding failure equates to approximately 15×10^{11} $Bq.m^{-3}$ I-131 eq. and 1×10^{13} $Bq.m^{-3}$ Σgas present in the reactor coolant.)

A.22.3 Basis for I-134 Limiting Values

The presence of I-134 in the primary circuit is the most sensitive indication of large defects on fuel rods. Iodine is not readily released from defective fuel rods due to its chemical and physical properties. Most of the I-134 present in rods with small defects will thus have decayed by the time it is released into the primary circuit due to its short half-life (T = 53 minutes). If however, the defect is large, some of the UO_2 may disperse into the primary coolant. This UO_2 will thus be in direct contact with the water and most of the I-134 from fission will escape into the water and will be detected before it decays.

The limit value is specific activity in excess of A1 + $1,0 \times 10^{10}$ $Bq.m^{-3}$ for I-134 noted during continuous operation, which is considered to represent fuel damage that is sufficiently serious to require a unit shutdown in the short term.

The value of $1,0 \times 10^{10}$ $Bq.m^{-3}$ I-134 is justified by the fact that $1,0 \times 10^{10}$ $Bq.m^{-3}$ corresponds to the limit value at the end of the cycle to avoid exceeding the set values on the accumulative average in eq. I-131.

Furthermore, the value of $1,0 \times 10^{10}$ $Bq.m^{-3}$ I-134 will limit the degradation of the fuel due to baffle jet fretting. The value of $1,0 \times 10^{10}$ $Bq.m^{-3}$ is lower than the values reached in the most serious cases of the degradation of the fuel by baffle jet fretting based on operating experience from EDF. However, Koeberg is an up-flow plant, i.e. coolant flows in an upward direction in the gap between the core barrel and the baffle; therefore, Koeberg would not be susceptible to baffle jetting.

To measure the increase in the I-134 activity due to new large defects, it is necessary to subtract residual I-134 activity coming from previous cycles. In order to exclude the contamination of the preceding cycles with defects and to take into account only the activity coming from the presence of a defect in the cycle in progress, the I-134 limit does not relate to an absolute value, but to an increase in the activity in I-134. (Tramp I-134 activity is expected to increase by a factor of 2 during a defect-free cycle.)

Activity A1 represents the theoretical value in I-134 activity coming from contamination. The change in activity is modelled by the linear relationship:

$$A_1 = A_0 \bullet (1 + K.Bu), \text{ where } Bu = \text{burn-up}$$

In this equation, *Ao* is the I-134 activity present at the beginning of cycle ‘n’ due to the residual deposit from the previous cycles (‘n’ – current cycle). This activity (*Ao*) corresponds to the lesser of:

- the first activity measured after stabilising at full power in the cycle under consideration (cycle ‘n’) or,
- the activity at the end of the previous cycle (cycle ‘n – 1’) after correcting for the fraction of reloaded assemblies in cycle ‘n’ that were present in cycle ‘n – 1’.

The slope of the equation is given by the co-efficient *K*, which depends on the age of the contamination and on the type of dispersed fuel. The values of the co-efficient *K* are determined from a calculation as a function of the theoretical isotopic changes taking place in the deposited oxide.

- $K = 0,7 \times 10^{-4}$, if the dispersion in UO_2 occurred in cycle ‘n – 1’
- $K = 0,25 \times 10^{-4}$, if the dispersion in UO_2 occurred in cycle ‘n – 2’

A.22.4 Basis for Tritium Limiting Values

Tritium is detected in the secondary system water as a result of known and quantified primary to secondary leak rates (SGLRs). The rigorous Radiation Protection (RP) requirements and practices employed to protect workers in the radiation control zones, are not required in the turbine hall under normal conditions because activity transferred via SGLRs to the secondary side is removed by the steam generator blowdown demineralisers. Tritium however cannot be removed by demineralisers. Therefore an administrative upper limit for tritium in the secondary water is stipulated in KGH-010 (Appendix 1, Surveillance 27 of Rev. 14a) to action RP to reassess the dose impact should the limit be exceeded.

Increases in steam generator leaks during 2017 have required a reassessment of the dose impact for tritium, and the basis for the revised limit for tritium in the secondary side is documented in the Radiation Protection Technical Assessment Report “Assessment of H-3 activity limit in titrated water (Possible primary to Secondary leak)”.

The **Limit Value** for Condenser Extraction System (CEX) Tritium is: $\leq 7{,}4 \times 10^8$ Bq/m^3 according to the RP reassessment [3]. The **Target Value** is $\leq 7{,}4 \times 10^7$ Bq/m^3, which is a KNPS Administrative value based on operating experience.

A.22.5 REFERENCES

[1] KWF-002: Evaluation of Failed Fuel Cladding Integrity

[2] Report: RFE-REP-2006-14: Background to the Applicable OTS radioactivity Limits in the Primary Coolant at Koeberg.

[3] TAR/001 Rev 0 Assessment of H-3 activity limit in titrated water (Possible primary to Secondary leak) doc no. 151746, E Khoza, April 2017

A.23 Chlorine

A.23.1 Objective and Strategy

Chlorine is added to various water systems as a biological sanitising agent to prevent the build-up of organisms (e.g. bacteria, viruses, fungi, protozoa, barnacle larvae etc.) in areas where these could accumulate and cause blockage of heat exchangers, damage to plant and contamination of process water.

The concentration of *free chlorine* should be optimised at the minimum level that meets the above mentioned objective while also adhering to the stringent environmental regulations for chlorine and chlorination by-product release into the environment.

A.23.2 Source

Free chlorine can be added by direct injection of chlorine gas, injection of hypochlorite solution, addition of solid hypochlorite granules or by electrolysis of sea water as is the case for CRF and SEC.

Chlorine dissolved in water ($Cl_2 + H_2O \rightleftharpoons HOCl + HCl$) gives hypochlorous acid (HOCl) and the hypochlorite ion (OCl^-) which is representative of the free chlorine concentration.

In the electrolysis of sea water (simplified as sodium chloride solution), the process at the CTE plant:

Cathode reaction = $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ and the anode reaction = $2Cl^- \rightarrow Cl_2 + 2e^-$. These together = $2NaCl + 2H_2O \rightarrow 2NaOH + H_2$ (gas) + Cl_2 (gas)

The hydrogen gas escapes as a by-product and is vented off, while the chlorine reacts with the sodium hydroxide to form hypochlorous acid; $Cl_2 + NaOH \rightarrow NaCl + HOCl$.

The hypochlorous acid reacts with the hydroxyl ions present; $HOCl + OH^- \rightarrow OCl^- + H_2O$, which gives the hypochlorite ion. The process can therefore be written as:

$Cl_2 + 2NaOH \rightarrow NaCl + NaOCl + H_2O$; i.e. sodium hypochlorite is produced.

A.23.3 Risks

Chlorine is a highly toxic gas that attacks the respiratory system, eyes, and skin. It is denser than air and therefore tends to accumulate at the bottom of poorly ventilated spaces. Chlorine gas is a strong oxidiser, which may react with flammable materials. Hypochlorite solution and solid material reacts rapidly with acid to form chlorine gas.

Free chlorine (hypochlorous acid and the hypochlorite ion) is harmful to the environment in high concentrations, therefore its release into the environment is restricted and there are national regulations that must be complied with.

Disinfection by-products (DBPs) from chlorination are known to cause chemical contamination of demineralised water systems in the power plant which could lead to the corrosion of plant components. DBPs are also harmful to the environment.

A.23.4 Basis for the Limit Values and Analysis Frequencies

The basis for the limit values, target values, and analysis frequencies for the systems are provided below.

A.23.4.1 Essential Services Water System (SEC)

Limit Value: 1,0 mg Cl_2.kg^{-1} maximum for the average of all trains in service [1] [2]. This complies with the Water Permit and accounts for the poor distribution of chlorine. Of concern to the environment is the total amount of chlorine released and thus the averaging of the lines in service is an acceptable approach also given the mixing that occurs in the CRF outfall.

0,2 mg Cl_2.kg^{-1} minimum is sufficient for the protection against biofouling. This is only considered out-of-specification low if below the limit for more than 16 hours. This is allowed because operating experience shows that there is no adverse biofouling related to the routine CTE maintenance activities which occur weekly lasting up to 24 hours at a time.

Target Value: 0,2 mg Cl_2.kg^{-1} to prevent biofouling of the heat exchangers.

Analysis Frequency: Shiftly analysis has proven to be sufficient for adequate monitoring. In the event that the CTE plant is out of service, no sampling is required, but the surveillance requirement will be met by reporting a result of 0 mg Cl_2.kg^{-1}, with the comment that the CTE plant was out of service.

A.23.4.2 Cooling Water System (CRF)

Limit Value: 0,5 mg Cl_2.kg^{-1} maximum for the average of all trains in service [1]. In addition, the monthly average should be 0,35 mg Cl_2.kg^{-1} maximum. The maximum limit value is a water permit requirement [1].

0,1 mg Cl_2.kg^{-1} minimum is sufficient for the protection against biofouling. This is only considered out-of-specification low if below the limit for more than 16 hours. This is allowed because operating experience shows that there is no adverse biofouling related to the routine CTE maintenance activities which occur weekly lasting up to 24 hours at a time.

Target Value: 0,2 mg Cl_2.kg^{-1} to prevent biofouling of the heat exchangers.

Analysis Frequency: Shiftly analysis has proven to be sufficient for adequate monitoring. In the event that the CTE plant is out of service, no sampling is required, but the surveillance requirement will be met by reporting a result of 0 mg $Cl_2.kg^{-1}$, with the comment that the CTE plant was out of service.

Chlorine must be checked within two hours after a CRF pump is started. Waterboxes 1, 3 and 5 are supplied by CRF 003 PO and waterboxes 2, 4 and 6 are supplied by CRF 001 PO. CRF 002 PO can take the place of either of the other pumps.

A.23.4.3 Potable Water Distribution (SEP)

Limit Value: 0,1 mg $Cl_2.kg^{-1}$ minimum and < 5 mg $Cl_2.kg^{-1}$. The minimum value has proven sufficient to prevent biofouling of the SEP tanks, and the maximum target value is to protect the activated carbon filters.

A.23.4.4 Sewage Plant (SEU)

Limit Value: 0,05 mg $Cl_2.kg^{-1}$ minimum and 0,50 mg $Cl_2.kg^{-1}$ maximum to ensure adequate sanitation as required by the national coastal guideline [3].

Target Value: 0,25 mg $Cl_2.kg^{-1}$ ensures adequate sanitation without excessive chlorine use and release.

Analysis Frequency: 2 × W, which is aligned to international practice for small / micro sewage plants.

A.23.5 References

[1] Water Permit 853N and Exemption 1133B for the Koeberg Power Station

[2] Changes to KNC-001 and 002, NS-023-15, 22 April 2015

[3] Chemistry Specification Basis: SEU, NCS-003-17, Deon Jeannes, March 2017 and the references sited therein

A.24 Lead, Manganese

A.24.1 Objective and Strategy

There is some industry concern regarding the acceleration of stress corrosion cracking of nickel alloys with respect to lead-accelerated stress corrosion cracking (PbSCC) of SG tubes [1].

During normal operation elemental iron, manganese and zinc and their radionuclides, Fe-55, Fe-59, Mn-54, Mn-56 and Zn-65 are predominantly present as soluble species in the reactor coolant, but iron and its radionuclides precipitate from solution once oxidizing conditions are established when hydrogen peroxide is added during the shutdown. Manganese and zinc and their radionuclides are not affected when oxidizing conditions are established and remain as soluble species [2].

A.24.2 Source

Foreign material is a potential source of lead.

Manganese’s principal source is metal surfaces undergoing steady state corrosion in the reactor coolant system.

A.24.3 Risks

PbSCC of SG tubes [1].

Manganese and lead may accelerate zirconium corrosion [2].

A.24.4 Basis for the Limit Values and Analysis Frequencies

For both lead and manganese, specific concentration limits cannot be technically justified, although gathering of data is considered useful for trending purposes.

It is recommended, but not a requirement, to analyse for Pb and Mn during operations once per cycle.

ATTACHMENT B
CHEMISTRY STRATEGIES DETAILS

This document is a living document and the detailed explanations of the strategies contained in this attachment will be developed with time.

Attachment	Strategy	Status
B.1	Primary Water Chemistry Management	Complete
B.2	Secondary Water Chemistry Management	Complete

B.1 Primary Water Chemistry Management Plan

The Primary Water Chemistry Management explains:

- how the chemistry control practices applied at KNPS support the Programme objectives (i.e. the four primary chemistry objectives stated in § 5),
- provides an historical overview of the changes that have impacted primary chemistry and,
- looks at technical issues and future initiatives to further optimise and develop the Programme.

For this, the reactor coolant system materials taken into consideration are:

- Nickel based alloys
- Zirconium based alloys
- Austenitic stainless steels

The steam generator tubes (3330 per SG), approximately 75% of the surface area of the reactor coolant system, are constructed of a nickel alloy, Inconel 600. On unit 1 SG 1 and SG 2 are 600 mill-annealed (MA) and SG 3 is thermally-treated (TT). On unit 2 all 3 SGs are 600MA.

The fuel cladding, approximately 20% of the surface area of the reactor coolant system (when in operation), is made of either Zircaloy-4, Zerlo or M-5 (depending on the fuel supplier).

The balance, approximately 5% of the surface area of the reactor coolant system is comprised of Austenitic stainless steel (304L and 316L). Internal surfaces of the reactor pressure head, penetrations (for CRDMs), etc. are lined with stainless steel and nickel-based alloys.

B.1.1 Primary Chemistry Control Practices in Support of the Programme Objectives

Associated with the main Programme objectives, the sub-sections below indicate the primary chemistry control practices applied at KNPS and the impacts of each.

B.1.1.1 Control of Primary System pH (at operating temperature (pH_T))

The pH_T programme is designed to minimise fuel deposits, fuel cladding and system materials corrosion, and out-of-core radiation fields. Lithium (as lithium hydroxide) is the controllable parameter for pH_T in co-ordination with the changing boron (as boric acid) concentration throughout the fuel cycle.

The maximum lithium concentration and control band shall be within the limit values as detailed in OTS-KCS (§ 3.2 [6]). For KNPS, an Alternate pH_T Programme is allowed for operational reasons such as to manage excessive primary to secondary leakage [4] [5].

Chemistry Programme Objective	**Impact of Control of pH_T**
Primary system pressure boundary integrity.	Decrease in corrosion. Positive impact.
Fuel cladding integrity and achievement of fuel design performance.	Lower corrosion product transport, therefore low fuel crud build-up.
Out-of-core radiation fields.	Reduces out-of-core radiation fields.
Plant condition for long-term-operation.	Supports long-term operation.

Table 1: Impact of pH_T control

B.1.1.2 Contaminant Minimisation – ALARA Chemistry

Contaminant species are minimised and maintained at as low as reasonably achievable (ALARA) levels. High quality water production standards and high purity plant chemicals support this practice. The station CRACK Programme is implemented to prevent harmful chemical species entering the plant systems [8]. Flag levels below the action levels in LIMS allow for pre-emptive action to be taken to avoid an out-of-specification condition.

A measured approach is taken since ALARA Chemistry involves higher cost, so it is applied rationally, ensuring that the plant remains comfortably within the technically justified limits and contaminants are kept as low as achievable.

For details regarding the specific sources, risks and effects of contaminants, see Attachment A (fluoride, chloride, sulphate, oxygen, silica, sodium, calcium, magnesium, aluminium)

Chemistry Programme Objective	**Impact of Contaminant Minimisation**
Primary system pressure boundary integrity.	Decrease in corrosion propagation. Increased cost.
Fuel cladding integrity and achievement of fuel design performance.	Lower corrosion product transport, therefore low fuel crud build-up. Increased cost.
Out-of-core radiation fields.	Reduces out-of-core radiation fields. Increased cost.
Plant condition for long-term-operation.	Supports long-term operation. Increased cost.

Table 2: Impact of ALARA Chemistry

B.1.1.3 Zinc Injection

The major effect of zinc injection is that it reduces out-of-core radiation fields. Zinc also has a mitigating effect on PWSCC. See Attachment A (Zinc).

Chemistry Programme Objective	**Impact of Zinc Injection**
Primary system pressure boundary integrity.	Slight decrease in corrosion (PWSCC).
Fuel cladding integrity and achievement of fuel design performance.	Associated with high silica, it is possible that deposits could accumulate thereby negatively impacting the fuel cladding.
Out-of-core radiation fields.	Significantly reduces out-of-core radiation fields. (This is the main reason for applying zinc)
Plant condition for long-term-operation.	Supports long-term operation.

Table 3: Impact of Zinc Injection

B.1.1.4 Shutdown / Startup Chemistry Control

Shutdown and Startup chemistry is carefully controlled by procedure [9] [10].

Chemistry Programme Objective	**Shutdown / Startup Chemistry Control**
Primary system pressure boundary integrity.	No major impact on corrosion with recommended parameter ranges.
Fuel cladding integrity and achievement of fuel design performance.	Deposit removal is enhanced by optimising the controls and CIPS risk is reduced. Some manoeuvers (e.g. lower pH_T during startup) could increase fuel crud.
Out-of-core radiation fields.	Minimal expected impact, i.e. ≤ 5% reduction if shutdown programme is optimised. Variations outside of recommendations (e.g. increase in lithium during shutdown could lead to hot-spot development due to particulate deposition.) Dissolved oxygen levels must be maintained after oxygenation to prevent silver contamination ($Ag\text{-}110^m$). Special precautions are required for damaged fuel.
Plant condition for long-term-operation	No major impact.

Table 4: Impact of Shutdown / Startup Control

B.1.2 Events Impacting Primary Chemistry

Table 5 provides the historical overview of the main changes that have impacted primary chemistry:

Event	Unit / Date	Purpose	Effect / Result
Operation at Reduced Temperature (ORT).	1994 Unit 1 Cycle 107 Unit 2 Cycle 207	To reduce the rate of PWSCC initiation time and the propagation rate.	Very effective in dropping initial crack growth rates. Efficiency of the heat exchange process is reduced, resulting in a loss of about 15 MWe per unit.
Increased target pH_T from 7,10 to 7,25.	2010 Unit 1 Cycle 119 Unit 2 Cycle 118	Reduce primary system corrosion and out-of-core radiation fields.	Fuel deposit loading was lower and reduction in plant dose rates.
Zinc injection.	2014 / 2015 Unit 1 Cycle 121 Unit 2 Cycle 221	Reduce plant dose rates.	Plant dose rate index has reduced. An increase in the primary to secondary leak rates has been observed.
Zinc injection suspended for U1.	2017 Unit 1 Cycle 123	To monitor the effect of zinc on the primary to secondary leak rates.	SG leak rates reduced, but cannot be attributed to stopping zinc alone.
Alternate pH_T strategy applied at 6,9 for U1.	2018 Unit 1 Cycle 124	To reduce the start-up primary to secondary leak rates.	The start-up SG leak rates were lower than at the previous start-up.

Table 5. Chemistry Changes and Effects

B.1.3 Technical Issues and Future Initiatives to Develop and Optimise the Programme

The following sub-sections discuss current technical issues and the future initiatives that will influence primary chemistry.

B.1.3.1 Continuing to Manage Primary to Secondary Leak Rates

The Steam Generator Health Care Working Group (SGHCWG) was re-established in 2016 to take care of all aspects related to SG health, with priority and focus on managing the station SGs towards their replacement.

Since Cycles 121 and 221 the startup primary to secondary leak rate has been high and, particularly during the startup of Cycle 123, where a peak leak rate of 19 $L.h^{-1}$ was reached on one steam generator (the technical specification limit is 30 $L.h^{-1}$ per SG), the technical specification limit of 30 $L.h^{-1}$ per SG was challenged.

Special startup plans with specific power ramp rates including power holds based on operating experience received from EDF are used to minimise primary to secondary leak rate.

The change in the leak rate patterns coincided with the implementation of zinc addition on both units. This aspect has been investigated during an EPRI on-site assessment and their report confirms a possible relationship between zinc injection and primary to secondary leak rate [11]. Zinc injection has therefore been temporally suspended on unit 1 (in 2017) to manage the increasing primary to secondary leak rate trend observed subsequent to the initiating Zinc Programme [6]. It is intended to recommence zinc injection into unit 1 in the cycle prior to steam generator replacement or earlier, after consideration by the SGHCWG.

For unit 2, since the primary to secondary leakage is lower, the Zinc Programme continues with a target of 5 ppb in the reactor coolant.

For KNPS an Alternate pH_T Programme at lower pH is allowed to manage excessive primary to secondary leak rate [4]. This is currently being implemented on unit 1 with consent from the fuel vendor [5].

B.1.3.2 Optimisation of Reactor Coolant Dissolved Hydrogen Concentration

The operational reactor coolant dissolved hydrogen control-point is below the optimum level for mitigation of PWSCC [1]. The reason for this is the limit on the volume control tank (VCT) pressure set-point. It is intended to increase the VCT pressure after implementation of a modification to the set-point [2].

However, since commencement of operation at reduced temperature (ORT) in 1994, Engineering has been monitoring the progression of axially oriented PWSCC (the dominant form of SG tube degradation experienced at KNPS, with over 43% of tubes cracked on SG 2 of unit 1). In the past 10 years the average crack growth rates have dropped to below 0,1 mm per cycle [3]. Steam generator engineering indicates that PWSCC is well under control and therefore the current dissolved hydrogen values are considered temporarily acceptable by Engineering, until the VCT modification is implemented.

B.1.3.3 Steam Generator Replacement

KNPS currently operates with the only remaining Mill Annealed Alloy 600 PWR SGs. Steam generator replacements (SGR) are planned for refuelling outage X25 in 2021. The safety studies for SGR have been completed and submitted to the regulator (NNR) for approval.

The plant chemistry aspects related to SGR are being monitored by the Chemistry Group and the associated actions are tabled at the Technical Review Committee (TRC) [7].

B.1.3.4 Reactor Pressure Vessel Head Replacement

The unit 2 reactor pressure vessel head must be replaced in the near future. Although there are no expected chemistry transients related to this, it is noted as a potential chemistry risk under the topic of large component replacement [7].

B.1.3.5 Thermal Power Uprating

Thermal Power Uprating of the units is being considered for implementation after SGR. This aspect is noted in that it may affect the primary chemistry strategy, but detailed actions for this have not yet been established. The TRC will track this topic.

B.1.3.6 Further increase in pH_T

It is intended to increase the pH_T to 7,4 from start of the cycle after SGR. Constant elevated pH_T reduces corrosion and corrosion product transport and hence also the production of activation products which lead to source term build-up, hot spots and high out-of-core radiation fields. To achieve this increase in pH_T, the current fuel manufacturer limitation on lithium exposure will need to be changed. Preliminary informal discussions with Reactor Fuel Engineering and the fuel manufacturer suggest that that there will be agreement and support for this change.

B.1.3.7 Use of Potassium Hydroxide for pH_T Control

Potassium hydroxide is being qualified by EPRI for use in PWRs. This will be more cost effective and limit the vulnerability to enriched ^7LiOH supply. Potassium has other advantages such as potentially being more beneficial for the fuel and reduces initiation of irradiation accelerated stress corrosion cracking because of lower lithium. This is to be considered after SGR.

B.1.4 References

[1] RCP Dissolved Hydrogen Increase Recommendation For Koeberg Power Station, NSC-019-16, N van Eeden, Eskom, September 2016

[2] Modification to Increase RCP DH, V Zatu, ECMC approved, 07 March 2017

[3] Email correspondence, RE: SG crack stabilisation, H Nicolson, September 2017

[4] Safety Screening S2016-0574, December 2016

[5] Email correspondence, RE: Koeberg Unit 1 Startup Chemistry Plan for cycle 24, R Carlsson, Westinghouse, May 2018

[6] KNPS Plant Chemistry Proposal for the Primary Coolant Zinc Injection Strategy to Manage Primary to Secondary Leak Rates, NSC-021-17, N van Eeden, Eskom, October 2017

[7] Technical Review Committee Minutes, H Morland, Eskom, TRC-06-2018, August 2018

[8] Chemical Restrictions and Control at Koeberg (CRACK) Programme, KAA-751

[9] Chemical Control of a Unit During Shutdown, KWC-CH-004

[10] Chemistry Control of a Unit During Startup from Normal Shutdown to Full Power Operation, KWC-CH-001

[11] EPRI Assessment of Primary Coolant Zinc at Koeberg NPS, 2017

B.2 Secondary Water Chemistry Management

Secondary Water Chemistry Management:

- Explains how the chemistry control practices applied at KNPS support the Programme objectives (i.e. the five objectives given in § 5);
- Provides an historical overview and milestones of secondary chemistry;
- Considers technical aspects and future initiatives to further optimise and develop the Programme.

The steam generators are prioritised because they are the pressure boundary between primary and secondary, which has nuclear safety significance. The other priority areas are those susceptible to FAC such as the moisture-separator-reheaters (MSRs), extraction lines and the feed-heaters.

The following key components are considered in the secondary chemistry programme in the order of priority based on the chemical environment and material:

Steam Generators, Moisture Separator Reheaters, High Pressure Extraction Lines, Low Pressure Extraction Lines, High Pressure Feed-heaters, Low pressure Feed-heaters, High Pressure Turbine, Low Pressure Turbines, Feedwater Piping, Condensate Piping, Condenser, Make-up Water-Treatment-System, SG Blowdown Demineraliser Vessels, Condensate Demineraliser Vessels and Chemical Feed System.

B.2.1 Secondary Chemistry Control Practices in Support of the Programme Objectives

To meet the objectives, KNPS maintains an alkaline pH in the secondary circuit and chemically reducing conditions in the steam generators. Ammonia and ethanolamine (ETA) are the pH control agents. Hydrazine is added into the feedwater to maintain reducing (low dissolved oxygen) conditions in the SGs to protect the nickel alloys. Reducing conditions support the formation of a magnetite protective oxide layer in the ferrous feed-trains. Magnetite is susceptible to FAC, and therefore ETA ensures that the two-phased regions are adequately protected thereby reducing iron transport into the SGs.

Contaminant minimisation (ALARA Chemistry) is practiced at KNPS. This lowers the amount of corrosion supporting species present in the SGs. A measured approach is taken since ALARA Chemistry involves higher cost, so it is applied rationally, ensuring that the plant remains comfortably within the technically justified limits and contaminants are kept as low as achievable.

During shutdown of the plant for refuelling outage, the plant is intentionally held in a low-temperature-soak for 12 hours to remove contaminants from the crevices and occluded areas in the SGs.

During outages the plant is conserved by implementing appropriate lay-up methods to prevent deterioration of the materials. Foreign material is kept excluded from the systems and cleanliness inspections are performed where intrusive work was performed. Only approved chemicals are used on the plant.

During startup, a Chemistry hold point is part of the plan to ensure that the systems are flushed and that the chemical specifications are met before increasing reactor power beyond the mid power level (> 30% Pn).

Chemistry Programme Objective	**Impact of Secondary Control**
Protect the SGs from degradation.	All chemical parameters are controlled within the target range. Reducing conditions protect the SG-tubing.
Minimise FAC and corrosion product transport.	ETA and ammonia are added to increase the pH. Alkaline conditions reduce magnetite solubility which reduces corrosion product transport.
ALARA Chemistry – Minimising Contaminants.	Good quality make up water and maintaining low impurities. Lower impurities results in less corrosion.
Long Term Operation – minimising ageing effects.	Favourable chemical conditions support LTO and minimise component ageing.

Table 1: Impact of Secondary Chemistry Control vs the Programme Objectives

The mandatory parameters for secondary system chemical control are; SG blowdown pH_{25}, cation conductivity and sodium. Feed-water dissolved oxygen and hydrazine are also mandatory control parameters.

These are control parameters with specific operating limits, action levels (ALs) and surveillance frequencies which are detailed in OTS-KCS (§ 3.2 [6]) along with the actions to take when entering ALs.

The performance indicators include; steam generator blowdown sodium (APG), chloride and sulphate and also feed-water (AHP) iron and copper. The current and historical data is on the Laboratory Information Management System (LIMS) database.

The technical basis for each parameter, action levels, surveillance frequencies and associated risks are provided in Attachment A.

Table 2 shows the average values for the main secondary chemistry parameters from recent cycles.

Cycle	**SG Na ppb**	**SG Cl ppb**	**SG SO_4 PPB**	**FW diss. O_2 ppb**	**FW N_2H_4 ppb**	**FW Fe ppb**
122	0,42	1,59	0,84	0,52	84,78	3,65
222	0,45	2,05	0,70	0,53	85,92	2,69
123	0,42	3,02	0,80	0,78	89,80	2,72
223	0,57	1,59	1,12	0,72	87,10	3,40

Table 2: Average secondary chemistry parameters for recent cycles for unit 1and 2

B.2.2 Events Impacting Secondary Chemistry

The units were commissioned in 1984 (unit 1) and 1985 (unit 2) under ammonia / hydrazine all volatile treatment (AVT). The contractor's secondary circuit $pH_{25°C}$ feedwater specification was 8,8 to 9,2, and the units were commissioned at a $pH_{25°C}$ of 9,2. Later the pH target was changed to 9,4 because of concerns over flow accelerated corrosion (FAC). Originally condensate polishing was at full flow but it was reduced to 40% (1500 $m^3.h^{-1}$) flow in 1986 to save on chemicals and regenerations, which had increased as a consequence of the increased ammonia concentration.

The inspection and monitoring programme that began in the second half of the 1980s confirmed that two-phase FAC was the major problem confronting KNPS and identified the moisture-separator-re-heaters as probably the most affected components at that stage. The target feed water $pH_{25°C}$ was raised to 9,65 in 1989 by increasing the ammonia dosing and reducing the condensate polishing to 27% (1000 $m^3.h^{-1}$) flow for normal operation. In 1994, it was decided to maintain the condensate polishing plant (CPP) in bypass mode and only place it in service when required.

Further changes to the secondary chemistry regime for FAC mitigation were considered. Hi-AVT by increasing feed water $pH_{25°C}$ to 10 with higher ammonia concentration was proposed but was judged to be impractical and uneconomical at the time. This related to CPP operation and certain copper alloy components that would have had to be replaced.

Another option was the use of advanced amines. Elecrtricité de France (EDF) had started using morpholine as alternative alkalising agent on several of their units. Morpholine was not deemed feasible for KNPS because of the probability of decreasing the service lifetime of the CPP resins, associated costs and other factors.

Experience from the United States was more favourable towards the use of ethanolamine (ETA) in that the measurements from plants operating with ETA could demonstrate significant reductions in iron transport to the SGs.

ETA was finally selected as the preferred pH agent for KNPS as opposed to the alternative secondary treatment technologies available at the time to combat FAC. Plant chemistry, design and financial aspects were considerations in the decision.

ETA testing began from August 1997 on unit 1. The objective was to maintain an ETA concentration of 4 $mg.kg^{-1}$ in the heater drains tank, and this was achieved by maintaining the feedwater ETA concentration at 2 $mg.kg^{-1}$.

The KNPS units were officially converted to ETA conditioning during 1999 (unit 1) and 2000 (unit 2) with hydrazine as oxygen scavenger, and the units were still supplemented by ammonia injection to achieve the target feedwater $pH_{25°C}$ of 9,60 – 9,65. The ETA concentration was intended to target a concentration of 3 mg $ETA.kg^{-1}$ as measured at the heater drains tank. This was determined to be sufficient to ensure an elevation of 1 pH unit above neutral in the most affected two phase areas (moisture separator-reheaters and bled steam lines to the second stage high pressure heaters).

In 2012 the secondary system chemistry was optimised based on the operating experience from Koeberg and international experience (§ 3.2 [18]).

At every refuelling outage the SGs are sludge-lanced and the sludge weight determined. The decrease in sludge removed gives an indication of the effectiveness of the treatment regime.

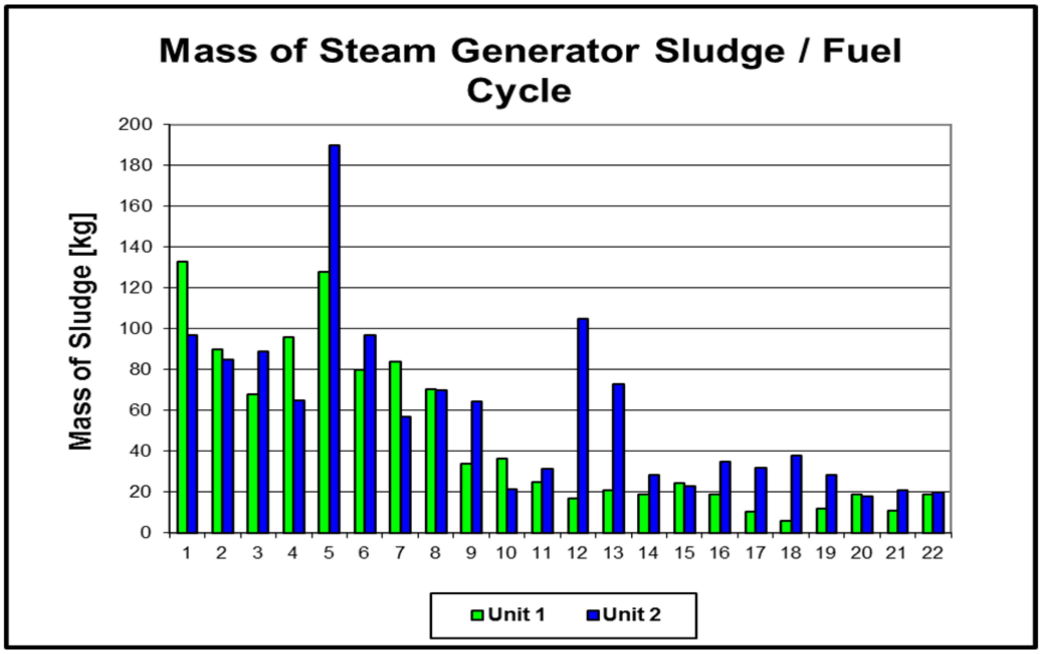


Figure 1. Sludge removed from SGs / Fuel Cycle

B.2.2.1 Contamination Events and Issues

There have been several notable contamination events over the years. Both units have experienced condenser tube leaks which have generally been well managed and contained by operating the condensate polishing plant followed by repair of the affected condenser water box by plugging the affected tubes.

On 21 June 2016 during re-commissioning of 2 APP 001 PO (electric feedwater pump) after the 6Y overhaul, Zone 5 on SG water sodium content was entered (126 ppb). OTS event, RP - APG 4 was declared with fallback to SD / SG within 1 hour and load had to be reduced to 950 MWe. The event occurred due to inadequate reinforcement of procedure usage requirements in Chemistry and incomplete reading of the *Note* in the procedure resulted in inadequate review of the procedure [1]. The SG blowdown (APG) specifications have subsequently been reviewed, and the zone diagrams have been replaced with Action Levels in (§ 3.2 [6]).

Component replacement and refurbishment work during outages has been a major source of sodium contamination on both units over several cycles.

Incidents after turbine replacements on both units gave chemistry transients on startup associated with the corrosion inhibitor being washed off with the steam.

During periods of high water use such as at startup of a unit, the SG chloride increases rapidly because of organochlorides being present it the makeup water [2].

The major source of contamination is maintenance work at refuelling outages [3]

Below is the CPI Chart showing contamination events:

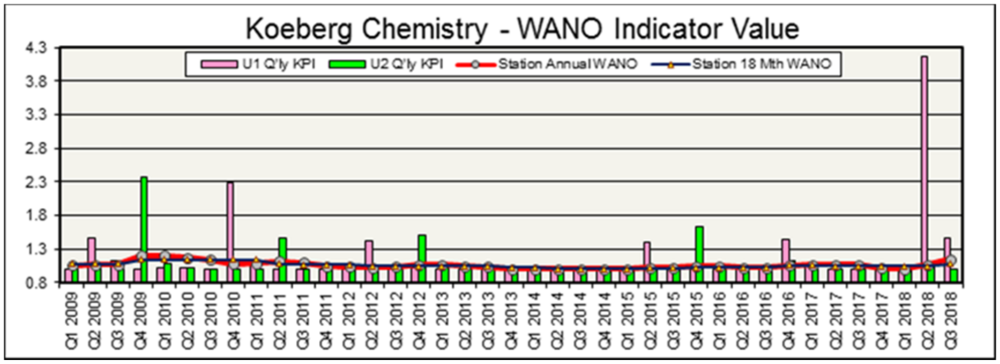


Figure 2. Chemistry Performance Indicator Chart showing contamination events

The peaks relate to plant start-ups after refuelling outages where there was component replacement, refurbishment and intrusive work performed on the secondary plant.

B.2.3 Technical Issues and Future Initiatives to Develop and Optimise the Programme

This section relates to technical aspects and future initiatives to develop and optimise the Programme.

B.2.3.1 Management of the effect of Primary to Secondary Leakage

The KNPS SGs are due for replacement. The current SGs have known tube leaks and these have an impact on the secondary plant chemistry.

A major technical item for KNPS for secondary plant chemical control is specifically the high primary to secondary startup leakrates. This influences the SG pH and also exhausts the blowdown demineralisers, prematurely releasing contaminants into the condenser. This release in turn increases the contaminant concentrations in the SGs.

On unit 1, approximately 4 kg per day of boric acid enters the secondary by leakage when the primary boron concentration is at its maximum (beginning of cycle). This same issue exists on unit 2 but the leak-rate is significantly lower and therefore the effect also proportionally less significant.

The plant chemists manage this situation by monitoring the steam generator chemistry closely and changing out the blowdown resins when they exhaust. Initially it is necessary to reduce ETA and increase ammonia, to reduce the loading on the blowdown demineralisers. The increased use of resin stresses the radioactive waste management team in terms of resources and space.

A detailed strategy has been developed to manage the secondary chemistry with primary to secondary leakage [4].

The objective is to optimise the SG chemistry within the limits (in KCS-OTS (§ 3.2 [6])) while also balancing plant constraints and operating considerations.

B.2.3.2 Future Initiatives

- Review of chemistry specifications for new materials associated with replacement steam generators.

- Considering film forming amine (FFA) application for conservation of plant during the SGR outages.

B.2.4 References

[1] Apparent Cause Evaluation Report from PN 93127 - Re-commissioning of 2 APP 001 PO, E Olivier, July 2016

[2] An Organic Profile of a Pressurised Water Reactor Secondary Plant, Power Plant Chemistry International Journal 14 (7), N van Eeden, MB Stwayi and G Gericke, 2012

[3] Apparent Cause Evaluation Report from CR 103483 - Elevated sodium concentration detected post maintenance period during outage 123, NP Daniels, July 2018

[4] Chemistry Management Strategy for Elevated SGLR, P Lotz, J Williams, F Matthee; K Pillay; K Ditlhake and M Stwayi, 05 January 2017

ATTACHMENT C
REVIEW AGAINST THE IAEA - SALTO ATTRIBUTES FOR AGEING MANAGEMENT

This Attachment is included as a review of the KNPS Chemistry Programme to ensure completeness and demonstrating that that the strategies and controls are aligned to the IAEA Safety Aspects of Long-Term Operation (SALTO) Attributes related to ageing management of nuclear power plant (§ 3.2 [21]). These Attributes are covered throughout the justification document and its attachments without specifically indicating which attribute is being addressed for each case. Therefore, interpretation is provided below using some of the examples for primary and secondary chemistry to show the rationale for how each attribute is being addressed.

C.1 Scope of the Ageing Management Programme

The chemistry strategy is designed to ensure that the ageing of materials is managed effectively taking into account the operational needs. E.g. corrosion mitigation is a key objective in primary and secondary chemistry. The Programme includes components in the reactor coolant system, the engineered safety features, the auxiliary systems, and the steam and power conversion system. This addresses the components subject to ageing management review that are exposed to a treated water environment controlled by the water chemistry programme.

C.2 Preventative Action to Minimise and Control Ageing Degradation

Limits are in place to minimise harmful impurity (ALARA Chemistry) entry into the systems. High purity chemical agents and effective water production are examples of preventive actions taken to minimise and control ageing degradation. For primary chemistry, elevated pH_T is another example.

For secondary plant chemistry, the application of ETA treatment for control of FAC is an example of a preventative action to minimise and control ageing degradation. ETA concentration, pH, conductivity and corrosion product transport are monitored under a specific documented surveillance programme.

Conservation of plant system is implemented to minimise and control ageing degradation during non-operational periods (outages).

C.3 Detection of Ageing Effects

The plant on-line and analytical chemistry routine surveillances detect any changes in plant chemistry that could cause accelerated ageing effects and provide early indications of deteriorating conditions. Analysis methods, analysis frequency, sampling methods, sampling locations and data collection are defined and documented.

C.4 Monitoring and Trending of Ageing Effects

Primary and secondary chemistry conditions are monitored continuously by on-line analysers and a laboratory grab-sampling routine which are trended by the personnel at the chemistry production meeting, by studying the LIMS graphs. Indications of deteriorating chemical conditions are noted and the necessary adjustments are made. The surveillance frequency and methodologies are defined according to industry guidance and operating experience. End of cycle reviews are also performed.

C.5 Mitigating Ageing Effects

The primary plant chemistry regime, e.g. the selected pH_T, mitigates ageing effects of the materials. Limiting exposure of the materials to impurities which can initiate corrosion also mitigates the ageing effect. The secondary plant chemistry regime, e.g. the selected chemical agents (ETA, ammonia, hydrazine), mitigates ageing effects of the materials.

These aspects are well entrenched into the strategy and are a focus area of the business. The Chemistry Performance Indicator and Chemistry Effectiveness Indicators (§ 3.2 [15]) are monitored and reported on in the month-end reports

C.6 Acceptance Criteria

All system chemical analysis parameters have documented acceptance criteria to ensure that the regime is maintained within the limits and that action is taken when the action levels and limit values are exceeded (§ 3.2 [6]). In addition, conservative target values are applied, providing a margin from the limit values to allow corrective action pre-emptively, thereby preventing entering action levels. The Chemistry Programme caters for all plant operational domains and non-operational periods.

C.7 Corrective Actions

When a chemical parameter is not within the permissible acceptance criteria, there are well defined and documented actions to take, to prevent damage to plant. The corrective action process (KAA-688) is applied and the condition is investigated and corrected as soon as practical. Where deemed necessary, a formal root cause determination and corrective actions to prevent recurrences are applied as part of the process. Chemistry corrective actions are reviewed for effectiveness.

C.8 Operating Experience Feedback and Feedback of Research and Development Results

Operating experience feedback and feedback of research and development are regularly monitored and incorporated into the chemistry strategy after technical and safety evaluations. KNPS has active membership with the EPRI PWR Chemistry Technical Strategy Group where industry research and experience is accessed. There is a close relationship with EDF with formal communication for technical exchanges. The Chemistry Group at KNPS has the TRC where the topics are tabled, discussed and appropriate actions are developed to improve various aspects of the business.

C.9 Quality Management

Chemistry methods are validated and results are reported subsequent to quality control (QC) samples passing statistical process control criteria. QC processes are documented for Radiochemistry and Analytical Chemistry. As part of the QC Programme, KNPS takes part in inter- and intra-laboratory comparison evaluations. A formal Quality Forum is established where all aspects related quality are discussed.

10.0 REVISION INFORMATION

EXISTING PAGE / PARA	NEW REV PAGE / PARA	
Rev. 0		First Issue
Rev. 0a		Change Number CCJ-059 – Safety Screening S2016-0574
4		Updated the table of contents page to include the Justification for Revision.
42-44 / A.5.1		Addition of an alternate lithium control strategy to the Justification for Koeberg Nuclear Power Station Chemistry Operating Specifications, KBA0022CHEMJUSTIF2.
93		Repagination due to an additional page being included into the document for Section 10.0 Justification for Revision.
Rev. 1 062-CCJ		Change number 062-CCJ – Safety Screening S2018-0058 Review and technological update to align with current international practice
22	23	A1: Boron updated for KER and SEK
38	39	A4: Oxygen updated for CEX, RRI, SRI, DEG, DEL and GST
49	51	A7: pH updated for RCP, AHP, RRI, SRI, SES, DEG, DEL, SEU, KER and SEK
52	56	A8: Conductivity updated for SEU
58	62	A11: Sodium updated for CEX, VVP and RCP/RRA
60	65	A12: Aluminium, Calcium, Magnesium added
70	77	A21: Trisodium Phosphate updated for RRI, SRI, SES, DEG and DEL
76	82	A23: Chlorine completed
79	87	B1: Primary Power Operation strategy added
83	91	B5: Secondary Plant Power Operation strategy added
throughout	throughout	Editorial: replaced “Inconel” with “nickel alloy”
throughout	throughout	Editorial: replaced “MPa” with “MPa(g)” as applicable
throughout	throughout	Repaginated for added pages
Rev. 2 074-CCJ		Change number 074-CCJ – Safety Screening S2019-0128 Review and technological update to align with current international practice
56	56	A.8: Conductivity in SEU updated
70	71	A15: Zinc added
71	73	A16: Ethanolamine and ammonia added
87	89	B1: Primary Water Chemistry Management added
91	96	B2: Secondary Water Chemistry Management added
		B2 to B4 were titles only and are removed, B5 becomes B2. B6 to B14 were titles only and are removed.
	102	Attachment C added, for the Chemistry Programme alignment to the SALTO Attributes for ageing management.
throughout	throughout	Editorial: replaced “/cm” with “.cm^{-1}”
throughout	throughout	Editorial: replaced “/kg” with “.kg^{-1}”

EXISTING PAGE / PARA	NEW REV PAGE / PARA	
Rev. 2a 080-CCJ		Change number 080-CCJ – Safety Screening S10551 Review and technological update to align with current international practice. Updates of A.10, A.13, A.14, A.22, A.19, A.20 and A.24
21	21, 22	Table extended to next page
22	23	Updated table
61	62, 63	A.10: Added Suspended Solids
69	71	A.13: Added Iron, Copper
70	72	A.14: Added Nickel, Cobalt, Chromium
78	80	A.19: Added Turbidity
79	81, 82	A.20: Added Total Organic Carbon
85	88	A.22: Included 22.4: Basis for Tritium Limiting Values
88	93	A.24: Added Lead, Manganese

11.0 Review Information

Name	Function
Nkani Mahlangu	Operating Procedures
Indrin Naidoo	Engineering Programmes
Herman Bosman	Probability Safety Analysis
Stephen Pietersen	Radiation Protection
Mandisi Stwayi	Nuclear Chemistry
Deon Jeannes	Nuclear Environmental – special review required for this ChemJustif2
Luqmaan Salie	Steam Generators Engineering Programme