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Title E3S Case Chapter 20: Chemistry		
<p>Executive Summary</p> <p>This chapter of the Environment, Safety, Security, and Safeguards (E3S) Case presents the overarching summary and information for the Chemistry of the Rolls-Royce Small Modular Reactor (RR SMR). The chapter outlines the Arguments and preliminary Evidence available at the Preliminary Concept Definition (PCD) design stage to underpin the high-level Claim that the RR SMR chemistry regime and development of the chemistry systems design, reduces risks during all normal operating modes and accident conditions for all phases of the lifecycle.</p> <p>The overall aims of the chemistry programme are summarised, which are to reduce, so far as reasonably practicable:</p> <ol style="list-style-type: none"> 1. Corrosion of structural materials, maintaining structural integrity and ensuing availability and reliability of Structures, Systems and Components (SSCs). 2. Fuel cladding corrosion, maintaining fuel cladding integrity. 3. Out of core radiation fields and generation of radioactive waste. <p>For the systems within the scope of this revision of Chapter 20, the chemistry regime at PCD is summarised, discussion of how the chemistry regime has been developed to reduce risks to As Low As Reasonably Practicable (ALARP) is presented, as well as the future development and verification activities that are required to substantiate the chemistry aspects of the RR SMR design. At this stage of design development, there is confidence that the Claims can be met when the full suite of Evidence is developed.</p>		



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20.1 Introduction

20.1.1 Introduction to Chapter

Chapter 20 of the Rolls-Royce Small Modular Reactor (RR SMR) Environment, Safety, Security and Safeguards (E3S) Case forms part of the Pre-Construction Safety Report (PCSR), and is a supporting reference to the Generic Environment Report (GER), as defined in E3S Case Chapter 1: Introduction, Reference [1].

From early concept design, an initial set of chemistry specifications were put in place to aid the RR SMR plant design. These chemistry specifications were based on Relevant Good Practice (RGP) and developed to meet the RR SMR design objectives. As the design and operating philosophy matures, the chemistry specifications are refined to ensure that they remain optimised. The chemistry specifications supporting Issue 1 of the E3S Case are presented in the Reactor Island and Turbine Island water quality specifications (References [2] and [3], respectively).

Chapter 20 presents the overarching summary and entry point to the design information for the chemistry of the Rolls-Royce Small Modular Reactor (RR SMR), as defined at Reference Design (RD) 5 level of design maturity. Issue 1 of Chapter 20 is predominantly based on RGP and operational experience (OPEX) (taken from References [4], [5], [6], [7], [8] and [9]); future development work will be reported in the Tier 2 and Tier 3 evidence documents, which will be incorporated and referenced into future revisions of this document.

20.1.2 Scope

Chapter 20 of the E3S Case provides a summary of the chemistry of the RR SMR design and presents the associated safety Claims and Arguments. Chapter 20 is the Tier 1 document within the E3S Case and is a summary of the underpinning information. The structure of the Chapter is aligned to the Tier 2 documentation that will be produced and includes the following sections:

1. Chemistry Specifications (Section 20.3)
2. Monitoring and Control (Section 20.4)
3. Reactor Coolant Chemistry (Section 20.5)
4. Reactor Island Auxiliary System Chemistry (Section 20.6)
5. Secondary Water Chemistry (Section 20.7)
6. Turbine Island Ancillary System Chemistry (Section 20.8)
7. Normal Operation Source Term (Section 20.9)

Upon completion, the chemistry E3S chapter will present the following information:

1. Definition and justification of the chemistry regime, including how the chemistry regime minimises risks As Low As Reasonably Practicable (ALARP) using Best Available Techniques (BAT) in relation to;

- a. Structural / Material integrity,
 - b. Fuel Integrity,
 - c. Radiation Fields, and
 - d. Waste generation.
2. The chemistry specification for each system (within scope). This will include:
- a. Identification of control and diagnostic parameters (for both chemical and radiochemical parameters)
 - b. Definition of expected values and lower/upper limit values
 - c. Frequency of sampling/monitoring
3. Design substantiation covering:
- a. Control of chemical parameters (addition and removal)
 - b. Sampling and monitoring of chemical and radiochemical parameters

In addition to defining the chemistry regime for each system, the following areas are also within the scope of Chapter 20 of the E3S Case:

1. Commissioning Chemistry
 - a. Objectives and available options for commissioning the Primary Coolant Systems (including Hot Functional Testing).
 - b. Objectives and available options for commissioning the Secondary Coolant Systems.
 - c. Note: Issue 1 of the E3S Case will not define the commissioning chemistry regime, as this is a decision that will require input from the future plant operator. Future revisions of the E3S Case will present RGP for commissioning Pressurised Water Reactors (PWRs) and demonstrate that the RR SMR plant design does not foreclose options.
2. Normal Operation Source Term
 - a. Coolant activities (Primary and Secondary Coolant Systems)
 - b. Deposit activities (piping and fuel)
 - c. Accumulated activity (filters and demineralisers)

Based on the above, the following is captured as an Assumption on the future dutyholder/licensee:

Assumption on Future Dutyholder/Licensee A20.1: *The final decision on the optimum commissioning chemistry regime for the RR SMR plant will require input from the future plant operator and will be deferred until the site-specific licensing period. During safety case and*

design development, RGP for commissioning PWRs will be presented and it will be demonstrated that the RR SMR design does not foreclose options.

Due to the level of maturity at Reference Design 5 (RD5) stage, commissioning chemistry is excluded from the scope of this issue and the topic will be deferred until later revisions.

The chemistry aspects of the following systems are included in the scope of Chapter 20 of the E3S Case (Reference Designation System for Power Plants (RDS-PP) coding given in square brackets):

1. Primary Coolant Systems:
 - a. Reactor Coolant System [JE]
 - b. Chemistry and Volume Control System [KB]
 - i. Normal Make-Up System [KBA]
 - ii. Chemistry Control System [KBD]
 - iii. Coolant Purification System [KBE]
 - c. Cold Shutdown Cooling System [JNA]
 - d. Component Cooling System [KAA]
 - e. Boron Supply System [JDK]
 - f. Low Pressure Injection System [JNG]
 - g. Emergency Make-Up System [JND]
 - h. Spent Fuel Pool [FAB]
 - i. Spent Fuel Cooling System [FAK]
 - ii. Spent Fuel Purification System [FAL]
 - i. Reactor Island Sampling System [KU]
2. Secondary Coolant Systems:
 - a. Steam Generation System [JEA]
 - b. Main Feedwater System [LA]
 - c. Main Steam System [LB]
 - d. Condensate System [LC]
 - i. Steam Generator Blowdown System [LCQ]
 - e. Turbine Island Sampling System [QU]

The chemistry aspects of the following systems are excluded from the scope of Chapter 20 of the E3S Case; however, these systems are included within the overall scope of the E3S Case. Information relating to these systems will be presented in E3S Case Chapter 11: Management of Radioactive Waste, Reference [10]:

1. Waste Treatment Systems (covered in the Radioactive Waste Management topic area):
 - a. Liquid Waste Treatment System [KN], including:
 - i. Processing & Treatment System for Primary Liquid Effluent [KNF10]
 - ii. Processing & Treatment System for Spent Liquid Effluent [KNF20]
 - b. Gaseous Waste Treatment System [KP], including;
 - i. Processing & Treatment System for Gaseous Radioactive Effluent [KPL]
 - c. Solid Radioactive Waste Processing Systems [KM].

Chemistry is a cross-cutting topic and is closely related to a number of other topic areas. The scope of this chapter covers the chemistry aspects of the RR SMR, with:

1. Materials selection and justification of the integrity of Structures, Systems and Components (SSCs) covered in E3S Case Chapter 23: Structural Integrity (Reference [11]).
2. Accident chemistry covered in E3S Case Chapter 15: Safety Analysis (Reference [12]).

Design/Programme Maturity

RR SMR design information presented in this Issue 1 of the E3S Case is largely based on the design definition at the end of Preliminary Concept Definition (PCD), which is an interim design stage representing RD5 level of design maturity. Development of the chemistry specifications and associated justifications are being progressed in line with the design programme to inform the design development and the demonstration that exposures to workers and the public are reduced to ALARP.

Further Development and Underpinning

In order to achieve the aims and objectives of the RR SMR project, Reference [13], a number of optimisations have been made to the RR SMR design. This includes the relatively novel aspects of the primary coolant chemistry regime, for a Western PWR, summarised as:

1. The adoption of a boron-free chemistry regime, with duty reactivity control being achieved via the control rods.
2. Potassium hydroxide as the alkali agent.

At this stage of the design programme, preliminary assessments have been undertaken to provide confidence in the baseline chemistry regime. A Validation and Verification (V&V) programme is being implemented in order to provide the underpinning justification for the RR SMR design, which includes a number of development activities related to chemistry.

The general aim of the materials and chemistry V&V programme is to demonstrate that the RR SMR chemistry regime (potassium hydroxide) is *no worse* than the widely adopted PWR chemistry regime of lithium hydroxide/boric acid. A large amount of operational experience and test data exists to underpin the lithium hydroxide/boric acid chemistry regime which will be leveraged as part of the underpinning for the RR SMR primary coolant chemistry regime.

Issue 1 of the chemistry chapter of the E3S Case is based on the key assumption that the future V&V activities will provide the required evidence to support development of the chemistry safety case and successfully demonstrate that potassium hydroxide is *no worse* than lithium hydroxide/boric acid. Further information on the V&V programme will be provided in the Tier 2 and Tier 3 documentation, as the E3S case is matured.

20.1.3 Claims, Arguments, Evidence Route Map

The Chapter level Claim for E3S Case Chapter 20: Chemistry, as defined in Reference [14], is:

Claim 20: the RR SMR chemistry regime and development of the chemistry systems design, reduces risks during all normal operating modes and accident conditions for all phases of the lifecycle.

The complete suite of evidence to underpin the Claims in the E3S Case will be generated through the RR SMR design and E3S Case programme and documented in the Claims, Arguments, Evidence (CAE) Route Map, Reference [15], described further in E3S Case Chapter 1: Introduction, Reference [1].

The overall purpose of the Tier 1 chemistry document is to summarise how the chemistry design (chemistry specification) contributes to achieving the fundamental E3S objective (*protect people and the environment from harm*) and delivery of the fundamental functions (*control of reactivity; cooling of radioactive material; confinement of radioactive material*).

An initial set of chemistry Claims and Arguments have been developed. A decomposition of Claim 20 into Sub-Claims, Arguments, and links to the relevant Tier 2 and Tier 3 Evidence is provided in Appendix A. For each lowest level Sub-Claim, the sections of this report providing the evidence summary are also identified. These Claims and Arguments have been developed based on the decomposition of the top-level Claim for chemistry, as well as alignment to the over-arching E3S Design Principles, Reference [16]. The chemistry CAE structure provides traceability from the top-level Claim all the way down to the resulting chemistry specifications that will be adopted for each system.

The chemistry CAE structure is based on a single top-level Claim, that is decomposed into four Arguments, with each Argument being further decomposed into Sub-Claims and lower-level Sub-Claims. The top-level Claim and Arguments are given in Figure 20.1-1 with a full breakdown given in Appendix A.

Chemistry is a broad subject that influences the whole RR SMR design. The applicability of each of the Arguments presented in Figure 20.1-1 to the relevant Power Station systems will be identified in the Sub-Claims that sit below each Argument.

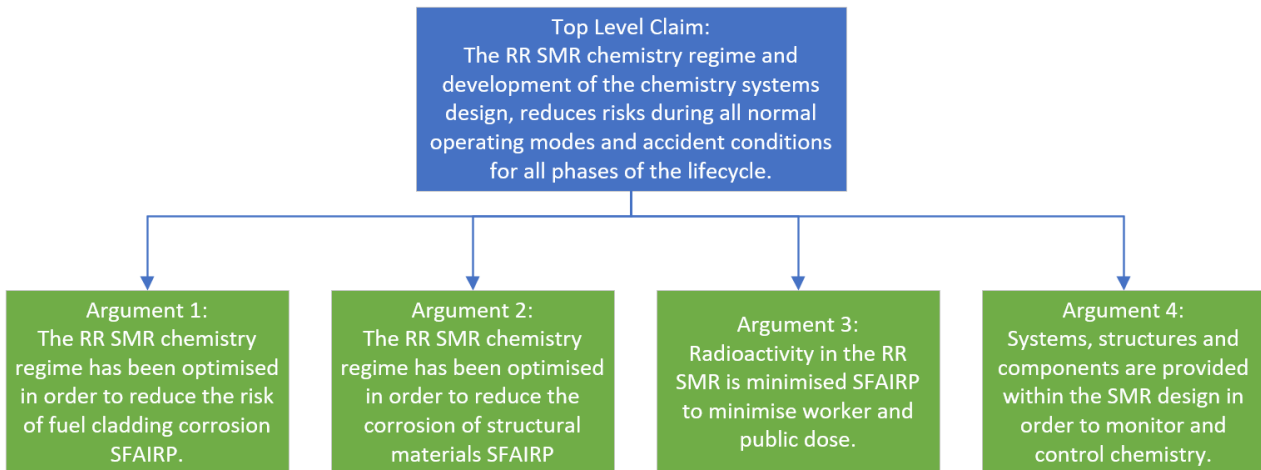


Figure 20.1-1: Chemistry Top-Level Claim and Decomposition to Arguments (*SFAIRP = so far as is reasonably practicable).

Reference [17] describes the proposed structure of the underpinning Tier 2 and Tier 3 documentation, which will be developed to provide the underpinning evidence to support the chemistry Safety Claims. Issue 1 of the Chemistry chapter of the E3S Case sets out the initial Claims and Arguments and presents the route map for how these will be further developed and underpinned. It is acknowledged that the Claims, as currently presented, are not finalised and will be refined as the Tier 2 and Tier 3 documentation are developed.

20.1.4 Applicable Regulations, Codes & Standards

E3S Case Chapter 3: E3S Objectives & Design Rules, Reference [18], outlines the E3S objectives and design rules applicable to the RR SMR. At PCD, the E3S Design Principles (Reference [16]) have been used to guide and inform the ongoing design development process and the RR SMR Engineering Management Plan (Reference [19]) presents the policy for the selection of codes and standards to ensure sound engineering in design. The following guidelines are also of particular relevance when considering development of the RR SMR chemistry regime:

1. International Atomic Energy Agency (IAEA) Specific Safety Guide (SSG)-13: Chemistry Programme for Water Cooled Nuclear Power Plants.
2. IAEA SSG-15: Storage of Spent Nuclear Fuel.
3. IAEA NF-T-3.6: Management of Damaged Spent Nuclear Fuel.
4. IAEA-TECDOC-1303: High Temperature On-Line Monitoring of Water Chemistry and Corrosion Control in Water Cooled Power Reactors.
5. IAEA-TECDOC-1505: Data Processing Technologies and Diagnostics for Water Chemistry and Corrosion Control in Nuclear Power Plants (DAWAC).
6. IAEA SSG-28: Commissioning of Nuclear Power Plants.
7. European Utility Requirements for Light Water Reactor (LWR) Nuclear Power Plants.



8. Electric Power Research Institute, in particular the PWR Primary Water Chemistry Guidelines, Reference [4], and the PWR Secondary Water Chemistry Guidelines, Reference [5].

20.2 Approach to ALARP

Chemistry is an important consideration for the safe, reliable operation of a nuclear power station. Appropriate chemistry control ensures the continued integrity, reliability, and availability of the SSCs that are important to safety and ensures that the plant operates within the design intent. For reactor chemistry, it also ensures that the accumulation of radioactive material and associated worker-dose are minimised. Chemistry therefore plays an important role in delivering the fundamental functions to support the E3S objective of *protecting people and the environment from harm*.

Operational experience that has been gained since the 1960s in operating nuclear power stations has shown that chemistry control can impact on the operation of a nuclear power station and has a significant impact on the economics of power generation. There have been numerous examples of corrosion failures resulting in costly downtime and replacement activities, as well as increased worker dose and additional waste discharge to the environment. This has resulted in an increased focus on chemistry control during the design stage and ensuring the risk to material degradation is reduced ALARP.

There is no single chemistry regime that can be universally applied to all fluid systems within a nuclear power station; the optimum chemistry regime will be dependent on the particular conditions within a system. For example, the following factors need to be considered when determining the chemistry regime:

1. The chosen chemistry regime will need to be compatible with the materials of construction, ensuring corrosion is reduced SFAIRP (for fluid systems that contact nuclear fuel, compatibility with the fuel cladding material also needs to be considered).
2. The operating environment within the system, in particular the temperature, pressure, flow conditions (e.g. turbulent flow, single/two-phase flow) and whether the fluid is exposed to irradiation.

The optimum choice for the RR SMR plant will be determined through optioneering and assessment (as described in Chapter 1 of the E3S Case, Reference [1]).

20.3 Chemistry Specifications

During early concept design, initial chemistry specifications were developed in order to support design development. These specifications were based on RGP and available information at the time, including previous revisions of the *Electric Power Research Institute (EPRI) Water Chemistry Guidelines*. The design maturity, operating philosophy and chemistry specifications are being developed in parallel and are continually reviewed to ensure alignment. No major design changes are expected as a result of further developing and refining the chemistry specification.

The chemistry specification tables are communicated to the wider RR SMR design teams as transverse requirements that are placed on the relevant plant systems; this ensures that the chemistry requirements are incorporated into the design and the ability to deliver these requirements is continually assessed as the design develops.

The chemistry specifications are within References [2] and [3]; at this stage specifications have been defined for the Plant Operational stage, i.e. Start-up, Power Operations, Shutdown and Refuelling Outage modes. Plant Pre-Operational and Commissioning, as well as Plant Final Shutdown chemistry has not yet been defined.

Action Levels

It is common for chemistry specifications to contain defined “*Action Levels*”, which enable defined actions to be taken in response to chemistry excursions, in a timely manner, ensuring that the chemistry stays within the bounds of the design envelope. Action levels and corrective actions to take in response to chemistry excursions will be developed as the design matures, considering the capability of the RR SMR design and in accordance with RGP.

20.4 Monitoring and Control

20.4.1 Sampling and Monitoring

There are two main sampling systems that are incorporated into the RR SMR design:

1. Reactor Island Sampling and Measurement System [KU].
2. Turbine Island Sampling System [QU].

The primary functional purpose of the Reactor Island Sampling and Measurement system [KU] is to representatively monitor key fluids within the reactor island for chemical and physicochemical parameters defined by the reactor island water chemistry specification, Reference [2].

The primary functional purpose of the Turbine Island Sampling System is to sample the feedwater, condensate and steam used within the Turbine Island at various sampling points, to confirm the quality of the water aligns with the turbine island chemistry specification, Reference [3].

The sampling systems will include a range of online instrumentation to provide continuous monitoring of selected chemistry parameters, as well as the ability to obtain local 'grab' samples that can be analysed within a laboratory.

The information within the chemistry specifications defines which chemistry parameters are monitored and the minimum frequency that is required. The future operator of the RR SMR plant will be responsible for implementing a *chemistry programme*, providing the means to collect, store and trend chemistry data in order to provide overall condition monitoring for the plant and enabling the early identification of adverse trends and anomalies.

This is captured in the following Commitment on the future dutyholder/licensee:

Commitment on Future Dutyholder/Licensee C20.1: *The future operator of the RR SMR plant will be responsible for implementing a chemistry programme*

Design Maturity

The Reactor Coolant Sampling System and the Turbine Island Sampling System will be included within the scope of E3S Case Chapter 9A: Auxiliary Systems, Reference [20] and E3S Case Chapter 10: Steam and Power Conversion Systems, Reference [21], respectively. These systems have not been included within the scope of E3S Case Issue 1, due to current low levels of design maturity.

20.4.2 Control of Chemistry Parameters

In order to ensure appropriate chemistry control, it is important that suitable chemical addition and purification systems are provided to ensure the chemistry specification for each system can be achieved.

Adequate capability should also be provided for the removal from the coolant of radioactive substances, including activated corrosion products and fission products deriving from the fuel, as well as non-radioactive substances.

The relevant RR SMR plant systems that are responsible for controlling the chemistry are described in sections 20.4.1, 20.5 and 20.6.1. These systems are comprised of:

1. Chemical addition systems, which add chemicals to the system in order to provide chemical conditioning
2. Purification systems, which remove chemical species from the system
3. Let down/blow-down systems, which remove water from the system, but do not directly perform a purification function

Design Maturity

These systems are at a maturity commensurate with the PCD design, broadly that requirement specifications are identified and understood, the design scope is defined and bounded, preferred concepts are selected and are likely to deliver requirements, or a plan for down-selection of multiple options is in place, and key verification activities are identified. Development of these systems will be informed by safety categorised functional requirements and non-functional system requirements (which includes transverse chemistry requirements) placed onto the design as the safety analysis is developed.

20.4.3 Tier 2 Documentation

Tier 2 documents will be produced entitled “*Primary Water Chemistry: Method of Monitoring and Control*” and “*Secondary Water Chemistry: Method of Monitoring and Control*”. These reports will summarise *how* the monitoring and control is achieved in order to ensure compliance with the chemistry specifications and will include Sub-Claims in support of the *Argument 20.4* relating to monitoring and control of chemistry parameters.

20.5 Primary Coolant Chemistry

20.5.1 Design Overview

The primary function of the Reactor Pressure Vessel (RPV) [JAA] is to interface with the reactor coolant system (RCS) [JE] so that cold coolant can flow to the core and hot coolant can be taken to the Steam Generators (SGs) [JEA]. The baseline architecture for the RCS [JE] consists of three vertical U-tube SGs [JEA] with associated pipework loops and a single Reactor Coolant Pump (RCP) [JEB] in each loop, mounted to the SG outlet. The configuration of the SG, pipework and pump layout in each loop ensures a robust thermal driving head for natural circulation flow in emergencies.

The primary function of the Chemical and Volume Control System (CVCS) [KB], is to control the chemistry and volume of the reactor coolant within the RCS [JE]. The system maintains reactor coolant chemistry within specification and maintains pressuriser level within a required operating band. The CVCS takes coolant from downstream of the RCPs [JEB], cools it, removes impurities, reheats it, and returns it upstream of the RCPs. The CVCS takes coolant from SG pipework loops and it is comprised of three sub-systems: the Level & Volume Control System [KBA]; the Chemistry Control System [KBD]; and the Coolant Purification System [KBE].

Further description of the RCS [JE] and associated systems can be found in E3S Case Chapter 5: Reactor Coolant System & Associated Systems [22].

20.5.2 Historical Development of the PWR Primary Coolant Chemistry Regime

The objective of the primary coolant chemistry regime is to:

1. Maintain the structural integrity of primary circuit SSCs by minimising corrosion
2. Maintain the integrity of the fuel cladding and fuel performance by minimising corrosion and crud (chalk river unidentified deposit) deposition
3. Minimise out-of-core radiation fields, waste, and discharges

Designing the optimal chemistry regime to deliver against all of these objectives may generate conflicting requirements. The optimal solution to achieve one objective may negatively impact the achievement of another. For example, chemicals are added in order to mitigate corrosion, but this increases the chemical loading in the reactor water, can increase the level of radioactivity and decrease the lifetime of ion-exchange resins (and therefore increases the volume of radioactive waste). Therefore, the optimised primary circuit chemistry regime must be a balance, and compromise, between these three objectives.

The primary coolant chemistry regimes for LWRs have evolved since the first reactors were developed in the 1950s. The early reactors adopted a pure water chemistry regime, without any chemical additions. The reactivity of the core was controlled by the control rods and it was believed that pure water (with low levels of impurities) would be sufficient to mitigate corrosion. However, a number of performance issues were encountered during the 1950s and 1960s,

which resulted in chemical additions being applied to the primary coolant, with continuous modifications continuing to the present day.

During the early operation of PWRs in pure water chemistry, it was observed that irradiated surfaces tend to accumulate corrosion products and heavy fuel deposits were observed [6]. The two main issues associated with heavy fuel deposits are an increase in flow friction, resulting in a pressure drop across the core, and localised overheating of the fuel cladding. The deposits are the result of corrosion of the structural materials and it was determined that operating under slightly alkaline conditions reduces the amount of corrosion and therefore reduces the amount of deposition on the fuel. Early investigations considered lithium hydroxide, potassium hydroxide and ammonia as the alkali agent.

During the development of the first LWRs, the susceptibility of structural materials to corrosion in an irradiated environment was not understood. Even in pure water conditions, with low levels of impurities, the oxidising environment that results from radiolysis of water is sufficient to drive corrosion, with Stress Corrosion Cracking (SCC) proving particularly problematic. In order to mitigate the harmful effects of corrosion, hydrogen addition was adopted in order to recombine with the oxidising species generated by radiolysis and create reducing conditions within the primary coolant.

As the design developed further, soluble boron (in the form of boric acid) was introduced into the primary coolant in order to provide a “chemical shim”. The boron provided reactivity control, reducing the number of control rods that were required. One of the main drivers for implementing a chemical shim was the cost savings achieved through the reduced number of control rods. In order to offset the acidity of the boric acid, higher concentrations of lithium hydroxide (PWR) or potassium hydroxide (Voda Voda Energo Reactor, VVER) are required in order to maintain slightly alkali conditions.

Finally, a more recent development in PWR chemistry during the mid-1990s was the implementation of zinc addition. Cobalt-60 is one of the main sources of operator dose during operation and maintenance of nuclear reactors. Cobalt-60 is released through corrosion and wear of structural materials and is subsequently incorporated into the oxide layers that are present on the surface of metallic components. It was found that at sufficiently high concentrations zinc is preferentially incorporated into the surface oxide films; the zinc replaces the cobalt which is then released back into the coolant and subsequently sequestered on the coolant purification system. This reduces the amount of cobalt-60 that is incorporated in the oxide films of plant surfaces thereby reducing the dose to operators during operation and maintenance activities. The majority of plants that have adopted zinc addition have applied it retrospectively, but a number of new build PWRs have chosen to implement it from the start of operations.

20.5.3 Structural Integrity

Although there are numerous degradation mechanisms relating to the RCS materials that must be managed, the two dominant corrosion mechanisms that have had the largest influence on the chemistry regime are:

1. General corrosion, which poses less risk to structural failure, but due to the surface area, results in large volumes of corrosion products being released into the primary coolant, which are redistributed through the system and contribute to the level of radioactivity in the plant.

2. Localised corrosion, which is the main threat to structural integrity and includes pitting corrosion, stress corrosion cracking and environmentally assisted fatigue.

Structural integrity and material degradation are addressed in E3S Case Chapter 23: Structural Integrity [11].

General Corrosion

General corrosion is an oxidation process that occurs almost uniformly over the metal surface, converting the base metal into a metal oxide. If the chemistry is appropriately controlled, the oxide film that is formed at the metal surface provides a stable barrier between the metal and fluid, reducing the rate of oxidation. As the oxide film thickens, the growth rate decreases and a steady-state equilibrium is reached between oxide thickness and corrosion rate. If the chemistry is appropriately controlled and the oxide film remains stable, then a very low corrosion rate is achieved that poses a low risk to material integrity.

Although the general corrosion rate is low, the large metallic surface area within the RCS (particularly within the steam generator tubes) means that the volume of corrosion product that is released is significant. Some of the corrosion products that are released will be transported to the reactor core, where they are deposited on the fuel surface. The deposits are exposed to irradiation and undergo activation, producing activation products that can be subsequently released and redistributed throughout the RCS. The activation products deposit on piping and component surfaces and increase the radiation dose rates during maintenance operations and outages (see Sub-Section 20.5.5).

“Crud” is a term that is commonly used to describe corrosion products that are deposited on the fuel surface and on structural surfaces throughout the RCS.

Within a PWR RCS, pH and oxygen concentration have the largest impact on the rates of general corrosion and generation of crud. The majority of the components within the RCS are constructed from austenitic stainless steel and nickel-base alloys, which have increased corrosion resistance in alkali conditions (pH >7). Oxygen is a driving force for corrosion, reacting with the metal to form nickel oxides and iron oxides, with the rate of oxidation increasing as the oxygen concentration is increased. Achieving high pH, deoxygenated conditions within the RCS therefore reduces the rate of general corrosion and reduces the volume of crud that is generated.

Localised Corrosion

Whereas general corrosion occurs uniformly over the surface of a metal, localised corrosion is concentrated into a small surface area. Localised corrosion occurs on materials that are generally resistant to corrosion; the bulk of the surface remains passive, with corrosion occurring at localised sites where defects (e.g. scratches or inclusions) are present, or in occluded regions where there is reduced flow and impurities can concentrate, creating localised aggressive environments. The material release rates are low, compared to general corrosion, but the risk of perforation and failure is significantly higher. Within PWRs, the majority of the RCS structural components are manufactured from austenitic stainless steels and nickel-base alloys and aggressive halide ions, particularly chloride and sulphate, are the dominant impurities that have resulted in the occurrence of localised corrosion. There are multiple mechanisms for localised corrosion that are of relevance to PWRs, including:

1. Pitting corrosion: localised pits form on the surface of the metal, which break through the surface oxide layer and penetrate into the underlying metal. At the expected operating chemistry for PWRs, with low concentrations of impurities, together with the corrosion resistant materials of construction, pitting corrosion presents a low risk of degradation and structural failure.
2. Crevice corrosion: occurs in crevices, such as flanges and bolts, where there is an occluded region with reduced flow. High concentrations of impurities can accumulate and result in very aggressive chemistries forming within the crevice. Crevice corrosion is generally mitigated through the plant design, removing the occurrence of crevices (e.g. using welded joints instead of bolted/flanged).
3. Stress Corrosion Cracking (SCC): requires a susceptible material, the presence of stress and a corrosive environment. The combination of stress and a corrosive environment result in a crack forming in the metal, that can grow and result in catastrophic failure of high pressure systems. Aggressive anions, such as chloride and sulphate, together with oxygenated conditions, acts as the driving force for SCC. Mitigation to SCC is achieved by the use of resistant materials, applying stress relaxation techniques, or removing the corrosive environment. From a chemistry perspective, SCC can be mitigated by maintaining low concentrations of impurities (in particular chloride and sulphate) and operating under reducing conditions. Under typical PWR operating conditions, nickel-base alloys have a superior resistance to SCC, compared to austenitic stainless steels.
4. Primary Water Stress Corrosion Cracking (PWSCC) is a particular form of SCC that occurs in nickel-base alloys at low redox potentials, even in the presence of low oxygen and low impurity concentrations. Alloy 600 was widely used for the steam generator tube material of older PWRs and this proved particularly susceptible to PWSCC. Alloy 690, with increased chromium content, has proved to have far superior resistance to PWSCC. It is generally accepted that material selection and the occurrence of stress are the dominant factors that influence PWSCC susceptibility, with chemistry being a secondary factor.

20.5.4 Fuel Cladding Integrity

Zirconium alloy is the most common fuel cladding material used in operational nuclear reactors, being highly corrosion resistant under PWR reactor circuit conditions and having a low neutron capture cross-section. Generally, under typical PWR operating chemistries and impurity concentrations, the zirconium cladding is resistant to corrosion and the risk of cladding failure is low. However, the presence of crud can create localised environments where the concentration of chemical species at the fuel cladding surface can be significantly increased from that of the bulk coolant.

Cladding Corrosion

The corrosion of zirconium alloy cladding results in two important processes occurring:

1. Thinning of the cladding and formation of an oxide layer (ZrO_2) on the cladding surface
2. Absorption of hydrogen into the zirconium alloy, which embrittles the cladding

The main parameters that control the rate of cladding corrosion are:

1. Temperature: as well as forming a barrier and maintaining containment of the fuel pellets and fission products, the cladding serves an important purpose in acting as the heat transfer medium, allowing heat from the fuel pellets to be transferred to the primary coolant. The temperature of the fuel cladding is always higher than that of the bulk coolant and the temperature at the metal/metal oxide interface at the cladding surface is the primary parameter controlling the rate of corrosion. As the oxide layer on the cladding surface thickens, the interface temperature increases and this results in an increased corrosion rate.
2. Material composition: any defects or local variations in the cladding material can impact on the rate of corrosion and therefore careful control is applied during the manufacturing process.
3. Lithium hydroxide: many PWRs operate with lithium hydroxide as the pH modifier and experimental testing has shown that high concentrations of lithium hydroxide can accelerate cladding corrosion. Fuel vendors place upper limits on the lithium hydroxide concentration allowable in the bulk coolant in order to reduce the risk of cladding failure.
4. pH: under typical PWR operating conditions, pH has been shown to have little direct impact on cladding corrosion. However, pH does have a large influence on the formation of fuel crud deposits, which can impact cladding corrosion.
5. Dissolved oxygen: the presence of dissolved oxygen creates oxidising conditions within the primary coolant, accelerating the rate of corrosion. Under typical PWR operating conditions, the low oxygen concentrations achieved should result in minimal impact on the rate of zirconium corrosion.
6. Dissolved hydrogen: at elevated dissolved hydrogen concentrations the rate of hydrogen adsorption into the cladding could increase, leading to hydrogen embrittlement and deterioration of the mechanical properties of the cladding. Although this is thought to be low risk, there is insufficient data to completely rule this out.
7. Chloride, fluoride, sulphate: Zirconium alloys have far greater resistance than austenitic stainless steels to chloride and sulphate induced SCC, although there may be some stainless steel components in the fuel assembly that are susceptible. High concentrations of fluoride have been shown to accelerate corrosion of zirconium alloys.
8. Aluminium, calcium, magnesium and silica: although having limited direct influence on cladding corrosion, these species can deposit on the fuel cladding surface and form thermally insulating layers, increasing the cladding temperature and indirectly increasing the corrosion rate.

Crud Formation

The RCS [JE] is designed so that heat from the fuel is transferred to the reactor coolant, which in turn transfers heat to the secondary system via the steam generator tubes. As discussed, the fuel cladding surface is always hotter than the bulk coolant and in addition to this, the upper region of the fuel assembly is hotter than the lower region. Depending on the core design, sub-cooled nucleate boiling can occur in the upper region of the fuel assembly; sub-cooled nucleate boiling is a type of boiling that occurs when the surface temperature is greater than the saturation temperature, but the bulk fluid remains below the saturation temperature. Bubbles are formed on the cladding surface that collapse as they are cooled by the bulk coolant.

As the primary coolant enters the lower core region and flows over the fuel, the temperature of the bulk coolant increases, which can influence the solubility of species dissolved in the primary coolant. Sub-cooled nucleate boiling acts as a driving force for most of the deposition of crud on the fuel, causing precipitation of solution species and accumulation of particulates. The crud layer is therefore typically thicker in the upper fuel assembly regions, compared to the lower regions.

Crud is an important factor in the performance of the fuel, as deposited crud will result in increased fuel cladding temperatures. Understanding crud behaviour and having the ability to model crud thickness and cladding temperatures is important to ensure compliance with the thermal limits and restrictions placed on the fuel.

Crud-Induced Localised Corrosion (CILC)

Crud-Induced Localised Corrosion (CILC) is a mechanism whereby the formation of thick, porous crud deposits can cause enhanced corrosion as chemical species can accumulate to high concentration, creating a localised aggressive corrosion environment within the crud layer. This can cause accelerated corrosion in the region where the crud is deposited, in the worst case resulting in fuel failure and release of fission products into the system.

Crud-Induced Power Shifts (CIPS)

Crud-Induced Power Shifts (CIPS), formerly known as Axial Offset Anomaly (AOA), occur as a result of boron-containing species precipitating within porous crud deposits under sub-cooled boiling conditions. By its nature, boron will dampen the reactivity of the neutrons released during nuclear fission reactions in the fuel. The presence of locally high levels of boron incorporated within crud means the reactivity within a crud region is suppressed and thus reactivity becomes non-uniform across the core height. The detrimental effect of this is less efficient operation of plant and / or loss of control of fuel rod reactivity. Alternatively, to control a CIPS event, power stations must operate under reduced power output.

20.5.5 Radioactivity

One of the main causes of out-of-core radiation fields in a PWR is the accumulation of activated corrosion products in oxide films on out-of-core surfaces, with Co-58 being the primary contributor to radiation fields in early plant life and Co-60 becoming the predominant source later in life. There are a number of processes that result in the build-up of activated corrosion products, which are as follows:

1. Corrosion of wetted primary circuit materials and release of corrosion products into the primary coolant
2. Transportation of corrosion products to the reactor core via the primary coolant
3. Deposition of corrosion products on in-core surfaces resulting in the accumulation of fuel deposits (fuel crud)
4. Activation of corrosion products in the reactor core. This includes those deposited on in-core surfaces, as well as those suspended in the primary coolant
5. Release of activated corrosion products from in-core surfaces back into the primary coolant

6. Deposition of activated corrosion products on out-of-core surfaces and incorporation into oxide films

While many factors influence this overall process, control of primary coolant chemistry over the course of a cycle is of particular importance, notably for stages 1, 3, 5 and 6 of the process stated above.

20.5.6 Chemistry Control Parameters

Sections 20.5.3 and 20.5.4 summarise the main chemistry-related parameters that influence corrosion of the structural materials within the primary coolant system, as well as fuel cladding integrity. The most significant parameters are pH, redox potential and impurities; controlling these parameters supports achievement of the overall three chemistry objectives of reducing structural corrosion, fuel cladding corrosion and radiation fields.

pH Control

Control of pH during the reactor cycle is important to minimise corrosion of the primary circuit materials, but also once corrosion products are formed, pH impacts the solubility of corrosion products in the primary coolant, the thermodynamics and kinetics of in-core deposition, and release and redeposition on out-of-core surfaces. The optimum pH regime is a balance between lowering plant radiation fields, controlling corrosion of structural materials and maintaining fuel cladding integrity.

As discussed, many PWRs operate with lithium hydroxide as the pH modifier and boric acid for reactivity control, both of which influence the pH that is achieved. At the start of the cycle, when core reactivity is highest, a higher concentration of boron is required in the primary coolant and the concentration of dissolved boron subsequently decreases over the course of the operating cycle. PWRs have operating experience of maintaining pH_T (where T is typically defined at 300°C, or at average at-power operating temperature, T_{av}) in the range of 6.9 to 7.4. pH is a temperature dependent parameter and pure water would be $\text{pH}_T \sim 5.7$. At 25°C, $\text{pH}_{25^\circ\text{C}}$ of pure water is 7.

The minimum of the pH target (pH_T 6.9) is to reduce the rate of general corrosion within the reactor circuit and reduce the corrosion of the fuel cladding. In recent years some plants have implemented 'elevated' pH regimes, where the pH_T is maintained >7.2 for the entire operating cycle.

As well as influencing the rate of general corrosion and the release of corrosion products, the pH has also been shown to influence the solubility of corrosion products within the core, therefore influencing the volume of crud deposited on the fuel. Increasing the pH has been shown to reduce the amount of crud deposited on the fuel, whereas operating at a $\text{pH}_T < 6.9$ results in increases in the amount of crud deposited. Experimental testing with pressurized in-pile loops has confirmed that out-of-core radioactivity is minimised by increasing the pH of the coolant, with observations from operating plants supporting this conclusion, with the majority of modern plants targeting an elevated pH_T .

In order to reduce the corrosion of primary coolant system materials, minimise the amount of crud deposition and out-of-core deposition, it is beneficial to operate at as high a pH as practicable. The majority of PWRs therefore adopt a pH_T between 6.9-7.4, with the upper limit imposed to control the maximum lithium concentration, usually driven by fuel vendor limits, due to concerns of accelerated cladding corrosion at high lithium concentrations.

Within the range 6.9-7.4, pH_T has been shown to have minimal influence on the rate of SCC and PWSCC.

For the RR SMR design, removing the requirement for soluble boron for reactivity control means that the primary coolant pH can be controlled by a strong base only. Potassium hydroxide is the pH raiser selected for the baseline design, which offers several benefits over lithium hydroxide. These benefits include:

1. Surety of chemical supply (potassium hydroxide vs lithium-7 hydroxide)
2. Mitigating known accelerated fuel cladding corrosion concerns, which are present in concentrated lithium hydroxide.
3. Reduction in tritium generation (neutron reactions with lithium are the second highest contributor to tritium generation in PWR coolant, with boron being the highest contributor), potentially resulting in substantially lower primary coolant discharge. As a result of eliminating soluble boron, the RR SMR does not require regular let down of primary coolant during a cycle in order to dilute boron as required for duty reactivity control. This provides the opportunity to explore the potential for a different type of operation, more akin to closed cycle operation. Closed cycle operation has minimal impact on steady state coolant concentrations of the majority of nuclides present in PWRs. The exception to this is tritium, as it is not removed by current technologies available in coolant purification systems.

The RR SMR will have a target pH_T of **{REDACTED FOR PUBLICATION}** and, as there will be no boric acid dosed, should be able to achieve a more stable pH range throughout the operating cycle, requiring a lower dose of potassium hydroxide (compared to the concentration of lithium hydroxide required in the presence of boric acid).

For the RR SMR, the removal of boron has removed the risk of CIPS events occurring, since this is dependent on boron-containing precipitates forming. The risk of CILC assessment and underpinning justification will be discussed in the Tier 2 and demonstrated in the Tier 3 documentation.

Redox Potential

In simplistic terms, the redox potential can be considered the driving force for corrosion; generally, metallics are more susceptible to corrosion when exposed to high redox potentials and are more resistant to corrosion at lower redox potentials. Chemical oxidising agents, such as oxygen, serve to raise the redox potential and can significantly impact on the corrosion susceptibility of components within the RCS [JE]. Even low concentrations of oxygen have a strong impact on the redox potential and this is of particular concern when in the presence of chloride and sulphate, which serve to enhance the susceptibility of austenitic stainless steels to SCC.

The susceptibility of austenitic stainless steels to SCC has long been recognised, with control of aggressive impurities and oxygen being considered in the design of early PWRs. The increased resistance to SCC of nickel-base alloys was a primary consideration in their use as the steam generator tubing material. However, the influence of radiation on the primary coolant and the generation of oxidising species as a result of radiolysis was not fully understood and this process has resulted in corrosion-related performance issues being encountered in numerous PWRs.

Radiolysis is the dissociation of molecules when exposed to radiation. In PWRs, water is used as both the primary coolant and the moderator; when exposed to radiation, the water molecules decompose into a number of products, most noticeably hydrogen, oxygen and peroxide. The radiolytic decomposition of water is a complex series of reactions.

Oxygen and peroxide are oxidants and increase the redox potential within the primary coolant, with operating experience showing that the increase is sufficient to promote SCC in austenitic steels, even in low concentrations of chloride and sulphate. The increase in redox potential has also proven to be sufficient to promote PWSCC in Alloy 600, which was widely used as the tubing material within the SGs.

The radiolytic decomposition of water involves a series of equilibrium reactions and when excess hydrogen is present, the reaction is suppressed and a steady state is reached where low concentrations of oxygen and peroxide are formed. Hydrogen injection is therefore implemented in order to promote reducing conditions within the primary coolant and mitigate SCC and PWSCC. The reducing conditions also have the advantage of reducing the rate of general corrosion of structural materials, reducing the release of corrosion products that could deposit on the fuel, as well as increasing the corrosion product solubility across the core, which again is beneficial for reducing the amount of crud deposition.

The minimum hydrogen concentration required to suppress radiolysis is dependent on the radiation levels within the reactor core; at lower radiation levels, less hydrogen is required to suppress radiolysis.

Although resistant, the RR SMR materials of construction are still susceptible to SCC and PWSCC under oxidising conditions and therefore hydrogen injection will be applied to the RR SMR [2] in order to suppress radiolysis, creating a reducing environment in order to reduce the risk of corrosion SFAIRP.

Zinc Injection

Evidence from plant measurements and experiential studies indicates that the rate of incorporation of radiocobalt into oxide films on out-of-core surfaces is significantly reduced due to the presence of zinc in the coolant. The likely mechanism for this is the competition between zinc and cobalt for available sites in the oxide films. Additional benefit is anticipated for plants operating with zinc injection from the first cycle, with zinc injected during hot functional testing leading to the uptake of zinc in fresh oxide films. The addition of zinc also appears to reduce the release rate of significant activated corrosion products from the fuel surface, as well as their incorporation into oxide films on out-of-core oxide surfaces.

It is anticipated that the RR SMR will inject zinc in the form of **{REDACTED FOR PUBLICATION}** from hot functional testing, such that the production of radiologically significant **{REDACTED FOR PUBLICATION}** is also minimised.

Impurity Control

Management of the chemical environment to minimise corrosive impurities is an important factor in mitigating the risk of SCC and fuel cladding failure, in conjunction with the inherent resistance of the materials of construction. The ionic impurities of chloride, fluoride and sulphate in the primary coolant are of most concern and must be carefully monitored.

1. Austenitic stainless steels are susceptible to SCC in the presence of chloride, with highly stressed components being susceptible even in low oxygen concentration.
2. The relationship of sulphate and SCC in the PWR environment is less well studied than that of chloride, but sulphate can also enhance the susceptibility of stainless steels, particularly sensitised stainless steel such as produced in welding, and nickel alloys to SCC in deaerated conditions.
3. Fluoride is controlled due to the increased risk of fuel cladding corrosion at elevated fluoride concentrations.

20.5.7 Start-Up and Shutdown Chemistry

The information presented in Sections 20.5.2 to 20.5.4 is predominantly focussed on chemistry control during at-power operations; although the principles of chemistry control that are outlined are applicable to all modes of operation, the changes that occur during mode changes have an impact on chemistry control.

Shutdown Chemistry for Refuelling Outage

As discussed, general corrosion of the RCS [JE] materials results in the formation of a protective oxide layer on the metal surface and the slow release of corrosion products into the primary coolant.

During a refuelling outage, the reducing conditions achieved during power operations cannot be maintained as the reactor circuit is opened to air when the reactor head is removed. The change in chemistry environment can cause changes to the oxide layer. Uncontrolled 'crud bursts' (release of corrosion products driven by changes in the chemistry environment) during shutdown can cause operational challenges, increased outage dose rates and extensions to the outage duration.

The approach to shutdown chemistry control and crud management will be informed as the RR SMR design and operating philosophy develops. The design will have the ability to inject peroxide during shutdown to achieve controlled oxidising conditions prior to reactor head removal. This will allow for controlled clean up and removal of any excessive corrosion products generated by a crud burst.

Start-Up Chemistry

During refuelling outages the head of the reactor is removed and flood-up occurs, enabling fuel to be removed and transferred to the spent fuel pool. The primary coolant is exposed to the environment within the reactor building, resulting in the dissolved oxygen concentrations increasing. In addition, impurities that are present can dissolve into the primary coolant, increasing the impurity concentrations.

Corrosion is a temperature dependent process, with the corrosion rate increasing with increasing temperature. During outages the primary coolant temperature and pressure are significantly reduced, compared to at-power operations. This means that the risk of corrosion is reduced during refuelling outages and a higher concentration of impurities and dissolved oxygen can be tolerated. However, it is important that the impurity concentrations are reduced before the reactor commences heat up and the transition to at-power operations.

On completion of refuelling operations, the reactor head is replaced, creating a sealed environment within the RCS [JE]. The coolant is circulated through the CVCS in order to remove impurities and condition the chemistry in preparation for heat-up operations. The primary coolant is deaerated in order to reduce the concentration of dissolved gases, most noticeably the dissolved oxygen concentration. As the reactor temperature and pressure are increased, dissolved hydrogen injection and pH raising are implemented in order to ensure alkaline, reducing conditions are achieved prior to transferring to at-power operations (mode 1).

In order to accelerate the removal of dissolved oxygen and reduce the outage duration, it is common practice for PWRs to inject hydrazine during warm-up operations. Hydrazine is an oxygen scavenger, reacting with oxygen to form water and nitrogen.

As the RR SMR design and operating philosophy develops, outage durations and target durations will be refined and confirmed. This will inform the approach to shutdown chemistry control and crud management. The design will have the ability to inject hydrazine during the start-up operations, in order to accelerate the removal of dissolved oxygen and to support reduced outage durations.

20.5.8 Design Development at PCD

At PCD, the baseline chemistry regime for the primary coolant is based on:

1. Potassium hydroxide as the alkali agent, increasing the pH to minimise corrosion and deposition of corrosion products onto the fuel.
2. Hydrogen addition, to suppress radiolysis and create a reducing environment within the primary coolant, mitigating SCC and PWSCC.
3. Zinc addition, to control out-of-core dose rates.
4. Control of impurities that may negatively impact on corrosion or fuel performance.

Further Development

As stated in Section 20.3, the design maturity, operating philosophy and chemistry specifications are being developed in parallel and are continually reviewed to ensure alignment. If evidence gaps are identified, or additional underpinning required, these will be considered for incorporation into the developing V&V strategy.

Structural integrity, including materials selection, is within the scope of Chapter 23 of the E3S case [11]. As part of the overall justification for the materials selection for the RR SMR, an “Ageing Management Plan” (AMP) will be produced which identifies the degradation mechanisms of relevance, as well as stating which Technical Justification (TJ) reports will be produced. The TJs will assess the material degradation risk, under the RR SMR operating conditions and chemistry regime, and will identify any gaps in the existing evidence. Further development work, including materials and chemistry test programmes, will be undertaken in order to fill these evidence gaps and provide the underpinning and justification for the RR SMR design.

20.5.9 Tier 2 Reports

In relation to the primary coolant chemistry regime, the following Tier 2 documents will be produced:

5. **Reactor Island Water Chemistry Specification Tables.** This report will contain the water chemistry specification tables (covering both chemical and radiochemical parameters) for the primary coolant systems within the Reactor Island, including the RCS [JE] for all modes of operation, as well as the primary coolant auxiliary systems that interface with the RCS [JE]. Expected values for each parameter will be stated, as well as lower and upper limit values, where relevant.
6. **Primary Water Chemistry: Minimisation of Radioactivity.** This report will provide a summary of how the primary circuit chemistry contributes to the minimisation of radioactivity. It will include Sub-Claims in support of the main Argument on minimisation of radioactivity, with a high-level summary of the detailed evidence in Tier 3 reports that support each of these Sub-Claims. The scope of the report covers all radionuclides including corrosion products, fission products, actinides and activation products, detailing how the primary circuit chemistry regime contributes to their minimisation in terms of generation, and how it impacts transport and accumulation within the systems in the RR SMR. The scope of this report also includes all modes of operation, including start-up and shutdown.
7. **Primary Water Chemistry: Minimisation of Fuel Cladding Corrosion.** This report will provide a summary of how the primary circuit chemistry contributes to the minimisation of fuel cladding corrosion. It will include Sub-Claims in support of the main Argument on minimisation of fuel cladding corrosion, with a high-level summary of the detailed evidence in Tier 3 reports that support each of these Sub-Claims. The scope of this report includes corrosive species (e.g. chloride), but also fuel crud and the impact this can have on cladding corrosion. This report will not calculate/define the amount and type of crud expected, instead it will summarise information that will be presented in lower-level modelling reports and technical assessments. The scope of this report also includes all modes of operation, including start-up and shutdown.
8. **Primary Water Chemistry: Minimisation of Corrosion of Structural Materials.** This report will provide a summary of how the primary circuit chemistry contributes to the minimisation of corrosion of structural materials. It will include Sub-Claims in support of the main Argument on minimisation of corrosion of structural materials, with a high-level summary of the detailed evidence in Tier 3 reports that support each of these Sub-Claims. The Tier 3 reports cover pH, impurities, redox potential and zinc injection. This report will summarise how each of these parameters have been optimised to minimise the risks associated with corrosion SFAIRP. The scope of this report also includes all modes of operation, including start-up and shutdown.

20.6 Reactor Island Auxiliary System Chemistry

In order to support design development of the reactor island auxiliary systems, initial chemistry specifications have been produced that are based on RGP. The design maturity, operating philosophy and chemistry specifications are being developed in parallel and will be continually reviewed to ensure alignment.

20.6.1 Component Cooling System and Essential Services Water System Coolant

The Component Cooling System (CCS) [KA] system provides cooling for multiple systems within Reactor Island with the Essential Service Water System (ESWS) [PB] functioning as the ultimate heatsink for CCS [KA] system.

The CCS [KA] is a closed loop system using demineralised water as the cooling medium. The CCS is not directly exposed to irradiation and the fluid does not contact the nuclear fuel. When determining the optimum material selection and chemistry regime for the CCS, there is greater flexibility (when compared to the primary coolant chemistry regime), as fuel integrity and radioactivity considerations are less significant.

The baseline position at PCD is that a combination of nitrite and molybdate will be dosed to the CCS [KA], with the pH to be controlled to alkaline conditions (~pH 9.5 measured at 25°C) [2]. This is based on the assumption that the CCS [KA] pipework will be carbon steel, with no copper alloys or aluminium being used in the system and no significant neutron field exposure to the system.

The ESWS [PB] is an open recirculating system utilising mechanical draught cooling towers. The system will use a chemical treatment, tailored to the local water supply specification. As a preliminary baseline, biocides will be dosed to control bacteria, specifically legionella growth, anti-scalants may need to be dosed to minimise scale and maintain cooling function and corrosion inhibitors will be dosed to maintain the integrity of metal components within the system.

20.6.2 Spent Fuel Pool and Spent Fuel Pool Cooling System Coolant

It is important to maintain the water quality of the refuelling pool to the same standard as the primary coolant, as the refuelling pool is connected to the Spent Fuel Pool (SFP) [FAB10] and will be connected to the RPV [JAA] during head lift and cavity flood up. To maintain this level of quality, the chemistry of the SFP [FAB10] is controlled to the same requirements as the primary coolant during refuelling operations. The pools will contain no soluble boron and to prevent criticality the fuel will be stored in borated stainless-steel racks. Further detail on this this will be provided as the RR SMR design develops.

The spent fuel pool cooling and clean-up systems maintain the chemistry conditions within the SFP [FAB10], comprising of:

1. Fuel Pool Cooling System (FPCS) [FAK]

2. Fuel Pool Purification System (FPPS) [FAL]
3. Fuel Pool Supply System (FPSS) [FAT]

Further information on these systems, including design development activities, is contained within E3S Case Chapter 9A: Auxiliary Systems [20].

20.6.3 Local Ultimate Heatsink Coolant

The Local Ultimate Heatsink System (LUHS) [JNK] comprises of three trains, each containing a LUHS tank and its associated ancillary equipment, including the provision of fill, drain and sampling functions. Each LUHS tank corresponds to a single Passive Containment Cooling (PCC) train.

The LUHS tanks are arranged such that each tank (and most of the supporting equipment) is currently located outside containment in the interspace, adjacent to the SG [JEA] with which it interfaces. Cross-connects are provided between each tank to enable the unused water in one tank to be gravity drained into a tank that is available to cool the plant. The final location and geometry of the LUHS tanks are still to be finalised.

The PCC heat exchangers are cooled by water from the LUHS tank, which circulates water in a closed loop between the LUHS tank and PCC heat exchanger via natural circulation.

The LUHS tanks are filled with demineralised water, with no chemical additives, and are constructed of corrosion resistant materials.

Further information on the LUHS systems, including design development activities, is contained within E3S Case Chapter 6: Engineered Safety Features [23].

20.6.4 Alternative Shutdown Function (ASF)

The objective of the Alternative Shutdown Function (ASF) [JD02] is to provide the secondary means of controlling reactivity during faulted operation by inserting negative reactivity in the form of liquid neutron absorbers (boron) into the reactor fuel, thereby shutting down the reactor.

The baseline architecture for the ASF [JD02] is comprised of the Emergency Boron Injection System [JDK]; with a boron storage tank, two supply lines and two metering pumps; and the High-Pressure Injection System (HPIS) [JND] high-head pumps to deliver boron into the Reactor System [JA]. The ASF [JD02] also utilises instrumentation predominantly within the RCS [JE] and response of the Reactor Control and Protection Systems [JY].

The function operation is split into two phases:

1. Phase 1: Concentrated boron solution injection into the Reactor System [JA] directly from the boron storage tank
2. Phase 2: Metered boron injection for any subsequent plant make-up

The required boron concentration is defined by the shutdown and hold down requirements for cold zero power. The boron will be provided as potassium tetraborate. The system will include

appropriate sampling and monitoring capability in order to monitor and confirm the boron concentration.

Further information on the ASF systems, including design development activities, is contained within E3S Case Chapter 6: Engineered Safety Features [23].

20.6.5 Tier 2 Reports

A Tier 2 report will be produced entitled *Chemistry Justification for Primary Auxiliary Systems* which will provide the technical basis for the chemistry regime adopted within the Primary Auxiliary systems. The majority of these systems will be low temperature, demineralised water systems (no chemical addition) that are made of stainless steel. Due to the commonalities in chemistry and corrosion, as well as the lower complexity compared to the primary and secondary chemistry requirements, all of the auxiliary systems will be covered in one report. Where required, this Tier 2 report will draw upon the detailed technical information within the Tier 3 reports. This Tier 2 report will summarise why the chemistry of these systems has been optimised in order to reduce the risk of corrosion, reduce the occurrence of deposition/fouling and support reliable system operation. The scope of this report will also include the chemistry aspects of the standby boron injection tank.

20.7 Turbine Island

20.7.1 Design Overview

The main plant items within the Secondary Coolant System include:

1. Steam Generation System [JEA]
2. Main Feedwater System [LA]
3. Main Steam System [LB]
4. Condensate System [LC]
 - a. Steam Generator Blowdown System [LCQ]
5. Turbine Island Sampling System [QU]

Heat from the nuclear fuel is transferred from the RCS [JE] to the secondary system coolant in the three SGs [JEA]. Feedwater present in the SGs [JEA] is converted to steam which is then routed through the high pressure and low pressure turbines. The turbines are coupled to and rotate a generator, thereby generating the plant's electrical output. The steam leaving the low pressure turbines is condensed by heat exchange with the cooling water in the Main Cooling Water System (MCWS) [PA] system. The resulting condensate is then deaerated, pre-heated, and fed back into the SGs [JEA].

There is a bleed from the SGs [JEA] through the Steam Generator Blowdown System (SGBS) [LCQ] to control impurities in the secondary system coolant. Feedwater is provided from the demineraliser plant.

Additional information on the design and maturity of these systems is provided in Chapter 10 of the E3S Case [21].

20.7.2 Historical Development of Secondary System Chemistry

The SG tubes facilitate the transfer of heat from the reactor coolant system to the secondary system coolant; this not only enables cooling of the nuclear fuel, but provides the heat required to convert the water in the secondary system to steam, providing the energy required to drive the steam turbines and ultimately generate electricity. As the boundary between the reactor coolant and secondary system coolant, the SG tubes also form part of the reactor coolant pressure boundary and prevent the spread of radioactivity.

The boiling of water that occurs within the SGs results in the concentration of non-volatile species, which can create corrosive environments and wastage of the SG materials, potentially resulting in failure of the tubes and the release of primary coolant into the secondary system coolant. Corrosion products from the steam, condensate and feedwater systems are also concentrated through boiling, resulting in fouling of the SG tubing and a reduction in heat transfer efficiency.

The two main objectives of chemistry control in the secondary system are to:

1. Reduce corrosion of the steam generator tube materials SFAIRP
2. Reduce performance losses within the secondary system by reducing corrosion in the water and steam system and subsequent transport of corrosion products into the SGs [JEA], SFAIRP

Due to its resistance to SCC under primary coolant conditions, early PWRs adopted Alloy 600 as the SG tubing material and carbon steels and low-alloy steels were widely used in the steam and feedwater systems. Secondary chemistry control in early PWRs was based on that in fossil stations, with most PWR units using disodium phosphate or sodium hydroxide to achieve alkaline conditions, combined with impurity and oxygen control (although plants using sodium hydroxide quickly changed to trisodium phosphate). Phosphate is a weaker base than sodium hydroxide, enabling phosphate to buffer contaminants entering the system. However, SG tubes that were constructed of Alloy 600 soon started to suffer from corrosion problem due to the presence of phosphate-riches sludges; these sludges consolidated onto surfaces within the SGs and had high compressive strength, meaning they were difficult to remove. The sludges allowed the accumulation of aggressive species that caused corrosion of the SG materials. Phosphates (and sodium hydroxide) have low volatilities, meaning that they accumulate in the water phase and do not evaporate and transfer to the steam phase, resulting in no chemical conditioning of the steam and condensates that form.

In order to prevent the formation of consolidated sludges, plants adopted an “All Volatile Treatment” (AVT) of the secondary system and phosphate dosing was phased out of PWRs from the mid-1970s to late 1980s. The two main components of an AVT are an alkalisng agent used to control the pH around the circuit, and an oxygen scavenger used to remove dissolved oxygen. The pH is optimised to protect the condensate and feedwater piping from corrosion and to minimise iron transport. An appropriate pH range for protection is selected according to the plant design, materials and operating conditions. A low oxygen concentration in the feedwater is important in reducing the susceptibility of plant materials to corrosion. Advantages of an AVT regime over a phosphate regime are that it generally results in less sludge formation within which impurities can concentrate, it causes less wastage and it results in less corrosion of steam lines, wetted turbine components, condensers and the condensate system. A disadvantage of an AVT regime is that, since the reagents are volatile, they will not concentrate in boiling crevices and protect these vulnerable areas. Early implementation of AVT typically used ammonia for pH control, combined with hydrazine for oxygen control.

Although ammonia is volatile and transfers into the steam system, it preferentially remains in the steam phase and only a small proportion transfers to water upon condensation. Ammonia therefore provides limited protection in the two-phase regions of the steam system. In order to provide additional corrosion protection within the two-phase regions, and therefore reduce the volume of corrosion products transferred to the SGs, alternative amines or a “high-AVT” have been adopted. Alternative amines, such as ethanolamine (ETA) or methiopropamine (MPA), have higher distribution coefficients, resulting in a greater proportion remaining in the water phase and therefore increased alkalinity of condensates in the two-phase regions of the steam system, providing increased corrosion protection. Alternative amines may be used alone, or in combination with ammonia. A high-AVT treatment uses higher concentrations of ammonia to increase the pH of condensates formed; due to the high ammonia concentrations, a high-AVT regime is not compatible with the condensate purification system being operated at full flow and is typically only in service during start-ups and to correct impurity ingress.

20.7.3 Corrosion of Steam Generator Tubes

Corrosion of the SG tubes has been the predominant issue that has influenced the evolution of the secondary system chemistry regime; this is due to SG tube corrosion being the most significant issue experienced in the secondary system, SGs being the most expensive/difficult component to repair in the secondary system and the important role that the SG tubes play in maintaining containment of the primary coolant. There has been a significant amount of research conducted on SG tubing corrosion, with the majority of work focussing on mill-annealed Alloy 600 (600MA), as this was the tubing material used in early PWRs and which has suffered a number of corrosion-related issues. In order to mitigate these issues, a number of alternative materials have been used; these all demonstrate similar properties to 600MA, but with increasing resistance to corrosion (*order from lowest to highest resistance*):

1. Mill-annealed Alloy 600 (600MA): operational experience has shown that this is the alloy that has experienced the most corrosion-related issues in PWR SGs, with InterGranular Attack (IGA) and SCC being the dominant corrosion mechanisms.
2. Stress relieved Alloy 600 (600SR): this alloy has experienced serious corrosion issues in operating PWRs, but to a lesser extent than 600MA.
3. Thermally treated Alloy 600 (600TT): this alloy has been used in SGs since 1980 and there have been limited cases of IGA/SCC. Although having increased resistance to secondary side IGA/SCC, laboratory testing has shown that this alloy is susceptible to PWSCC.
4. Nuclear grade Alloy 800 (800NG): this alloy has been used in SGs since 1972 and experienced some corrosion issues whilst operating with phosphate chemistry. There have been limited cases of IGA/SCC under AVT, although other issues have been encountered.
5. Thermally treated Alloy 690 (690TT): this alloy has been used in SGs since 1989 and to date, there have been no confirmed cases of IGA/SCC. 690TT has a high resistance to IGA/SCC, even under aggressive test conditions, and also has increased resistance to PWSCC.

The main alloying elements present in alloys 600, 800 and 690 are nickel, chromium and iron. Under typical secondary system operating chemistries, nickel, chromium and iron all experience greater stability as oxides, rather than metals. Although the metals are reactive under secondary system chemistry conditions, the formation of the protective oxide films provide protection and results in low corrosion rates being experienced. The protective films result in high resistance to general forms of corrosion, but if the film is damaged, the materials can be susceptible to localised forms of corrosion. IGA and SCC are the two main localised corrosion mechanisms of concern regarding the SG tubes, with the main chemistry parameters that influence corrosion being:

1. pH: The pH of the system influences both general corrosion and localised corrosion. At typical SG operating temperatures (i.e. 280-300°C) chromium, nickel and iron are susceptible to general corrosion when exposed to low and high pHs, but form stable oxides at mid-range pHs (~pH 6-9). Experimental testing has shown that at low pH, Alloy 600 is susceptible to acidic attack and vulnerable to SCC under oxidising conditions, whilst at higher pHs the alloy is susceptible to alkaline SCC and IGA under oxidising and reducing conditions
2. Redox Potential: in common with the primary coolant system, corrosion of SGs tubes is accelerated under highly oxidising conditions (high redox potentials) but forms a stable

protective oxide when redox potentials are reduced. As the alloys rely on a stable oxide layer for corrosion protection, some mildly oxidising conditions are beneficial, as this provides the driving force for corrosion and the formation of the oxide film. However, if the redox potential increases and conditions become highly oxidising, then the alloys are susceptible to SCC and IGA, with the stable oxide film breaking down and localised corrosion occurring

3. **Aggressive Species:** aggressive species can accelerate the rate of corrosion by affecting the local conditions experienced, by changing the pH and/or redox potential. Some aggressive species affect the corrosion rate by impacting on the formation and integrity of the protective oxide layer that is formed on the SG tube material.

pH and Oxygen Control

As described in section 20.7.2, a high-AVT or alternative amine regime are commonly used for secondary system chemistry control. The amines are dosed into the feedwater to achieve a mildly alkaline regime at SG operating temperatures, which is equivalent to a pH of ~10 at 25°C.

Within the secondary system, the presence of dissolved oxygen has the greatest effect on the redox potential. Although the secondary system operates under vacuum conditions, dissolved oxygen is present in the make-up water and general ingress into the system. Hydrazine is injected into the feedwater system in order to act as an oxygen scavenger, ensuring a low dissolved oxygen concentration is achieved when the feedwater enters the SGs. The exact concentration of hydrazine required is dependent on the oxygen concentration, with the ratio of hydrazine:oxygen being considered more significant than the specific hydrazine concentration.

A mildly alkaline pH and low dissolved oxygen concentrations provide the optimum conditions for the formation of a protective oxide to form on the SG tube materials, ensuring passivity to general and localised forms of corrosion.

Aggressive Species

There are a number of chemical species that, when present in the secondary system coolant, have been shown to increase the risk of SG tube corrosion. The main species that can impact on the integrity of the SG tubes are:

Caustics: concentrated caustics can result in rapid IGA and SCC of SG tube materials, especially when exposed to oxidising conditions. Caustics (e.g. sodium hydroxide) have low volatility and can concentrate in the water phase under boiling conditions in the SG, as well as concentrating under deposits and within crevices.

Lead: although the effect is not fully quantified and exact limits are not technically underpinned, there is concern that the presence of lead can increase the susceptibility to SCC for nickel-base alloys.

Sulphur: oxidised sulphur species (i.e. sulphates) can affect the local pH and therefore the susceptibility to IGA and SCC. Reduced sulphur species can interfere with the formation of the protective oxide layer, therefore increasing susceptibility to corrosion.

Chlorides: although typical tubing alloys (Alloys 600MA, 600TT and 690TT) have high resistance to chloride-induced SCC due to the high nickel content, austenitic stainless steels

may be present in the SGs and these alloys are susceptible. If high chloride concentrations and oxidising conditions achieved as a result of fault conditions (e.g. condenser tube leakage and ingress of cooling water), then both nickel-base alloys and austenitic stainless steels can be susceptible to pitting corrosion, especially if sludge deposits are present in the SGs.

20.7.4 General Corrosion and Flow-Accelerated Corrosion (FAC)

Although localised corrosion (IGA/SCC) is the degradation mechanism of primary concern for the SG tubes, FAC is the main degradation mechanism that impacts on the feedwater and steam systems, as well as impacting on some components within the SGs themselves.

Under typical secondary system chemistry regimes, carbon steel undergoes oxidation to form either magnetite (deoxygenated conditions) or haematite (oxygenated conditions), which provide reasonable corrosion protection at system operating temperatures. The rate of general corrosion (i.e. uniform corrosion across the surface) is predictable and can be managed by ensuring that pipework wall thicknesses have an appropriate corrosion allowance.

Carbon steels are susceptible to FAC, which has resulted in significant operational issues at operational nuclear and fossil power stations. FAC is the accelerated corrosion that occurs under turbulent flow conditions and causes higher than predicted rates of corrosion. Although a passive film can form on the carbon steel, this is degraded by the turbulent flow conditions, resulting in localised attack of the metal. If undetected, this can result in catastrophic failure of feedwater and steam system pipework.

The main parameters that influence the occurrence of FAC in carbon steel pipework are:

1. Temperature: experimental studies have shown that a bell shaped dependence on temperature is observed, with the FAC rates increasing at temperatures above ~100°C, reaching a peak at ~180°C and then decreasing at higher temperatures (noting the exact temperatures will be dependent on plant and system specific details). At low temperatures the rate of corrosion is generally low and any degradation that occurs is attributed to wear/impingement, rather than corrosion. At high temperatures the carbon steel suffers increased rates of general corrosion, so localised FAC rates decrease.
2. Flow conditions: FAC requires turbulent flow conditions, with the turbulence resulting in accelerated breakdown of the protective oxide film on the carbon-steel surface.
3. Oxygen concentration: under deoxygenated conditions, the oxide layer formed on the carbon steel surface is magnetite, which is susceptible to FAC. Under oxygenated conditions, a haematite oxide layer forms on the carbon steel surface, which has increased resistance to FAC.
4. pH: alkaline conditions promote the formation of a stable oxide layer, and therefore higher pH conditions result in increased resistance to FAC.
5. Chromium content: increasing the chromium content of carbon steels results in chromium being present in the oxide layer. Low-alloy steels have sufficiently high chromium content that they are resistant to FAC.

6. Fluid phase: FAC can occur in both single phase (water) and two phase (water/steam) conditions, with higher rates possible in two-phase regions due to the increased temperature and high steam flow rates.

Sludge Deposition

At the PCD stage, the baseline assumption is that the secondary system will utilise low-alloy steels to provide resistance to FAC. Although the risk of failure of low-alloy steel pipework and components is low, low rates of FAC still occur and due to the surface area, this generates large amounts of corrosion products that are transported to the SGs. The boiling that occurs in the SGs results in concentration of the corrosion products, resulting in sludge deposition and build-up within the SG internals. The presence of sludge can have a negative impact on SG corrosion, as the sludge deposits can accumulate aggressive species and result in localised aggressive conditions being formed. It is therefore important that the secondary system chemistry regime is optimised in order to reduce the rate of FAC occurring in the feedwater system and two-phase regions of the steam system.

From a chemistry perspective, the two parameters that can be varied in order to control FAC are the pH and the dissolved oxygen content. Historically, many plants back-fitted oxygen injection systems in order to increase the dissolved oxygen content of the feedwater and promote the formation of a haematite oxide layer. For PWRs, this is not desirable, as dissolved oxygen creates oxidising conditions, increasing the risk of corrosion occurring in the SG tubes. pH is therefore the only chemistry parameter that can be controlled in order to reduce the rate of FAC (and general corrosion) of low-alloy steel pipework and reduce the generation and transportation of corrosion products.

As described in section 20.7.2, AVT and alternative amines have the advantage of being volatile, evaporating on boiling and transferring to the steam phase. This provides increased protection against two-phase FAC and general corrosion within the steam and condensate system and is beneficial in reducing the quantities of SG sludge deposits.

20.7.5 Design Development at PCD

At PCD, the baseline chemistry regime for the secondary system is based on:

1. High-AVT treatment to increase the pH of the system, providing corrosion protection to the single phase and two phase regions
2. Hydrazine injection to scavenge oxygen and lower the redox potential within the SGs, promoting the formation of a passive oxide layer and reducing the risk of IGA and SCC.

The chemistry control parameters, expected values and limit values for secondary system coolant are defined in Reference [3]. The justification for these values, and the overall chemistry regime, was based on RGP and information that was available at the time.

Further Development

Although the baseline position for the secondary system chemistry is based on an ammonia-based high-AVT regime, the positive and negatives of ammonia use versus alternative amines will be re-assessed as the design matures.

As the RR SMR SGs and turbine systems design develops, the secondary chemistry requirements and limits may be refined to ensure corrosion control and optimum system performance for their specific design.

20.7.6 Tier 2 Reports

In relation to the Turbine Island chemistry regime, the following Tier 2 reports will be produced:

1. **Turbine Island Water Chemistry Specification Tables.** This report will contain the water chemistry specification tables for the secondary coolant systems within the Turbine Island. Expected values for each parameter are stated, as well as lower and upper limit values, where relevant.
2. **Secondary Water Chemistry: Minimisation of Corrosion of Structural Materials.** This report provides a summary of how the secondary system chemistry contributes to the minimisation of corrosion (including Flow Accelerated Corrosion). It includes Sub-Claims in support of the main Argument on minimisation of corrosion, with a high-level summary of the detailed evidence in Tier 3 reports that support each of these Sub-Claims.

20.8 Turbine Island Ancillary Systems

The turbine island ancillary systems are included within the scope of Chapter 9 of the E3S case [20]. Due to the level of design maturity, limited information is provided within Issue 1 of Chapter 9.

In order to support design development of the reactor island auxiliary systems, initial chemistry specifications have been produced that are based on RGP and currently available information. The design maturity, operating philosophy and chemistry specifications are being developed in parallel and will be continually reviewed to ensure alignment.

20.9 Normal Operation Source Term

20.9.1 Purpose

The source term describes the types, quantities and physical and chemical forms of the radionuclides present in a nuclear reactor that have the potential to give rise to exposure to ionising radiation to workers, the public and the environment.

The purpose of the RR SMR source term is to quantify the radioactive inventory of the RR SMR so that the radioactive hazard in the reactor, supporting systems and circuits can be understood. The source term is used to support the development of the design and the E3S case to demonstrate that risks relating to radioactivity have been reduced SFAIRP and As Low As Reasonably Achievable (ALARA) using BAT.

The normal operation source term is a sub-set of the overall source term for the RR SMR which also consists of the:

1. Activated structures source term: Which covers the concentration of radionuclides activated within structural materials subject to neutron flux, e.g. RPV internals.
2. Spent fuel source term: Which covers the radionuclide inventory of partially and fully spent fuel assemblies.

Both the activated structures source term and the spent fuel source term will be covered in E3S Case Chapter 12: Radiation Protection, Reference [24], as part of the Radiation Protection topic area.

The normal operation source term is used to underpin assessments related to the following technical areas:

1. Waste management;
 - a. Radioactive waste system design,
 - b. Waste categorisation (package assessment),
 - c. Disposability assessments.
2. Radiation protection;
 - a. Worker dose (internal and external),
 - b. Public dose from direct shine,
 - c. Shielding design.
3. Routine environmental discharges;
 - a. Aqueous and gaseous radioactive effluent discharge limit assessments,
 - b. Radiological impact assessment.

4. Decommissioning;
 - a. Decommissioning waste disposability assessments,
 - b. Decommissioning shielding design.
5. Fault Studies;
 - a. Design basis event dose assessments,
 - b. Design extension condition dose assessments.

20.9.2 Radionuclide Groups

The normal operation source term is comprised of the following four radionuclide groups:

1. Fission Products (FP): This covers radionuclides that originate from fission of fissile materials in the reactor core. FPs can be present in the primary coolant due to the presence of tramp uranium on the fuel assembly surface, uranium impurities in the fuel cladding material, migration and release through small cladding defects or through fuel failures.
2. Corrosion Products (CP): This covers radionuclides that originate from the surface degradation (e.g. wear and corrosion) of primary circuit materials. During operation, primary circuit materials will corrode and release metallic impurities into the primary coolant. Some of these impurities will deposit on the fuel surface and subsequently become activated and re-released into the coolant, while some remain suspended in the coolant and can become activated while flowing through the reactor core.
3. Activation Products (AP): This covers radionuclides that originate from the activation of the primary coolant, as well as impurities contained in the primary coolant. It also covers activation of substances that are purposefully injected into the primary coolant to control its chemistry.
4. Actinide Products (ActP): This covers radionuclides that are produced as a result of neutron activation of uranium, subsequent activation and radioactive decay. ActPs can be present in the primary coolant due to the presence of tramp uranium on the fuel surface, uranium impurities within the fuel cladding or due to fuel failures.

The radionuclide list (and related methodology) associated with the normal operation source term for the RR SMR is documented in the Normal Operation Source Term Radionuclide Selection Report [25]. The development of this list takes account of RGP in the form of codes and standards, and datasets from similar technologies, and considers design choices specific to the RR SMR.

20.9.3 Categories of Source Term Value

Given one of the primary functions of the normal operation source term is to inform technical areas and facilitate technical assessments to support and develop the design, more than one type of source term value is required to be derived for each of the radionuclide groups outlined above. The source term values are subdivided into the following categories for all radionuclides:

1. Best Estimate (BE): This gives an overall best estimate of the source term expected in the RR SMR. This is a representative condition that is realistic so as not to result in over-specification of the source term for plant systems. The BE value is used for areas such as disposability assessments and routine environmental discharges.
2. Design Basis (DB): This gives a conservative maximum value for the source term which is considered to be a bounding limit for the plant design. The DB value is not expected to be exceeded during operation, even during transients and when expected events such as fuel failures occur. The DB value is important for key safety related applications such as shielding calculations to ensure that doses to the operators and public are minimised.
3. Cycle Average (CA): This gives a source term that is averaged over the entire fuel cycle, including start-up, power operation, shutdown and refuelling outage phases. The CA values are determined for both BE and DB values and include expected events such as fuel failures and unplanned shutdowns.

20.9.4 Source Term Types

The normal operation source term is derived for multiple locations around the RR SMR primary circuit and supporting plant systems that contain radioactivity. The source term is derived focussing on the source term in the reactor core and using this as a basis for deriving the source term for supporting plant systems. The overall source term for the RR SMR is made-up of the following constituent source terms:

1. Primary Source Term (PST): The PST considers the initial formation of radionuclides in the primary coolant in the reactor core. It includes fission products, corrosion products, activation products and actinides. The PST represents the most important dataset in the source term suite and is used as the starting point for all other system source terms subsequently derived, as summarised below.
2. Primary System Source Term (PSST): The PSST covers the radioactive inventory in the coolant and gaseous streams in primary circuit systems, as well as any deposited radioactivity on the inner surface of system components which become fixed on primary circuit surfaces by absorption into primary circuit materials.
3. Secondary System Source Term (SSST): The SSST covers the radioactive inventory in the coolant and steam of secondary circuit systems which may be produced by a SG tube leak.
4. Fuel crud Source Term (FCST): The FCST covers the radioactive inventory of the fuel crud (deposited material on the surface of the fuel, predominately made up of CPs). Fuel deposits impact the PST due to the activation and resuspension of deposited material from the fuel surface.

20.9.5 Source Term Derivation Methodology

Primary Source Term

The PST will be largely based on Operating Experience (OPEX) from analogous plants. Where relevant OPEX data are not available or applicable for aspects of the source term, industry-validated computer codes/models will be used to support the derivation of the source term, as well as calculation from first principles.

The FP and ActP PST represents operation with intact fuel for BE values. This reflects the presence of FPs in the primary coolant due to recoil and knock-on reactions from tramp uranium and uranium impurities within the fuel cladding. Given the physical nature of these release mechanisms, the FP and ActP PST will be predominantly derived from OPEX data. Conversely, DB values are representative of operation with failed fuel, based on a maximum fuel pin inventory (derived using the SCALE Code System) and a series of experimentally derived escape rate coefficients. The resulting steady-state concentration of FPs and ActPs will be normalised using the plant limiting condition for operation for Dose Equivalent Iodine (DEI).

CPs will predominantly be present in the coolant due to the corrosion and release of metallic impurities into the primary coolant and subsequent activation in the reactor core. One of the primary methods of controlling corrosion in PWRs is chemistry control. As the RR SMR will operate with a boron-free primary chemistry regime and KOH as the pH raising agent, limited OPEX data are available from “like-for-like” plants. However, the CP PST will be developed based on OPEX data on the basis that corrosion and release rates for a KOH regime are equal to or less than a standard lithium-boron regime given similarities in the target pH, redox regime and material selection. An experimental programme has been established that has the primary objective of understanding the difference in material release rates and oxide deposition rates between the RR SMR chemistry regime and that employed in standard PWRs. The outcome of this work will validate the use of OPEX data from analogous plants for CP radionuclides and support the development of an Activity Transport Model that simulates the behaviour of CP radionuclides under RR SMR primary circuit conditions.

APs are produced due to activation of the coolant as well as impurities that are unavoidably and intentionally present in the coolant. These radionuclides are only produced in the presence of a neutron flux and do not exhibit transient behaviour. The PST for all APs will be calculated using FISPACT-II code coupled with design data to reflect removal from the primary coolant.

In addition to this, tritium is considered as an AP, primarily due to its production via activation of deuterium in the primary coolant. However, unlike other radionuclides in the AP group, there are a number of other sources in the primary coolant which need to be considered – diffusion from the fuel through the fuel cladding and release from the fuel in the event of a fuel failure. The contribution from both phenomena will be assessed using a fuel pin inventory derived using the SCALE Code System.

Primary System Source Term

The PSST covers the radioactive inventory in the coolant of primary circuit systems, as well as any deposited radioactivity on the inner surface of system components. The PSST also covers the inventory of any gaseous volumes in the primary circuit.

The PSST is split into primary circuit systems with a number of calculation points for each primary system. Typically, there is a calculation point that captures each of the key operations of a system, e.g. there is a calculation point upstream and downstream of the demineralisers in the CVCS.

The coolant PSSTs are calculated using a primary circuit mass and activity balance model, taking the PST as the principal input and applying operational parameters to assess the source term at each calculation point. The model takes account of radioactive decay and system operations.

The piping deposit PSSTs will be calculated based on the coolant PSSTs and the Activity Transport Model. The model will utilise a series of deposition coefficients, one for each relevant CP radionuclide. These deposition coefficients will be based on a mixture of OPEX, experimental data and coefficients published in the literature as well as experimental data produced as part of the related RR SMR experimental programme.

Secondary System Source Term

The SSST covers the radioactive inventory in the coolant and steam of secondary systems. The SSST also covers the inventory of any gaseous volumes in the secondary system.

Like the PSST, the SSST will be split into secondary coolant systems with a number of calculation points for each secondary system with a calculation point that captures each of the key operations of a system.

The coolant SSSTs will be calculated by assuming the presence of SG tube defects that result in radionuclide concentrations in the secondary coolant, with the PST used as one of the principal inputs along with a primary-to-secondary leak rate. A secondary circuit mass and activity balance model will then be used to assess the SSST at each relevant calculation point by applying operational parameters that reflect the operation of the RR SMR secondary system.

Fuel Crud Source Term

The FCST covers the radioactive inventory of any deposited material on the surface of the fuel. The Activity Transport Model will be used to quantify the mass and composition of fuel deposits (crud) by simulating boiling based on a core wide average sub-cooled nucleate boiling rate derived using VIPRE code. This model will be coupled with EPRI's BOA code once mature to include changes in boiling rate associated with the evolution of crud on the fuel surface.

20.9.6 Design Maturity

Due to the lack of publicly available OPEX data to support the development of the normal operation source term prior to Final Concept Definition (FCD), an initial PST dataset has been derived based on the methodology outlined in ANSI/ANS 18.1 (2020) [7]. This standard consists of taking a source term dataset for a reference plant and applying a series of adjustment factors to reflect differences in the design of the reference plant relative to the RR SMR. Adjustment factors reflect differences in aspects such as thermal power, primary coolant mass, purification flow rates and purification efficiencies.

The primary coolant concentrations for the reference plant in ANSI/ANS 18.1 are based on data collected between 1999 and 2015 for ten worldwide PWRs and include contribution from normal operating events such as fuel pin failures and mid-cycle outages.

This initial PST dataset has facilitated the development of the design of the RR SMR up to the FCD stage. The forward strategy and methodology for developing the Normal Operation Source Term is defined in Reference [26].

20.10 Conclusions

20.10.1 Conclusions

Evidence is presented to support the overall chapter Claim that ‘the RR SMR chemistry regime and development of the chemistry systems design, reduces risks during all normal operating modes and accident conditions for all phases of the lifecycle’, which contributes to the overall E3S objective to protect people and the environment from harm, and the demonstration that risks are reduced ALARP.

During early concept design, initial chemistry specifications were developed in order to support design development (References [2] and [3]). These specifications were based on RGP and available information at the time, including early revisions of the *EPR Water Chemistry Guidelines*. The design maturity, operating philosophy and chemistry specifications are being developed in parallel and are continually reviewed to ensure alignment.

The complete suite of evidence to underpin the Claim will be developed in line with CAE Route Map and reported in future revisions of the E3S Case.

20.10.2 Assumptions & Commitments on Future Dutyholder/Licensee

Table 20.10-1: Assumptions and Commitments on Future Dutyholder/Licensee

Assumption/ Commitment	ID	Description
Assumption	A20.1	The final decision on the optimum commissioning chemistry regime for the RR SMR plant will require input from the future plant operator and will be deferred until the site-specific licensing period. During safety case and design development, RGP for commissioning PWRs will be presented and it will be demonstrated that the RR SMR design does not foreclose options
Commitment	C20.1	The future operator of the RR SMR plant will be responsible for implementing a chemistry programme

20.11 References

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- [21] RR SMR Report, SMR0003880/001, E3S Case Chapter 10: Steam and Power Conversion Systems, March 2023.
- [22] RR SMR Report, SMR0003984/001, E3S Case Chapter 5: Reactor Coolant System and Associated Systems, March 2023.
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- [26] SMR0000867 Issue 1: Normal Operation Source Term Strategy Report.
- [27] EDNS01000919142: Small Modular Reactor Commissioning Strategy in Concept Phase, Issue 1, February 2021.
- [28] SMR0000150 Issue 1: Water Quality Specification for the UK SMR Turbine Island Secondary Circuit and Ancillary Systems Specification Tables, May 2022.

20.12 Appendix A: CAE Route Map

20.12.1 Chapter 20 Route Map

A preliminary Claims decomposition from the overall Chapter 20 Claim is summarised in Table 20.12-1, including the Tier 2 Evidence underpinning the Claims at PCD (i.e., summarised in Revision 1 of this report) and further Tier 2 Evidence still to be developed.

Table 20.12-1: CAE Route Map

Level 1 Claims	Argument	Level 2 Claims	Level 3 Claims	Evidence Summary within Chapter 20	Underpinning Tier 2 Evidence <i>*at PCD</i>	Underpinning Tier 2 Evidence <i>*to be developed</i>
20. The RR SMR Chemistry regime and development of the chemistry systems design, reduces risks during all normal operating modes and accident conditions for all phases of the lifecycle	20.1 The SMR chemistry regime has been optimised in order to reduce the risk of fuel cladding corrosion SFAIRP.	20.1.1 Impurities and Additives within the Reactor Coolant that could Result in Fuel Clad Degradation are Identified, Operating Ranges Defined and Concentrations Controlled (i.e. control parameters)		Section 20.5.4	Reactor Island Water Chemistry Specification Tables [2]	Reactor Island Water Chemistry Specification Tables [2]; Primary Water Chemistry: Minimisation of Fuel Cladding Corrosion
		20.1.2 The CVCS Removes Corrosion Products in Order to Control Fuel Cladding Deposition		Section 20.5.1	Reactor Island Water Chemistry Specification Tables [2]	Primary Water Chemistry: Technical Justification for Control of Impurities



Level 1 Claims	Argument	Level 2 Claims	Level 3 Claims	Evidence Summary within Chapter 20	Underpinning Tier 2 Evidence <i>*at PCD</i>	Underpinning Tier 2 Evidence <i>*to be developed</i>	
		21.1.3 Impurities and Additives within the SFP that could Result in Fuel Clad Degradation are Identified, Operating Ranges Defined and Concentrations Controlled (i.e. control parameters)		Section 20.6.2	Reactor Island Water Chemistry Specification Tables [2]	Reactor Island Water Chemistry Specification Tables [2]; Primary Water Chemistry: Minimisation of Fuel Cladding Corrosion	
		21.1.4 The Reactor Coolant pH is controlled through additions of KOH, reducing the risk of fuel cladding corrosion SFAIRP.		Section 20.5.6	Reactor Island Water Chemistry Specification Tables [2]	Reactor Island Water Chemistry Specification Tables [2]; Primary Water Chemistry: Minimisation of Fuel Cladding Corrosion	
	20.2 The SMR chemistry regime has been optimised in order to reduce the corrosion of structural materials SFAIRP	20.2.1 The Reactor Coolant Chemistry is Optimised in Order to reduce Corrosion of Structural Materials SFAIRP	20.2.1.1 Passivation is Undertaken During Hot Functional Testing in Order to reduce General Corrosion SFAIRP		Claim initially presented to support structuring of the chemistry safety case, but due to the level of design maturity, there is currently no evidence to underpin this Claim.	No work was undertaken relating to commissioning chemistry during the PCD phase. The overarching commissioning strategy is presented in reference [27]	Chemistry Commissioning Strategy
			20.2.1.2 Hydrogen is Injected into the Reactor Coolant in Order to Mitigate PWSCC		Sections 20.5.6	Reactor Island Water Chemistry Specification Tables [2]	Primary Water Chemistry: Minimisation of Corrosion of Structural Materials

Level 1 Claims	Argument	Level 2 Claims	Level 3 Claims	Evidence Summary within Chapter 20	Underpinning Tier 2 Evidence <i>*at PCD</i>	Underpinning Tier 2 Evidence <i>*to be developed</i>
			20.2.1.3 The Concentration of Impurities in the Reactor Coolant are Controlled in Order to Reduce Corrosion SFAIRP	Sections 20.5.6	Reactor Island Water Chemistry Specification Tables [2]	Primary Water Chemistry: Minimisation of Corrosion of Structural Materials
			20.2.1.4 The Concentration of Oxygen in the Reactor Coolant is Controlled (Both Mechanically and Chemically) in Order to Reduce the Corrosion SFAIRP	Sections 20.5.6	Reactor Island Water Chemistry Specification Tables [2]	Primary Water Chemistry: Minimisation of Corrosion of Structural Materials
			20.2.1.5 The Reactor Coolant pH is controlled through additions of KOH in order to reduce corrosion SFAIRP.	Sections 20.5.6	Reactor Island Water Chemistry Specification Tables [2]	Primary Water Chemistry: Minimisation of Corrosion of Structural Materials
		20.2.2 The secondary circuit chemistry is optimised in order to reduce corrosion of structural materials and fouling of heat transfer surfaces SFAIRP	20.2.2.1 The secondary circuit chemistry is controlled in order to reduce corrosion of the steam generator materials SFAIRP	Section 20.7.3	Water Quality Specification for the UK SMR Turbine Island: Secondary Circuit and Ancillary Systems [3]	Turbine Island Water Chemistry Specification Tables [28]; Secondary Water Chemistry: Minimisation of Corrosion of Structural Materials
			20.2.2.2 The secondary circuit chemistry is controlled in order to reduce corrosion in the water and steam system and subsequent transport of corrosion products into the steam generators, SFAIRP	Section 20.7.4	Water Quality Specification for the UK SMR Turbine Island: Secondary Circuit and Ancillary Systems [3]	Turbine Island Water Chemistry Specification Tables [28]; Secondary Water Chemistry: Minimisation of Corrosion of Structural Materials



Level 1 Claims	Argument	Level 2 Claims	Level 3 Claims	Evidence Summary within Chapter 20	Underpinning Tier 2 Evidence <i>*at PCD</i>	Underpinning Tier 2 Evidence <i>*to be developed</i>
		20.2.3 The SFP Chemistry is Optimised in Order to reduce Corrosion of Structural Materials SFAIRP	20.2.3.1 The Concentration of Impurities in the within the spent fuel pool are Controlled in Order to Reduce Corrosion of structural materials SFAIRP	Section 20.6	Reactor Island Water Chemistry Specification Tables [2]	Primary Water Chemistry: Minimisation of Corrosion of Structural Materials
		20.2.4 The Chemistry of the Ancillary Systems is Optimised in Order to Minimise Corrosion of Structural Materials	20.2.4.1 The chemistry of the closed cooling water systems is controlled in order to reduce corrosion of structural materials SFAIRP	Section 20.6	Reactor Island Water Chemistry Specification Tables [2]	Primary Water Chemistry: Minimisation of Corrosion of Structural Materials
	20.3 Radioactivity in the RR SMR is minimised SFAIRP to minimise worker and public dose.	20.3.1 Generation of radionuclides in the Reactor Coolant is minimised SFAIRP.		Claim initially presented to support structuring of the chemistry safety case, but due to the level of design maturity, there is currently no evidence to underpin this Claim. See Sections 20.5.5 and 20.9.	Normal Operation Source Term Strategy Report [26]	Primary Water Chemistry: Minimisation of Radioactivity
		20.3.2 Deposition of radionuclides in the primary circuit is minimised SFAIRP.		Claim initially presented to support structuring of the chemistry safety case, but due to the level of design maturity, there is currently no evidence to underpin this Claim. See Sections 20.5.5 and 20.9.	Normal Operation Source Term Strategy Report [26]	Primary Water Chemistry: Minimisation of Radioactivity

Level 1 Claims	Argument	Level 2 Claims	Level 3 Claims	Evidence Summary within Chapter 20	Underpinning Tier 2 Evidence <i>*at PCD</i>	Underpinning Tier 2 Evidence <i>*to be developed</i>
		20.3.3 Accumulation of radionuclides in the Reactor Coolant is minimised SFAIRP.		Claim initially presented to support structuring of the chemistry safety case, but due to the level of design maturity, there is currently no evidence to underpin this Claim. See Sections 20.5.5 and 20.9.	Normal Operation Source Term Strategy Report [26]	Primary Water Chemistry: Minimisation of Radioactivity
		20.3.4 Accumulation of radionuclides in the secondary coolant is minimised SFAIRP.		Claim initially presented to support structuring of the chemistry safety case, but due to the level of design maturity, there is currently no evidence to underpin this Claim. See Sections 20.5.5 and 20.9.	Normal Operation Source Term Strategy Report [26]	Primary Water Chemistry: Minimisation of Radioactivity
		20.3.5 Accumulation of radioactivity in the spent fuel pool is minimised SFAIRP.		Claim initially presented to support structuring of the chemistry safety case, but due to the level of design maturity, there is currently no evidence to underpin this Claim. See Sections 20.5.5 and 20.9.	Normal Operation Source Term Strategy Report [26]	Primary Water Chemistry: Minimisation of Radioactivity



Level 1 Claims	Argument	Level 2 Claims	Level 3 Claims	Evidence Summary within Chapter 20	Underpinning Tier 2 Evidence <i>*at PCD</i>	Underpinning Tier 2 Evidence <i>*to be developed</i>
		20.3.6 Release of radioactivity to the environment is minimised SFAIRP.		Claim initially presented to support structuring of the chemistry safety case, but due to the level of design maturity, there is currently no evidence to underpin this Claim. See Sections 20.5.5 and 20.9.	Normal Operation Source Term Strategy Report [26]	Primary Water Chemistry: Minimisation of Radioactivity
	20.4 Systems, structures and components are provided within the SMR design in order to monitor and control chemistry.	20.3.1 Sampling and monitoring systems are designed to provide representative data on the concentrations of chemical and radiochemical species within plant systems.		Section 20.4	Reactor Island Water Chemistry Specification Tables [2]; Water Quality Specification for the RR SMR Turbine Island: Secondary Circuit and Ancillary Systems [3]	Reactor Island Water Chemistry Specification Tables [2]; Primary Water Chemistry: Method of Monitoring and Control Turbine Island Water Chemistry Specification Tables [28]; Secondary Water Chemistry Method of Monitoring and Control
		20.3.2 Chemical and radiochemical species that are important to plant operation are defined and sampled/monitored at defined frequencies		Section 20.4	Reactor Island Water Chemistry Specification Tables [2]; Water Quality Specification for the RR SMR Turbine Island: Secondary Circuit and Ancillary Systems [3]	Reactor Island Water Chemistry Specification Tables [2]; Primary Water Chemistry: Method of Monitoring and Control Turbine Island Water Chemistry Specification Tables [28]; Secondary Water Chemistry: Method of Monitoring and Control

20.13 Acronyms and Abbreviations

ActP	Actinide Products
AP	Activation Products
ALARA	As Low As Reasonably Achievable
ALARP	As Low As Reasonably Practicable
AMP	Ageing Management Plan
AOA	Axial Offset Anomaly
ASF	Alternative Shutdown Function
AVT	All-Volatile Treatment
BAT	Best Available Techniques
BE	Best Estimate
CAE	Claims, Arguments, Evidence
CCS	Component Cooling System
CILC	Crud-Induced Localised Corrosion
CIPS	Crud-Induced Power Shifts
Crud	Chalk River Unidentified Deposit (fuel deposit)
CP	Corrosion Products
CVCS	Chemical and Volume Control System
CA	Cycle Average
DB	Design Basis
DEI	Dose Equivalent Iodine
E3S	Environment, Safety, Security and Safeguards
EPRI	Electric Power Research Institute
ESWS	Essential Services Water System
ETA	Ethanolamine
FAC	Flow-Accelerated Corrosion
FCD	Final Concept Definition
FCST	Fuel Crud Source Term
FP	Fission Products

FPCS	Fuel Pool Cooling System
FPPS	Fuel Pool Purification System
FPSS	Fuel Pool Supply System
GER	Generic Environment Report
HPIS	High-Pressure Injection System
IAEA	International Atomic Energy Agency
IGA	Inter-Granular Attack
LUHS	Local Ultimate Heat Sink
LWR	Light Water Reactor
MPA	Methiopropamine
MCWS	Main Cooling Water System
OPEX	Operating Experience
PCC	Passive Containment Cooling
PCD	Preliminary Concept Definition
PCSR	Pre-Construction Safety Report
PWR	Pressurised Water Reactor
PST	Primary Source Term
PSST	Primary System Source Term
PWSCC	Primary Water Stress Corrosion Cracking
RCP	Reactor Coolant Pump
RCS	Reactor Coolant System
RD	Reference Design
RDS-PP	Reference Designation System for Power Plants
RGP	Relevant Good Practice
RPV	Reactor Pressure Vessel
RR SMR	Rolls-Royce Small Modular Reactor

SSST	Secondary System Source Term
SFAIRP	So Far As Is Reasonably Practicable
SFP	Spent Fuel Pool
SG	Steam Generator
SGBS	Steam Generator Blowdown System
SCC	Stress Corrosion Cracking
SSC	Structure, System and Component
SSG	Specific Safety Guide
TJ	Technical Justification
V&V	Validation and Verification
VVER	Voda Voda Energo Reactor