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Content

Page

1. Introduction.....	6
2. Supporting Clauses	7
2.1 Scope	7
2.1.1 Purpose.....	8
2.1.2 Applicability	8
2.1.3 Effective date	8
2.2 Normative/Informative References.....	8
2.2.1 Normative.....	8
2.2.2 Informative	9
2.3 Definitions	12
2.4 Abbreviations	14
2.5 Roles and Responsibilities	15
2.6 Process for Monitoring	15
2.7 Related/Supporting Documents	15
3. Introduction – Feasibility Study.....	15
3.1 Existing Design	15
3.2 Problems / Opportunities with the Existing Design	16
3.3 Benchmarking	17
3.3.1 EDF Position	17
3.3.2 Position of other utilities / Statutory and Regulatory Requirements	20
3.4 Options considered	26
4. Success Criteria	27
4.1 Preliminary classification.....	27
4.2 Quality Requirements.....	27
4.3 General Design Criteria.....	27
4.4 Performance Criteria	28
4.5 Safety and Environmental Requirements.....	28
4.5.1 Nuclear Safety	28
4.5.2 Conventional Safety.....	28
4.5.3 Environmental requirements	28
4.6 Supplier Development and Localisation (SD&L)	29
4.7 Testing and Commissioning.....	29
4.8 Other Critical Success Criteria	29
5. Rationale for selection of options	30
6. Description of Options	30
6.1 Option 1 – Maintain the status quo – Do nothing option	30
6.1.1 Technical Description.....	30
6.1.2 Description of Operation	31
6.1.3 Risks	31

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6.2	Option 2 - Replace hydrazine with another wet lay-up oxygen scavenger	31
6.2.1	Technical Description.....	31
6.2.2	Description of Operation	34
6.2.3	Risks	34
6.3	Option 3 - Significantly reduce the need for an oxygen scavenger during wet lay-up conditions.....	35
6.3.1	Technical Description.....	36
6.3.2	Description of Operation	48
6.3.3	Risks	48
6.4	Option 4 - Chemical decompose hydrazine into inert components before conventional discharge.....	63
6.4.1	Technical Description.....	63
6.4.2	Description of Operation	64
6.4.3	Risks	65
7.	Decision Matrix Table	67
8.	Cost Analysis of Option	69
8.1	Option 1 – Maintain the status quo – Do nothing option	69
8.2	Option 2 - Replace hydrazine with another wet lay-up oxygen scavenger	69
8.3	Option 3 - Significantly reduce the need for an oxygen scavenger during wet lay-up conditions.....	70
8.4	Option 4 - Chemical decompose hydrazine into inert components before conventional discharge.....	70
9.	Conclusions	70
9.1	Option 1 – Maintain the status quo – Do nothing option	70
9.2	Option 2 - Replace hydrazine with another wet lay-up oxygen scavenger	70
9.3	Option 3 - Significantly reduce the need for an oxygen scavenger during wet lay-up conditions.....	71
9.4	Option 4 - Chemical decompose hydrazine into inert components before conventional discharge.....	72
10.	Recommendations.....	72
11.	Acceptance.....	73
12.	Revisions	73
13.	Development Team	73
14.	Acknowledgements	73
15.	Appendices.....	73

Figures

Figure 1: Decomposition of carbohydrazide at elevated temperatures.....	33
Figure 2: Decomposition of carbohydrazide below 100°C	34
Figure 3: Octadecylamine (ODA), CAS-No. : 124-30-1	36
Figure 4: N-oley 1, 3-propanediamine (OPDA), CAS-No. : 7173-62-8	36

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Figure 5: Phase diagram for ODA in water [18]	37
Figure 6: Micelle formation and structure in water	38
Figure 7: Schematic representations of FFA films: monoamine (left), polyamine (right)	39
Figure 8: Surface complex formation between an amine and an oxidized iron surface – dashed lines indicate ionic interaction / hydrogen bonding.	40
Figure 9: Appearance of a boiler tube with a “good” hydrophobic coating. The angle between the side of the bubble and the vertical reportedly should be less than 90°, or greater than 90° when measured from the horizontal plane inside the bubble to edge of the bubble-water-surface interface.	41
Figure 10: Appearance of a boiler tube with a “moderate” hydrophobic coating.	42
Figure 11: Appearance of a boiler tube with a “poor” hydrophobic coating.	42
Figure 12: Contact angles measured on (a) the bare carbon steel and (b) carbon steel treated ODA	43
Figure 13: Relative increase in the measured heat-transfer coefficient.....	47

Tables

Table 1: Preliminary Purity Specifications for Film Forming Products (FFA products)	51
Table 2: Decision Matrix Table for reduction of hydrazine discharges at KNPS.....	68

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1. Introduction

The internal surfaces of the feedwater sections of the secondary side plant (ARE, ABP, AHP, APA, APP and CEX) systems, and secondary side of the RCP steam generators at KNPS are susceptible to secondary side corrosion. This challenges the integrity and efficiency of the plant. As such, a stringent chemistry regime is employed to prevent general corrosion of the mainly carbon steel feed-train and to maintain low dissolved oxygen concentration to protect the steam generator nickel-alloy tubing material [6], [7]. The current secondary side chemistry programme is an all-volatile treatment in a reducing environment (as it relates to ORP) which, amongst others, seeks to control the oxidation of iron, and promote the formation of a protective magnetite (Fe_3O_4) film. During normal operation this is achieved through maintaining a pH of between 8.0 – 10.5, using ammonia and/or alkalising amine dosing, and a reducing agent, hydrazine.

Hydrazine is an inorganic compound with the chemical formula N_2H_4 . It is a colourless, flammable liquid with an ammonia-like odour. It is a strong reducing agent and is used as an oxygen scavenger to control concentrations of dissolved oxygen to reduce corrosion. Hydrazine requires a dosing ratio of at least 1:1 (scavenger to: O_2 ratio). The following reactions are predominant [20]:



During wet lay-up, hydrazine is also added as a wet lay-up chemical (in mg/kg concentrations) for the conditioning and conservation of feedwater sections of the secondary side plant systems. It is also used on the auxiliary boilers (XCA) and the secondary side of the steam generators (SGs) during periods of non-operation (e.g., outages or standby mode for the auxiliary boilers). It is used in the secondary side water at power operations (in $\mu\text{g/kg}$ concentrations) and is introduced as an oxygen scavenger in the primary system at start-up following an outage, where any residual hydrazine thermally decomposes during at power operations. Hydrazine is a toxic substance to both marine ecology and humans and is dangerously unstable unless handled in solution.

The National Environmental Management: Integrated Coastal Management Act of 2008 requires the approval of a section 69 Coastal Waters Discharge Permit (CWDP) for the discharge of effluent into the sea from KNPS. As part of the CWDP application, a marine dispersion and ecological assessment was performed for the CWDP against the assessment criteria set out by the environmental authorities. The assessment showed that the current hydrazine discharges, arising from the use of hydrazine as an oxygen scavenger for wet lay-up and auxiliary boiler preservation, do not meet the ecological criteria at the end of the initial mixing zone. As a result, the specialists have recommended that the hydrazine discharges are reduced [4].

Currently, for outage preservation, only one type of lay-up practice is chosen per outage. This is typically dependent on whether feed train maintenance is scheduled for the outage. Once wet lay-up has been implemented (which is preferred), it is extremely labour intensive and difficult to implement dry lay-up, and impossible to re-implement wet lay-up during the same outage. Also, if dry lay-up has been implemented from the start of the outage to allow for feed train maintenance, it is impossible to implement to wet lay-up during the same outage. EPRI has stated that dry lay-up is only to be considered for long outages [19], and where strict environmental controls can be maintained at all times.

Due to the method in which wet lay-up needs to be applied, i.e., during unit shutdown, (which is in-line with good international practice and also the only practical way of ensuring the entire feed train is protected) it is not possible to implement wet lay-up and then do feed train maintenance and

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effectively protect the feed train thereafter. It is also not possible to re-dose hydrazine into the feed train and obtain a homogeneously mixture without at least one CEX pump in-service [71].

To this end, a project has been raised to reduce hydrazine (and other specific) discharges at KNPS. This feasibility study focuses on reduction of hydrazine related to its use as a wet lay-up oxygen scavenger for the feed train. This project does not focus on the reduction of hydrazine during at power operations, primarily due to the significantly lower concentrations used compared to wet lay-up (three orders of magnitude less). The use of hydrazine during power operations is still regarded as good practise and the concentration of hydrazine during power operations will not result in a discharge that exceeds ecological guidelines at the point of discharge. Notwithstanding the above, it is recommended that as a separate study, carbohydrazide be considered and investigated as a safer alternative to hydrazine (from a personnel point of view) as an oxygen scavenger for use during at power operations, and for boiler preservation, without draining prior to start-up. No recommendation is made on the use of carbohydrazide as a primary side start-up oxygen scavenger, as the thermal decomposition with CO₂ as by product will have unwanted implications on primary side chemistry, and lead to C¹⁴ production; a radiological isotope to be avoided.

The work done in this feasibility study recognizes that the options identified could offer some benefits across wet lay-up and during at power operations, however the optimization of those benefits does not form part of the scope of this feasibility study. Any positive benefit for at power operations are unintended and the specific studies required for implementation for at power operations are excluded from the scope of this feasibility study and should implementation during at power operations be desired, it will require further study at a later stage.

This feasibility study compares four options, namely:

- Do nothing option, i.e., maintain status quo,
- Replace hydrazine with another wet lay-up oxygen scavenger. This replacement chemical would need to be as effective as hydrazine for dissolved oxygen and ECP / ORP control, and less toxic than hydrazine with respect to human health and the marine environment.
- Reduce the need for an oxygen scavenger during wet lay-up conditions by inhibiting the oxygen oxidation process at the metal surface, i.e., using a barrier chemical. This would be possible using film forming amines (specifically ODA) to form a hydrophobic layer on the wetted surface of components.
- Use mechanical and chemical methods (or a combination of the two) to completely eliminate/decompose hydrazine into inert components (nitrogen and water) before discharge through KER and SEK systems into the CRF outfall.

Based on the scope of work and the decision matrix table discussed in Section 7, this feasibility study determines that use of film forming amines (FFAs), specifically those based on octadecylamine (CAS-no.: 124-30-1), is the most feasible solution to reduce hydrazine discharges at KNPS, to within the site specific ecological criteria, and satisfy the criteria set out in this feasibility study.

2. Supporting Clauses

2.1 Scope

This feasibility study focuses on reduction of hydrazine related to its use as a wet lay-up oxygen scavenger. This feasibility study differs from most at KNPS, in that its scope is limited to the assessment of alternative chemicals and chemical methods related to the use of hydrazine as a wet

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lay-up oxygen scavenger and does not cover the feasibility of various implementation options or methods. The implementation studies will be covered under a commercial enquiry following the acceptance of the recommendations and conclusions in this feasibility study. This feasibility study further does not focus on the reduction of hydrazine during at power operations, primarily due to the significantly lower concentrations used when compared to wet lay-up (three orders of magnitude less).

The work done in this feasibility study recognizes that the options identified could offer some benefits across wet lay-up and during at power operations, however the optimization of those benefits does not form part of the scope of this feasibility study. Any positive benefit for at power operations is unintended and the specific studies required for implementation thereof is excluded from the scope of this feasibility study. Should implementation during at power operations be desired, it will require further study at a later stage.

2.1.1 Purpose

The main purpose of the feasibility study is to:

- Document success criteria and compare the selected options against their success criteria to determine the most feasible option.
- Providing sufficient technical and operational detail about the selected option to ensure that the option can be implemented and without compromising nuclear/conventional safety.
- Outlining the main project strategies, the risk, and the implementation strategy of the options.
- Provide the necessary information on costing.

This feasibility study specifically excludes the reduction of hydrazine on the Auxiliary Steam Production (XCA) system boilers as these are being covered under a specific test application as described in Reference [74].

2.1.2 Applicability

This document is applicable to the Koeberg Nuclear Power Station.

2.1.3 Effective date

The document is effective from authorisation date.

2.2 Normative/Informative References

2.2.1 Normative

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2.3 Definitions

- 2.3.1 Adsorption:** A surface phenomenon involving the adhesion of atoms, ions, or molecules onto the surface of another substance. This process creates a film of the adsorbate on the surface of the adsorbent. The adsorption process is generally classified as physisorption (characteristic of weak van der Waals forces) or chemisorption (characteristic of covalent bonding). It may also occur due to electrostatic attraction.
- 2.3.2 Aliphatic:** Any chemical compounds belonging to the organic class in which the atoms are connected by single, double, or triple bonds to form nonaromatic structures. Besides hydrogen, other elements can be bound to the carbon chain, the most common being oxygen, nitrogen, sulphur, and chlorine.
- 2.3.3 Alkyl:** An alkyl is a functional group of an organic chemical that contains only carbon and hydrogen atoms, which are arranged in a chain.
- 2.3.4 Carboxylic acid:** A carboxylic acid is an organic acid that contains a carboxyl group attached to an R-group. The general formula of a carboxylic acid is R-COOH, with R referring to the alkyl group.
- 2.3.5 Controlled Disclosure:** Controlled disclosure refers to disclosure of information to external parties (either enforced by law or discretionary).

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- 2.3.6 Fatty acid:** A fatty acid is a carboxylic acid with a long aliphatic chain, which is either saturated or unsaturated.
- 2.3.7 Film Forming Amine:** FFAs belong to chemical substances of the class of oligo alkylamino fatty amines, the simplest one being Octadecylamine (ODA).
- 2.3.8 Film Forming Amine Product:** FFA products are blends of FFAs and other products such as alkalizing amines, stabilisers, preservatives, or solubilising agents, which are combined to achieve successful industrial application as specific, chemically pure FFAs on their own might not achieve the desired result on their own on an industrially scale.
- 2.3.9 Hydrophilic:** A hydrophilic molecule, or portion of a molecule, is one whose interactions with water and other polar substances are more thermodynamically favourable than their interactions with oil or other hydrophobic solvents. They are attracted to water molecules and tend to dissolve in water. They are typically charge-polarized and capable of hydrogen bonding.
- 2.3.10 Hydrophobic:** A hydrophobic molecule, or portion of a molecule, is one whose interactions with nonpolar substances are more thermodynamically favourable than their interactions with water or other hydrophilic solvents. They repel water molecules and tend to dissolve in oil, alcohol, and other nonpolar solvents. Hydrophobic substances generally aggregate and do not disperse when placed in water.
- 2.3.11 Leidenfrost effect:** A physical phenomenon in which a liquid, close to a surface that is significantly hotter than the liquid's boiling point, produces an insulating vapour layer that keeps the liquid from boiling rapidly. As it relates to nucleate boiling, this is undesirable.
- 2.3.12 Lipid:** Is chemically defined as a substance that is insoluble in water (polar solvent) and soluble in alcohol, and other nonpolar solvents.
- 2.3.13 Micelle:** Lipid molecules that arrange themselves in a spherical form in aqueous solutions. The formation of a micelle is a response to the amphipathic nature of fatty acids, meaning that they contain both hydrophilic regions (polar head groups) as well as hydrophobic regions (the long hydrophobic chain). Micelles cannot form below the Krafft temperature (Refer to Figure 5 and Figure 6.)
- 2.3.14 Oxidation:** The loss of electrons from an atom or molecule, typically in a chemical reaction.
- 2.3.15 Redox potential:** Also known as Oxidation-Reduction Potential (ORP). A numerical index of the intensity of oxidizing or reducing conditions within water systems containing different types of oxidizing and reducing substances. ORP is measured in millivolts (mV). Positive values for ORP indicate oxidizing conditions, whereas negative values indicate reducing conditions.
- 2.3.16 Side Effect:** In this context the term side effect refers to a relatively minor issue exclusive of a safety concern.
- 2.3.17 Surfactant:** Surfactants are molecules that spontaneously bond with each other to form sealed bubbles. Surfactants are compounds that lower the surface tension between two liquids, between a gas and a liquid, or between a liquid and a solid.

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2.3.18 All-Volatile Treatment: AVT is defined as the exclusive use of volatile conditioning agents. Volatile chemicals evaporate from the water into the steam in a gaseous form. AVT water treatment can generally be divided into two categories: AVT (R) for reducing services and AVT (O) for oxidizing services. When steam condenses, the chemicals dissolve into the water. They do not form a solid phase and thus they do not form a scale or deposit on heat transfer surfaces.

2.3.19 AVT (R): Is defined as All Volatile Treatment that employs a reducing agent such as hydrazine or other oxygen scavengers. This results in a low (highly negative) electrochemical potential (ECP) or oxidation/reduction potential (ORP). Thus, the highest possible oxidation state iron in the oxide layer is magnetite.

2.4 Abbreviations

Abbreviation	Explanation
ABP	Low pressure feedwater heater system
AHP	High pressure feedwater heater system
APA	Motor-driven feedwater pump
APP	Turbine-driven feedwater pump
ARE	Feedwater flow control
ATE	Condensate polishing system
AVT(R)	All Volatile Treatment (Reducing)
C	Carbon
CEX	Condenser extraction system
CWDP	Coastal Waters Discharge Permit
EDF	Electricité de France
EIS	Electrochemical impedance spectroscopy
ETA	Ethanolamine
FAC	Flow-accelerated corrosion
Fe	Iron
FFA	Film Forming Amine
H	Hydrogen
KER	Monitoring and discharge of nuclear island liquid radwaste
KNPS	Koeberg Nuclear Power Station
IPD-K	Integrated Plant Design - Koeberg
LMWOA	Low molecular weight organic acid
N	Nitrogen
Na	Sodium
O	Oxygen
ODA	Octadecylamine (C ₁₈ H ₃₇ NH ₂)
ORP	Oxidation-Reduction Potential
PLCM	Project Life-Cycle Management

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Abbreviation	Explanation
PPE	Personal Protective Equipment
RCP	Reactor coolant system
S	Sulphur
SEK	Monitoring and discharge of conventional island liquid waste
SG	Steam generator
XCA	Auxiliary steam production system
XPS	X-ray photoelectron spectroscopy

2.5 Roles and Responsibilities

NPM

- i) Providing project management and PLCM process support for the project, in line with Nuclear Project Management's FOS/mandate.

Chemistry

- i) Providing plant operational support as it relates to the plant chemistry parameters and data, in line with the Chemistry department's FOS/mandate.

Design engineering

- i) Providing the engineering and technical support, compiling the feasibility study, technical requirements, performing the technical tender evaluation and compiling technical tender evaluation documents for the project, in line with the Design Engineering department's FOS/mandate.

2.6 Process for Monitoring

- KNC-001, Chemistry Operating Specifications For Safety Related Systems
- KNC-002, Chemistry Operating Specifications For Availability Related Systems
- KSC-003, The Chemistry Programme

2.7 Related/Supporting Documents

N/A

3. Introduction – Feasibility Study

3.1 Existing Design

The internal surfaces of the feedwater sections of the secondary side plant (ARE, ABP, AHP, APA, APP and CEX) systems, and secondary side of the RCP steam generators at KNPS are susceptible to secondary side corrosion. This challenges the integrity and efficiency of the plant. As such, a stringent chemistry regime is employed to prevent general corrosion of the mainly carbon steel feed-train and to maintain low dissolved oxygen concentration to protect the steam generator nickel-alloy tubing material [6], [7]. The current secondary side chemistry programme is an all-volatile treatment

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in a reducing environment (as it relates to ORP) which, amongst others, seeks to control the oxidation of iron, and promote the formation of a protective magnetite (Fe_3O_4) film. During normal operation this is achieved through maintaining a pH of between 8.0 – 10.5, using ammonia and/or alkalising amine dosing, and a reducing agent, hydrazine.

Hydrazine is an inorganic compound with the chemical formula N_2H_4 . It is a colourless, flammable liquid with an ammonia-like odour. It is a strong reducing agent and is used as an oxygen scavenger to control concentrations of dissolved oxygen to reduce corrosion. Hydrazine requires a dosing ratio of at least 1:1 (scavenger to: O_2 ratio). The following reactions are predominant [20]:



During wet lay-up, hydrazine is also added as a wet lay-up chemical (in mg/kg concentrations) for the conditioning and conservation of feedwater sections of the secondary side plant systems. It is also used on the auxiliary boilers (XCA) and the secondary side of the steam generators (SGs) during periods of non-operation (e.g., outages or standby mode for the auxiliary boilers). It is used in the secondary side water at power operations (in $\mu\text{g}/\text{kg}$ concentrations) and is introduced as an oxygen scavenger in the primary system at start-up following an outage, where any residual hydrazine thermally decomposes during at power operations. Hydrazine is a toxic substance to both marine ecology and humans and is dangerously unstable unless handled in solution.

3.2 Problems / Opportunities with the Existing Design

Hydrazine is a toxic substance to both marine ecology and to human and dangerously unstable unless handled in solution. It is a known carcinogen, methanogenic, is repro-toxic and requires the strict use of PPE, include respiratory protection.

The National Environmental Management: Integrated Coastal Management Act of 2008 requires the approval of a section 69 Coastal Waters Discharge Permit (CWDP) for the discharge of effluent into the sea from KNPS. As part of the CWDP application, a marine dispersion and ecological assessment was performed for the CWDP against the assessment criteria set out by the environmental authorities. The assessment showed that the current hydrazine discharges, arising from the use of hydrazine as an oxygen scavenger for wet lay-up and auxiliary boiler preservation, do not meet the ecological criteria at the end of the initial mixing zone. As a result, the specialists have recommended that the hydrazine discharges are reduced [4]. The draft CWDP also requires that hydrazine practices are investigated for improvement. See Appendix C for the draft CWDP.

The introduction of new coastal environmental legislation as discussed above, establishes new standards for effluent management. This will require changes to Koeberg's effluent management practices. If these changes are not adopted the effluent release permit (referred to as the CWDP) may be withdrawn, directives issued by the Department of Environment Fisheries and Forestry, and the shutdown of the power station required [3].

To this end, a project has been raised to reduce hydrazine (and other specific) discharges at KNPS. This project focuses on reduction of hydrazine related to its use as a wet lay-up oxygen scavenger [2].

Currently, for outage preservation, only one type of lay-up practice is chosen per outage. This is typically dependent on whether feed train maintenance is scheduled for the outage. Once wet lay-up has been implemented (which is preferred), it is extremely labour intensive and difficult to implement dry lay-up, and impossible to re-implement wet lay-up during the same outage. Also, if

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dry lay-up has been implemented from the start of the outage to allow for feed train maintenance, it is impossible to implement to wet lay-up during the same outage. Dry lay-up of the feed train is extremely labour intensive and difficult to implement and maintain, and EPRI has stated that it is only to be considered for long outages [19], and where strict environmental controls can be maintained at all times.

Due to the method in which wet lay-up needs to be applied, i.e. during unit shutdown, (which is in-line with best international practice and also the only practical way of ensuring the entire feed train is protected) it is not possible to implement wet lay-up and then do feed train maintenance and effectively protect the feed train thereafter. It is also not possible to re-dose hydrazine into the feed train and obtain a homogeneously mixture without at least one CEX pump in-service [71].

A solution is therefore sought to allow the feed train to be suitably protected, and if necessary drained at short notice, independent of length of time after shutdown, to perform maintenance, while still protecting the feed train thereafter.

3.3 Benchmarking

3.3.1 EDF Position

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3.3.2 Position of other utilities / Statutory and Regulatory Requirements

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3.4 Options considered

Details regarding the options are discussed in Section 5, Section 6 and Section 9. The options considered are based on the chemical mechanism and physical and chemical effect of the existing oxygen scavenging chemical, namely hydrazine. The options considered also take into account international operating experience regarding implementation. The proposed options include:

- Do nothing option, i.e., maintain status quo,
- Replace hydrazine with another wet lay-up oxygen scavenger. This replacement chemical would need to be as effective as hydrazine for dissolved oxygen and ECP / ORP control, and less toxic than hydrazine with respect to human health and the marine environment.
- Reduce the need for an oxygen scavenger during wet lay-up conditions by inhibiting the oxygen oxidation process at the metal surface, i.e., using a barrier chemical. This would be possible using film forming amines (specifically ODA) to form a hydrophobic layer on the wetted surface of components.
- Use mechanical and chemical methods (or a combination of the two) to completely eliminate/decompose hydrazine into inert components (nitrogen and water) before discharge through KER and SEK systems into the CRF outfall.

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4. Success Criteria

4.1 Preliminary classification

The most stringent classification for components affected on the RCP system (secondary side of the steam generators, 1/2 RCP 001, 002 and 003 GV) is for components under classification number 0082/89Q:

- Importance Category: CSR
- Safety Class: 3
- Seismic Class: 1A
- Environmental: NEV
- Quality Level: Q2

4.2 Quality Requirements

The quality requirements for chemicals to be used in secondary side systems at KNPS are predominantly concerned with chemical purity and how this affects the associated limits on concentrations of chemicals controlled under the station chemistry performance indicators (CPI). This is done to maintain plant integrity and is discussed in References [6], [7] and [68]. In addition, chemicals to be used must undergo CRACK registration [67] and limitations on use may be imposed.

It is recommended that in line with EPRI guidance, as contained in References [18] and [19], impurity levels for the FFA to be used must be kept in line with existing limits for ETA, and that the impurity levels for hydrazine alternatives must be kept in line with existing limits for hydrazine. This is due to the dosing concentrations for FFA being similar with those of ETA.

As part of the test application for the use of FFAs in the XCA boilers, octadecylamine, has been registered as CRACK approved in July 2020. [72], [73].

4.3 General Design Criteria

The general design criteria used in deciding on the various options are:

- The option must be compatible with the existing chemistry regime [6], [7], [67], [68].
- The option must maintain plant integrity during lay-up conditions, through either:
 - Preventing oxygen from reacting with the metal surface through either the use of an oxygen scavenger, i.e., a replacement for hydrazine, or
 - Preventing oxygen from reaching the metal surface/s, i.e., the use of a physical coating or chemical barrier.
- The option must not have an unacceptable negative impact on normal plant integrity and operations during at power conditions.
- The chemical to be used must have a track record for the intended use within the nuclear power generating industry.
- The option must meet the objectives as it relates to environmental requirements identified in Section 4.5.3.

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4.4 Performance Criteria

The operational performance criteria used in deciding on the various options are:

- Operator burden must be consistent with current duties.
- The option must be compatible with the existing chemistry regime [6], [7], [67], [68].
- Any chemicals must be non-toxic to marine organisms or be discharged at a concentration and rate which is not harmful to marine organisms, as defined by the ecological studies as part of the CWDP and its appendices [4].
- If a coating is selected, application or dosing must be done during the period prior to outage, and not require reapplication during the outage or lay-up period.
- Maintenance of the feed train must be readily possible without the need for burdensome lay-up practices, at any point during an outage.

4.5 Safety and Environmental Requirements

4.5.1 Nuclear Safety

There is no nuclear safety impact associated with this feasibility study. The design criteria in Section 4.3 ensure that the proposed solution does not adversely affect the corrosion protection of the SGs and feed train. A Safety Screening and Safety Evaluation will be performed for the implementation, as they will include changes to KBA0022CHEMSPEC00, Koeberg Chemistry Specifications.

4.5.2 Conventional Safety

The options considered in this feasibility study introduce no new, unmitigated, conventional safety risks as it relates to personnel safety, hazardous locations, electrical shock, fire, and hazards associated with the storage and handling of chemicals. This is based on the MSDS sheets for the chemicals used in these options. The known and potential technical risks associated with the options considered in this feasibility study are discussed in Sections 6.1.3, 6.2.3, 6.3.3 and 6.4.3. Should an unacceptable risk be identified, which cannot be suitably mitigated, it would be grounds to disqualify an option.

4.5.3 Environmental requirements

The National Environmental Management: Integrated Coastal Management Act of 2008 requires the approval of a section 69 Coastal Waters Discharge Permit (CWDP) for the discharge of effluent into the sea from KNPS. As part of the CWDP application, a marine dispersion and ecological assessment was performed for the CWDP against the assessment criteria set out by the environmental authorities. The assessment showed that the current hydrazine discharges, arising from the use of hydrazine as an oxygen scavenger for wet lay-up and auxiliary boiler preservation, do not meet the ecological criteria at the end of the discharge point and that the affected zone is very large. As a result, the specialists have recommended that the hydrazine discharges are optimised, ideally below 0.0025 mg/l in CRF, before discharge.

As part of the assessment of the various options in the feasibility study, an ecological assessment on the marine impact associated with the use of the FFA octadecylamine (in the product form ODACON®) was performed [13]. Based on this assessment, even at FFA dosing of 5 ppm (which is

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more than twice the maximum anticipated dosing concentration and before any adsorption or dilution of residual FFA in CRF), ODACon poses very low risk to the marine environment and poses less toxicity risk than hydrazine. In addition, the projected concentration at the discharge point meets the ecological criteria.

4.6 Supplier Development and Localisation (SD&L)

This feasibility study contains no specific requirements on the local content and development of local suppliers in the project through all the stages of the project execution as mentioned in 240-89333427: Nuclear Project Sourcing Work Instruction I – Supplier Development and Localisation. Market research, through the RFI KBG2048, has however indicated that only foreign suppliers are capable of supplying scope of work for the engineering services and studies, and the application of FFA products. As part of the commercial process, staff will receive theoretical and on-job training during the first application, including application and monitoring of FFA.

4.7 Testing and Commissioning

At this stage, it is anticipated that the FFA will be injected/ dosed into the feed train close to the end of an operating cycle, while in stretch-out conditions. The exact details of the implementation such as the dosing concentrations, the locations of the specific dosing points, duration of dosing, monitoring during dosing and various implementation options etc., will form part of the implementation studies which will be covered under a commercial enquiry following the acceptance of the conclusions and recommendations in this feasibility study. Modifications to the plant are expected to be minimal and limited to the inclusion of specific injection points along the feed-train and associated equipment and control. The implementation design will be performed by a suitable vendor, to be identified using the commercial process.

A test application for the use of the FFA product, ODACon® to preserve the XCA boilers is currently being developed for implementation [74].

4.8 Other Critical Success Criteria

A Technical Requirements Specification for the implementation of FFA at KNPS will be compiled and submitted with the request for proposal under the commercial process, following the acceptance of the conclusions and recommendations in this feasibility study. The TRS will be developed based on the User Requirement Specifications for RFI budget quote associated with the use of Film Forming Amines for secondary side feedwater protection at KNPS, which was compiled for the RFI KBG2048. The factors critical to the success of this project include those listed below.

- The supplier must have a proven, demonstrable track record of a nuclear qualified process in the successful application of FFAs on PWR secondary steam / water systems, similar in design to KNPS.
- The compatibility of the FFA treatment with the established water chemistry regime as documented in References [6], [7] and [68] must be established in the design, by the vendor.
- A design justification and technical basis of FFA application must be provided. This must include the strategy and objectives, basis for the target value, basis for the limiting values, basis for the analysis frequency and actions to take when the limits are exceeded.

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- Clear direction on how to deal with possible chemical excursions resulting from the FFA treatment, specifically on the control parameters that have implications on limiting conditions of operation must be provided.
- A risk assessment in the form of a FMEA and HAZOP analysis, KNPS Safety screening and a mitigating strategy for associated risks, for applying FFA must be provided as part of the FFA application.

5. Rationale for selection of options

The options considered are based on the chemical mechanism and physical and chemical effect of the existing oxygen scavenging chemical, namely hydrazine. The options considered also take into account international operating experience regarding implementation. The proposed options include:

- Do nothing option, i.e., maintain status quo,
- Replace hydrazine with another wet lay-up oxygen scavenger. This replacement chemical would need to be as effective as hydrazine for dissolved oxygen and ECP / ORP control, and less toxic than hydrazine with respect to human health and the environment.
- Reduce the need for an oxygen scavenger during wet lay-up conditions by inhibiting the oxygen oxidation process at the metal surface, i.e., using a barrier chemical. This would be possible using film forming amines (specifically ODA) to form a hydrophobic layer on the wetted surface of components. ODA is selected as the most suitable FFA as it is the only FFA to have been implemented in the nuclear industry [17], [18], [21], specifically in PWRs.
- Use mechanical and chemical methods (or a combination of the two) to completely eliminate/decompose hydrazine into inert components (nitrogen and water) before discharge through KER and SEK systems into the CRF outfall.

6. Description of Options

6.1 Option 1 – Maintain the status quo – Do nothing option

This option considers maintaining the status quo.

6.1.1 Technical Description

The internal surfaces of the feedwater sections of the secondary side plant (ARE, ABP, AHP, APA, APP and CEX) systems, and secondary side of the RCP steam generators at KNPS are susceptible to corrosion, which challenges the integrity and efficiency of the plant. As such, a stringent chemistry regime is employed to prevent general corrosion of the mainly carbon steel feed-train and maintain low dissolved oxygen concentration to protect the steam generator nickel-alloy tubing material. The current secondary side chemistry regime is an all-volatile treatment in a reducing environment (AVT (R)) (as it relates to ORP) which, amongst others, seeks to control the oxidation of iron, and promote the formation of a protective magnetite (Fe_3O_4) film, through maintaining a pH of between 8.0 – 10.5, using ammonia and/or alkalising amine dosing, and a reducing agent, hydrazine. Hydrazine is an inorganic compound with the chemical formula N_2H_4 . It is a colourless, flammable liquid with an ammonia-like odour. It is a strong reducing agent and is used as an oxygen scavenger to control concentrations of dissolved oxygen to reduce corrosion.

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6.1.2 Description of Operation

Hydrazine is used in the secondary side water at power operations (in µg/kg concentrations) and is introduced as an oxygen scavenger in the primary system at start-up following an outage. Any residual hydrazine thermally decomposes during at power operations.

Hydrazine is also added as a wet lay-up chemical (in mg/kg concentrations) for the conditioning and conservation of feedwater sections of the secondary side plant systems, the auxiliary boilers (XCA) and the secondary side of the steam generators (SGs) during periods of non-operation (e.g., outages or standby mode for the auxiliary boilers). After or during outages, the secondary side systems and SGs that were preserved in wet lay-up are usually drained to SEK in preparation for unit start-up. At that point, hydrazine content can be above 100 mg/l [4].

6.1.3 Risks

Hydrazine is a toxic substance to both marine ecology and humans and is dangerously unstable unless handled in solution. It is a known carcinogen and requires the strict use of PPE, include respiratory protection.

The National Environmental Management: Integrated Coastal Management Act of 2008 requires the approval of a section 69 Coastal Waters Discharge Permit (CWDP) for the discharge of effluent into the sea from KNPS. As part of the CWDP application, a marine dispersion and ecological assessment was performed for the CWDP against the assessment criteria set out by the environmental authorities. The assessment showed that the current hydrazine discharges, arising from the use of hydrazine as an oxygen scavenger for wet lay-up and auxiliary boiler preservation, do not meet the ecological criteria at the end of the discharge point. As a result, the specialists have recommended that the hydrazine discharges are reduced.

A CURA risk, titled, "Coastal water discharge permit will be withdrawn leading to plant shutdown", CURA number R034025 (CURA level II) has been raised because of the anticipation of authorities issuing a draft CWDP to KNPS, with permit condition which KNPS will not be able to meet unless mitigation is put in place. Since raising the CURA risk, a draft CWDP has been issued for comment which specifically requires an investigation into the reduction of hydrazine also to show that the requirement to optimise discharges is met. Should KNPS not comply, the risk exists that the CWDP will be withdrawn, leading to extended plant shutdown, caused by Koeberg's design not meeting standards set by authorities, controlled by advocacy and environmental assessment.

It is therefore expected that the use of hydrazine as an oxygen scavenger, following the existing practices for wet lay-up, will not be a solution once a CWDP has been issued since reasonable alternatives have been identified as feasible. This option is therefore not viable.

6.2 Option 2 - Replace hydrazine with another wet lay-up oxygen scavenger

This option considers replacing hydrazine with another wet lay-up oxygen scavenger, which would need to be as effective as hydrazine for dissolved oxygen and ECP / ORP control, and less toxic than hydrazine with respect to human health and the environment.

6.2.1 Technical Description

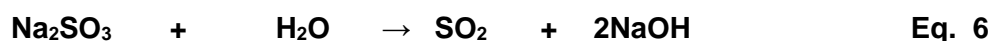
Several alternative chemicals to hydrazine, as it relates to oxygen scavenging, exist, and are used commercially in various nuclear (albeit very limited) and non-nuclear applications. These include:

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- Sodium Sulphite
- Diethylhydroxylamine (DEHA)
- Methylethylketoxime (MEKO)
- N-Isopropylhydroxylamine (NIPHA)
- Hydroquinone
- Carbohydrazide

(i) Sodium Sulphite

Sodium sulphite is an oxygen scavenger which is used in low quality steam and low-pressure applications and is not considered as a potential direct replacement to hydrazine application for high pressure applications. It requires a dosing ratio of at least 8:1 (scavenger to: O₂ ratio). The following reactions are predominant [20]:



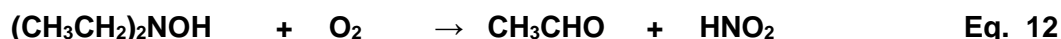
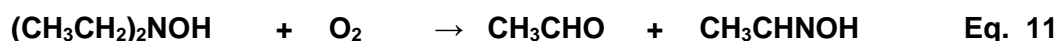
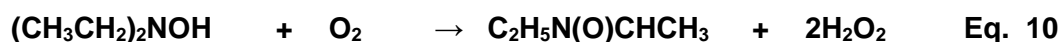
(ii) Hydroquinone:

Hydroquinone is considered as a potential replacement to hydrazine. It requires a dosing ratio of at least 6.9:1 (scavenger to: O₂ ratio). The following reaction is predominant [20]:



(iii) Diethylhydroxylamine (DEHA), Methylethylketoxime (MEKO) or N-Isopropylhydroxylamine (NIPHA)

Diethylhydroxylamine (DEHA), Methylethylketoxime (MEKO) and N-Isopropylhydroxylamine (NIPHA) are oxygen scavengers having a hydroxylamine structure and are considered as potential replacements to hydrazine. DEHA requires a dosing ratio of at least 1.2:1 (scavenger to: O₂ ratio). MEKO requires a dosing ratio of at least 5.4:1 (scavenger to: O₂ ratio). NIPHA requires a dosing ratio of at least 7:1 (scavenger to: O₂ ratio). The following reactions for DEHA are predominant [20]:



The following reactions for MEKO are predominant [20]:



The following reactions for NIPHA are predominant [20]:



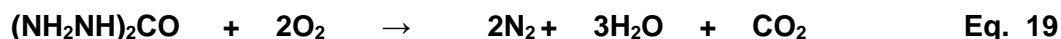
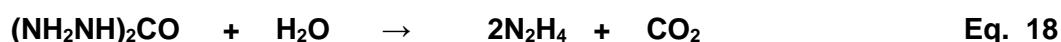
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(iv) Carbohydrazide

Carbohydrazide is considered as a potential direct replacement to hydrazine. It requires a dosing ratio of at least 1.4:1 (scavenger to: O_2 ratio). Carbohydrazide has been in use as an oxygen scavenger in the power industry since the early 1980s [20]. At elevated temperatures (above 135°C), carbohydrazide readily decomposes (refer to Figure 1) to yield hydrazine and carbon dioxide as follows in Equation 16. At lower temperatures (i.e., less than 135°C), carbohydrazide will react directly with oxygen according to the reaction in Equation 17.

The following reactions are predominant [20]:



The use of carbohydrazide is expected to provide oxygen scavenging capabilities similar to those of hydrazine at elevated temperatures (at power operations).

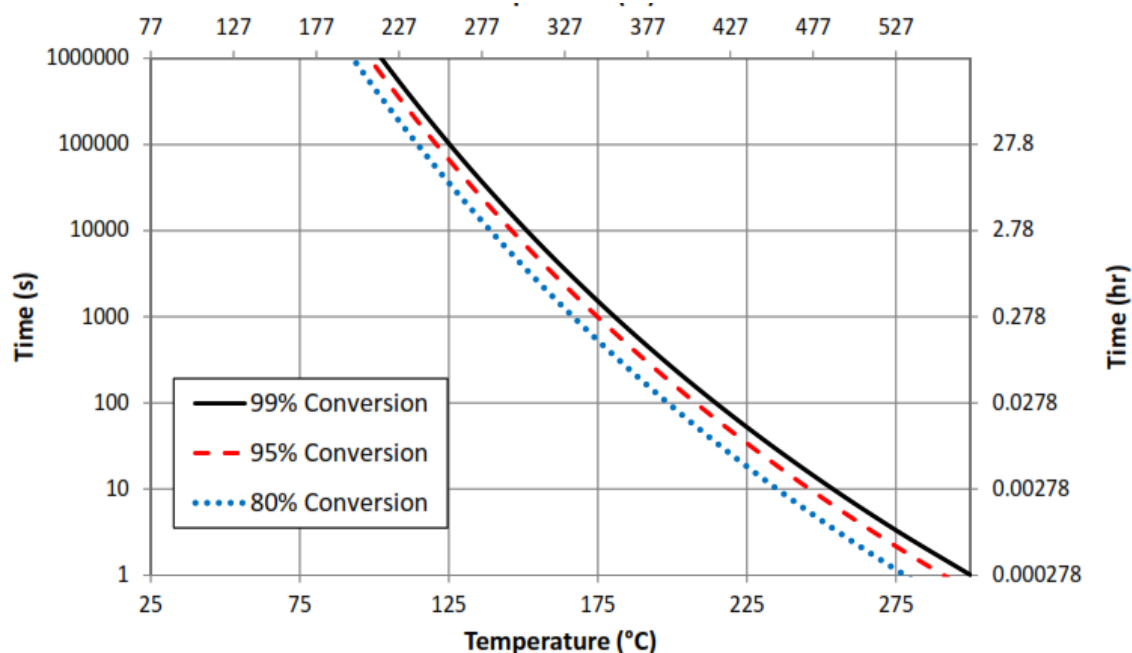


Figure 1: Decomposition of carbohydrazide at elevated temperatures

Figure 2 shows the results of a similar analysis for lower temperatures ($\leq 100^\circ\text{C}$). This analysis indicates that there is likely to be very little hydrazine generation at low temperatures even over very long time periods. For example, 100 days at 50°C , only about 5% of the carbohydrazide would be converted to hydrazine. The implication is that even for long outages, carbohydrazide can be used without concern of significant hydrazine generation.

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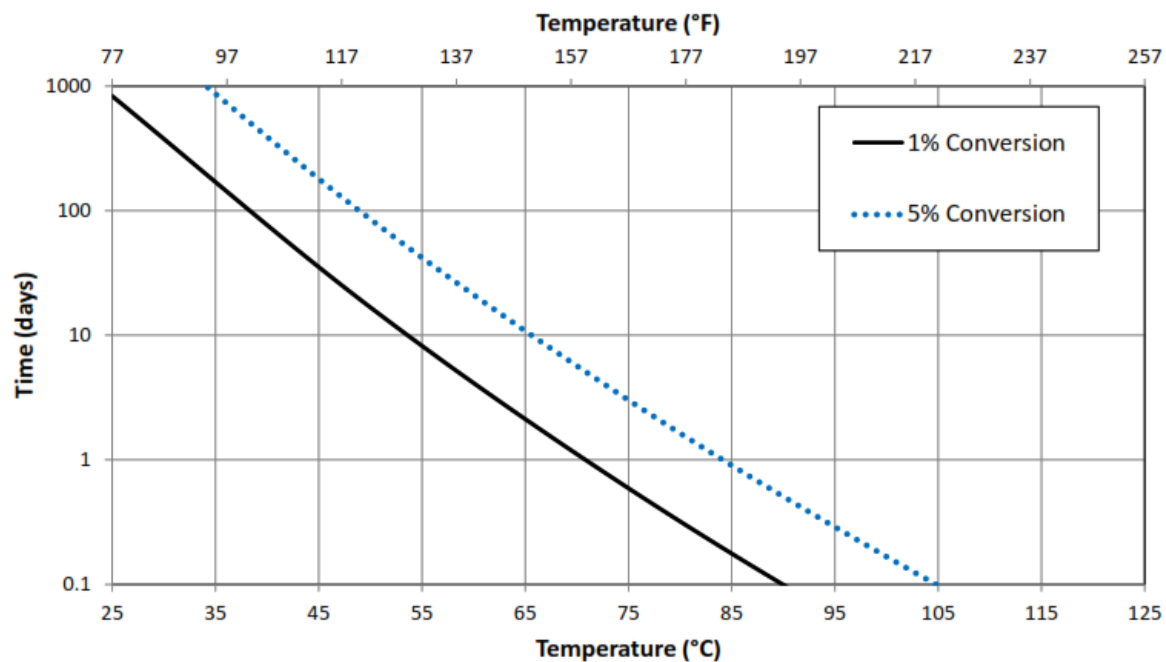


Figure 2: Decomposition of carbohydrazide below 100°C

Carbohydrazide has successfully used at three nuclear power plants (Kewaunee, Cook and TKPNPP) for multiple cycles [20], [28]. Use was discontinued at Kewaunee because of batch of chemically contaminated carbohydrazide, and at Cook because carbohydrazide decomposition led to measured elevated cation conductivity in the steam system, which was not compatible with their chemistry programme. Under at power operations and wet lay-up conditions, carbohydrazide hydrolysis into hydrazine and carbon dioxide, as described in Eq. 17. During at power operations the residual hydrazine thermally decomposes or reacts and is of no concern a, however at ambient conditions it remains present. Several stations have also used carbohydrazide for SG lay-up [20].

6.2.2 Description of Operation

All options considered here would require almost identical operational practices to the current setup used to dose hydrazine (via the SIR system), with the exception of potentially adding a portable industrial scale to weigh out carbohydrazide before mixing with deionized water, the latter which is available at the existing hydrazine dosing facility using the SIR system, and minor changes to the chemistry dosing procedures for feed train and SG lay-up would be required.

6.2.3 Risks

The following risks are associated with the options considered in replacing hydrazine with another wet lay-up oxygen scavenger:

(i) Sodium Sulphite

During its oxygen scavenging function sodium sulphite reacts with oxygen to form water insoluble sodium sulphate, which would contribute to solids in the feed train. The solids will accumulate at the bottom of the SG tube plate during start-up, as it is non-volatile, requiring significantly more APG blowdown to remove. In addition, it is most often used with cobalt sulphate as a catalyst for the oxygen scavenging reaction and is not compatible with the alkaline chemistry regime for secondary

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side plant systems as it causes the cobalt sulphate to precipitate contributing to more solids in the feed train.

Sodium sulphite is not suitable for high pressure boilers (>10MPa), as it decomposes chemically as described in Eq. 5 and 7, resulting in the formation of sulphur dioxide and hydrogen sulphide. Both are corrosive gases which leave the boiler with steam, resulting in low pH in the steam and condensate and potential corrosive attack throughout the system. Sulphite is an effective oxygen scavenger, but it is non-volatile and is not carried over in the steam phase, thus providing no protection in the condensate system. Sulphite also does not reduce hematite to magnetite and is ineffective in re-passivating boilers with existing internal surface corrosion.

Sodium concentration in the feed train is strictly measured (through online and offline feedwater analysis) and controlled in line with the existing chemistry programme [6], [68]. The use of sodium sulphite is therefore also excluded on grounds of incompatibility with existing chemistry programme [68].

While the main risks associated with the use of sodium sulphite are of concern with its use as an oxygen scavenger during at power operations, the effects of its use as an oxygen scavenger during wet lay-up conditions will carry through, especially as power and secondary side pressure is increased.

(ii) Hydroquinone

Hydroquinone as an oxygen scavenger has not been used in the nuclear industry. The reaction kinetics is complex and involves multiple intermediate reactions and contributes to the total organic carbon loading in the feedwater and is not compatible with the current chemistry regime for at power operations, or wet lay-up [6], [68]. Hydroquinone is considered more toxic than hydrazine with respect to aquatic life and equivalent to hydrazine with respect to ingestion [20]. It is therefore excluded on environmental grounds.

(iii) DEHA, MEKO and NIPHA

DEHA, MEKO and NIPHA contribute significantly to the total organic carbon loading in the feedwater as they decompose and are therefore not compatible with the current chemistry regime for at power operations, or wet lay-up [6], [68]. They are therefore excluded on the grounds of non-compatibility with the existing chemistry programme [68].

(iv) Carbohydrazide

Carbohydrazide may result in the increase in cation conductivity due to its decomposition according to Eq. 16 and 17, and the associated formation of CO₂ [20], [28]. The method of application for carbohydrazide as an oxygen scavenger is almost identical to the existing method to application for hydrazine as an oxygen scavenger for wet lay-up. This means that the use of carbohydrazide as a wet lay-up oxygen scavenger does not allow the feed train to be suitably protected and if necessary drained at short notice, independent of length of time after shutdown, to perform maintenance, while still protecting the feed train thereafter. It is therefore excluded on the grounds of not meeting the flexibility on outage feed train related maintenance criteria.

6.3 Option 3 - Significantly reduce the need for an oxygen scavenger during wet lay-up conditions

This option considers reducing the need for an oxygen scavenger during wet lay-up conditions by inhibiting the oxidation process at the metal surface through means of a barrier chemical. This would be possible using film forming amines to form a hydrophobic layer on the wetted surface of components.

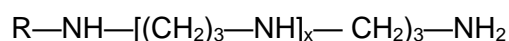
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Film forming amines have been reported to provide an excellent potential for lay-up of steam generators in the nuclear, fossil power and steam generation sectors, due to their specific mode of action. The film forming molecules adsorb onto the surface and thereby creating a barrier on the surface against corrosive media. Practical experiences in steam generators with frequent short-term shutdowns have encouraged the extension of the application to dry lay-up of several months with a sharply simplified procedure, i.e., without nitrogen blanketing or keeping the steam generators and feed train warm and dry.

6.3.1 Technical Description

6.3.1.1 Chemical structure

A film forming amine can be said to be an aqueous dispersion of high molecular weight monoamine or polyamines from the types of straight chain aliphatic alkyl polyamine represented by:



Where:

R is a radical of 12 to 18 C saturated or unsaturated

X can be zero or an integer from 1 to 5

FFAs belong to chemical substances of the class of oligo alkylamino fatty amines [19], the simplest one being the well-known octadecylamine (ODA) (Refer to Figure 3), a mono-amine containing a single amine functional group. Polyamine FFAs, such as N-oleyl 1, 3-propanediamine (oleyldiamine or OPDA), contain multiple amine functional groups (Refer to Figure 4.)



Figure 3: Octadecylamine (ODA), CAS-No. : 124-30-1

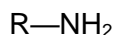


Figure 4: N-oleyl 1, 3-propanediamine (OPDA), CAS-No. : 7173-62-8

In the commercially available FFA compounds, the R radical typically is derived from a long chain fatty acid, obtained from either natural fat or oil sources, or petrochemical raw material sources. The fatty acid is decarboxylated and reacts with the desired amine functionality, to form the FFA. This explains the origin of the name fatty amines that sometimes is used to identify these compounds.

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In contrast, a neutralizing amine typically corresponds to a formula of the type:



Where:

R is an aromatic, cyclic, or aliphatic group generally with no more than eight carbons.

6.3.1.2 Chemical and physical properties

(i) Solubility in water

The molecules have relatively long hydrocarbon backbones with one, two, or more amino groups. The chemical and physical properties of the FFA family of compounds are complex as the amino groups' end of the FFA is hydrophilic, and the long alkyl chain is hydrophobic. Due to their organic component, FFAs are not readily soluble in water; however, solubility can vary dependent on the ratio of amino groups to alkyl groups. Solubility at room temperature (wet-lay-up conditions) is typically very low [30].

In Figure 5 [17], [30], the area bounded by (I) and the concentrations and temperatures above the saturation curve, two phases coexist: FFA (undissolved/suspended) and the corresponding saturated solution at temperature of the FFA in water. Inside this zone (I), at any given temperature T, the FFA (undissolved/suspended) is in equilibrium with a saturated solution of FFA at the saturation concentration corresponding to T. In this area, the concentration axis provides only the numerical total concentration of FFA (undissolved/suspended) in the system, not the saturated solution concentration. The saturated solution concentration is given by the intersection of T with the saturation curve [17].

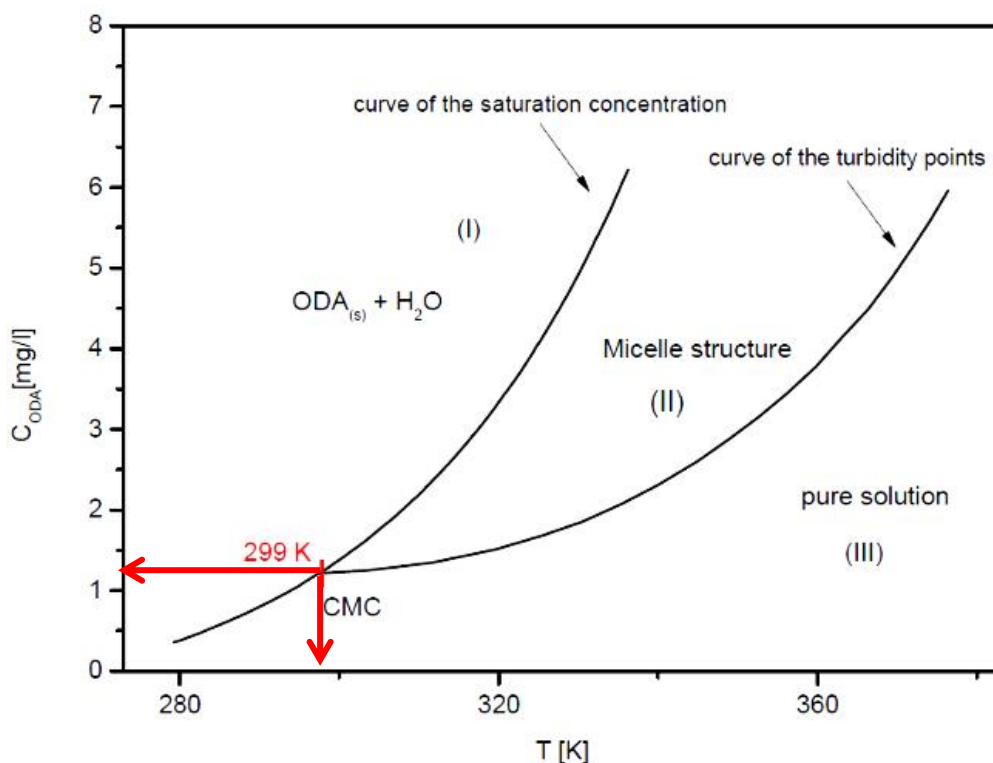


Figure 5: Phase diagram for ODA in water [18]

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The Krafft point is the minimum temperature at which micelles form, i.e., solubility is equal to its critical micelle concentration (CMC). Inside the area (II), FFA micelles coexist with a solution of FFA in water. Micelles can be pictured as soluble aggregates of FFA and associated water. For any point inside area (II), FFA concentration as read in the vertical axes is the total concentration of FFA in the system, and thus represents neither the concentration of FFA in solution nor the concentrations of the FFA in the micelles but rather the total FFA in micelles plus FFA dissolved in water. No additional solubility data for other FFAs were in the literature.

The zone of concentration/temperature that defines area (III) is the region of temperatures and concentrations where a solution exists of FFA molecules that are soluble in water.

Dosing concentrations during application are such that they fall within area (III). In this area of the phase diagram, a solution of water and molecules of FFA exists and the attraction between the FFA and the metal surface is greater than the attraction forces between molecules (which would lead to micelle formation).

It is important to note that different FFA products have different CMCs, and thus different dosing concentrations.

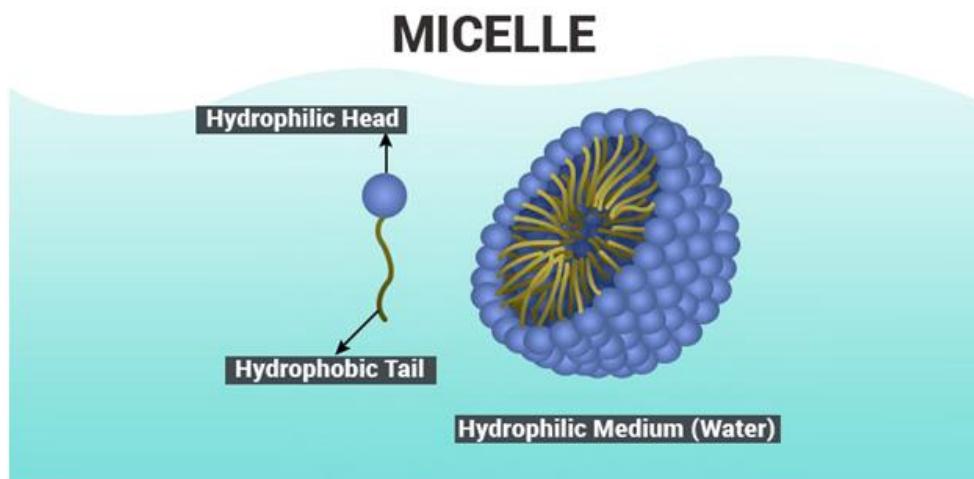


Figure 6: Micelle formation and structure in water

(ii) Electrochemical and adsorption properties

A study of the adsorption properties of mono-, di- and tri-amines on carbon steel, stainless steel and copper was performed to establish adsorption isotherms for the different systems at several temperatures [42]. All three metals adsorbed the FFA readily, with stainless steel samples generally having the lowest propensity, at roughly one third of that of carbon steel [43].

In the conditions predominant in the water/steam cycles where the water is alkaline, as is the case at KNPS, stable, bare metal surfaces do not normally exist. All metal surfaces are covered by hydrated oxides. The current secondary side chemistry regime at KNPS [68] promotes the formation of a protective magnetite (Fe_3O_4) layer of carbon steel piping. When a solution of FFA in water (alkalized or not) is put in contact with components of the water/steam cycle, a hydrophobic film is formed [17]. Literature reports present a persistent (often described in as tenacious) film formation under both laboratory and field conditions. Considering that it is known that such film is adhesive, stable at high temperatures (in relation to lay-up temperatures as well as operating temperatures for secondary feed water system at KNPS), not easily dissolved, and resistant to hydrodynamic shear forces of the fluid in the pipelines, it is evident that the force of

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interaction between the metal/metal oxides and the FFA must be of a strong nature. This discounts Van der Waals forces (as well as hydrogen bonding) and tends to indicate the existence of an ionic molecular bond between the metal/metal oxides and the FFA.

FFAs are known for their tendency to adsorb on metal/metal oxides surfaces by sharing the free electron pair of the amine nitrogen with the positively charged iron ions. The protective film has been described as a mono-molecular hydrophobic film adsorbed on the surfaces. The aliphatic chain creates a homogeneous, hydrophobic, physical barrier that prevents water, oxygen and other corrosive agents to reach the metal surface [17], [19]. Refer to Figure 7.

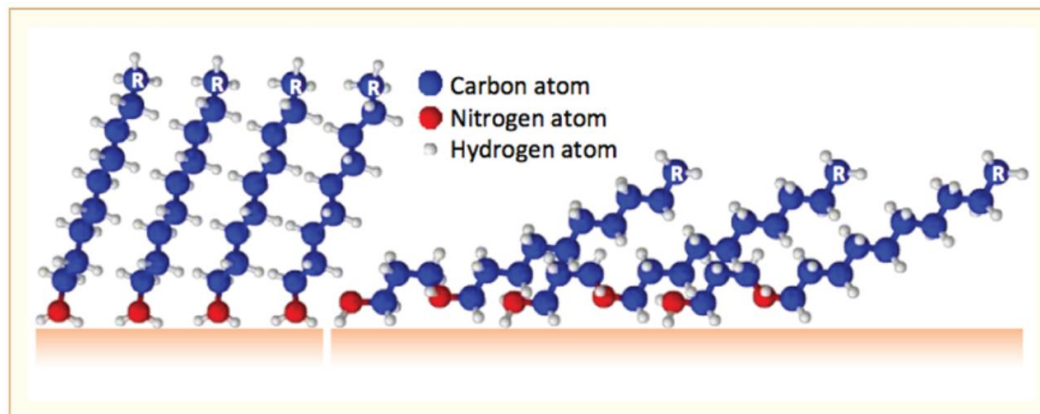
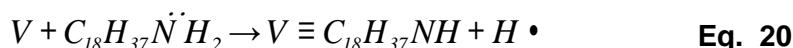


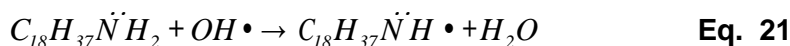
Figure 7: Schematic representations of FFA films: monoamine (left), polyamine (right)

While the above holds true under atmospheric conditions, research by EPRI [18] and Betova [31] has shown that several factors influence the ability of FFAs to form films on surfaces. These include pH, temperature, concentration of impurities, contact time, FFA concentration, as well as the exposed materials composition, oxidation state and surface condition (e.g., presence of oxide and deposit layers).

The FFA-surface attraction model discussed above does not explain why the composition and adhesiveness of films are temperature-dependent. Betova et al. [31] introduced the following mechanism as an alternative, with ODA used as an example FFA. At low temperatures (40–80°C), free valence electrons from the surface bond with the amine, releasing a radical hydrogen. Radical hydrogen proceeds to donate its electron to the surface or to the surface complex of a different amine. This produces another nitrogen to surface bond and the release of another radical hydrogen.



At temperatures greater than 100°C, the dissociation of water leads to the presence of many hydroxide radicals. Because of this dissociation, a different mechanism, shown in Equation 21 and 22, governs the release / adsorption of the amine. In this case, a hydroxide radical reacts with the amine to produce water and a radical amine. The radical amine then reacts with the metal surface (M) and leaves the radical (valence electron) on a nearby surface site. The neighbouring surface site can then react with another amine [30].



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As suggested in both References [17] and [31], both of these reaction mechanisms are chain reactions that could explain the influence of pH and temperature on the growth of a filming layer. Although the mechanism is unknown, the films formed by these amines can be maintained even after the concentration in the bulk fluid decreases. This property makes them particularly valuable in protecting surfaces during start-up and shutdown periods.

Research by Bohnsack [32] has reported, using infrared spectral measurements, that the metal oxides and polyamine FFAs form a complex chelate type of three-dimensional membranes between the ions of the metal oxides and the FFA [17], [32]. Refer to Figure 8. This agrees with the findings as discussed above.

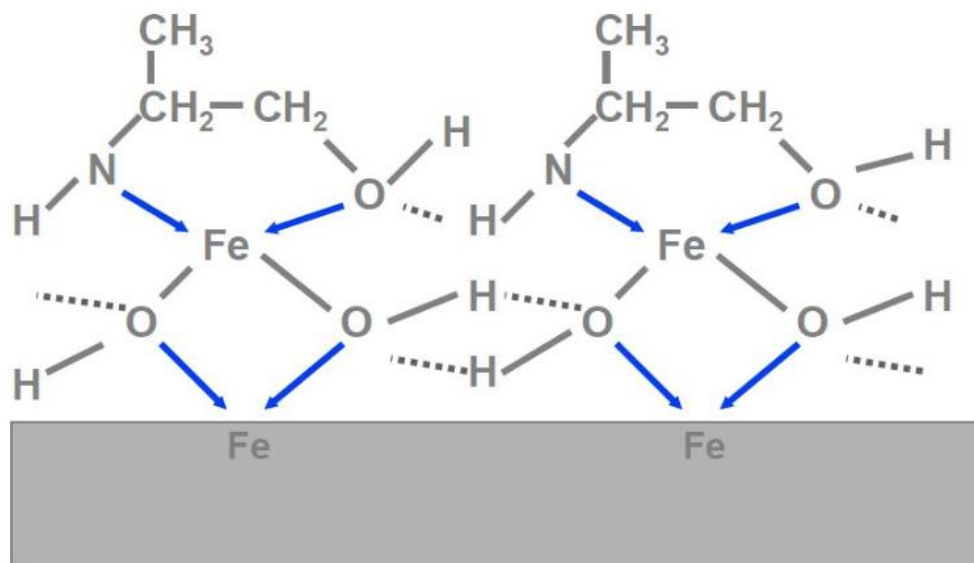


Figure 8: Surface complex formation between an amine and an oxidized iron surface – dashed lines indicate ionic interaction / hydrogen bonding.

This hydrophobic layer impedes mass transfer, i.e., the diffusion to and from the metal / metal oxide surface to the treated water in the water / steam cycle. The slowdown in diffusion applies to corrosive substances such as oxygen, carbon dioxide, and other contaminating ions such as chlorine, sodium, and silica. The result is an observed decrease in the corrosion rate observed in systems treated with FFAs [17].

(iii) Hydrophobicity, film presence verification and thickness measurements

The existence of the film has been corroborated macroscopically by measuring the change in properties of the metal/metal oxides layer before and after FFA treatment [17]. A few microscopic and spectroscopic techniques have also been used to try to identify the nature of the film on ex-situ test samples. There is considerable evidence that indicates the changes in the properties measured before and after using different techniques to determine film presence and properties [17], [40], [41]. These changes are due to the FFA film.

During experiments performed in Reference [55] under conditions similar to those found in the feed train during dosing, judging by the carbon and nitrogen signals from the glow-discharge optical emission spectroscopy, an estimate of the ODA film thickness at the oxide/water interface would be in the range of 50-150 nm [55].

Physically checking for hydrophobicity to confirm the presence of the adsorbed film can be performed during offline periods (e.g., Outages). Water applied to a hydrophobic surface will form

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beads rather than wet the surface as shown in Figure 9, Figure 10 and Figure 11. A hydrophobicity test can be performed using a bottle of water during equipment inspections. [17].

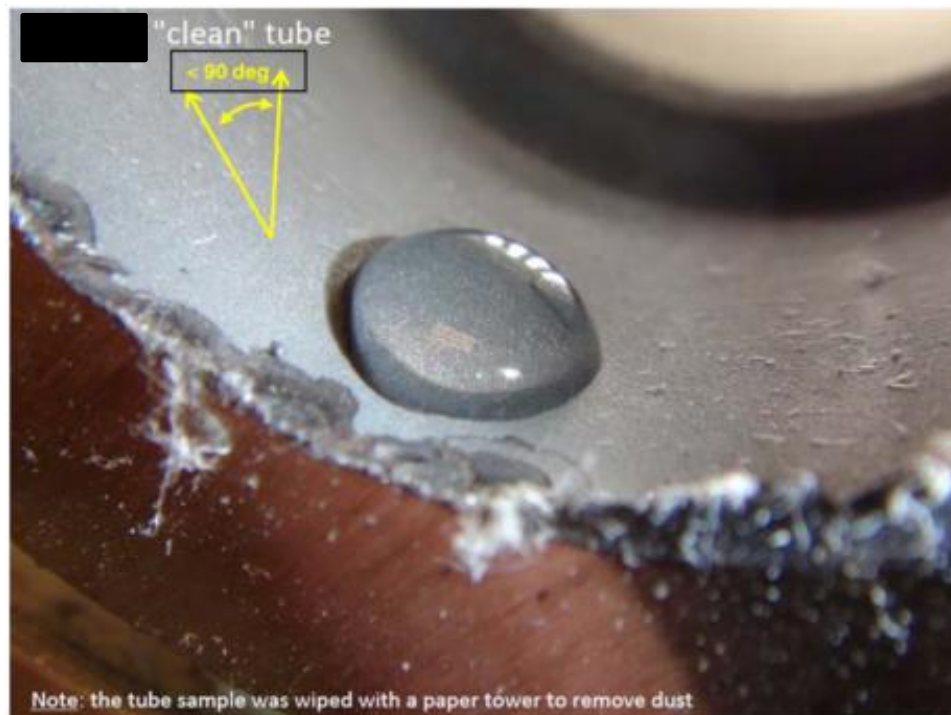


Figure 9: Appearance of a boiler tube with a “good” hydrophobic coating. The angle between the side of the bubble and the vertical reportedly should be less than 90°, or greater than 90° when measured from the horizontal plane inside the bubble to edge of the bubble-water-surface interface.

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Figure 10: Appearance of a boiler tube with a “moderate” hydrophobic coating.



Figure 11: Appearance of a boiler tube with a “poor” hydrophobic coating.

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Contact angle measurements (measured from the horizontal plane inside the bubble to edge of the bubble-water-surface interface) performed on the bare carbon steel surface and on the ODA treated sample was conducted in Reference [41]. See Figure 12. For the bare steel, the surface presented a hydrophilic character with a contact angle value of $39^\circ \pm 5^\circ$. For the ODA treated sample the contact angle value is $93^\circ \pm 2^\circ$ showing that the surface lost its hydrophilic character, which is a well-known effect of the ODA adsorption [31]. The weak variation of the contact angle for the ODA treated sample indicates that the hydrophobic film is homogeneous even in the presence of ODA aggregates on the surface.

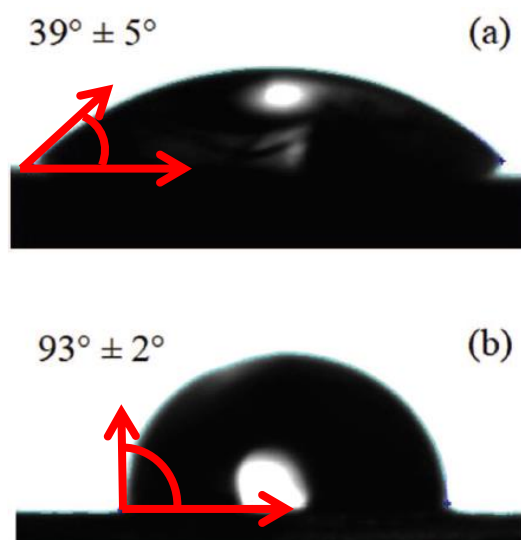


Figure 12: Contact angles measured on (a) the bare carbon steel and (b) carbon steel treated ODA

Reference [49] reported estimates for the extent of FFA surface coverage (i.e., the mass of FFA adsorbed per unit area of metal surface) for several FFAs. These estimates were developed by comparing the initial FFA concentration to that reached upon equilibrium. In particular, three oleylamines with different numbers of amine groups were evaluated. The findings included the following:

- The adsorption was linearly dependent on the FFA concentration in solution up to a loading of about 2 g/m^2 .
- The number of amines in the FFA molecule (1, 2, or 3) did not significantly affect the extent of adsorption.

(iv) Distribution Coefficient/Volatility

Based on literature, there is conflicting information on whether film formation also takes place in areas of superheated steam; in some studies, steam circuits were found protected, possibly because of the presence of water in the steam during start-ups and shutdowns. Studies in an industrial boiler under controlled conditions clearly showed the presence of FFA on tubes exposed to superheated steam, thus strongly indicating the adsorption of FFA on metal surfaces also from the gas phase [18].

FFA can be steam volatile, and their volatility depends on their chemical structure with monoamines being less volatile than diamines [39, 42]. Due to their volatility, FFA can protect evaporator surfaces, the condensate system, and the steam turbine at locations with high

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steam moisture. It is not fully confirmed whether film formation also takes place in areas of superheated steam; sometimes steam circuits are found protected possibly because of the presence of water in the steam during start-ups and shutdowns [48].

Available data for the dissociation constant (describing the degree of ionization in water, which relates to the basicity of the amine) and the distribution coefficient (describing the partitioning between liquid and vapour phases in water-steam two-phase systems) are presented by EPRI in Reference [18]. In general, the apparent distribution coefficients are time dependent due to the time required to reach equilibrium between FFA adsorbed onto metal / metal oxide surfaces, and free FFA in solution. The distribution coefficients reported are assumed to reflect the approximate equilibrium coefficients determined experimentally after an extended period (except in cases where the time dependence is explicitly specified).

EPRI has tested two FFAs in an autoclave experimental setup to determine volatility in the form of steam-water phase distribution coefficient. They were found to have apparent distribution coefficients similar to ETA at 250°C and 350°C, simulating typical PWR secondary side conditions. [21]

Laboratory experimental and literature research conducted by Dooley and Lister (2018) has indicated that unless dosed continuously during at power operations, the reduction in FAC associated with FFA usage is limited in time duration (in the order of days) while at power operations. The on-line carbon steel measuring probe used to monitor FAC in the experiments, when dosed at concentrations consistent with industrial application of ~ 800 ppb and continuously while steady state conditions were observed, were coated with FFA as confirmed by hydrophobicity tests, and a laser-Raman microscope. EPRI investigated the potential of the FFA product Cetamine® V219 as a corrosion inhibitor for two-phase FAC during at power operations. FAC can be caused by both flowing water and wet steam and can result in wall thinning and significant material loss. KNPS currently limits FAC through pH control using ETA during at power operations. FFA products were investigated for FAC protection because it was thought that the protective film could provide protection in addition to that provided by pH-control amines. As detailed in Reference [44], this conclusion was confirmed for testing completed at 140°C, but was not confirmed at 200°C. In the latter tests, Cetamine® did not significantly affect the rate of FAC above the protection provided by the pH-control amine. One potential reason for this finding at the higher temperature may be that the FFA film was unable to fully form or to remain intact in the turbulent environment—or it could be that the film was not able to prevent FAC at the higher temperature [18], [44].

Given the lack of definitive knowledge on the ability of FFA to robustly coat the superheated steam sections of the secondary side (and the gaps in definitive knowledge on the steam/water distribution ratio of FFAs), it is recommended that existing turbine and steam system outage lay-up practices continue as it relates to purging with dehumidified air [38] and the existing Koeberg procedure, KBA1217GCA001 [9], until further empirical data from application at KNPS as well as other reputable sources can be obtained.

6.3.1.3 Other considerations

(i) Dosing

In general, FFAs are not added as pure, individual substances but rather as blended commercially available solutions or products, such as Anodamine™ HPFG, Cetamine®, HELAMIN®, ODACON®, PowerFilm™ 10000, and Steamate™, containing various combinations with neutralizing amines, dispersants, and reducing agents. The ammonia and the neutralizing amines remain in solution, volatilize, and aid in maintaining appropriate alkaline pH

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in different parts of the water/steam circuit [17]. This approach is consistent with the AVT-(R) chemistry regime at KNPS [6], [7], [68]. At the same time the blended chemicals serve to provide the necessary storage stability of the formulations and there is typically no need for additives whose sole function is to stabilize the formulations [31]. FFAs are applied as solutions (normally with very low concentrations), emulsions, or suspensions in water except for Russian VVERs which use pure ODA [17].

The dosing of FFAs is usually adjusted in a manner, so that a small amount of residual product can be detected in the condensate and feed water. In most cases, the presence of the smallest reliably detectable amount of amine suffices. Dosing concentrations for outage preservation are dependent on the FFA product to be used, dosing conditions and plant design and can be in order of 300-900 µg/l (ppb) for pure ODA but may be as high as 1ppm. Other FFA products such as Cetamine may be 2-5ppm, and Anodamine may be as high as 25-50ppm. However, dosing must occur in the concentration range of area (III) in Figure 5 (if ODA is used) as described in Section 6.3.1.2 (i). Dosing commences shortly before outage, while at full power or in stretch out conditions.

Once a steady state or equilibrium has been reached dosing is stopped. It is however important that the minimum duration be determined in the design phase. Once the protective film has formed it remains intact even after the dosage has been stopped. Increasing dosing beyond that which is required to achieve the mono-layer thickness does not increase layer thickness or effectiveness [31], and will result in the formation of micelles as described in Section 6.3.1.2 (i).

Dosing can be accomplished by feeding directly into the condenser hot well using system vacuum. EPRI has reported that several of the utilities used this short-term dosing protocol [53]. Literature reports that film presence can be confirmed with a hydrophobicity test, but due to complexity in assessing film thickness in-situ, surface coverage is estimated by a mass balance comparing residual FFA concentration in condensate to the inlet, this is however not an absolute indication of FFA bonding with the surfaces.

The exact dosage locations and amounts need to be determined taking into consideration the plant specifics such as secondary side water and steam volumes, pH, temperature, linear velocity of the fluid, condenser pressure (as it affects the phase transition zone), and the specific FFA product to be used.

EPRI has found that direct dilutions from as-received product are preferred over multi-step solutions to prevent filming of intermediary containers when preparing dosing concentrations prior to testing and application. This recommendation is atypical for low miscibility solutions in which large aliquots of each successive dilution are used to ensure representative sampling. [21]

(ii) Thermal stability

For the purposes of this feasibility study, which focuses on the use of FFA during wet-lay-up, low temperature stability is of more concern than high temperature stability [18], however, high temperature thermal stability must be considered due to the potential contribution of breakdown products in increasing steam cation conductivity (which is monitored to provide indications of strong acid anion contamination (e.g., Cl⁻, SO₄²⁻, etc.) of the steam) in order to protect the steam turbines. This includes the thermal decomposition of any blended neutralizing amine, when also present in the product, into low molecular weight organic acids (LMWOAs). KNPS currently operates a secondary chemistry regime using amines (specifically ETA), that decompose into acetate and formate, which are the same principal decomposition products that are expected from FFAs. The high temperature thermal stability requirements for FFAs should ensure that any decomposition of it is not excessive compared to the pH-control amines currently in use, i.e., ETA. This is discussed under chemical purity in Section 6.3.3.2.

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Based on research conducted in Reference [51], only very low levels of thermal decomposition of ODA were observed at temperatures below 300°C in pH neutral solutions. However, in the presence of alkaline solutions at this temperature, a thermal conversion process occurs which leaves the long-chain carbon backbone of ODA intact. This thermal conversion involves ODA molecules combining to form di- and tri- ODA by elimination of ammonia at temperatures above 325°C.

Rapid, complete thermal decomposition (to NH₃, H₂, CO₂, and CH₄ [50]) occurs in aqueous solutions at temperatures above 450–470°C [51] [52]. This was also confirmed in References [30] and [46].

Reference [46] indicates that no increases in the concentrations of organic acids or carbon dioxide were detected during the field applications of ODA CON® as would be anticipated in the context of significant thermal decomposition.

NOTE: *There are reports that attempt to establish the decomposition products by studying the thermal breakdown in the laboratory by heating the product at an elevated temperature for a length of time. Such static experiments can yield results that do not reproduce the results in the plant cycle because the mechanisms of decomposition could change. In a dynamic plant steam/water cycle, the decomposition products, especially if they are volatile, would not accumulate as they would in static autoclave experiments. In addition, the residence times are generally short in the steam/water cycle.*

(iii) Chemical stability

Chemical stability and half-life are of concern when an FFA product is used for outage preservation / wet lay-up. For these applications, the half-life of the FFA in a FFA product must be at least several times greater than the duration of the planned lay-up (or the planned interval between lay-up chemistry adjustments / refreshments) in order to meet efficacy requirements, and not pose a risk to the plant if oxidizing conditions are allowed to develop uncontrolled in the feed train. Reference [46] states that ODA CON® has an effective shelf life of approximately 2 years when stored at temperatures above 0°C, and below 25°C.

(v) Effects on Thermal Performance

Literature indicates that FFAs can influence the thermal efficiency of plant components through several physical phenomena. These include:

- Increased Boiling Efficiency

FFAs have also been shown in some cases to enhance the heat transfer coefficient over a range of heat fluxes [17], [19]. Research conducted in Reference [45] showed that the presence of OPDA (in Cetamine® V211) at concentrations of 0.5–1 ppm, led to an increase in the bulk bubble density (i.e., activation of more nucleate boiling sites), which significantly raised the measured heat-transfer coefficient in boiling experiments relative to that measured for a reference phosphate chemistry (see Figure 13). High-speed video of the experiments confirmed this interpretation. These results have clear relevance to PWR SGs, in which heat is transferred on the secondary side predominantly through boiling.

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It is important to note that when the number of nucleate boiling sites is relatively low, bubbles coalesce to form gas pockets along the heated surface. The resultant steam layer prevents liquid from reaching the wall and limits the overall heat-transfer coefficient (Leidenfrost effect). The hydrophobicity of FFAs causes bubbles to dissociate from the wall more rapidly than in the absence of FFAs, thus limiting bubble size. The release of the smaller bubbles reduces the degree to which steam blankets the heat-transfer surface, increasing the number of available nucleation sites and allowing new bubbles to form more efficiently, and be carried away from the surface.

Independent experiments conducted by Gasnier and Lister [47] using an unnamed FFA product demonstrated that FFA addition at 1 ppm led to improved boiling efficiency in benchtop beakers. The investigators found that the bubble nucleation frequency increased in the presence of the FFA.

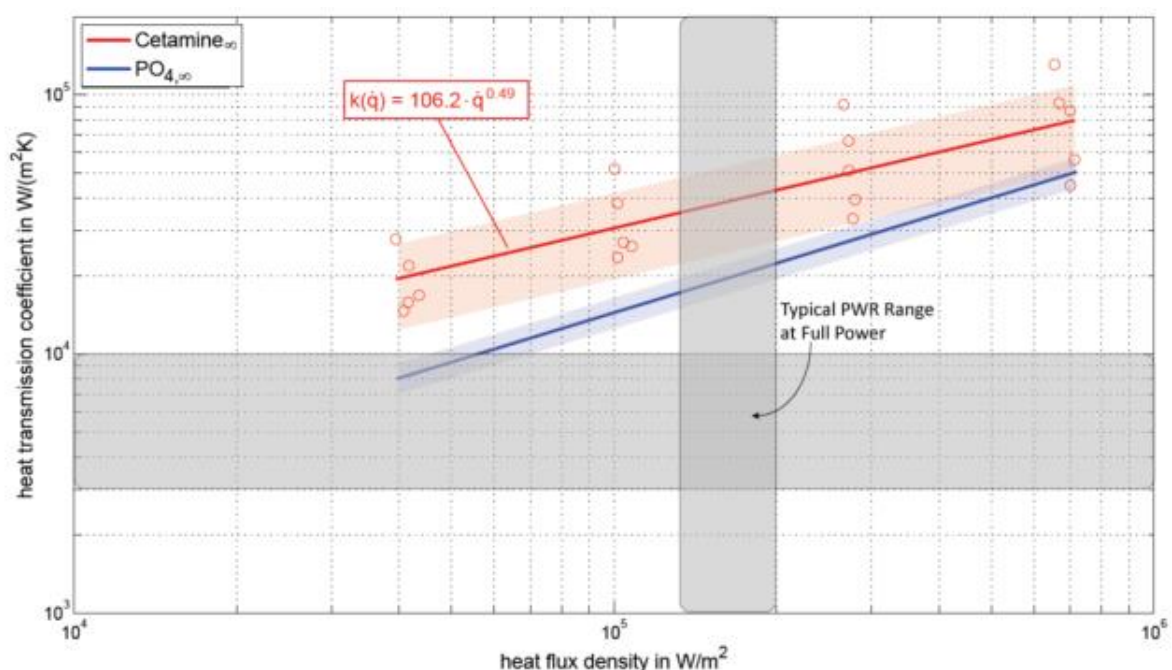


Figure 13: Relative increase in the measured heat-transfer coefficient

Rudolph et al. report that analytical work employing computational fluid dynamics (CFD) and the DLVO colloid-surface interaction theory concluded that the use of FFAs such as ODA can be expected to alter the size distribution of iron oxide particulates, resulting in generally smaller particles. A similar phenomenon was also postulated for polymeric dispersant addition as noted in Reference [17], based on the expectation that dispersant-coated iron particles would be less likely to agglomerate, though no confirmatory data are known to be available regarding this hypothesis. Measurements of particle size during FFA application (which are said to have been conducted at Almaraz, although access to the data is not possible) were consistent with this predicted shift toward smaller particles. Although the specific effects of this phenomenon on steam generator heat-transfer performance are not well understood, the effect could be a contributing cause to the improvement in thermal efficiency observed at Almaraz, for example by altering the properties of the SG tube deposit layers.

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- Decreased Hydraulic Resistance

Research reported in Reference [21] showed that the hydraulic resistance of FFA-treated surfaces was reduced relative to a similar untreated surface. This effect was shown to reduce the differential pressure of flow through a treated pipe and would have the potential to improve heat-exchanger thermal efficiency, due to decreased hydraulic resistance. The authors concluded that the surface-active product used, FFA, intensifies bubble formation, while at the same time, it has a dispersing effect on the surface of the oxide layer.

6.3.2 Description of Operation

In the case of use of FFAs in lay-up, injection/dosing is limited to a short period, in the order of two-three weeks prior to unit shutdown [27] that is sufficient to establish, with confidence, the protective film prior to a scheduled outage. The primary goal is to achieve a reduction in corrosion rates for certain susceptible components during lay-up and to reduce the need for resource intensive lay-up practices (e.g., dehumidified air during dry layup). The success criteria are discussed in Section 4.

In the absence of a detailed design for application, it is anticipated that the FFA will be injected/dosed into the feed train close to the end of an operating cycle, while in stretch-out conditions. The exact details of the dosing concentrations, the locations of the specific dosing points, duration of dosing, monitoring during and after dosing and various implementation options etc., will form part of the implementation studies will be covered under a commercial enquiry following the acceptance of the conclusions in this feasibility study. Training of chemistry and operating personnel will take place prior to FFA application on the plant.

Modifications to the plant are expected to be minimal and limited to the inclusion of specific injection points along the feed-train and associated equipment and control of the dosing system. The implementation design will be performed by a suitable vendor, to be identified using the commercial process.

6.3.3 Risks

With very few exceptions, the applications of FFA products reported in the literature show overall beneficial effects in steam boilers [53]. The two essential goals of performing technical assessments for new PWR secondary chemical additives are obtaining answers to the following basic questions as expressed at the beginning of Chapter 4 in the scoping study for PWR secondary filming product use [18], namely:

- Safety – The question which needs to be answered as a minimum is: “Is the chemical safe for use with exposed plant components, equipment, personnel and (if relevant) the outside environment?” This may be restated in a more complete way: “Are the mitigated risks of unacceptable, adverse consequences associated with use of the chemical on the following items sufficiently low or negligible:
 - the integrity and function of major or critical plant components, equipment, and systems and,
 - the health and safety of plant workers and the public?”
- Efficacy – The question which needs to be answered as a minimum is: “Is the chemical effective in providing one or more benefits to the plant, either by maintaining or improving component reliability or increasing plant performance, and do these benefits outweigh any possible adverse side effects?”

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For the purposes of this feasibility study, the focus is on lay-up protection as described in Section 6.3.2. According to EPRI [27], from a safety perspective, the risks of a number of adverse effects are judged lower for lay-up type applications, including the formation of solid agglomerations/micelles and reductions in the accuracy or reliability of chemistry analysers and other instruments such as flow measurement devices [27].

In addition to the series of criteria for technical qualification of FFAs used in PWR secondary systems as described by EPRI [18], [27] and the technical description of, other literature and KNPS specific plant design considerations and knowledge have been used to identify potential risks associated with the use of FFAs. These include:

- Marine toxicity and compliance to the CWDP,
- Product Purity,
- Overdosing,
- Poor surface coverage,
- Measuring residual FFA during dosing,
- Macroscopic Fouling,
- Instrumentation and secondary flow measurement device accuracy,
- Condensate polishing plant,
- Effects on SG materials,
- Effects on other metals,
- Effects on non-metallic materials and gaskets,
- Disruption to condenser vacuum,
- Handling and storage of chemicals,
- Effects on secondary chemistry conditions and measurements of key chemistry parameters, and
- Effects on the turbine.

These risks will be included in the Technical Requirements Specification for the implementation of FFA at KNPS which will be compiled and submitted with the request for proposal under the commercial process, following the acceptance of the conclusions and recommendations in this feasibility study.

The TRS will require the specific risks mitigation steps to be further developed as part of the implementation design which will be performed by a suitable vendor, to be identified using the commercial process. In addition, it will require the vendor to report and mitigate to other risks known by the vendor, and other international operating experience in the nuclear and conventional power generation sectors.

6.3.3.1 Marine toxicity and compliance to CWDP

Based on the scientific studies performed as part of the CWDP application, and the identified need to reduce hydrazine discharges to the environment, it is expected that the use of hydrazine as an oxygen scavenger and following the existing practices for wet lay-up (i.e., the “do nothing option”, will no longer be allowed once a CWDP has been issued given that reasonable alternatives are

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feasible. This option is therefore not viable, on the grounds of it not meeting the intent of the project, i.e., reduce hydrazine discharges at KNPS.

As part of the assessment of the various options in the feasibility study, an ecological assessment on the marine impact associated with the use of the FFA octadecylamine (in the product form ODACON®) was performed [13]. Based on this assessment, even at FFA dosing of 5 ppm (which is more than twice the maximum anticipated dosing concentration and before any adsorption or dilution of residual FFA in CRF), ODACON poses very low risk to the marine environment and poses less toxicity risk than hydrazine. The projected concentration at the discharge point also meets ecological guidelines.

6.3.3.2 Product purity

Some commercial FFA products contain both types of FFAs and alkalizing amines or other solubilising agents, which could result in an increase in cation conductivity due to the breakdown products of the neutralizing amines, primarily, formate and acetate organic acid anions, i.e., LMWOAs. This needs to be considered in the FFA product purity specifications. KNPS currently operates a secondary chemistry regime using amines (specifically ETA), that decompose into acetate and formate, which are the same principal decomposition products that are expected from FFAs.

Commercial FFA products used in fossil or nuclear plant applications are described in Section 3.3.2 iv a) to f). Each is listed below together with its FFA chemical constituent and other components:

- Anodamine™ HPFG: proprietary “single substance” – constituents not publicly disclosed
- Cetamine®: OPDA + pH-control amine(s) + dispersant(s)
- HELAMIN®: OPDA + pH-control amines + dispersants
- ODACON®: ODA / HDA / monoamines
- PowerFilm™ 10000: proprietary composition – constituents not publicly disclosed
- Steamate™: OPDA + pH-control amines + (optional) dispersant(s)

It is recommended that in line with EPRI guidance, as contained in References [18] and [19], impurity levels for the FFA to be used be kept to those in line with existing limits for ETA. Refer to in Table 1: Preliminary Purity Specifications for Film Forming Products (FFA products). ETA is a pH-control amine which is applied at feedwater concentrations in the low single digit ppm range [6]. This is around the same range as anticipated dosing concentrations for FFAs. Further, because ETA is specified as 40–85 wt.% while the preliminary FFA product specification is for an effective 100 wt.% concentration, the ETA limits would be expected to result in up to 2.5 times higher feedwater impurity concentrations than the FFA product limits proposed here. While the 50ppb limit for lead is a factor of 10 lower than the ETA limit for lead, it is the same as the lead limit for methoxypropylamine (MPA, another pH control agent), suggesting that it is likely to be achievable and economically feasible.

These limits are however defined for use during at power operations and are more stringent than the requirements for use during outages. This is because the total ingress and accumulation of the impurities in the steam generators during an operating cycle is of greater concern rather than the short-term impurity concentration in the feedwater with limited time exposure (and thus less accumulation). Therefore, for outage periods it is possible that less stringent impurity limits could be accepted for such FFA applications. It is still however recommended that impurities be kept as low as reasonably practicable. Should the limits as prescribed by EPRI not be economically feasible, it

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is possible to use the existing KNPS specification for ETA, also reported in Table 1: Preliminary Purity Specifications for Film Forming Products (FFA products).

Table 1: Preliminary Purity Specifications for Film Forming Products (FFA products)

Impurity	Recommended Max. Conc. (ppm) EPRI	Max. Conc. In ETA (ppm) Limit in DSG-317-090
Sodium (Na)	0.5	1
Chloride (Cl ⁻)	0.5	1
Fluoride (F ⁻)	0.5	2
Sulphate (SO ₄ ²⁻)	0.5	1
Copper (Cu)	0.5	1
Iron (Fe)	1	1
Lead (Pb)	0.05	10

6.3.3.3 Overdosing

The main disadvantages of pure octadecylamine include:

- Its poor ability to enter more complex formulations, which makes the addition of acetic acid or other solubilising agents necessary to introduce it in ionic form, and,
- The marked sensitivity to overdose above the CMC [31].

Overdosing occurs where dosing is high enough to promote the formation of micelles, as described in Section 6.3.1.2 (i). These micelles can accumulate in steam traps and cause rapid, macroscopic blocking of filters and resin beds, as well as blockage of monitoring instrumentation, sampling, and dosing tubing and potentially small-bore piping [17]. The mitigated risk of overdosing is low, provided that the dosing concentration has been accurately determined (in line with the scientific data related to the specific FFA Krafft point/CMC as described in Figure 5) by qualified personnel who have experience in the field of FFA application, and that freely available FFA is constantly kept below this concentration. It is also reduced by using an FFA product such as ODAICON or other FFA which is not highly sensitive to overdosing, and not pure octadecylamine. The dosing concentration will be determined a part of the implementation design which will be performed by a suitable vendor, to be identified using the commercial process, and will be verified by Eskom.

6.3.3.4 Poor surface coverage

Poor surface coverage of FFAs is associated with two main issues: FFA under dosing and poor FFA emulsion stability.

Under dosing is associated with dosing concentrations which are too low, insufficient dosing locations points and insufficient dosing duration. The mitigated risk of under-dosing is low, provided that the dosing concentrations, the locations of the specific dosing points, duration of dosing and monitoring during and after dosing have been accurately determined by qualified personnel who have experience in the field of FFA application. The exact details of the dosing concentrations, the locations of the specific dosing points, duration of dosing, monitoring during and after dosing and

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various implementation options etc., will form part of the implementation studies, and will be verified by Eskom.

Poor emulsion stability leads to the FFA not adsorbing onto the system being treated and is caused by rapid film formation, i.e., the film forms too rapidly in areas adjacent to dosing points (due to not being compatible with the operating conditions during dosing), or by the formation of micelles, in the dosing vessel leading to insufficient free FFA. Poor emulsion stability is typically associated with FFA products where dilution prior to application should be prevented but has not. The mitigated risk of poor emulsion stability is low, provided that the correct FFA product is chosen for the plant's parameters. It is also mitigated by following the manufacturer's directions where there should be no dilution prior to application of the FFA product, as well as by using an FFA product such as ODACON or other FFA which forms a stable emulsion, i.e., not pure octadecylamine.

6.3.3.5 Measuring residual FFA during dosing

The measurement of filming amine residuals in the steam/water cycle is not trivial, and a reliable, commercially available online methodology has not yet been established [27], [53]. It is not however necessary to utilise online analysis and manual sampling can be used. The most commonly used methods include:

- Spectrophotometry – A spectrophotometric method involves pre-treatment of the FFA sample to produce a coloured complex that can be analysed using UV-visible spectrophotometer. The process also requires maintaining of pH using buffer solution.
- Gas Chromatography – Gas chromatography is a direct injection method however this is not suitable for long chain filming amines.
- Fluorometry – Fluorometric method also requires pre-treatment of the FFA solution and maintaining of pH using buffer solution, and the reagents can be expensive.
- Rose Bengal (colorimetry) – Rose Bengal method is a proprietary colorimetric method, reagents can be purchased only from Taylor Technologies, and it also requires specific instrumental set up.
- Liquid chromatography mass spectrometry.

Framatome (the ODACON® F application vendor) uses a modified version of British Standard No. BS 2690 Part 117:1983 to measure ODA concentrations during periods of ODACON® F addition in nuclear applications [27]. Framatome has provided EPRI with additional details concerning this method [27]:

- It is a photometric technique based on the reaction between ODA and methyl orange.
- The response is linear with FFA concentration for values below approximately 2–3 ppm and curvilinear at higher concentrations.
- The method is time-consuming to carry out and relies on analyst-specific practices which are difficult to standardize or automate, making readings subject to wide variability and analyst bias. This latter shortcoming is not considered problematic regarding the typical application protocol in use, as high levels of precision in FFA concentration measurements are not considered a requirement by Framatome.
- Like other FFAs ODACON tends to form films on glass and many plastics, often compromising measurement accuracy, though the use of PTFE bottles can limit this problem [27].

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Manual sampling is not without limitations however: the same characteristic of FFAs (the affinity for adsorption on metal surfaces in a monomolecular layer) that makes them valuable as corrosion inhibitors greatly complicates the analysis in water for them. Previous researchers have reported that the adsorption of filming amine on even non-metallic sampling and analysis container walls is greatly affected by the composition of the FFA product, the range of detection required, the container material, the cleanliness of the cleanliness of all the containers, the purity of the reagents (especially the dye purity when using the Bengal Rose method [17]), the temperature of the sample, and pH [17], [53]. This can be mitigated by users keeping in mind the possibility of these interferences prior to and when sampling and analysing. The analysis should be conducted soon after sample collection, using high-density polyethylene (HDPE), PTFE and not polyethylene terephthalate (PET) or glass sample bottles.

Containers and Spectro photographic cells must be rinsed thoroughly at least twice with isopropanol followed by deionized water before reuse. According to the authors, the purity of the Bengal Rose dye is very important because the results and the sensitivity of the test can be impacted. They recommended using only the high purity grade of the dye [17]. Research by EPRI has also shown that for all practical purposes, the neutralizing amines do not interfere with the determination of the FFA concentrations [17]. It is recommended that dependent on availability of gas chromatography equipment, that the ASTM 4983 method be used. If this is not possible, ASTM 2327 should be used. It might also be necessary to consult the specific vendors for verified and accurate test methods.

6.3.3.6 Macroscopic Fouling

Fouling associated with FFA is linked to overdosing, as discussed in Section 6.3.3.2, and is limited to the formation microscopic micelles and macroscopic “gunk balls” within the water phase. The effects of overdosing are discussed in Section 6.3.3.2 and not here. Surface fouling, i.e. in a similar way to bulk deposits onto surfaces (such as fouling due to scale deposits) is not possible due to the way in which the film mono-layer is adsorbed onto the surface, as discussed in Section 6.3.1.2(ii) and (iii). Mitigation of this risk is thus the same as that for mitigating the risk of overdosing.

6.3.3.7 Instrumentation and secondary flow measurement device accuracy

An important aspect to consider is whether the FFA use has any impact on the reliability of the common online sensors and instruments used to monitor and control feedwater flow and cycle chemistry [17], [27]. Other chemical additives, especially polymeric dispersants (chemicals used for boiler scale and corrosion deposit control) have shown the tendency to affect the accuracy of some secondary flow measurement instruments [27].

Even when FFA films have a beneficial effect with respect to surface corrosion, given that FFAs by nature produce a film on many of the surfaces they contact, a similar effect could occur in secondary feedwater and steam side instrumentation following addition of these chemicals. The changes induced in the properties of the protected surfaces have the potential to affect the accuracy of the two common types of devices used to measure secondary mass flow rates:

- Differential-pressure (DP) devices such as orifices, venturi elements and flow nozzles
- Ultrasonic flow meters (UFMs), including those based on both transit-time technology and those based on cross-correlation technology.

Changes in key surfaces associated with these instruments, due, e.g., to the removal of (or changes in the properties of) existing corrosion product deposits, could potentially affect frictional pressure drop, which would influence the accuracy of DP-type instruments, and/or the rate or strength of transmission of ultrasonic signals through the secondary piping, which could adversely affect the

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readings of UFM's [27]. Since KNPS does not use UFM's for secondary heat balance calculations, this is not of concern. The presence of a film could cause a change in flow characteristics upstream and/or within DP-type flow elements which affects the pressure within the flow element and/or the permanent pressure loss between the relevant pressure taps.

As noted above, secondary mass flow rate measurements that employ these instruments are used as an input to the secondary heat balance calculations that PWRs like KNPS use to control reactor power. (The secondary heat balance inputs for KNPS include feedwater flow rates. In other PWRs steam flow rates are used.) Other flow instrumentation (e.g., that used for measuring SG blowdown flow rates, condensate flows, etc.) could also be affected by FFA films, though the effects would not significantly influence the secondary heat balance calculations [59]. Bias errors of this kind could affect the accuracy of the secondary heat balance calculation (which is used to control reactor thermal power in PWRs). These effects are related to safety rather than efficacy [27].

Due to the complex microscopic (on a nanometre scale) nature of the adsorption mechanism it is practically impossible to theoretically quantify the exact impact on each type of instrument, to within the specific error band of the instruments. This includes pressure sensors and flow sensors in the ARE system. The pressure taps associated with the ARE flow measuring orifices and venturi have an inner diameter of 13mm. It is however anticipated that the effects of the film thickness on secondary heat balance and the risk of exceeding licensed thermal power will be negligible, due to, i) orifice inner diameter reduction of 5e-8m (50nm reduction on orifice diameter) being insignificant (1.95e-5 %) and ii) the dosing occurring at stretch-out (end of core life) when the reactor power is operated below maximum licensed rated power, i.e. if there were any error in SHB it would not place the station at risk of exceeding the power. In addition, the probes will not be required during wet-lay-up periods.

To mitigate this, EPRI [27], [59] recommends an independent engineering assessment of trends in critical secondary side parameters before, during, and after FFA product addition in order to understand instrument indications and how these are affected control systems and to develop a base against which to determine any effects that FFA product application may have. These parameters must include the readings of online chemistry instruments (e.g., temperature, sodium, cation conductivity, pH, etc.), various flow measurement devices (for which anomalous readings could be an indicator of solids fouling), and filter differential pressure readings. This recommendation by EPRI has also been supported by Electrabel/Engie in a utility benchmarking event hosted by Eskom in June 2021. EPRI recommends a maximum change in instrumenting accuracy of 0.3% for both feedwater and steam flow rate instruments because of exposure to FFAs and other non-amine filming products [27], [59]. Changes larger than this threshold would exceed the typical range of daily scatter and would therefore carry a substantial risk that a thermal power derating could be required in response until mitigating actions can be taken. If the direction of the bias error creates false high indications, then the thermal power level would be incorrectly decreased anyhow.

This requirement could be relaxed for the instruments that do not provide inputs to the secondary heat balance calculations, i.e., are not SR or CSR related.

EPRI [27] and Engie also recommend that visual inspections in a selection of secondary components following FFA product addition with a focus on identifying any unusual deposit accumulations, or any areas where coating has not occurred. Candidate targets for the inspection include components such as the SGs, the turbines, the condenser, the feedwater heaters, ion exchange resins, DP flow meter pressure taps, and filters for signs of unusual deposit build-up. It is expected that particle filters and ion exchange resin vessels would be included in the post-FFA product application inspection scope.

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Those probes which require physical contact with the media may also be affected due to the FFA barrier formation affecting the probe. This includes temperature sensors and on-line conductivity analysers and is described in Section 6.3.3.14.

No relevant, publicly disclosed information is believed to be available on the potential effects of ODACON® F on secondary flow instrument accuracy, consistent with FP vendor input [27]. As indicated in Section 4.2.1.7 of [18], the operating utility for Almaraz is not known to have reported any adverse effects on secondary flow instrumentation since initial application of ODACON® F in 2011–2012. However, no supporting data are currently available to evaluate this issue independently [27].

6.3.3.8 Condensate polishing plant

The same properties that allow FFAs (as described in Section 6.3.1.1 and 6.3.1.2) to coat surfaces within the steam/water cycle of a power plant can also cause them to inhibit ionic mass transport or to interact chemically with ion-exchange resins used in the condensate polish plant (ATE).

As filming may occur on all contacted surfaces, especially electrically charged surfaces, the potential risks of FFAs on especially condensate polishing plant ion-exchange resin performance needs to be determined. For optimal ion-exchange resin performance, no limitations to ionic mass transfer from the bulk water to the ion-exchange site should exist. FFAs can potentially reduce the efficiency of ion-exchange resins by numerous mechanisms, including:

- physical, macroscopic level surface blockage of a pore or gel structure,
- permanent filling of space within the resin beads,
- establishment of a surface charge or zeta potential that repulses diffusing ions, and
- permanent bonding of exchange sites within the beads that reduces effective exchange capacity.

Even if bonding is non-permanent and the amine is removable—by means of a typical resin regeneration acid or caustic treatment—there could still be reduced operating time between regenerations if internal exchange sites are obstructed by external filming. This blocking effect would reduce the effective capacity of the resin to remove contaminants.

Note: *The effects on the demineralised water production plant (SDA) cation and anion resins are not considered as there is no possible flow path from the secondary system back to the SDA plant. Only ATE and APG resins could be affected.*

EPRI has conducted laboratory research on two proprietary FFAs, to evaluate potential impacts on condensate polisher ion-exchange spherical bead resins (Dowex MS 650C (H) and 550A (OH)) and a commercially available resin used for the measurement of online cation conductivity [22]. The formulation for one of the products contained only a FFA, while the second formulation consisted of a FFA and a neutralizing amine. Comparative studies were performed using the non-proprietary commercial filming amine octadecylamine (ODA). Due to their formulation, the FFA products required dissimilar dosing concentrations (by volume), to ensure that the resins were exposed to similar amine mass [22].

Experimentation with resins before and after exposure to FFAs included measurements of the mass transfer coefficient (MTC), exchange capacity, and hydrophobicity, as well as evaluation of physical material changes, such as moisture, density, bead cracking, and swelling. The FFA product concentrations, for the MTC determinations, were selected to be in line with several scenarios, namely:

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- The values suggested by the supplier for the low dosing application applied typically during at power conditions. For FFA product 1 this was 0.5-1ppm and 5ppm for FFA product 2.
- The values suggested by the supplier for the higher dosing application applied over a short period prior to a unit shutdown, i.e., like those in preparation for wet-lay-up. For FFA product 1 this was 5ppm and for FFA product 2 this was 15-100ppm.
- Very high concentrations (50, 250, 1500ppm and 2500ppm) to simulate gross overdosing and accumulation over an extended period were also tested.

As a reference, pure ODA was used at a concentration of 0.5ppm, due to the poor solubility of ODA in water. This is also in line with what is required to prevent micelles/gunk balls as described in Section 6.3.1.2 (i).

Following exposure to the two proprietary FFAs, cation resins showed both adsorption and ion exchange of the amine on and within the resin. Cationic capacity could be recovered by regeneration (at the maximum regenerating agent concentrations as specified by the resin manufacturer), and the mass transfer coefficient (MTC) could be improved but not restored to initial values, or values on par with spent resin which had been regenerated. For pure ODA, reductions in capacity and the MTC were permanent, i.e., regeneration had little effect on recovering cation resin performance.

The FFA product which contained the neutralizing amine indicated a larger reduction in cation resin salt-split capacity and less recovery following regeneration than the product containing only a filming amine. This is expected as neutralizing amines are known to affect cation resins. Anion resins, which do not have an affinity for amines, showed minor impact because of adsorption. The reduction in salt-split capacity and recovery following regeneration for the anion resin was similar for both products [22].

Results suggest that condensate polishers containing bead resins should not be exposed to FFA products at these higher concentrations (5-10 times the supplier's prescribed concentration). In cases where contact does occur, the study reported provided qualitative and limited quantitative information about the potential to recover mass transfer and capacity properties [22].

EPRI also funded industry research that investigated the use of dodecylamine (DDA) to inhibit fouling of steam generator tubes [24]. This chemical showed promise in enhancing boiling heat transfer and corrosion protection, however, significant resin performance degradation was observed for typical cation resins (Dowex MS 650C H and Amberjet 1600 H) exposed to DDA [24].

EPRI [23] has conducted laboratory experiments to evaluate potential impacts on bead resin at low-level dosages of the FFA (Cetamine V219), similar to the concentrations that would be expected during normal plant operation for continuous application. The research also covered two proprietary FFAs and their interactions on condensate polisher ion-exchange powdered resins. As powdered resins are not used at in the condensate polishing plant at KNPS that portion of the research was not applicable to this feasibility study. While the research focussed on the continuous application of FFA during at power conditions, the concentration of FFA tested (1ppm) is in line with what the anticipated concentration which would be used during application at KNPS for feed train outage lay-up [23].

Two experimental columns (control and test) were loaded with Dowex 650C (H) cation-exchange resin, backwashed, regenerated using hydrochloric acid, and rinsed with DI water prior to both the service and evaluation cycles. The results indicate that there is little to no significant impact of low-concentration (1ppm) Cetamine V219 exposure on the cation bead resin, when compared to the control [23].

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In addition, two experimental columns (control and test) were loaded with 2/3 Dowex 650C (H) cation-exchange resin and 1/3 Dowex 550A (OH), regenerated separately, rinsed, mixed, added to the columns as a mixed resin slurry, and rinsed with DI water prior to both the service and evaluation cycles. The rationale for this choice was to match the resin volume required in the ASTM method for evaluating the ion-exchange resins: ASTM Method D6302 – 98 (2009) The results indicate that there is little to no significant impact of low concentration (1ppm) Cetamine V219 addition for the mixed-bed resin exposure. [23].

It must be noted that the existing chemistry regime during at power operations [6], [68] makes use of ETA as a water-steam phase pH control amine. ETA is known to severally impact the longevity (useable life) of ion-exchange resins [6], [7], [19], however, effective administrative operating procedures have been put in place to ensure that the secondary side is not in an ETA regime when the condensate polishing plant (ATE) is required to be in service.

The mitigated risk of negatively affecting the condensate polishing plant is low, provided that administrative operating procedures are effective (similar to those used during the ETA regime), and plant status controls have been put in place to ensure that the condensate polishing plant (ATE) is not in service, or bypassed [17] during the FFA dosing application prior to outages or directly following unit start-up.

6.3.3.9 Effects on SG materials

EPRI observed the effects of Dodecylamine (DDA) on the electrochemical behaviour of Alloy 600 indicates that DDA addition to water will not jeopardize SG tube integrity and showed promise in enhancing boiling heat transfer and corrosion protection. The report by EPRI states that the target concentration of DDA (<1mg/kg) may improve the localized-corrosion resistance of Alloy 600 [24].

Rohani-Rad et al [56], [57], conducted laboratory testing using weight loss and electrochemical tests to determine the anticorrosive behaviour of octadecylamine (ODA) on carbon steel, brass, and austenitic stainless steel. The corrosive solution was soft water with 1 ppm Fe, 240 ppm Cl, 445 ppm Na, 4 ppm K, 0.5 ppm PO₄, 5.75 ppm O₂, 730 ppm SO₄, 1270 ppm TOC, 280 ppm HCO₃, 2 ppm Ca, and 2 ppm Mg. The pH was 8.27 and ODA concentration of about 10 ppm. Coupon testing was performed on steel 20, brass and 18/10 steel over 1100 hours with average rates determined over 100 hours. Reported corrosion rates for test coupons of Steel 20, Brass, and 18/10 Steel with and without Octadecylamine present indicated that significant reduction in corrosion rate, as high as 94.5%, were obtained in the series of experiments where the FFA was present. For surfaces that were coated with ODA before lay-up began, the optimum concentration of ODA for protection while out of surface was found to be 0.2 ppm [56].

Research was conducted by Jundong et al of the Suzhou Nuclear Power Research Institute, Suzhou, in China [60], using the high temperature slow strain rate test (SSRT) method to evaluate the influence of ODA on the stress corrosion cracking behaviour of two conventional island materials for PWR nuclear power plants. These two metal materials are the heat exchange tube materials of the high-pressure heater and steam generator in the high-temperature operation area of the secondary circuit of a nuclear power plant: TP 439 stainless steel and 690 TT alloy. The test results indicated that:

- (i) Under the condition of slow strain rate, the stress corrosion behaviour of the two materials is relatively consistent in the two environments of FFA and non-FFA, and neither shows obvious stress corrosion sensitivity.
- (ii) Under the test conditions, the FFA (<5mg/kg) will not significantly affect the SCC behaviour of TP 439 stainless steel and 690 TT alloy under the condition of slow strain rate.

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- (iii) In actual application, the general dosage is lower than the FFA concentration used in the experiment. Therefore, there is no concern about the obvious impact on the SCC behaviour of TP 439 stainless steel and 690 TT alloy

6.3.3.10 Effects on other metals

With the exception of ion exchange resins, which is discussed in the Section 6.3.3.8, no test programs are known to have been conducted specifically to investigate the potential for unintended, adverse increases in corrosion or degradation rate that might occur in plant materials in the context of ODAICON® F addition. Rather, all materials testing has primarily been focused on establishing efficacy.

In preparation of the FFA application at Embalse in late 2015, AREVA performed laboratory testing to demonstrate the essential compatibility of ODAICON® with a selection of secondary plant materials. The purposes of this testing were to confirm that a stable film could be established in conditions prototypical of the long layup planned for Embalse and to confirm that this film would reduce rates of corrosion under these conditions. The following bullets cover available information relevant to this topic in the context of the major material classifications:

- Testing data for Carbon steel, stainless steel, and low-alloy steel these materials include:
 - Laboratory testing published in 2017 [64] evaluated corrosion rates of carbon steel samples at 228°C and 300°C in a static autoclave with and without ODA at concentrations of 1 ppm to 5 ppm in the test solution. Coupon weight loss measurements and electrochemical impedance spectroscopy (EIS) measurements (i.e., film thickness measurements) reported by the investigators indicated a decrease in the corrosion rate which ranged from about 40% to 70%).
 - Layup corrosion testing. As described in References [46] and [65], this testing for Embalse involved exposure of treated coupon specimens, together with virgin and pre-oxidized control coupons, to simulated dry layup conditions characterized by a range of relative humidity (RH) levels (10%, 40%, and 80%), adjusted using chloride salts, consistent with exposure to a marine air environment. The tested materials were as follows:
 - A-106 Gr. B: CS pipe.
 - SA-285 Gr. C: CS plate.
 - 410 SS.
 - 316L SS.
 - CDA-443: admiralty brass.
 - Siemens turbine blade specimens (Details of this testing were not reported).

These tests qualitatively demonstrated film protection for two carbon steels and two stainless steels based on the visual appearance of the exposed samples compared to control specimens. No film thickness tests were conducted.

- Testing data for Copper and Cu alloy materials include:
 - The dry layup testing noted above also included admiralty brass specimens (nominally 69 Cu–30 Zn–1 Sn). As with the Carbon Steel and Stainless-Steel samples, exposure of the treated coupons resulted in apparent protection based on visual appearance.

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At both Almaraz and Embalse, ODACON® F has been added in a diluted form, meaning that injection line components are exposed to this diluted concentration (i.e., a lower value than the 5% present in the FP formulation). The Almaraz injection line components, reflecting an injection location just downstream of the condensate pump discharge at ambient temperature are known to be constructed of SS materials. No qualitative information from this OE indicating any incompatibility between the injection line materials and these FP exposures has been reported to date for either station. Each Almaraz unit has added ODACON® F a total of at least four times since 2011–2012, meaning that the accumulated period of injection at these units is currently at least 8 weeks [27], with no incompatibility reported.

6.3.3.11 Effects on non-metallic materials and gaskets

Many non-metallic materials are used in the secondary side, including BOP elastomers (e.g., gaskets): Viton A, ethylene propylene diene monomer (EPDM), nitrile rubber (Buna-N), polychloroprene (neoprene), styrene-butadiene, natural rubber, etc. [27].

In 2016 Framatome reported that compatibility between ODACON® F and, some elastomers was verified through laboratory testing prior to the first Almaraz application in 2011 at the request of the utility [27]. Although details of this test exposure are not publicly available, nor available via EPRI, the results are understood to have shown no appreciable adverse effects. Subsequently, AREVA indicated that the utility has not reported any integrity problems with elastomeric seals, which has been interpreted as an absence of a significant incompatibility with ODACON® given its use since 2011–2012 at Almaraz Units 1 and 2 [18].

Extensive experience in PWR secondary systems gained over many years with pH control amines such as ETA—which have chemical similarities to filming amines—suggest that amine- containing products are likely to have some degree of compatibility with commonly used elastomers. In addition, experience with various amine-based products indicates their affinity for adhering to a wide variety of materials, suggesting a high likelihood that exposed elastomers would also be filmed [27]. For these reasons, a systematic evaluation of elastomer compatibility is considered a minimum requirement prior to routine FFA use in nuclear units [27]. The expected method for this evaluation is a low-temperature laboratory test series similar to that carried out as part of technical assessments completed for PAA (see Appendix D of Reference [66]):

- Specimen material: At least three commonly used elastomers (e.g., Viton A, EPDM, nitrile rubber, neoprene, styrene-butadiene, etc.)
- Specimen surface condition: As recommended by the elastomer vendor (e.g., untreated, coated with a specified lubricant, etc.)
- Test type: Low-temperature (atmospheric pressure) laboratory exposure followed by physical property evaluations
- Test conditions: Low temperature (e.g., between 25°C and 100°C), atmospheric pressure, and representative pH control amine concentration, together with FFA concentrations ranging from
- 1 to 100 times the expected target feedwater concentration. Depending on the results, additional sets of test conditions could be added (including a high-temperature environment such as an autoclave) to reflect the prototypical water-steam circuit conditions more closely, but such additional test conditions are not considered a minimum requirement.

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- Elastomer property evaluation: Weight change, tensile strength at break, elongation at break, and hardness (see Appendix D of Reference [65] includes some additional details on the test protocols used for qualifying PAA). Changes in additional properties may also be evaluated as a supplement—e.g., volume swell, thermal properties, visual appearance, compression set, usable lifetime, etc. It is expected that replicate specimens will be necessary to address statistical scatter and also that control specimens exposed to the same conditions (without the FFA) would be tested. Depending on the results, an assessment of the elastomer surface to characterize the presence of any FP film might also be performed (though this is not considered a minimum requirement) [27].

Verification of effects on non-metallic materials would need to be conducted as part of the application at KNPS.

6.3.3.12 Disruption of condenser vacuum

If the condenser hot-well were used as an FFA dosing point, it could be possible to increase condenser pressure (i.e., increase absolute pressure / departure from vacuum) should the FFA dosing tank be allowed to run dry. This can be avoided by ensuring that the FFA dosing tank does not run dry. As the dosing frequency is only once every fuel cycle per unit, and occurs in batches, this mitigation can be implemented by ensuring that the level in the dosing tank is checked frequently during dosing, in accordance with the dosing rate and volume to be dosed, and that the dosing tanks is topped up, or the dosing isolated at the appropriate time.

6.3.3.13 Handling and storage of chemicals

The handling of FFAs is complicated by both their physical and chemical properties. The handling and storage of FFAs poses a unique set of challenges as it relates to long term storage of the chemicals, in that the filming of storage containers and containers used for decanting for performing analyses must be considered. Low miscibility with water, container filming, and solution viscosity must all be considered when handling FFAs, however most FFA products contain a sufficient concentration of a neutralizing amine to keep the FFA in solution [21]. This challenge is posed more by chemically pure FFAs, such as ODA, DDA, etc.

In power plants using FFAs, handling and sampling of the condensate, feedwater, boiler/evaporator, and steam-conditioned samples should not present the challenges mentioned above unless FFAs are overfed. At the typical recommended treatment concentrations, emulsions and other sampling-related issues are usually not encountered. [21]

Most suppliers indicate that storage container filming can be minimized if Teflon or Teflon-lined sampling containers are used. Due to the expense of Teflon bottles, PTFE sample containers can be used, as suggested by EPRI [21]. To minimize filming on the plastic containers, samples should be taken and analysed within two hours of dilution from the as-received solutions.

6.3.3.14 Effects on secondary chemistry conditions and measurements of key chemistry parameters

This topic involves two distinct areas [27], namely:

- The potential effects of FFA product addition on the actual chemistry conditions in the secondary water-steam circuit,
- The potential effects of FFA product exposure on instruments used to monitor secondary chemistry parameters, and

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A third area does exist, namely the ability to effectively implement the desired FFA product addition protocol through measurement of residual FFA concentrations. This is discussed in detail in Section 6.3.3.5.

As all these areas involve the potential for adverse side effects or poor FFA implementation, secondary chemistry issues are judged to be primarily related to safety rather than efficacy as defined at the beginning of this chapter.

(i) Effects on the actual chemistry conditions in the secondary water-steam circuit

- Cation conductivity

As discussed in the Section 6.3.1.2 (i) regarding the thermal stability of FFAs, the decomposition of the FFAs, and any blended neutralizing amines in the FFA product, results in the formation LMWOAs. Reference [17] reports that in most of the cases where a FFA product was used, the cation conductivity increased by 0.2 to 0.4 $\mu\text{S}/\text{cm}$. There is evidence that the increase cation in conductivity could also be due to impurities in the FFA product [17], [18]. This risk is mitigated through the selection of the correct FFA product, which if utilising a neutralizing amine, must account for thermal decomposition, as well as the risk of introducing chemical impurities, as discussed in Section 6.3.3.2. It is also important to note that this is of greater concern when FFA products are used continuously during at power operations, then during outage lay-up conditions.

(ii) Effects on instruments used to monitor secondary chemistry parameters

Due to the wide range of instruments used, it is considered impracticable to develop any generic statement on effects or basis requirements for each individual item [27]. However, as indicated in Section 6.3.3.7 (as referenced form Reference [27]), it is recommended that, as a minimum, all critical chemistry parameters be monitored and trended for at least one cycle, preferably two prior to FFA application, and that an engineering assessment on trends in online chemistry instruments before, during, and after FFA product addition be conducted[27]. The risk of FFA product induced effects on chemistry instrumentation performance can be assessed through analyses of trends in individual readings during FFA product use compared with pre-FFA product time periods. Due to the potential for slowly developing issues, such analyses may require data collected over relatively long time periods both before and after FFA product addition (e.g., weeks to months) [27].

Research, in the form of controlled laboratory tests, was performed to ascertain the impact of three different brands of FFAs on system parameters and online measurement instrumentation [39]. This research followed an attempt to perform similar research in the field, which was deemed inconclusive as the recorded data showed too much operational noise, combined with the fact that only one FFA was used. In the laboratory set-up, specific conductivity, pH drift, cation resin retention, pH stability, sodium step response, sodium calibration, oxygen sensor response and ORP probe response were considered. Differences in some results depending on the FFA used were noted. The report concluded that while with some measurements no negative influence could be observed, with other equipment there was a minor loss of sensitivity and speed of response time due to FFA coating effects. No negative influence was observed on pH, ion-selective sodium measurement and Clark-type oxygen probes, however, slight loss of sensitivity and speed of response due to coating effects were observed during measurement of ORP [39].

At Almaraz NPP application of ODAICON® F was found to adversely affect the accuracy and performance of the platinum probes in the original Almaraz sodium analysers in use at the time of initial addition. Replacement of these analysers with another model coupled with frequent

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probe cleaning was reported to resolve this issue. It was further observed that other Pt-containing probes (from alternative suppliers) were affected but could be used if the probes were cleaned frequently (e.g., every few days during the application period—although the necessary frequency is expected to be strongly plant-dependent).

6.3.3.15 Turbine

The accumulation of damage due to localized corrosion (pitting, stress corrosion cracking (SCC) and corrosion fatigue) in low pressure steam turbines (LPST) components, such as blades, discs, and rotors, has consistently been identified as being among the main causes of turbine unavailability [38].

The phase transition zone (PTZ) in the LP turbine, where the expansion and cooling of the steam leads to condensation, is particularly susceptible. Several processes that take place in this zone such as precipitation of chemical compounds from superheated steam, deposition, evaporation, and drying of liquid films on hot surfaces, lead to the formation of potentially corrosive surface deposits [38].

Pitting of turbine components is initiated through the combined action of oxygen and contaminants, such as chlorides, in the moist environment occurring in the turbine during shutdown. Use of dehumidified air, a method advocated by many turbine manufacturers, appears to be the preferred approach for protection in fossil plant applications.

Reduction and elimination of moisture on surfaces of the turbine components prevent the formation of concentrated electrolytic films containing oxygen, which are precursors to disruption of the passive films and pit formation. EPRI research and modelling has demonstrated that stress corrosion cracking and corrosion fatigue cracks initiate from micropits on the surface of the metal [38].

Elimination of moisture following shutdown presents a major challenge as the steam environment naturally exceeds the 60% humidity level at ambient conditions. The objective is to condition the turbine environment beginning at the initiation of shutdown and control the moisture levels below 40%. Use of nitrogen to eliminate oxygen presence in a turbine is deemed, by most utilities, too hazardous to personnel safety to be a viable alternative [38]. FFA could benefit in this regard, by preventing oxygen and moisture from contacting the metal surface.

EPRI has funded research that investigated the effects of two filming amines (Anodamine HPFG and Cetamine BL8101) on chloride related pitting in the phase transition zone (PTZ) of a fossil unit. This testing was performed with a reference chemistry in which ammonia was the pH agent. This study found that, although the filming amines did not eliminate corrosion, they did significantly reduce it [25].

According to EPRI, current industry posture is that SCC and corrosion fatigue in PWR turbines are not due to improper water chemistry but rather are due to the materials and design of the turbines. The specific concentrations of impurity contaminants (sodium, chloride, sulphate, and silica) which may affect turbine performance are discussed extensively in Reference [36]. With respect to organic acids produced by decomposition of amines, calculations have been performed by EPRI to evaluate whether net acidification (due to the formation of formate and acetate) is expected (i.e., relative to use of ammonia). These calculations indicate that acidification is not predicted under normal chemistry conditions when amines are used [61], [62], and not greater than the use of ETA, as is currently the case at KNPS. Independent reviews of field experience by EPRI and a turbine vendor [63] have concluded that there are no amine-specific corrosion effects likely to affect turbine materials at typical operating conditions when using FFAs for lay-up or during at power conditions.

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EPRI has reported that Siemens's turbine blade specimens were included in dry layup testing conducted with ODAICON [18]. The test specimens treated with ODAICON exhibited an intact FFA film as well as greater corrosion resistance than untreated controls following 3 weeks of exposure to a humid environment with elevated chloride levels). In addition, the results of visual inspections after multiple FFA refreshments showing the LP turbine in apparently good condition in each case indicate some level of material compatibility for at least materials used in the LP turbine at Almaraz. [18]

Despite the potential benefits, and no major drawbacks as discussed above, it is still recommended that existing turbine and steam system outage lay-up practices continue as it relates to purging with dehumidified air [38] and the existing Koeberg procedure, KBA1217GCA001 [9], until further empirical data from application at KNPS can be obtained.

6.4 Option 4 - Chemical decompose hydrazine into inert components before conventional discharge

6.4.1 Technical Description

This option considers the use of mechanical and chemical methods (or a combination thereof) to significantly reduce hydrazine into inert components (nitrogen and water) before discharge through KER and SEK systems into the CRF outfall. This would entail the implementation of modifications to several mechanical and electrical systems and civil structures, changes to existing as well as compiling of new operating and chemistry procedures, changes to waste liquid management practices (generating, blending storage, treatment, and discharge), and introduce further limiting conditions of operations as it relates to availability of liquid effluent collection tanks to eliminate/neutralize hydrazine. The ways in which the reduction occurs could be one of the following:

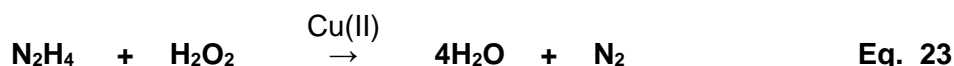
- Reaction with hydrogen peroxide or another oxidizing agent,
 - Thermally decomposing hydrazine in the prior to start-up, or,
 - Significant reduction of hydrazine through sparging with compressed air either prior to or inside the waste tanks.
- (i) Significant reduction of hydrazine with hydrogen peroxide or another oxidising agent

Several oxidising agents can theoretically be used to significantly reduce hydrazine in the discharge. These include chlorine bleach, calcium hypochlorite, its derivatives, catalysed charcoal, ferric chloride, oxygen, and hydrogen peroxide. Some of these reactions require catalysts to increase the reaction rate to be industrially viable. The most common catalyst is copper sulphate, which is used in the reaction with oxygen and the reaction with hydrogen peroxide. Based on work completed by EDF [12], it was identified that the reaction of hydrazine and chlorine bleach or chlorine bleach derived chemicals or with ferric chloride as oxidising agents needs very large quantities of these chemicals, which requires bulk chemical handling. It would also result in an increase above the maximum allowed discharges quantities for chlorides to the environment. For these reasons they have not been considered any further.

Based on work completed by EDF [12], it was identified that (as it relates to reacting hydrazine with an oxidising agent) the only technically viable option would be to use hydrogen peroxide to eliminate/neutralize hydrazine in the presence of a copper (II) catalyst. This could occur within roughly 24 hours, by adding about 700 to 800 litres of 30 % hydrogen peroxide solution per 100 kg hydrazine to eliminate. To achieve this reaction time, it would also require copper sulphate as a catalyst, at levels between 100 to 200 µg/kg (minimum levels required),

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and an optimal level of 500 µg/kg. The copper sulphate would have to be added if copper is not present in the waste. Without the addition of copper sulphate as catalyst, the reaction rate is significantly slower, and requires at least 72 hours (and is more dependent on reaction temperature).



- (ii) Thermally decomposing hydrazine during unit start-up.

Instead of draining the feed train and SGs, the water used during wet lay-up can technically be used during unit start-up, provided it meets the chemical purity requirements. The residual hydrazine would thermally decompose (crack) according to the reactions below. Reaction 25 is the most favoured, while reaction 24 and 26 occur, but to a much lesser degree:



- (iii) Eliminating/neutralizing of hydrazine through sparging with compressed air.

In this method, the hydrazine is destroyed by a reaction with the oxygen in the air, at specific conditions and in the presence of copper sulphate as a catalyst. This is performed as a batch process. Oxygenation of the solution to be treated is carried out by continuous mixing, during the treatment period, using a circulating pump and air sparger.



Operating experience [54] shows that hydrazine destruction by air sparging is less effective in terms of reaction kinetics and conversion, than with hydrogen peroxide, but is safer and cheaper, reduces the risk of reaction between the hydrogen peroxide and the other products, such as the organic or chlorinated compounds.

6.4.2 Description of Operation

This would entail the implementation of modifications to several systems and buildings, changes to existing as well as compiling of new operating and chemistry procedures, changes to waste liquid management practices (generating, blending storage, treatment, and discharge), and further limiting conditions of operations as it relates to availability of liquid effluent collection tanks.

- (i) Significant reduction of hydrazine with hydrogen peroxide or another oxidising agent

This could occur within 24 hours, by adding 700 to 800 litres of 30 % hydrogen peroxide solution per 100 kg hydrazine to eliminate. To achieve this reaction time, it would also require copper sulphate as a catalyst, at levels between 100 to 200 µg/kg (minimum levels required), and an optimal level of 500 µg/kg. The copper sulphate would have to be added as copper is not present (only present in trace amounts and nowhere near the required level) in the waste at KNPS. Without the addition of copper sulphate as catalyst, the reaction rate is significantly slower, and requires at least 72 hours (and is dependent on temperature, with optimal reaction conditions above 50°C).

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The wet lay-up waste for the SGs would require a dedicated KER tank and exceptionally strict waste treatment practices prior to treating the effluent. Due to limitations in treating activated liquids the waste would need to be treated in batches, which could influence outage duration. Each SG generates roughly 70 m³ (at 20 °C) of hydrazine contained effluent, resulting in 210 m³ for all three SGs per unit. The SGs would need to be drained to the additional, dedicated KER tank, where the copper sulphate catalyst is added to optimise the reaction kinetics.

The wet lay-up waste from the feed train and secondary side would require exceptionally strict waste treatment practices prior to treating the effluent, as well as a dedicated SEK tank to avoid treating effluent in batches and for prolonged periods, which could influence outage duration. The feed train and condenser volume drained when under wet lay-up is approximately 800 m³.

The mixing of strong oxidising and strong reducing agents, such as hydrogen peroxide and hydrazine are typically avoided in industry, as the resulting reactions are highly exothermic.

(ii) Thermally decomposing hydrazine during unit start-up.

Instead of draining the feed train and SGs, the water used during wet lay-up can technically be used during unit start-up, provided it meets the chemical purity requirements. Hydrazine will decompose to ammonia and nitrogen and possibly hydrogen. It is recommended that this thermal cracking be performed during start-up in domain SD-SG, with steam being dumped via GCT to atmosphere, to vent small amounts of non-condensable ammonia and hydrogen gas. This operation does rely heavily on the absence of any corrosion by-products during start-up, and a feed train which is free of any foreign material, as well as the optimal operation of all blow-down related systems. It is also important to note that high ammonia concentrations, resulting from the thermal decomposition of hydrazine can lead to premature exhaustion of the ATE and APG cation and mixed bed resins [19], which needs to be accounted for.

(iii) Significant reduction of hydrazine through sparging with compressed air.

This is performed as a batch process. Oxygenation/Aeration of the hydrazine containing effluent to be treated is carried out by continuous mixing (during the treatment period) using a circulating pump and air sparger, located in the effluent collection sumps and requires exceptionally strict waste separation and treatment practices prior to treating the effluent.

SAT air can be injected to increase the kinetics of the reaction and reduce the treatment time. Copper sulphate is used as a reaction catalyst between hydrazine and oxygen. To increase the kinetics of the reaction with oxygen from the atmosphere, the hydrazine must be destroyed at an elevated pH, i.e., basic environment and in the presence of a copper sulphate catalyst. Copper sulphate would need to be added with injection of 5 ppm in principle being regarded as sufficient, as it is not present in the waste. The effluent collecting sumps and tanks must be kept completely free of oil and free of any effluent of unknown composition, e.g., laundry detergents [54]. As an absolute minimum, they must be cleaned prior to treating the hydrazine effluent. This helps avoid all interaction by the hydrazine with other chemical substances (in particular with detergents) to prevent froth formation.

6.4.3 Risks

Based on the work performed by EdF [12], [54], options

(i) Significant reduction of hydrazine with hydrogen peroxide or another oxidising agent

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The significant reduction of hydrazine with hydrogen peroxide poses many occupational health and safety risks, and requires very strict precautions which must be adhered to, to guarantee personnel safety, owing to the physical and chemical properties of hydrogen peroxide, specifically:

- Raising personnel awareness of the chemical risk,
- Wearing additional personal protection equipment,
- The installation of a water rinsing system nearby to deal with an accidental spillage of hydrogen peroxide.
- Using dedicated storage tanks, piping and equipment made from series 316 stainless steel.
- Correct storage of bulk quantities of strong oxidising agents.

Without the addition of copper sulphate as catalyst, the reaction rate is significantly slower, and requires at least 72 hours (and is dependent on temperature, with optimal reaction conditions above 50°C). The addition of copper sulphate would require additional dosing facilities.

While the reaction kinetics of hydrazine and oxygen is sufficient above 50°C, it would require major and costly modifications to implement this method, i.e., heaters to the SEK and KER tanks, as well as thermally insulating these tanks and ancillary equipment. This also has negative implications on the discharge temperatures into the environment, which was also identified as an environmental hazard during the CWDP application process.

The wet lay-up waste for the SGs would require a dedicated KER tank and exceptionally strict waste treatment practices prior to treating the effluent. Due to limitations in treating activated liquids the waste would need to be treated in batches, which could influence outage duration. Each SG generates roughly 70 m³ (at 20 °C) of hydrazine contained effluent, resulting in 210 m³ for all three SGs per unit. The SGs would need to be drained to the additional, dedicated KER tank, where the copper sulphate catalyst is added to optimise the reaction kinetics.

The wet lay-up waste from the feed train and secondary side would require exceptionally strict waste treatment practices prior to treating the effluent, as well as a dedicated SEK tank to avoid treating effluent in batches and for prolonged periods, which could influence outage duration. The feed train and condenser volume drained when under wet lay-up is approximately 800 m³.

The addition of copper sulphate would have to be added if copper is not present (only present in trace amounts and nowhere near the required level) in the waste at KNPS. Without the addition of copper sulphate as catalyst, the reaction rate is significantly slower, and requires at least 72 hours (and is dependent on temperature, with optimal reaction conditions above 50°C).

While the chemistry change may be theoretically possible, the risk of cross-contamination with wastes from impossible to characterise sources is high. This cross contamination of the waste to be treated with unknown origin from sumps and other drains will require excess hydrogen peroxide, require exceptionally strict waste separation practices from workers (without real methods to prevent cross-contamination) prior to treating the effluent and the possibility of side reactions with unknown consequences.

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This option further increases the burden on plant operators prior to unit start-up due to the additional limitations it places on waste treatment practices.

(ii) Thermally decomposing hydrazine during unit start-up.

Good practice at KNPS dictates that the feed train and condenser are usually drained after each outage to flush any corrosion by-products as well as any foreign material which may have been introduced during feed train SSC maintenance during outages.

The option to thermally decomposing hydrazine during unit start-up is thus not considered best-practice by KNPS.

(iv) Significant reduction of hydrazine through sparging with compressed air.

Previous engineering studies have identified that preventing contamination of sumps is practically very difficult and time-consuming, especially during outages, prior to when the effluent will need to be treated.

Copper sulphate would have to be added as copper is not present (only present in trace amounts and nowhere near the required level) in the waste at KNPS. Without the addition of copper sulphate as catalyst, the reaction rate is significantly slower, and requires at least 72 hours (and is dependent on temperature, with optimal reaction conditions above 50°C).

7. Decision Matrix Table

The decision matrix below was developed to assist with the option evaluation and selection process. It is used to rank and score technical and project criteria to conclude on a preferred technical option. The decision matrix table has been developed using the technical and project criteria as defined in the SOW as well as other criteria for success described in Section 4, and rational for selection described in Section 5.

The criteria are weighted where the most important criteria are given a higher weighting, with the total adding up to 100%. Compulsory criteria that must be met to meet the intent of the project, the failure of which would result in an option being disqualified, are given a weight of "C". Compulsory criteria are not allocated a score, instead it is indicated if they meet the criteria, "yes", or not, "no". If an option does not meet compulsory criteria, then the option is considered as not technically feasible.

Each option is scored as to how it meets the specific criteria, with a score of 0% to 100%. The option that best satisfies the criteria is scored 100%. The other options are then given a proportional score dependant on how the criteria were met by the specific option in relation to the option that scored a 10. Scores are then weighted and summed.

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Table 2: Decision Matrix Table for reduction of hydrazine discharges at KNPS

	Success Criteria	Importance Weight Factor	Option 1 – Do Nothing		Option 2 – Replace hydrazine		Option 3 – Use of FFA		Option 4 – Decompose hydrazine	
			Score	Weighted score	Score	Weighted score	Score	Weighted score	Score	Weighted score
Compulsory Criteria	Chemicals must be non-toxic to marine organisms or be discharged at a concentration and rate which is not harmful to marine organisms. *	C	No	FAIL	Yes	PASS	Yes	PASS	Yes	PASS
	Must be compatible with the existing chemistry regime	C	Yes	PASS	Yes	PASS	Yes	PASS	Yes	PASS
	Must maintain plant integrity during lay-up conditions	C	Yes	PASS	Yes	PASS	Yes	PASS	Yes	PASS
Qualitative Criteria	Must not have a more than minimal negative impact on normal plant integrity and operations during at power conditions.	30%	100%	30%	100%	30%	90%	27%	100%	30%
	Operator burden must be consistent with current duties.	10%	100%	10%	90%	9%	100%	10%	30%	3%
	Conventional safety associated with handling and storage chemicals.	5%	10%	1%	100%	5%	100%	5%	20%	1%
	Must allow maintenance of the feed train at any point during an outage without the need for burdensome lay-up practices.	30%	0%	0%	0%	0%	100%	30%	0%	0%
	The chemical to be used must have a track record for the intended use within the nuclear power generating industry.	15%	100%	15%	85%	13%	85%	14%	50%	8%
	Cost	10%	0%**	0%	100%	10%	50%	5%	50%* **	5%
Qualitative Criteria Totals				56%		67%		90%		47%

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	Success Criteria	Importance Weight Factor	Option 1 – Do Nothing		Option 2 – Replace hydrazine		Option 3 – Use of FFA		Option 4 – Decompose hydrazine	
			Score	Weighted score	Score	Weighted score	Score	Weighted score	Score	Weighted score
	Compulsory Criteria			FAIL		PASS		PASS		PASS
	Overall							<i>Most feasible</i>		

* As defined by the ecological studies as part of the CWDP and its appendices [4].

** Even though Option 1 has the lowest relative operational cost from a chemical consumption point of view, a cost rating of 0% has been allocated to it in line with the CURA risk.

*** No design related costs were available.

8. Cost Analysis of Option

The budget cost or approximate costs for the design, equipment and installation are detailed below for each technically feasible option.

8.1 Option 1 – Maintain the status quo – Do nothing option

This option is not costed as it is not considered feasible, as described above.

8.2 Option 2 - Replace hydrazine with another wet lay-up oxygen scavenger

The costing for the use of alternative wet lay-up oxygen scavengers, i.e., replacing hydrazine with another chemical which is deemed as effective as hydrazine for dissolved oxygen and ECP / ORP control and less toxic than hydrazine with respect to human health and the environment discussed below:

- Sodium Sulphite

This option is not costed as it is not considered feasible.

- Diethylhydroxylamine (DEHA), Methylketoxime (MEKO) and N-Isopropylhydroxylamine (NIPHA)

This option is not costed as it is not considered feasible.

- Hydroquinone

This option is not costed as it is not considered feasible.

- Carbohydrazide

Based on the description of the operation as described in Section 6.2.1 and 6.2.2, and a bulk chemical price of R75/kg excluding VAT, the direct replacement with carbohydrazide would cost roughly R920,000.00 per year.

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8.3 Option 3 - Significantly reduce the need for an oxygen scavenger during wet lay-up conditions

Based on the description of the operation as described in Section 6.3.1 and 6.3.2, and a budget quote by Framatome obtained through RFI KBG2048m, this option would cost € 975.653,00 (R16,859,283.84 as on 25.03.2021 with an exchange rate of R17.28/€). This quite includes all safety studies, design, and implementation.

8.4 Option 4 - Chemical decompose hydrazine into inert components before conventional discharge

- (i) Significant reduction of hydrazine with hydrogen peroxide or another oxidising agent

Based on an internal cost estimate compiled by an Eskom QS this option is determined to have a capital only cost of R 2 020 275.00.

- (ii) Thermally decomposing hydrazine during unit start-up.

This option is not costed as it is not considered feasible.

- (iii) Significant reduction of hydrazine through sparging with compressed air.

This option is not costed as it is not considered feasible.

9. Conclusions

The conclusion will summarise the effectiveness of each option at achieving the required goals. The conclusion will also summarise the outcomes of the “decision matrix” in producing a recommended concept.

9.1 Option 1 – Maintain the status quo – Do nothing option

Based on the scientific studies performed as part of the CWDP application, and the identified need to reduce hydrazine discharges to the environment, it is expected that the use of hydrazine as an oxygen scavenger and following the existing practices for wet lay-up (i.e., the “do nothing option”, does not meet the draft CWDP requirement to optimise discharges. This option is therefore not viable, on the grounds of it not meeting the intent of the project, i.e., reduce hydrazine discharges at KNPS.

9.2 Option 2 - Replace hydrazine with another wet lay-up oxygen scavenger

The use of alternative wet lay-up oxygen scavengers, i.e., replacing hydrazine with another chemical which is deemed as effective as hydrazine for dissolved oxygen and ECP / ORP control and less toxic than hydrazine with respect to human health and the environment is not considered as viable as discussed below:

- Sodium Sulphite

As discussed in Section 6.2.3 (i), the use of Sodium Sulphite is not compatible with the existing chemistry programme [6], [68] as it results in the increase of sodium concentration in the feed train, which is strictly measured (through online and offline feedwater analysis) and controlled. This option is therefore not viable, on the grounds of non-compatibility with the existing chemistry programme [6], [68].

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- Diethylhydroxylamine (DEHA), Methylethylketoxime (MEKO) and N-Isopropylhydroxylamine (NIPHA)

As discussed in Section 6.2.3 (iii) DEHA, MEKO and NIPHA contribute significantly to the total organic carbon loading in the feedwater as they decompose, and are therefore not compatible with the current chemistry regime for at power operations, or wet lay-up [6], [68]. This option is therefore not viable, on the grounds of non-compatibility with the existing chemistry programme [6], [68].

- Hydroquinone

As discussed in Section 6.2.3 (ii)(iv) the oxygen scavenging reactions for Hydroquinone are complex and contribute to the total organic carbon loading in the feedwater, and is not compatible with the current chemistry regime for at power operations, or wet lay-up [6], [68]. Hydroquinone is considered more toxic than hydrazine with respect to aquatic life and equivalent to hydrazine with respect to ingestion [20]. This option is therefore not viable, on the grounds of non-compatibility with the existing chemistry programme [6], [68] and not meeting the intent of the reduction in environmental impacts on the marine environment.

- Carbohydrazide

As discussed in Section 6.2.3 (iv) the method of application for carbohydrazide as an oxygen scavenger is almost identical to the existing method to application for hydrazine as an oxygen scavenger for wet lay-up. This means that the use of carbohydrazide as a wet lay-up oxygen scavenger does not allow the feed train to be suitably protected and if necessary drained at short notice, independent of length of time after shutdown, to perform maintenance, while still protecting the feed train thereafter. It is therefore excluded on the grounds of not meeting the flexibility on outage feed train related maintenance criteria.

It is recommended that as a separate study, carbohydrazide be considered and investigated as a safer alternative to hydrazine (from a personnel point of view) as an oxygen scavenger for use during at power operations, and for boiler preservation, without draining prior to start-up. It is also recommended that, if for some reason it would be necessary to provide additional wet lay-up protection for the SGs (over and above the use of FFAs), carbohydrazide be used.

9.3 Option 3 - Significantly reduce the need for an oxygen scavenger during wet lay-up conditions

FFAs are considered the most feasible option in achieving the project criteria as described in Section 4, provided the risks identified in Section 6.3.3 of this feasibility study are mitigated. These risks will be included in the Technical Requirements Specification for the implementation of FFA at KNPS which will be compiled and submitted with the request for proposal under the commercial process, following the acceptance of the conclusions and recommendations in this feasibility study.

The TRS will require the specific risks mitigation steps to be further developed as part of the implementation design which will be performed by a suitable vendor, to be identified using the commercial process. In addition, it will require the vendor to report and mitigate to other risks known by the vendor, and other international operating experience in the nuclear and conventional power generation sectors.

Notwithstanding the above, it is highly recommended that an Eskom/KNPS engineering assessment of trends in critical secondary side parameters be conducted before, during, and after FFA product addition to understand instrument indications and how these are affected control systems and to develop a base against which to determine any effects that FFA product application may have. These

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parameters must include the readings of online chemistry instruments (e.g., temperature, sodium, cation conductivity, pH, etc.), various flow measurement devices (for which anomalous readings could be an indicator of solids fouling), and filter differential pressure readings.

9.4 Option 4 - Chemical decompose hydrazine into inert components before conventional discharge

(iv) Significant reduction of hydrazine with hydrogen peroxide or another oxidising agent

Given the personal risks associated with handling large volumes of strong oxidizing agents in large quantities, the anticipated modifications to the plant in the form of chemical off-loading facilities, storage tanks and additional dosing piping, and the fact that copper sulphate will need to be added to ensure optimum reaction kinetics in quantities which would be out of line with environmental discharge limits, this option is not considered feasible.

(v) Thermally decomposing hydrazine during unit start-up.

Good practice at KNPS dictates that the feed train and condenser are drained after each outage to flush any corrosion by-products as well as any foreign material which may have been introduced during feed train SSC maintenance during outages.

The option to thermally decomposing hydrazine during unit start-up is thus not considered good-practice by KNPS and therefore not feasible.

(vi) Significant reduction of hydrazine through sparging with compressed air.

To increase the kinetics of the reaction with oxygen from the atmosphere, the hydrazine must be destroyed at an elevated pH, i.e., basic environment and in the presence of a copper sulphate catalyst. Copper sulphate would need to be added with injection of 5 ppm in principle being regarded as sufficient, as it is not present in the waste. The effluent collecting sumps and tanks must be kept completely free of oil and free of any effluent of unknown composition, e.g., laundry detergents [54].

The fact that copper sulphate will need to be added to ensure optimum reaction kinetics in quantities which would be out of line with environmental discharge limits, this option is not considered feasible.

10. Recommendations

FFAs are considered the most feasible option in achieving the project criteria as described in Section 4, provided the risks identified in Section 6.3.3 of this feasibility study are mitigated. These risks will be included in the Technical Requirements Specification for the implementation of FFA at KNPS which will be compiled and submitted with the request for proposal under the commercial process, following the acceptance of the conclusions and recommendations in this feasibility study.

The TRS will require the specific risks mitigation steps to be further developed as part of the implementation design which will be performed by a suitable vendor, to be identified using the commercial process. In addition, it will require the vendor to report and mitigate to other risks known by the vendor, and other international operating experience in the nuclear and conventional power generation sectors.

Notwithstanding the above, it is highly recommended that an Eskom/KNPS engineering assessment of trends in critical secondary side parameters be conducted before, during, and after FFA product addition to understand instrument indications and how these are affected control systems and to

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develop a base against which to determine any effects that FFA product application may have. These parameters must include the readings of online chemistry instruments (e.g., temperature, sodium, cation conductivity, pH, etc.), various flow measurement devices (for which anomalous readings could be an indicator of solids fouling), and filter differential pressure readings.

It is recommended that as a separate study, carbohydrazide be considered and investigated as a safer alternative to hydrazine (from a personnel point of view) as an oxygen scavenger for use during at power operations, and for boiler preservation, without draining prior to start-up. No recommendation is made on the use of carbohydrazide as a primary side start-up oxygen scavenger, as the thermal decomposition with CO₂ as by product will have unwanted implications on primary side chemistry, and lead to C¹⁴ production; a radiological isotope to be avoided.

11. Acceptance

This document has been seen and accepted by:

Name	Designation
Nestor Van Eeden	Chief Scientist Nuclear Support
Deon Jeannes	Nuclear Environmental Manager
Nomaninzi Msumza	Chemistry Manager (Acting)
Abdul-Aleem Obaray	Feedwater systems system engineer
Nazier Allie	Feedwater systems and GSS system engineer
Luqmaan Salie	Steam Generator Programme Owner
Neelan Rama	Primary Circuit system engineer
Oscar Khathide	CEX, CVI, SIR system engineer
Mark Courtney	Turbine systems system engineer
Brandon Douwie	ATE system engineer

12. Revisions

Date	Rev.	Compiler	Remarks
March 2023	1	Robert Moffat	New document

13. Development Team

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

- N/A

14. Acknowledgements

Nestor van Eeden

15. Appendices

List all appendices used in this document.

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- Cost Estimate Calculation
- The Expanded Decision Matrix Table
- Draft CWDP issued to Eskom in September 2022

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Appendix A. Cost Estimate Calculations

Base date of indicative pricing: 25.03.2021

Scope deliverable	Indicative Price			Ccy.	CPA	Local Content % (As per SCATT)
	First unit	Following unit	Total			
Engineering studies	60.830,00	36.500,00	97.328,00	€		
Implementation design	174.680,00	104.808,00	279.488,00	€		20
Full technical support for the first on-line application	221.945,00	171.945,00	393.889,60	€		
Detailed application instructions and monitoring / operating procedures so that KNPS may be able to independently perform future applications	35.200,00	35.200,00	70.400,00	€		
Training of KNPS line staff on the application and monitoring during the first and subsequent applications	22.935,00	-	22.935,00	€		
Supply of materials	55.805,00	55.805,00	111.610,40	€		
Others						
Total	571.395,00	404.258,00	975.653,00	€		

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[illegible]

Appendix B. The Expanded Decision Matrix Table

	Success Criteria	Importance Weight Factor	Option 1 – ...		Option 2 – ...		Option 3 – ...		Option 4 – ...	
			Score	Weighted score	Score	Weighted score	Score	Weighted score	Score	Weighted score
Compulsory Criteria	Any chemicals must be non-toxic to marine organisms, or be discharged at a concentration and rate which is not harmful to marine organisms, as defined by the ecological studies as part of the CWDP and its appendices.	C	No	FAIL	Yes	PASS	Yes	PASS	Yes	PASS
	Must be compatible with the existing chemistry regime	C	Yes	PASS	Yes	PASS	Yes	PASS	Yes	PASS
	Must maintain plant integrity during lay-up conditions	C	Yes	PASS	Yes	PASS	Yes	PASS	Yes	PASS
Qualitative Criteria	The option must not have an unacceptable negative impact on normal plant integrity and operations during at power conditions.	30%	100%	30%	100%	30%	90%	27%	100%	30%
	Operator burden must consistent with current duties.	10%	100%	10%	90%	9%	100%	10%	30%	3%
	Conventional safety associated with handling and storage chemicals.	5%	10%	1%	100%	5%	100%	5%	20%	1%
	Maintenance of the feedtrain must be readily possible without the need for burdensome lay-up practices, at any point during an outage.	30%	0%	0%	0%	0%	100%	30%	0%	0%
	The chemical to be used must have a track record for the intended use within the nuclear power generating industry.	15%	100%	15%	85%	13%	85%	13%	50%	8%
	Cost	10%	0%	0%	100%	10%	50%	5%	50%	5%
				FAIL		PASS		PASS		PASS
				56%		67%		90%		47%
	Totals	100%								

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Appendix C. Draft CWDP issued to Eskom in September 2022

SECTION B: PERMIT HOLDER'S DETAILS

Permit Holder	:	Eskom Holdings SOC Limited
Address	:	Private Bag X10, Kernkrag, 7441
Contact Person	:	Mr Deon Jeannes
Designation	:	Nuclear Environmental Manager
Tel	:	(021) 550 5027
E-mail	:	deon.jeannes@eskom.co.za

SECTION C: ACTIVITY DETAILS

Effluent Classification	:	Cooling Water, Brine, Industrial and Municipal Effluent
Location of Discharge	:	Surf Zone
Daily Discharge volume	:	8 200 000 m ³ per day (mid-tide)

SECTION D: DESCRIPTION OF THE PROCESS, LOCATION OF SITE, AND DISCHARGE POINT

1. Koeberg Nuclear Power Station (KNPS) is located 30km north of Cape Town, on the West Coast of South Africa. The main waste streams of the effluent from the Koeberg Nuclear Power Station include effluent from the Circulating Water Circuit (CRF), Essential Service Water System (SEC), industrial effluent, oily water process effluent, demineralised water production effluent, domestic effluent and desalination effluent.
2. The operation of KNPS requires approximately 90m³/s of cooling water to condense steam used by the turbines that generate electricity which gets exported to the national grid. The cooling water is abstracted from the Atlantic Ocean and passes through condensers and then returns to the sea with temperature above the abstracted sea water temperature. The cooling water effluent, which is generated from cooling the turbine steam and turbine auxiliaries, is referred to as the Circulating Water Circuit (CRF). The second cooling water stream, which cools the Nuclear Island is referred to the Essential Service Water System (SEC). The effluent that is generated from the CRF and the SEC contain residual oxidants that arise from the chlorination of the incoming water in order to mitigate the build-up of biofouling within the cooling system.
3. In addition to the cooling water effluent, industrial effluent is produced from the primary and secondary circuits. This waste stream comprises of chemical effluent and radiological contaminants. The treatment systems at KNPS are designed to reduce radioactivity from primary circuit effluent prior to discharge with the cooling water. The radioactivity release limits are set by the National Nuclear Regulator (NNR).
4. The oily water process effluent comprises of water that is potentially contaminated with oil from working areas where hydrocarbons are used. This effluent stream is directed to an oil skimmer or weir that is used to filter off all the oil, after which the effluent is discharged with the cooling water effluent. The remaining oil fraction that has been separated is sent for final disposal at an appropriately licenced waste management facility.

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5. The demineralised water production effluent is generated from demineralising potable water for use in process operations. The effluent generated, which is characterised by high or low pH is treated by neutralisation using acids and alkalis before being discharged with the cooling water. This permit also makes provision should KNPS replace the obsolete reverse osmosis plant for groundwater or seawater desalination purposes. The desalination effluent consists of brine and chemicals used in the treatment of groundwater and/or seawater.
6. The domestic effluent which consists out of grey water from showers and black water from sewage. This effluent is treated at the on-site Wastewater Treatment Plant (WWTP) before being discharged with the cooling water. Laundry water is currently not treated but is discharged via the SEK and KER systems.
7. The total effluent volume that is discharged via the Koeberg Cooling Water Outfall Basin is approximately 8 200 000 m³ per day (mid-tide).



Figure 1: Aerial photograph showing Koeberg Nuclear Power Station, Storm water discharge and the Koeberg Cooling Water Outfall Basin

SECTION E: GENERAL CONDITIONS

1. This permit is issued to the permit holder as stipulated in Section B, for the activity stipulated in Section C and at the locations stipulated in Section D of this permit.
2. This permit may not be transferred or assigned to any other person or organisation, except with prior written permission from this Department.
3. An appeal against this permit does not suspend the effect of this permit, unless directed otherwise by the Minister.

4. The permit holder will be liable for an annual fee as prescribed by the Minister in the Government Gazette from time to time, as contemplated in Section 83 (2) and (3) of the ICM Act, for the purpose of covering the cost to the Department of monitoring compliance with permit conditions.
5. Access to the site must be granted to any authorised official representing the Department who requests access for the purposes of assessing and / or monitoring compliance with the conditions of this permit or to collect monitoring samples, at any reasonable time during the validity or review period of this permit.
6. A copy of this permit must be kept at the Koeberg Nuclear Power Station and must be produced to any authorised official representing the Department or any employee or agent of the permit holder who works or undertakes work at the site upon request.
7. The Department reserves the right to revoke, suspend or cancel this permit or to amend any condition of this permit, other than the permit validity period, if –
 - 7.1 The holder of the permit contravenes or fails to comply with a condition subject to which this permit is issued;
 - 7.2 The permitted use is in conflict with a relevant coastal management programme or will significantly prejudice the attainment of a relevant coastal management objective;
 - 7.3 Changes in circumstances require such revocation, suspension, cancellation or amendment of the permit. These circumstances include, *inter alia*, if action is necessary or desirable to prevent deterioration or further deterioration of the quality of the coastal environment and / or if it is in the interest of the whole community; and / or
 - 7.4 It is necessary to meet the Republic's international obligations.
8. The Department reserves the right to instruct the permit holder to modify any monitoring programme or to implement any supplementary monitoring if the Department suspects that the monitoring programme implemented by the permit holder:
 - 8.1 does not meet the requirements of this permit,
 - 8.2 does not meet the environmental quality objectives for the receiving environment, and
 - 8.3 does not provide adequate information to determine the effects of the effluent on the receiving environment.
9. If a major incident, occurs (whether the requisite permission has been obtained from the Department or not), the permit holder must report the incident immediately to the Department, or where that is not possible, at the earliest opportunity, which must be within seven calendar days, providing full details of the:
 - 9.1 cause of the incident,
 - 9.2 alternatives considered other than the discharge of effluent,
 - 9.3 the volume of effluent released,
 - 9.4 the location of the effluent released, and
 - 9.5 any other information requested by the Department subsequent to the reporting of the emergency.
10. The permit holder must, in addition to condition 9 above, comply with the requirements of Section 30 of the National Environmental Management Act, 1998 (Act No. 107 of 1998) ("NEMA"), where applicable.
11. The permit holder must ensure compliance with the provisions of the duty of care and remediation stipulated in Section 58 of the ICM Act and Section 28 of NEMA.

12. The term 'incident' in this permit is defined in Section 30 of the National Environmental Management Act (NEMA) (1998) (Act No. 108 of 1998).
13. All reports and correspondence to the Department relating to this permit must be submitted to: The Deputy-Director General: Oceans and Coasts, Department of Forestry, Fisheries and the Environment, P. O. Box 52126, Victoria and Alfred Waterfront, Cape Town, 8002, for the attention of: The Director: Coastal Pollution Management or electronically to cwdp@environment.gov.za and copy Rueben Molale (Email: rmolale@dfre.gov.za), Tandise Jacobs (Email: tjacobs@dfre.gov.za) and Bongumenzi Gumbi (Email: bgumbi@dfre.gov.za).
14. Any written agreements entered into between the permit holder and the Department relating to this permit must be attached to the permit as appendices and must be considered to form part of these permit conditions.

SECTION F: SPECIFIC CONDITIONS

1. ABBREVIATIONS

1.1 The following abbreviations are applicable to this permit

Table 1: Abbreviations used in this permit.

AE	Alcohol Ethoxylates
AES	Alcohol Ethoxysulfates
BG	Background
BOD	Biological Oxygen Demand
BWRO	Brackish (Ground) Water Reverse Osmosis Plant
COD	Chemical Oxygen Demand
CRF	Circulating Water System
DBNPA	Dibromonitropropionamide
DEG	Chilled Water Production and Distribution System
DEL-N	Chilled Water Plant Electrical Building (North)
DEL-S	Chilled Water Plant Electrical Building (South)
FOG	Fats, Oil, Grease
KER	Nuclear Island Liquid Waste Monitoring and Discharge System
LAS	Linear Alkylbenzene Sulfonate
NNR	National Nuclear Regulator
RRI	Component Cooling Water System
SDA	Demineralization Plant
SDX	Reagents Neutralisation System
SEC	Essential Cooling Water System
SEK	Conventional Island Liquid Waste Monitoring and Discharge System
SES	Hot Water System
SEU	Sewage Treatment Plant
SRI	Secondary Component Cooling System
SWRO	Sea Water Reverse Osmosis Plant
TRO	Total Residual Oxidant
TSS	Total Suspended Solids
U1	Unit 1
U2	Unit 2
XCA	Boiler System

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2. EFFLUENT QUANTITY (FLOW)

2.1 The permit holder must not exceed the daily average discharge volume of 8 200 000 m³ per day (mid-tide).

3. EFFLUENT QUALITY

- 3.1 No material other than the effluent and its constituents authorised by this permit that may adversely affect the receiving marine environment may be discharged from the discharge point described in Section D apart from detergent containing surfactant Ethoxylated Alkylphenol which shall be phased out within 6 (six) months after this permit is issued.
- 3.2 The maximum limits prescribed in **Table 2**, for the constituents of the effluent to be discharged via the Koeberg Cooling Water Outfall Basin must not be exceeded.

Table 2: Effluent Emission Limits for constituents and Physico-Chemical Properties of the final combined effluent and the reference to effluent monitoring requirements

Substance / parameter	Limits to be complied with prior to discharge into coastal waters	Reference to Monitoring Requirements
pH	7,3 – 8,2	No monitoring required
Temperature increase	11,8 °C	See Table 3
Temperature increase: CRF pump(s) unavailable	21,2 °C (limited to 14 days per event)	See Table 3
Free Chlorine (TRO)	0,60 mg/L	See Tables 3 and 4
Free Chlorine (TRO): Shock	6,6 mg/L (limited to 30 minutes)	See Table 4
Free Chlorine (TRO) abnormal	0,84 mg/L (limited to 8 hours once per week)	See Table 4
Total Suspended Solids	4,7 mg/L	See Tables 6, 7, 9, 10 and 15
Hydrazine	0,11 mg/L	See Tables 6 and 8
Hydrazine release (during refuelling outages)	0,20 mg/L	See Tables 6, 8, 12 and 13
Sulphate	2750 mg/l	No monitoring required
Sodium	10900 mg/L	No monitoring required
Ammonia	0,23 mg/L	See Tables 6, 7, 8, 12 and 13
Chloride	19500 mg/L	No monitoring required
Boron	5,02 mg/L	See Tables 5 and 6
Lithium	0,05 mg/L	No monitoring required
Phosphate	0,87 mg/L	See Tables 5, 6 and 11

Detergents-LAS	0,03 mg/L	See Tables 5, 6 and 7
Detergents- AES	0,61 mg/L	See Tables 5, 6 and 7
Detergents- AE	0,133 mg/L	See Tables 5, 6 and 7
Aluminium	0,0053 mg/L	See Tables 5, 6 and 9
Copper	0,0009 mg/L	See Tables 5 and 6
Chromium	0,0043 mg/L	See Tables 5 and 6
Iron	0,0038 mg/L	See Tables 5 and 6
Manganese	0,0011 mg/L	See Tables 5 and 6
Nickel	0,0048 mg/L	See Tables 5 and 6
Lead	0,0033 mg/L	See Tables 5 and 6
Zinc	0,0033 mg/L	See Tables 5 and 6
Ethylenediaminetetraacetic acid	0,31 mg/L	No monitoring required
Citric Acid	0,71 mg/L	No monitoring required
Ethanolamine	0,012 mg/L	See Table 6
Nitrates	0,71 mg/L	See Table 6
Nitrites	0,026 mg/L	See Table 6 and 15
Faecal Coliforms	0,46 counts/1000mL	See Table 7
Chemical Oxygen Demand	3,62 mg/L	See Tables 5, 6, 9 and 10
Biological Oxygen Demand	1,30 mg/L	No monitoring required
Fat/Oil / Grease	0,33 mg/L	See Tables 5 and 6
Silica	0,66 mg/L	No monitoring required
Octadecylamine	0,0012 mg/L	See Tables 6 and 8
Sodium Metabisulphate	0,03 mg/L	See Tables 14 and 15
Phosphonate Antiscalant	0,05 mg/L	See Tables 14 and 15
DBNPA	0,02 mg/L	See Tables 14 and 15
Peroxyacetic acid	0,01 mg/L	See Tables 14 and 15
Low pH cleaner	0,03 mg/L	See Tables 14 and 15
High pH cleaner	0,03 mg/L	See Tables 14 and 15
Total Organic Carbon	1,2 mg/L	No monitoring required
Anionic Polymer	0,02 mg/L	See Tables 14 and 15
Ferric Chloride (as Fe)	0,04 mg/L	No monitoring required
Salinity	35,2 psu	No monitoring required

3.3 The monitoring required in Table 2 is not required if the constituent is absent in the discharge.

3.4 Tanks that require sampling shall be sampled prior to release but the analysis is only required after release.

3.5 The concentration of the various constituents that requires monitoring (Table 2) shall be estimated using upstream monitoring results from Tables 3 to 15. Dilution factors and background concentrations from report

'Koeberg Nuclear Power Station: Coastal Process Technical Information in Support of the Coastal Waters Discharge Permit Application: Dispersion Modelling of Thermal, Chemical, Sediment and Radiological Discharges', dated 4 September 2017 shall be used to estimate outfall concentration.

3.6 The formulas to be used for the various constituents and taking plant configuration into account are as follows:

- 3.6.1 Temperature = average of CRF trains at 6 hour and 12,5 minute intervals. Every two subsequent readings will be averaged to determine the mid-tide average.
- 3.6.2 The normal and shock free chlorine (TRO) will be estimated per 8-hour period using the higher result of the two equations:
- 3.6.2.1 Free Chlorine (TRO) = (average of CRF trains)/(1,04 for two-unit or 1,09 for one unit operation) + (average of SEC trains)/(27 for two-unit or 14 for one-unit operation).
- 3.6.2.2 Free Chlorine (TRO) = (1*SEC average+(11 for both units, 6 for U1 and 3 for U2)*(CRF average/(1,04 for two units or 1,09 for one unit))/(12 for both units, 7 if U1 operating, 4 if U2 operating)).
- 3.6.3 TSS = (highest SEU measurement in month)/(4417 for two unit-operation or 2159 for U1 or 2604 for U2) + (highest SEK measurement in month)/(989 for two-unit operation or 504 for U1 or 521 for U2) + (highest SDX measurement in quarter)/(820 for two-unit operation or 410 for one unit operation) + (highest SDA measurement in quarter)/(3279 for two-unit operation or 1639 for one unit operation) + (highest SWRO measurement in month)/(237 for two-unit operation or 121 for one-unit operation) + (highest BWRO measurement in month)/(3092 for two-unit operation or 1512 for one unit operation) + (BG of 4).
- 3.6.4 Hydrazine or Octadecylamine = highest of:
- 3.6.4.1 (highest XCA in month)/(5465 for two-unit ops or 2732 for one-unit ops), or
- 3.6.4.2 (highest of highest SEK or highest steam generator or highest feed-train measurement in month)/(989 for two-unit operation or 504 for U1 or 521 for U2).
- 3.6.5 Ammonia = (highest SEU measurement in month)/(4417 for two-unit operation or 2159 for U1 or 2604 for U2) + (highest of SEK or steam generator or feed-train measurement in month)/(989 for two-unit operation or 504 for U1 or 521 for U2) + (highest XCA in month)/(5465 for two-unit ops or 2732 for one-unit ops) + (BG of 0,015).
- 3.6.6 Boron = (highest KER in month)/(11360 for two-unit ops or 5309 for U1 or 4916 for U2) + (highest SEK measurement in month)/(989 for two-unit operation or 504 for U1 or 521 for U2) + (BG of 4,5). If discharges are not overlapping then the higher of KER and SEK shall be used. If the SEK boron is more than 225 mg/kg a lower discharge flow rate shall be used in proportion to the boron concentration and the SEK discharge concentration will be estimated: Outfall boron from SEK = SEK tank boron concentration * (flow rate m³/h / 300) / (989 for two-unit operation or 504 for U1 or 521 for U2).
- 3.6.7 Phosphate = (highest KER in month)/(11360 for two-unit ops or 5309 for U1 or 4916 for U2) + (highest SEK measurement in month)/(989 for two-unit operation or 504 for U1 or 521 for U2) + (highest DEL-N in month)/(16394 for two-unit operation or 8197 for one-unit operation) +

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- (highest DEL-S in month)/(6184 for two-unit ops or 3023 for one-unit operation) + (BG of 0,037). If the discharges are not overlapping then the highest discharge of only one (the highest) phosphate system shall be used.
- 3.6.8 Detergent (surfactant) = (highest KER in month)/(11360 for two-unit ops or 5309 for U1 or 4916 for U2) + (highest SEK measurement in month)/(989 for two-unit operation or 504 for U1 or 521 for U2) + (highest SEU measurement in month)/(4417 for two-unit operation or 2159 for U1 or 2604 for U2).
- 3.6.9 Aluminium = (highest KER in month)/(11360 for two-unit ops or 5309 for U1 or 4916 for U2) + (highest SEK measurement in month)/(989 for two-unit operation or 504 for U1 or 521 for U2) + (highest SDX measurement in month)/(820 for two-unit operation or 410 for one-unit ops) + (BG of 0,001).
- 3.6.10 Metals (all except Aluminium) = (highest KER in month)/(11360 for two-unit ops or 5309 for U1 or 4916 for U2) + (highest SEK measurement in month)/(989 for two-unit operation or 504 for U1 or 521 for U2) + (BG of 0,0008 for copper, 0,00008 for chromium, 0,003 for iron, 0,0007 for manganese, 0,00056 for nickel, 0,00015 for lead and 0,0012 for zinc).
- 3.6.11 ETA = (highest SEK measurement in month)/(989 for two-unit operation or 504 for U1 or 521 for U2).
- 3.6.12 Nitrate = (highest SEK measurement in month)/(989 for two-unit operation or 504 for U1 or 521 for U2) + (BG of 0,67).
- 3.6.13 Nitrite = (highest SEK measurement in month)/(989 for two-unit operation or 504 for U1 or 521 for U2) + (highest BWRO measurement in month)/(4947 for two-unit operation or 2418 for one-unit operation) + (BG of 0,017).
- 3.6.14 Faecal Coliform = (highest SEU measurement in month)/(4417 for two-unit operation or 2159 for U1 or 2604 for U2).
- 3.6.15 COD = (highest KER in month)/(11360 for two-unit ops or 5309 for U1 or 4916 for U2) + (highest SEK measurement in month)/(989 for two-unit operation or 504 for U1 or 521 for U2) + (highest SEU measurement in month)/(4417 for two-unit operation or 2159 for U1 or 2604 for U2) + (highest SDX measurement in quarter)/(820 for two-unit operation or 410 for one unit operation) + (highest SDA measurement in quarter)/(3279 for two-unit operation or 1639 for one unit operation) + (highest XCA in quarter)/(5465 for two-unit ops or 2732 for two-unit ops).
- 3.6.16 FOG = (highest KER in month)/(11360 for two-unit ops or 5309 for U1 or 4916 for U2) + (highest SEK measurement in month)/(989 for two-unit operation or 504 for U1 or 521 for U2).
- 3.6.17 Peroxyacetic acid or Sodium Metabisulphate or Phosphonate Antiscalant or DBNPA or Low pH cleaner or High pH cleaner = (highest SWRO measurement in month)/(237 for two-unit operation or 121 for one-unit operation) + (highest BWRO measurement in month)/(4947 for two-unit operation or 2418 for one unit operation).
- 3.6.18 Anionic Polymer = (highest SWRO measurement in month)/(237 for two-unit operation or 121 for one-unit operation) + (highest BWRO measurement in month)/(3092 for two-unit operation or 1512 for one unit operation).

4. MONITORING

4.1 Compliance with monitoring requirements

- 4.1.1 Failure to comply with the monitoring requirements of this permit may affect the decision to amend, revoke, suspend or cancel the permit during the compliance review and may affect the decision to renew the permit / issue a new permit once the validity period has lapsed.
- 4.1.2 The Department reserve the right to request additional monitoring should the audit monitoring or compliance monitoring render unsatisfactory results.
- 4.1.3 Failure to comply with the monitoring requirements of this permit is an offence in terms of Section 79 of the ICM Act and the permit holder may be liable, upon conviction, of the penalties prescribed in Section 80 of the ICM Act.

4.2 Effluent quantity (flow) monitoring

- 4.2.1 The quantity of effluent discharged must be estimated as follows:

- 4.2.1.1 The CRF flow volume shall be estimated using pump running hours over a 3-month period and a mid-tide flow estimate of 81 972 m³/h per pump. The daily average shall be determined (CRF flow / 90 days = m³/d). The highest SEC flow shall be estimated by recording an instantaneous flow measurement every 24-hours and then ensuring that the maximum hourly flow does not exceed 12 700 m³/d. If this SEC data is not available, then the highest SEC flow rate over a 3-month period using pump running hours and a flow rate of 2750 m³/h per pump shall be used to determine average daily SEC flow (m³/d). The CRF daily average shall be added to the SEC daily average and this shall be less than the limit in Section 2. Given that the CRF and SEC combined flow contributes to about 99,9% of total effluent discharge the other sources can be ignored when comparing to the limit in Section 2.

- 4.2.1.2 The KER flow shall be estimated using flow totaliser divided by pump running hours over a 3-month period. The hourly average shall be less than 25 m³/h. This ensures that the assumption used to determine dilution factors and to estimate outfall concentrations remains valid.

- 4.2.1.3 The SEK bypass and tank flow rate shall be estimated using bypass flow totaliser and SEK tank volumes discharged over a three-month period divided by 2160 hours. The hourly average flow rate shall be less than 300 m³/h. This ensures that the assumption used to determine dilution factors and to estimate outfall concentrations remains valid.

- 4.2.1.4 The SEU flow rate shall be estimated using flow totaliser over a 3-month period (SEU total volume / 2160 hours = m³/h). The hourly average shall be less than 28 m³/h. This ensures that the assumption used to determine dilution factors and to estimate outfall concentrations remains valid.

- 4.2.1.5 The SWRO and BWRO flow rates shall be estimated using weekly recorded flow readings. The SWRO brine discharge flow rate shall be less than 1250 m³/h, BWRO brine discharge shall be less than 25 m³/h and the BWRO pre-treatment effluent discharge shall be less than 40 m³/h. This ensures that the assumption used to determine dilution factors and to estimate outfall concentrations remains valid.

- 4.2.1.6 No flow monitoring is required for the SDA, SDX, CTE, XCA, DEL systems.

4.3 Effluent quality monitoring

- 4.3.1 The quality of the effluent discharged via the Koeberg Cooling Water Outfall Basin (including discharges into the intake basin that are pulled into the cooling water) must be monitored at the following monitoring points:
- 4.3.1.1 CRF (at CRF condenser water box)
 - 4.3.1.2 SEC (at RRI heat exchanger)
 - 4.3.1.3 KER (KER discharge tanks)
 - 4.3.1.4 SEK (SEK tank or SEK tank bypass)
 - 4.3.1.5 SEU (at SEU chlorination basin)
 - 4.3.1.6 XCA (XCA boiler)
 - 4.3.1.7 SDX (SDX discharge sump)
 - 4.3.1.8 DEL (DEL system)
 - 4.3.1.9 SRI (at SRI system)
 - 4.3.1.10 SES (at SES system)
 - 4.3.1.11 SWRO (SWRO discharge)
 - 4.3.1.12 BWRO (BWRO discharge)
- 4.3.2 The date, time and monitoring points in respect of each sample taken must be recorded, together with the results.
- 4.3.3 The permit holder must appoint an independent external auditor to determine compliance with Table 2 emission limits every twelve (12) months.
- 4.3.4 The sampling and analysis frequency, type of sampling and sampling and analysis details must be complied with in Table 3 to 10 below.

Table 3: CRF System Monitoring Requirements

Substance / parameter	Minimum frequency of monitoring	Type of monitoring	Comments
Temperature	Continuous	Estimate	Record reading every 6 hour and 12,5 minutes and average every two readings to get mid-tide value. All trains in service are to be monitored and the average of all trains is determined.
Total Residual Oxidant	Every 8 hours	Grab Sample	All trains in service are to be monitored and the average of all trains is determined

Table 4: SEC System Monitoring Requirements

Substance / parameter	Minimum frequency of monitoring	Type of monitoring	Comments
Free Chlorine (TRO)	Every 8 hours	Grab sample	All trains in service are to be monitored and the average of all trains is determined.
Free Chlorine (TRO) Shock	Every shock event	Grab sample	

Table 5: KER System Monitoring Requirements

Substance / parameter	Minimum frequency of monitoring	Type of Monitoring	Comments
pH @ 25°C	Every tank prior to release	Grab sample	pH used to flag high phosphate events and trigger phosphate analysis. All tanks shall be monitored.
Boron	Every tank prior to release	Grab sample	All tanks to be released shall be monitored.
Aluminium	Monthly	Grab sample	Only one tank that is to be released is required to be sampled on a monthly frequency
Copper	Monthly	Grab sample	
Chromium	Monthly	Grab sample	
Iron	Monthly	Grab sample	
Manganese	Monthly	Grab sample	
Nickel	Monthly	Grab sample	
Lead	Monthly	Grab sample	
Zinc	Monthly	Grab sample	
Phosphate	Monthly and when pH is high	Grab sample	See pH monitoring above. All tanks for release shall be monitored for PO ₄ with high pH but only one tank is required to be sampled on a monthly frequency
Detergents (surfactant)	Monthly	Grab sample	Monitoring can be done in the service drains tanks upstream instead. Only one tank for release is required to be sampled on a monthly frequency
Chemical Oxygen Demand	Monthly	Grab sample	Only one tank for release is required to be sampled on a monthly frequency
FOG	Monthly	Grab sample	

Table 6: SEK System Monitoring Requirements

Substance / parameter	Frequency of monitoring	Type of monitoring	Comments
pH @ 25°C	Prior to every tank release	Grab sample	
Boron	Prior to every tank release	Grab sample	All tanks for release shall be monitored
Aluminium	Monthly	Grab sample	
Copper	Monthly	Grab sample	
Chromium	Monthly	Grab sample	
Iron	Monthly	Grab sample	
Manganese	Monthly	Grab sample	
Nickel	Monthly	Grab sample	
Lead	Monthly	Grab sample	
Zinc	Monthly	Grab sample	
Hydrazine	Monthly	Grab sample	If bypass is not sampled and used, only one SEK tank per month requires analysis
Phosphate	Monthly	Grab sample	
Ethanolamine	Monthly	Grab sample	
Ammonia	Monthly	Grab sample	
TSS	Monthly	Grab sample	
COD	Monthly	Grab sample	
Detergents (surfactant)	Monthly	Grab sample	
Nitrate	Monthly	Grab sample	
Nitrite	Monthly	Grab sample	
FOG	Monthly	Grab sample	
Octadecylamine	Monthly	Grab sample	

Table 7: SEU System Monitoring Requirements

Substance / parameter	Frequency of monitoring	Type of monitoring	Comments
Ammonia	Monthly	Grab sample	
Total Suspended Solids	Monthly	Grab sample	
Faecal Coliforms	Monthly	Grab sample	
Chemical Oxygen Demand	Monthly	Grab sample	
Detergents (surfactant)	Monthly	Grab sample	Only when plant laundries routed to SEU

Table 8: XCA System Monitoring Requirements

Substance / parameter	Frequency of monitoring	Type of monitoring	Comments
Ammonia	Twice per month	Grab sample	All boilers not under maintenance shall be monitored
Hydrazine	Twice per month	Grab sample	
Octadecylamine	After dosing	Grab sample	

Table 9: SDX System Monitoring Requirements

Substance / parameter	Frequency of monitoring	Type of monitoring	Comments
Aluminium	Quarterly	Grab sample	
COD	Quarterly	Grab sample	
TSS	Quarterly	Grab sample	

Table 10: SDA System Monitoring Requirements

Substance / parameter	Frequency of monitoring	Type of monitoring	Comments
COD	Quarterly	Grab sample	
TSS	Quarterly	Grab sample	

Table 11: SES, SRI and DEL System Monitoring Requirements

Substance / parameter	Frequency of monitoring	Type of monitoring	Comments
Phosphate	Monthly	Grab sample	All trains in service require monitoring

Table 12: Steam Generator (Wet Layup) Monitoring Requirements

Substance / parameter	Frequency of monitoring	Type of monitoring	Comments
Hydrazine	After dosing	Grab sample	All steam generators placed in wet layup require monitoring
Ammonia	After dosing	Grab sample	

Table 13: Secondary System Feed-Train (Wet-Layup) Monitoring Requirements

Substance / parameter	Frequency of monitoring	Type of monitoring	Comments
Hydrazine	After dosing	Grab sample	All trains placed in wet lay-up require monitoring
Ammonia	After dosing	Grab sample	

Table 14: SWRO System Monitoring Requirements

Substance / parameter	Frequency of monitoring	Type of monitoring	Comments
Phosphonate antiscalant	Monthly	Grab sample	All trains require monitoring
Sodium metabisulphate	Monthly	Grab sample	
Peroxyacetic acid	Monthly	Grab sample	
Low pH cleaner	Monthly	Grab sample	
High pH cleaner	Monthly	Grab sample	
DBNPA	Monthly	Grab sample	
TSS	Monthly	Grab sample	

Table 15: BWRO System Monitoring Requirements

Substance / parameter	Frequency of monitoring	Type of monitoring	Comments
Phosphonate antiscalant	Monthly	Grab sample	All trains require monitoring
Sodium metabisulphate	Monthly	Grab sample	
Peroxyacetic acid	Monthly	Grab sample	
Low pH cleaner	Monthly	Grab sample	
High pH cleaner	Monthly	Grab sample	
DBNPA	Monthly	Grab sample	
Nitrite	Monthly	Grab sample	
Total Suspend Solids	Monthly	Grab sample	
Ferric Chloride	Monthly	Grab sample	
Anionic Polymer	Monthly	Grab sample	

5. RECEIVING ENVIRONMENT QUALITY

5.1 The permit holder must submit a monitoring programme to the Department for approval within 18 (eighteen) months of the date of issue of this permit.

5.1.1 The monitoring programme must include, as a minimum, the following aspects:

- 5.1.1.1 Validation of the findings of the dispersion modelling study;
- 5.1.1.2 Management strategies and actions to ensure compliance with the permit conditions,
- 5.1.1.3 Management strategies and actions to ensure compliance with the environmental quality objectives as per the South African Water Quality Guidelines for Coastal Marine Waters (Volume 1): Natural Environment and Mariculture Use, published by the Department of Environmental Affairs in 2018, or any amended version thereof and effectiveness thereof,
- 5.1.1.4 Assessment of potential marine impact resulting from the effluent discharged from KNPS,
- 5.1.1.5 Trends, status and changes in the receiving environment related to the health of important ecosystems and designated beneficial uses;

5.1.2 Additional sampling points may be requested by the Department if deemed necessary;

5.1.3 The monitoring programme may, upon written agreement by the Department, be conducted in conjunction with any other institution.

5.1.4 The monitoring programme (s) mentioned above, must be implemented by a suitably qualified person(s) appointed by the permit holder.

5.1.5 The Department may request investigations of any other issues regarding effluent discharge and the marine environment if and when it is considered necessary.

CONTROLLED DISCLOSURE

5.1.6 The Marine Impact Assessment (MIA) must take into account the historical baseline data to determine the impact of the effluent at each monitoring location and must be conducted every year from the date of issue of this permit.

5.1.7 The monitoring programme, referred to above, must not be changed or amended without prior written permission from the Department.

6. ANALYSIS OF SAMPLE

- 6.1. All chemical, physical and biological analysis must be initiated within 6 (six) months after receipt of this permit either (1) in accordance with methods prescribed by and obtainable from the South African National Accreditation System, in terms of the Standards Act, 1982 (Act No. 30 of 1982), unless another comparable method has been approved of, in writing, by the Department, (2) analysed by an accredited laboratory or (3) quality assured by an annual, inter-lab proficiency test.
- 6.2. The permit holder must give access to the Department's official / representative undertaking any audit sampling at any given time.
- 6.3. The methods of analysis may not be changed without prior notification to, and written approval from the Department.
- 6.4. The Department may request the method of analysis to be changed depending on new technologies and requirement.

7. STORMWATER

- 7.1 The permit holder must take full responsibility for storm water leaving the permit holder's premises and any contamination thereof by any substance (whether such substance is a solid, liquid, vapour or gas or a combination thereof which is produced, used, stored, dumped or spilled on the premises).

8. MAINTENANCE

- 8.1. Flow metering, recording and integration devices (SEC, KER, SEK, SEU) must be maintained in a proper functioning order.
- 8.2. These devices must be calibrated using appropriate methods. The calibration of SEU flow meter shall be in place 6 (six) months after the issuing of this permit.

9. MALFUNCTIONS / ABNORMAL CONDITIONS

- 9.1. Accurate, up-to-date records of all system malfunctions resulting in the disposal of effluent not in accordance with the requirements of this permit must be kept.
- 9.2. The permit holder must conduct monitoring as normal during upset / abnormal conditions as specified in this permit
- 9.3. The following headings must be used for the above records, accompanied by a full explanation of all contributory circumstances and proposed / implemented mitigation measures:

- 9.3.1. operating errors;
- 9.3.2. mechanical failure (including design, installation, inspections and maintenance);
- 9.3.3. environmental factors (e.g. floods, storms, lightning, etc.)
- 9.3.4. loss of supply services (e.g. power failure, water supply failure, etc.);
- 9.3.5. other causes; and undetermined.

10. CONTINGENCY PLANS

- 10.1. The permit holder must submit a contingency plan to the Department for approval, 6 (six) months after the receipt of this permit, and must consist of stipulated procedures, schedules and responsibilities which include, *inter alia*:
 - 10.1.1. standard operating procedures for detection of problems and responding to emergency incidents as well as upset conditions;
 - 10.1.2. staff schedules;
 - 10.1.3. programmes for the maintenance, replacement and surveillance of the physical condition of equipment and facilities;
 - 10.1.4. standby / alternative personnel / service companies for the continued operation and maintenance of effluent discharge facilities during employee shortages (strikes, incidents, ill-health, etc.);
 - 10.1.5. stock lists and suppliers for chemicals, spare parts and equipment components that can adequately ensure the continued operation of the effluent discharge facility during an emergency or breakdown;
 - 10.1.6. emergency standby power facilities for high-risk areas;
 - 10.1.7. emergency standby pumps; and
 - 10.1.8. provision for sufficient storage capacity to cope with the normal or typical load for the area during power failures, etc.
 - 10.1.9. schedule of monitoring and sampling analyses when emergency or upset conditions occur at the plant.
- 10.2. The permit holder must provide the details on the type of mitigating measures to be implemented for discharge into the coastal environment that exceeds the limits prescribed in this permit.
- 10.3. Clear action plan(s) on mitigating measures to protect other users of the affected coastal environment (such as site notice boards or media releases (newspapers, radio or television) informing users (public) of the potential risks; demarcation of polluted areas, if required; notification of industrial users of seawater and marine aquaculture farms, as well as procedures to be followed in assisting with protection of such facilities against pollution), must be provided by the permit holder.
- 10.4. The permit holder must outline reporting procedures and protocols for reporting events of malfunctioning / breakdown of the effluent disposal system, as well as pollution events. These include internal procedures as well as reporting to responsible authorities on local, regional, and national levels (including, but not limited to the reporting of emergency incidents in terms of Section 30 of the National Environmental Management Act (NEMA) (1998) (Act No. 108 of 1998).

CONTROLLED DISCLOSURE

- 10.5. The permit holder must ensure that the contingency plan, once approved by this Department, is immediately implemented at the facility mentioned in Section B.

11. REPORTING REQUIREMENTS

- 11.1. All reporting to the Department must occur on prescribed forms, where available or in a format as agreed to, in writing, by the Department.
- 11.2. The permit holder may establish or join an effluent discharge monitoring forum (or equivalent body). Such a body must meet, as a minimum, once quarterly, to discuss any breach of permit conditions, current and future monitoring initiatives and reporting requirements as well as general effluent issues. This forum may be facilitated by an independent facilitator and comprise of the permit holder (or a representative), interested and affected parties (such as NGO's, local interest groups, etc.) and relevant government institutions. Effluent discharge monitoring forums may be established for either a single outfall (i.e. one permit holder) or a receiving environment (i.e. several permit holders).
- 11.3. The following must be reported on or presented quarterly to the Department:
- 11.3.1. The estimated volume discharged, showing average daily final discharge outfall, and estimated average hourly discharge volumes in accordance with Condition 4.2;
 - 11.3.2. Incidences that have occurred during emergency, malfunction or upset conditions.
 - 11.3.3. All minutes emanating from the effluent discharge monitoring forum, where established.
 - 11.3.4. The result / findings of the monitoring requirements in terms of this permit and where further monitoring is required.
- 11.4. The following must be reported on or presented annually to the Department:
- 11.4.1. A report on the monitoring of trends and incidents as well as the results of the marine impact assessment, as soon as it becomes available, but not later than 4 (four) months after marine impact assessment unless otherwise agreed to, in writing, by the Department.
- 11.5. A report detailing the results of the independent audit monitoring, must be submitted / presented annually to the Department.
- 11.6. The following must be reported on and presented at the compliance review meeting (as and when requested by the Department) to the Department:
- 11.6.1. A report detailing compliance with Section F of this permit.
 - 11.6.2. Calibration results for flow meter, recording and integrating devices as listed in Condition 4.2.
 - 11.6.3. Any investigations carried out in terms of Section F: condition 13 at the compliance review and upon submission of a renewal / new application.
- 11.7. Any defects or deficiencies in terms of the Koeberg Cooling Water Outfall Basin must be reported to the Department quarterly. Where necessary, repairs must be carried out on the Koeberg Cooling Water Basin as and when required.
- 11.8. Failure to submit any required report may affect the Department's decision to renew or to issue a new permit upon expiry of this permit.

12. INVESTIGATIONS

- 12.1. The permit holder must investigate methods for continuous improvement of the effluent quality. These investigations must include, *inter alia*:
- 12.1.1. Whether there are benefits to modifying the chlorination procedures and the hydrazine discharge practices
 - 12.1.2. waste minimisation and cleaner technology initiatives.
- 12.2. The permit holder must investigate means of optimising dispersion at sea and minimising the impact on the receiving environment.
- 12.3. The Department reserves the right to instruct the applicant to implement any improvements identified in the investigations required in Section F: Condition 13.

13. DECOMMISSIONING

- 13.1. The permit holder must provide a decommissioning plan for outfall basin one year prior to the actual date of decommissioning of the outfall basin, to the Department.

14. PERMIT VALIDITY

- 14.1. This permit is valid for a period of **10 (ten) years**, subject to a compliance review at **30 (thirty) months** or as deemed necessary by the Department during the validity period of this permit.
- 14.2. The permit holder must submit a renewal application at least **6 (six) months** before the expiry of this permit to the Department. Where a renewal application has been submitted to the Department before the lapsing of the validity period, the validity of this permit will automatically be extended ("the period of administrative extension") from the day before this permit would otherwise have lapsed, until the renewal application has been decided.

SECTION G: APPEALS

In terms of Section 74 (2) of the ICM Act:

"A person who is dissatisfied with any decision taken to issue, refuse, amend, suspend or cancel an authorisation, may lodge a written appeal against that decision with –

- (a) the Minister, if the decision was taken by a person exercising powers which have been delegated by the Minister to such person in terms of this Act"

Formal, motivated appeals must be made in writing within **30 (thirty) calendar days** of the date of issuing of this permit by means of one of the following methods:

By hand: Department of Forestry, Fisheries and the Environment
East Pier Building
East Pier Road
V&A Waterfront
Cape Town
8002

If the appellant is not the permit holder, the latter must be informed of the appeal within the appeal period referred to above and the appellant must provide the permit holder with reasonable access to a full copy of the appeal, if requested.

Appeals should be addressed to and appeal forms can be obtained from:

Adv. Mokete Rakgogo

Director: Appeals and Legal Review

Department of Environmental Affairs

E-mail: Mrakgogo@environment.gov.za / Appeals@environment.gov.za

SECTION H: REASONS FOR THE DECISION

1. During the validity period of this permit, the discharge of effluent into coastal waters from **Koeberg Nuclear Power Station** is unlikely to:
 - 1.1 Cause irreversible or long-lasting adverse effects that cannot satisfactorily be mitigated;
 - 1.2 Prejudice significantly the achievement of any coastal management objectives contained in a coastal management programme or;
 - 1.3 Be contrary to the interests of the whole community.
2. In reaching its decision, the Department, *inter alia*, considered the following:
 - 2.1 The information contained in the application for a coastal waters discharge permit, dated 2 October 2017, and the following supporting information:
 - 2.1.1 Technical Assessment Report of the Existing Coastal Discharge via the Cooling Water Outlet Basin at Koeberg Nuclear Power Station, dated September 2017 compiled by Advisian Worley Parsons Group
 - 2.1.2 The Koeberg Nuclear Power Station Marine Discharge Assessment in Support of the CWDP Application Marine Ecology Specialist Study, dated 29 August 2017, that was compiled by Lwandle Marine Environmental Services.
 - 2.1.3 The Koeberg Nuclear Power Station: Coastal Processes Technical Information in support of the Coastal Waters Discharge Permit Application, dated 4 September 2017 compiled by PRDW Consulting Port and Coastal Engineers.
 - 2.1.4 The Koeberg Nuclear Power Station: Coastal Processes Technical Information in support of the Coastal Waters Discharge Permit Application: Addendum Report: Dispersion Modelling of

Additional Thermal Discharges, dated 13 February 2019 compiled by PRDW Consulting Port and Coastal Engineers.

2.1.5 Koeberg Nuclear Power Station CWDP: Assessment of Additional Thermal Discharge Scenarios, dated 5 February 2019 compiled by Lwandle Marine Environmental Services.

2.1.6 Koeberg Nuclear Power Station CWDP: Evaluation of Toxicity Risks associated with the discharge of film forming amine (FFA) to the marine environment, dated 31 October 2019, compiled by Lwandle Marine Environmental Services.

2.2 The objectives and requirements of relevant legislation, policies and guidelines, including 69 of the ICM Act and Section 2 of the NEMA.

SECTION I: DISCLAIMER

The Department of Forestry, Fisheries and the Environment is exempt from any claims against loss or damage incurred by the permit holder in applying for, obtaining and complying with the conditions of this permit or any non-compliance thereof.

-----END OF PERMIT-----

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