ONR GUIDE		
CHEMISTRY OF OPERATING CIVIL NUCLEAR REACTORS		
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1. INTRODUCTION

1.1 The Office of Nuclear regulation (ONR) has established its Safety Assessment Principles (SAPs) which apply to the assessment by ONR specialist inspectors of safety cases for nuclear facilities that may be operated by potential licensees, existing licensees, or other duty-holders. The principles presented in the SAPs are supported by a suite of guides to further assist ONR's inspectors in their technical assessment work in support of making regulatory judgements and decisions. This Technical Assessment Guide (TAG) is one of these guides.

2. PURPOSE AND SCOPE

2.1 The Safety Assessment Principles (SAPs) [1] for Nuclear Facilities provide a framework to guide regulatory decision-making in the permissioning process and ONR's inspectors use the SAPs, together with the supporting Technical Assessment Guides (TAGs), to guide regulatory decision making. The outcome of an assessment in ONR is to reach an independent and informed judgement on the adequacy of a nuclear safety case [2]. This will involve the use of the Inspector's professional regulatory judgement, within the framework of ONR's assessment process.

2.2 This TAG contains guidance to advise and inform ONR staff in the exercise of their regulatory judgement. This TAG is intended to support the SAPs [1] and to provide general guidance on the main issues to be considered by nuclear safety inspectors in the assessment of safety submissions relating to chemistry in operating civil nuclear power plant. This guide refers to "reactor chemistry", so as not to confuse it with the other aspects of chemistry. For the purpose of this guide "reactor chemistry" means the influence of coolant chemistry on reactivity, pressure boundary integrity, fuel and core component integrity, radioactive waste generation and radiological doses to workers and the public. In this sense reactor chemistry is a broad topic, overlapping with several other topic areas, such as structural integrity and radiological protection. This guide does not attempt to discuss these areas in detail, but does indicate where such overlaps exists and may be considered by the inspector as necessary. This guide considers radiochemical aspects under the broader topic of chemistry, as these functions are often intimately linked to the operating chemistry and on a practical sense are often provided by the same group of licensee staff.

2.3 This Assessment Guide is broadly applicable both to new plant throughout the design, construction and commissioning phases, and to existing operating reactors, through to their eventual decommissioning. Similarly the principles described in this guide are applicable through all modes of operation, from cold shutdown to hot operations and back again.

2.4 The guide does not attempt to provide details for particular chemistry regimes which may be applied to a particular reactor design, but rather concentrates on the fundamental principles which may require consideration by the Licensee in preparing their safety cases and hence may be subject to assessment by ONR. Summary information on the various types of chemistry regimes applied to UK nuclear power reactors is given in Appendices 3 to 9.

2.5 While the effects of chemistry can be important in accident situations, often influencing the rate and ultimate consequences of a particular fault, this guide only considers operational chemistry matters. Some of the general guidance herein may be applicable in the assessment of other nuclear plant and situations where chemistry should be considered as part of the safety case. As for all guidance, inspectors should use their judgement and discretion in the depth and scope to which they employ this guidance.

3. RELATIONSHIP TO LICENCE AND OTHER RELEVANT LEGISLATION

Site Licence Conditions

3.1 The standard conditions associated with nuclear site licences are described in [3]. The majority of licence conditions are potentially relevant to a reactor chemistry assessment; however, the purpose of a number of licence conditions (LC) which are particularly relevant are summarised below:

- **Licence Condition 14: Safety Documentation** - The safety case for the plant, including the justification of reactor chemistry and those systems which are used to control, monitor and change the operating chemistry is produced and assessed by the Licensee under this condition, which also requires documentation to be submitted to ONR on request. The safety case should consider the relevant phase of operations for the plant (i.e. design, construction, manufacture, commissioning, operation or decommissioning). This will affect the scope and depth to which reactor chemistry is considered in the safety case.

- **Licence Condition 15: Periodic Review** - As part of their periodic review process, the adequacy of the Licensee's safety case, where it addresses reactor chemistry, should be reviewed to demonstrate that it takes into account the lessons and implications from the previous periods and for future periods and that it does not invalidate the safety case.

- **Licence Condition 21: Commissioning** - Commissioning can be a particularly important period for reactor chemistry and this should be considered as part of the "adequate arrangements" required under this LC. Control of chemistry during commissioning can have a significant impact on the subsequent safety of the plant. Appropriate commissioning tests should be carried out to ensure, for example, that design criteria, and where practicable, the safety functional requirements claimed within the safety case have been met (e.g. dosing rates, purification performance, etc.).

- **Licence Condition 23: Operating Rules** - For all reactor chemistry parameters that can affect nuclear safety, limits and conditions of operation should be clearly defined, typically as a concentration within a target range. LC 23 defines limits and conditions as operating rules, with the term operating rules used henceforth. Consideration should be given to corrective actions if operating rules are approached, including the tolerable time in such states. Certain Licensees present a part of their reactor chemistry operating rules in operating instructions, dependent upon the relative importance of these parameters to safe operation of the plant.

- **Licence Condition 25: Operational Records** - Operational records of the key reactor chemistry parameters affecting safety should be maintained. These may include, for example, records of operating history (concentrations, pH, temperature, etc.), number of hours in service, etc. Consideration should be given to the automatic recording of measurements of any parameters that are important to safety.

3.2 In addition the following LCs may also be of relevance, depending upon the scope of the assessment:

- Licence Condition 7: Incidents on the Site
- Licence Condition 10: Training
- Licence Condition 12: Duly authorised and other suitably qualified persons
- Licence Condition 19: Construction or Installation of New Plant
- Licence Condition 20: Modification to Design of Plant under Construction
- Licence Condition 22: Modification or Experiment on Existing Plant
- Licence Condition 24: Operating Instructions
- Licence Condition 26: Control and Supervision of Operations

- Licence Condition 27: Safety Mechanisms, Devices and Circuits
- Licence Condition 28: Examination, Inspection, Maintenance and Testing
- Licence Condition 30: Periodic Shutdown
- Licence Condition 32: Accumulation of Radioactive Waste
- License Condition 34: Leakage and Escape of Radioactive Material and Radioactive Waste

Other Relevant Legislation

3.3   Regulation 9 of the Ionising Radiation Regulations (IRRs) 2017 is concerned with restriction of exposure to ionising radiation. Adequate control of reactor chemistry can play a key role in demonstrating this has been achieved, by minimising the activity at source.

3.4   Other legislation which is potentially of relevance to a reactor chemistry assessment, but is not expected to form part of a nuclear safety assessment, includes:

- Control of Substances Hazardous to Health (CoSHH) Regulations 2002
- Dangerous Substances and Explosive Atmospheres Regulations (DSEAR) 2002
- Control of Major Accident Hazards Regulations (COMAH) 2015

4.   RELATIONSHIP TO SAPS, WENRA REFERENCE LEVELS AND IAEA SAFETY STANDARDS ADDRESSED

Safety Assessment Principles

4.1   The Safety Assessment Principles (SAPs) [1] provide nuclear inspectors with a framework for making consistent regulatory judgements on nuclear safety cases, including the principal legal requirement of reducing risks so far as is reasonably practicable.

4.2   In the 2014 revision of the SAPs, there are four specifically related to chemistry. These include:

- **ECH.1: Safety cases** – This SAP highlights ONR's expectation that safety cases should identify and analyse how chemistry can impact safety in normal operations and fault conditions, with demonstration as to how chemistry is controlled. The key output of this should be any identified operating rules, consistent with the requirements of LC 23.
- **ECH.2: Resolution of conflicting chemical effects** – Specifically for chemistry assessment, there can be occasions where a change to one chemistry based parameter to improve safety can be to the detriment of another hazard or risk. This SAP outlines ONR's expectations in these circumstances. The SAP essentially expects an ALARP demonstration to be made, proportionate to the level of risk and hazard, where there a number of chemistry options available.
- **ECH.3: Control of chemistry** – This SAP describes ONR expectations regarding how, once the chemistry based operating rules are derived from the safety case, adequate provisions are in place to ensure the plant is designed, and can be operated within the safe operating envelope defined in the safety case. This SAP covers systems, processes and procedures.
- **ECH.4: Monitoring, sampling and analysis** – This SAP requires that adequate provisions are in place (systems, processes and procedures) to ensure that the required level of chemistry control for safety will be effectively implemented, including obtaining and maintaining the required quantity and quality of data to support decision making, throughout all phases of the

operational life of a nuclear facility. This is an important part of demonstrating adequate chemistry control.

4.3   There are a number of other SAPs which are related to the potential consequences of operating a nuclear reactor with poor chemistry controls and hence signify that reactor chemistry is an important consideration. Of these there are some which are often the most relevant and important to consider, dependent upon the particular safety case under assessment, including:

- **ECM.1** – This SAP describes ONR expectations in regard to commissioning of plant and equipment. This is often the first time that such equipment will operate under the environment of its expected duty. Control of the chemistry during these periods can influence the subsequent behaviour of the plant or equipment.
- **EAD.1 to EAD.4** – The deterioration of materials over their lifetime should be considered, including the effects of the chemical environment. This should include consideration of factors such as lifetime, degradation rates and methods for monitoring that any such deterioration is within the safety case assumptions.
- **EMC.2, EMC. 3, EMC.13, EMC16, EMC.21, EMC.22 and EMC.25** – The claims made regarding protection provided to structures by the operating chemistry should be considered, particularly for the most safety critical features such as pressure boundaries and fuel integrity. The effects of detrimental chemical contaminants on metal components important to safety should also be considered.
- **EGR.1, EGR.2 and EGR.7 to EGR.9** – The operating reactor chemistry plays an important role in assuring that graphite components continue to be able to perform their safety functions.
- **ENM.1 to ENM.7** – reactor chemistry has a role to play in the control of nuclear matter, including its distribution, generation or accumulation around the reactor plant. The sampling, characterisation and control of nuclear matter are important aspects covered by these SAPs.
- **ERC.1, ERC.3 and ERC.4** – The influence of reactor chemistry on the core of a reactor is vital to consider in terms of the three fundamental requirements of reactivity control, heat removal and containment of radioactivity. These SAPs relate to ensuring that the core components (i.e. coolant, fuel, control rods, etc.) continue to operate within their safety limits.
- **EHT.4 and EHT.5** – The coolant within heat transport systems needs to minimise the potential for any failures or radioactivity accumulation or transport within the plant. Implementation of an adequate reactor chemistry regime will have an important influence on the fulfilment of the requirements of these SAPs.
- **ECR.1** – Chemical reactions, solvent evaporation, solute precipitation and other chemical phenomena can impact on the presence of neutron poisons and/or the control of fissile material, including the quantity and behaviour of moderators present, such as water.

4.4   Reactor chemistry can also have a role in helping to fulfil the Fundamental Principles (FP.1 to FP.8) and a number of related SAPs, including: SC.1 to SC.8, EKP.1 to EKP.5, ECS.1 to ECS.5, EMT.1 to EMT.8, ECV.1 to ECV.10, EPE.1, EPE. 3 to EPE.5, RP.1 to RP.6, FA.2, FA.7, FA.9, FA.15, FA.16, AV.1 to AV.8, AM.1, RW.1, RW.2, RW.4, RW.5, DC.1, DC.5 and DC.6.

4.5   Additional or related issues not directly addressed in the SAPs may be of equal importance in specific circumstances and these aspects of a thorough nuclear safety

assessment may need to be identified and considered by an experienced and qualified nuclear assessment inspector.

Technical Assessment Guides

4.6   There are many TAGs which are of potential relevance to reactor chemistry, due to the large number of SAPs which are of potential relevance. A full list is provided in Appendix 1, but the most relevant are listed below:

- NS-TAST-GD-005 – ONR guidance on the demonstration of ALARP (As Low As Reasonably Practicable) [4]
- NS-TAST-GD-016 – Integrity of metal components and structures [5]
- NS-TAST-GD-035 – The limits and conditions for nuclear plant safety (operating rules) [6]
- NS-TAST-GD-038 – Radiological protection [7]

WENRA Reference Levels

4.7   This TAG considers the Western European Nuclear Regulators Association (WENRA) Reference Levels [8] for specific applicability. Section 4 of NS-TAST-GD-005 [4] states that the WENRA Reference Levels are identified as relevant good practice for existing civil nuclear reactors. While the SAPs are intended for both existing and new facilities, the WENRA reference levels are intended for existing reactors. Notwithstanding the above, there are no WENRA reference levels directly relevant to this guide. However, reactor chemistry assessment will contribute to meeting the following Reference Levels:

- Issue E: Design Basis Envelope of Existing Reactors
- Issue H: Operational limits and conditions (operating rules)
- Issue I: Ageing Management
- Issue K: Maintenance, in-service inspection and functional testing

4.8   It is expected that assessments carried out in line with the SAPs in combination with this guidance will meet the requirements of the WENRA Reference Levels.

IAEA Safety Standards

4.9   The IAEA have published Specific Safety Requirements for nuclear power plants during design [9] and commissioning and operations [10] and both of these contain requirements relevant to reactor chemistry. The latter of these documents, for commissioning and operations [10], is more relevant and includes Requirement 29, which states that: "*Requirement 29: Chemistry programme. The operating organization shall establish and implement a chemistry programme to provide the necessary support for chemistry and radiochemistry.*"

4.10   To support this requirement, IAEA have also produced a Safety Standard on Chemistry Programmes [11]. This guidance contains much valuable information on the development, implementation and attributes for a successful chemistry programme. While this standard is only applicable to water cooled nuclear power plants, some of the generic guidance is applicable to other types of reactors.

4.11   A number of other IAEA guidance documents and standards contain information of relevance to reactor chemistry assessments. These are not described fully here, but more information is provided in Appendix 2.

4.12   This guide is consistent with these requirements and standards, and the inspector should consider these documents as appropriate as they are judged to provide relevant good practice in operational chemistry.

5.   ADVICE TO INSPECTORS

Introduction

5.1   This guide is concerned with the assessment of the chemistry aspects of safety cases for civil nuclear power plants. It covers those aspects where failure to carry out operations in a controlled and safe manner could affect nuclear safety. It is therefore not limited solely to the operating chemistry of the primary circuit, but also those systems which provide safety functions, provide cooling or allow the chemistry to be controlled or monitored. Important outputs from the chemistry aspects of the safety case include any operating rules necessary in the interests of safety and the chemistry programme (as described for ECH.1 in para 4.2 above), including the operating procedures.

5.2   Chemistry aspects of the safety case are an essential element in the safe operation of a nuclear power plant. An adequate operating chemistry ensures that the integrity, reliability and availability of those safety relevant systems and components are maintained, in accordance with the plant safety case. This is achieved by minimising the harmful effects of chemical impurities and corrosion on plant structures, systems and components; minimising the generation and accumulation of radioactive material; and limiting the environmental impact of any discharges.

5.3   The advice that follows is not specific to a particular phase of reactor operations. It should be considered throughout all phases, as appropriate, including:

   ■   commissioning
   ■   start-up
   ■   normal operation
   ■   shutdown
   ■   transients
   ■   stand-by
   ■   outages

Terminology

5.4   The following terminology is used throughout this guide, and is defined here for clarity:

   ■   **Reactor Chemistry** – the influence of coolant chemistry on reactivity, pressure boundary integrity, fuel and core component integrity, radioactive waste generation and radiological doses to workers and the public.
   ■   **Chemistry Regime** – the set of conditions (parameters) which define the particular chemistry environment to which the plant will be exposed.
   ■   **Chemistry Programme** – the totality of provisions which allow the Licensee to control and monitor the status of the Chemistry regime.

Reactor Chemistry Safety Case

5.5   Reactor chemistry interacts with many other aspects of the safety case, hence it is common for the chemistry aspects to be spread throughout the safety case for existing plants. Another approach is to have specific section(s) which deal exclusively with reactor chemistry, with links to their interactions. ONR would consider the latter approach to be relevant good practice for new facilities. For either approach the

fundamental requirements for a reactor chemistry safety case for a nuclear power plant should include:

■ The safety case should apply a systematic process to address all aspects of chemistry important to safety (ECH.1). This should clearly state what claims are being made on chemistry for nuclear safety. It is important to distinguish what claims are made for non-safety related reasons, for example for asset protection or commercial concerns. This should include consideration of all the relevant hazards, including:

(i) The use and control of neutron poisons within the coolant.
(ii) The integrity of structures, systems and components important to safety, particularly those related to the fuel, pressure boundary or containment.
(iii) The generation and build-up of radioactive material to reduce dose rates at the plant and hence radiation doses to personnel, to reduce the activity of wastes and to reduce the discharges to the environment.

■ Defining what the chemistry needs are to achieve those claims, including defining any operating rules that are necessary to ensure nuclear safety.
■ Demonstrating how the chemistry will be maintained within acceptable limits during all modes of operation (ECH.3, e.g. how does the Licensee add/remove the chemicals/nuclides, correct the chemistry when out of specification, and over what timescale, etc.).
■ Linked to the above, suitable and sufficient systems, processes and procedures should be in place to ensure chemistry parameters important to safety are properly controlled via monitoring, sampling and analysis (ECH.4).
■ Consideration of the potential long-term impact of the operating chemistry on Structures, Systems and Components important to safety (EAD.1 – 4). This may influence the Examination, Maintenance, Inspection and Testing (EIMT) arrangements for the plant. This could include incorporation of relevant Operational Experience Feedback (OEF).

5.6 The first step, of defining the claims for chemistry, is vital to the safety case. There are many potential reasons for applying a particular chemistry, including some that may not be safety related. However it is often found that the most appropriate choice for a particular safety issue leads to less than optimum conditions for other potential safety concerns. Thus the most appropriate chemistry regime will be a holistic balance between all the safety aims, with due priority given to those which are the most relevant, likely to occur and have the potential to lead to the largest consequences. This aspect is an important element of the overall ALARP (As Low As Reasonably Practicable) justification for the operating chemistry (ECH.2). Further guidance on ALARP can be found in the associated ONR TAG [4].

5.7 The influence of reactor chemistry on reactivity, material integrity, radioactivity and other hazards is described in more detail in the following sections.

5.8 After defining chemistry claims, the chemistry regime necessary to achieve such claims should be defined and justified. In addition to the requirements to define the operational chemistry parameters, the operational chemistry regime should consider the following points:

■ The design of each circuit is often unique and the chemistry regime should demonstrate how the specifics of the plant under consideration have been accounted for.
■ The radiation environment can lead to activation or break-down of coolant chemicals and the extent and products of this should be considered. Similar effects can also occur for high temperatures.

- Use of make-up sources of appropriate purity is an important input and the safety case should demonstrate that these are provided.
- The control of the chemistry regime often involves the chemical treatment of the coolant, to add or remove species as required. The impact of these steps, both on the coolant and the resultant waste produced should be considered including the effectiveness of any coolant clean-up provisions.
- Measures taken to minimise the ingress of impurities and consequences thereof.
- Quality assurance for the purity of chemicals used in coolant systems and the use of only specified chemicals in specific areas of the plant (compatibility constraints).
- Specification of operating parameters for all the potential modes of operation, including definition of "action levels" for control and corrective actions, including timescales.
- The adequacy and ability to measure the parameters needed to control the chemistry regime within the specified limits, either via sampling or on-line analysis. This should consider the type of sample (e.g. liquid, gas, particulate, etc.), concentrations, accuracy and reliability of measurement as well as the adequacy of sampling equipment and facilities.

5.9   Definition of a suitable chemistry regime(s) should form part of the plant design process, to ensure compatibility with the materials and to ensure that the design is suitable to achieve the design intent for chemistry. The scope of this definition will therefore be proportional to the development stage of the design. For operating plants this often puts constraints on the available chemistry regimes under which the plant can safely operate.

5.10   Demonstrating that the plant and operators are capable of controlling the operating chemistry within the specified operating rules is a vital part of the safety case. This involves an assessment of the adequacy of those systems responsible for the control of the operating chemistry, for all modes of operations, including accident safety systems (for example, in a PWR primary circuit this could include the chemical and volume control system, nuclear sampling system, safety injection systems, etc.). ONR expects systems providing safety functions to possess appropriate levels of redundancy, diversity and segregation. This may involve other ONR inspectors with expertise in areas such as fault studies, mechanical engineering or C&I and consideration of other SAPs such as ECS (safety classification and standards) or ESS (safety systems) [1].

5.11   The EIMT arrangements are described in another TAG [12]; however it is expected that reactor chemistry would input into these arrangements, as appropriate.

Reactor Chemistry influence on reactivity

5.12   A distinction should be made between the influence of the coolant on reactivity, which is factored into the plant and core design, and the purposeful or accidental influence on reactivity by additives or impurities in the coolant. Reactor chemistry assessment is only concerned with this latter category. For example:

- Purposeful additions of neutron poisons to control reactivity can affect the chemistry of the coolant.
- Safety systems may add additional quantities of neutron poisons to the coolant in order to arrest the nuclear reaction.
- Adventitious impurities can affect reactivity, if not controlled; however generally significant localised concentrations are required.

5.13   The inspector may consider if the following factors have been adequately addressed by the Licensee in terms of the reactor chemistry influence on reactivity:

■   Where the coolant is used as part of the reactivity control provisions, the influence of the neutron poison on the chemistry of the coolant is factored into the chemistry regime and any potential safety detriments quantified. The poison concentration required to achieve a sub-critical shutdown state will be specific to the nuclear power plant and should be documented in the safety analysis.

■   Purification and clean-up systems are compatible with the coolant, including the reactivity control provisions. The effects of process variables (e.g. operating temperature) which could affect the reactivity control provisions should be considered.

■   If such a control requires a particular isotope (e.g. ^{10}B) then the controls over this particular isotope merit attention, particularly the quality control, purity and measurement arrangements (ECH.4 and ERC.4). The isotopic concentrations of neutron poisons should be verified prior to their introduction into the reactor system, to ensure that their isotopic concentrations are equal to, or higher than, that required in the safety case. Factors such as isotopic dilution should be considered.

■   Where safety systems inject additional neutron poison into the coolant in accident situations, the control, monitoring and adequacy of these systems should be considered (ECH.3 and ECH.4). The chemistry regime of active and passive safety systems that contain neutron absorbers (boric acid tanks, containment sprinkler system, bubble stacks, etc.) should be maintained in accordance with the safety case, with account taken of the fact that correction to the chemistry within these reservoirs can generally only be made infrequently at specified times (e.g. during an outage).

■   The effect of impurities in the coolant on reactivity should be considered (ECH.1). This is particularly relevant for those which can accumulate within the core, especially on the fuel surface (e.g. Crud Induced Power Shifts (CIPS) in PWRs).

■   Chemical effects (e.g. precipitation, evaporation, reactions, etc.) which can remove the neutron poison should be considered as part of the safety case (ECR.1).

Reactor Chemistry influence on material integrity

5.14   The majority of radioactivity generated in a nuclear reactor is produced within the fuel. Maintaining the integrity of the fuel and its cladding is therefore a major objective for plant operational safety as this is the first barrier to releases of fission products and fuel materials to the coolant from where they can ultimately be released to the environment.

5.15   It is also vital that safety related structures, systems and components retain their integrity. This is particularly important to those materials in a nuclear power plant which provide a pressure boundary or whose structure maintains or supports the reactor core or other safety critical structures or components.

5.16   Corrosion can threaten the integrity of materials if the rates or type of damage is sufficient. The types of material changes brought about by corrosion are diverse. A distinction is generally made between uniform and non-uniform surface corrosion, pitting, selective corrosion, and cracking. Of these, the local corrosion processes are particularly critical as they are often more difficult to detect and can proceed at high rates. The reactions are mainly electrochemical, although they can also involve chemical or metallo-physical processes. Kinetic barriers, mainly provided by the formation of protective layers, often make metals resistant to corrosion. However, a

corrosive reaction with the environment can be brought about by erosion of protective coatings (erosive corrosion). Material changes due exclusively to mechanical effects are attributable to wear rather than to corrosion.

5.17   The inspector may consider if the following factors have been adequately addressed by the Licensee in terms of the reactor chemistry influence on material integrity:

■   The Licensee has adequately identified and reviewed the corrosion threats to the plant, based on the materials of construction and operating environment (ECH.1). This is specific to the plant design, including operating conditions and should consider all modes of operation. Where the operating chemistry has a direct influence on these the safety case should adequately justify that an appropriate chemistry regime and operating rules have been adopted.

■   It is important that the local conditions are considered when assessing corrosion threats, as opposed to the bulk (e.g. under intense heat transfer conditions local boiling may result, etc.). Similarly physico-chemical changes brought about by changing operating conditions (i.e. start-up and shutdown) should be considered.

■   The corrosion threats have been graduated on the basis of safety significance, likelihood and potential severity.

■   The concentrations of the chemical inhibitors that are added to cooling systems should be adequately controlled and monitored (ECH.3). The chemistry parameters that indicate proper treatment and the presence of impurities should be controlled to minimise corrosion of the systems and loss of integrity.

■   The use of chemicals in the plant, including chemicals brought in by contractors, need to be kept under close control (ECH.3). This is needed to ensure compatibility with the plant materials. The appropriate control measures need to be put in place to ensure that the use of chemical substances and reagents does not adversely affect equipment or lead to its degradation. Similar considerations should apply to materials in contact with the coolant (e.g. lead blankets).

■   The impact of corrosion should also consider:

(i)   Effects on purification systems.
(ii)   Transfer of corrosion products around the circuit (particularly to heat transfer surfaces).
(iii) Accumulation of corrosion products as a location for impurity build-up.

■   During outages, equipment should be maintained under adequate lay-up conditions (e.g. by means of chemicals or inerting), depending on the lay-up duration, and in accordance with safety requirements. Lay-up parameters should be monitored and corrective measures for deviations should be implemented.

■   The surface finish or treatments of materials, particularly if applied to reduce the corrosion rates, need to be adequately justified. Surface finishes may also be applied in order to reduce the tendency for deposit accumulation.

■   While the avoidance of leakage or unintentional releases of coolant should be avoided, the consequence of such release on the integrity of external surfaces of safety systems should be considered when such leakage is possible. This is particularly important when such surfaces are not expected to be in contact with the coolant and are made of incompatible materials (e.g. leakage of PWR primary coolant and its effect on carbon or low-alloy steels [13]).

Reactor Chemistry influence on radioactivity

5.18   All nuclear power plants must be operated, inspected, maintained and decommissioned in accordance with the regulations relating to the safe use of ionising

radiations (IRRs). A fundamental part of this is the strategy to restrict radiation exposure, including the minimisation of sources of radiation. Radiation exposure by workers is the product of time, distance and intensity of radiation to which workers are exposed. Reactor chemistry has some influence over the time and distance elements by limiting the need for maintenance and repair works but can more directly influence the intensity of radiation by minimising the out of core radiation field.

5.19   The sources of radiation in the primary circuit of an operating reactor can be broadly classified as either:

- Radioactivity released from the fuel.
- Activation of the coolant itself.
- Activation of additives or impurities carried by the coolant.

5.20   The influence of reactor chemistry on fuel integrity, and hence the release of radioactivity from the fuel is described above. The speciation and form of any such released activity can also influence the potential consequences and can be influenced by the coolant chemistry.

5.21   An appropriate reactor chemistry regime can also influence the second and third of these sources. Ultimately any material which is subjected to the core radiation field can be subject to activation, the extent of which would depend on its exposure. The chemistry regime can restrict both the quantity and form of any such material carried by the coolant, but can also influence the extent of its exposure by removing it or restricting its transport around the plant. Additions can be made to the coolant to control the radioactivity and means are often available in the plant design to remove activity from the coolant during operations.

5.22   The inspector may consider if the following factors have been adequately addressed by the Licensee's arrangements for the influence of chemistry on radioactivity:

- Corrosion can be an important source of material for activation. Even trace levels which are insignificant in terms of material integrity can be significant from a radiation viewpoint, especially given the large surface areas over which the release can occur:

    (i)   For new plant or equipment, the material surfaces in contact with the coolant are an important aspect that should be considered by the Licensee in their safety case. Past experience has shown that much can be achieved by restricting levels of easily activatable materials released by corrosion or wear. The Licensee should consider the relative contribution from both bulk and trace elements on the overall release (i.e. small releases from large surfaces versus large releases from small surfaces). For example PWRs have been shown to reduce out of core radiation fields significantly by applying careful controls over cobalt based materials and residual trace cobalt levels in structural materials. This could indicate replacement materials, but any substitute material would need to be appropriately qualified for its intended duty and would need to be justified on an ALARP basis.

    (ii)   For operating plants one of the main controls that can be applied to reduce radiation fields is the operating chemistry. In addition to its influence on general corrosion rates, the bulk operating chemistry regime can influence many relevant parameters which can affect controls on the transport, deposition or distribution of activity around a plant. This can also apply to other radioactivity carried by the coolant, not only that which is produced via corrosion (e.g. iodine released from damaged fuel elements).

- In addition to the composition, the surface finish applied to materials can directly influence the quantity of material released through general corrosion, with rougher surfaces having a greater area available to corrode or act as a deposition site. Similar improvements can be made by applying appropriate surface coatings, but consideration needs to be given to potential detriments of this technique and the longevity and stability of such coatings.
- Preconditioning surfaces before and during initial start up is important, involving careful control of chemistry throughout this period. The formation of initial surface oxides on metal components can influence subsequent releases during operating cycles and can act as an effective barrier to further rapid degradation.
- The bulk coolant may itself be subject to activation or radiolysis, requiring modifications to the operating chemistry to mitigate any detrimental effects. Examples include the addition of methane to AGRs and hydrogen to PWR primary coolants respectively.
- The additives present in the coolant as part of the chemistry regime (e.g. lithium, zinc, etc.) can also be a source of activation products. The impact of these on the operating chemistry, purification systems and discharges should be considered.
- Impurities in the primary coolant may be negligible on a concentration scale, but could be significant from a radiological viewpoint.
- The purification system performance can have important consequences on the minimisation of radioactivity generation. The performance of such systems needs to be shown to reduce activity SFAIRP. Over concentration of activity in waste streams and discharges should be considered.
- The effects of transient periods on the release of radioactivity should be considered as part of the safety case. This is particularly important for start-up and shutdown periods when the chemical and physical parameters of the coolant can change dramatically.
- The control of EIMT activities should ensure that activatable materials are not introduced into the coolant. This can result from activities such as valve maintenance.
- The use of chemicals in the plant, including chemicals brought in by contractors, needs to be kept under close control. This is needed to ensure compatibility with the plant materials. The appropriate control measures need to be put in place to ensure that the use of chemical substances and reagents does not adversely affect equipment or lead to its degradation.

Reactor Chemistry influence on other hazards

5.23   In addition to its influence on reactivity, material integrity or radioactivity it is important that the safety case also considers other potential hazards which could result from operation of the plant or from the chemicals used in the chemistry regime (e.g. hydrogen or methane). The safety case should identify any foreseeable toxic, reactive or energetic products that may threaten plant or worker safety or prevent safe operations as an input to relevant fault studies, internal hazards or other safety analysis.

Operating Rules, Control and Monitoring of Reactor Chemistry

5.24   An important output from the safety case is the definition of operating rules (ECH.1). This will require judgement in the importance of the various parameters to maintaining safety and is clearly linked back to the claims made in the safety case. Further guidance on operating rules can be found in the associated TAG [6], and more specifically for chemistry in operating reactors in Appendix 9 of this TAG. The

operating rules defined in the safety case should be implemented by the plant operating instructions and procedures.

5.25 Chemistry control includes not only the correct application of the chemistry regime (ECH.3), but relates to the ability to manage the plant chemistry regime, including the ability to detect and rectify deviations. The interpretation of "control" should not be restricted to the need for control and instrumentation (C&I) systems, but all operations that provide a degree of control over the operating chemistry, such as sampling and analysis (see ECH.4).

5.26 Chemistry monitoring should be conducted at the plant to verify the effectiveness of chemistry control in plant systems and to verify that structures, systems and components important to safety are operated within the specified chemical limit values.

5.27 The inspector may consider if the following factors have been adequately addressed by the Licensee's arrangements for chemistry related operating rules, control and monitoring:

■ The hierarchy applied by the Licensee in determining the relative importance to safety of the various chemical parameters is an important pre-requisite of a successful definition of chemistry related operating rules (ECH.1). These need to be based on the consideration given to the influences described more fully above and should be in accordance with the safety case.

■ Relatively few reactor chemistry related parameters are expected to be in the highest category of operating rules (i.e. High Hazard Operating Rules [6]), and may be presented by some Licensees in operating procedures. The correct application of this hierarchy of operating rules is an important aspect of the safety case, which should be fully justified.

■ Limits for chemistry parameters and conditions for operational and safety systems (operating rules) should be defined by the Licensee for all phases of operation.

■ Operating rules for parameters should not be exceeded; if a parameter exceeds its limit, appropriate actions should be taken to recover its normal operating value within a specified time (ECH.3). A subsequent assessment of any consequential effects may then be necessary. In extreme cases this may require the plant to be shut down.

■ The parameters used as the basis of control should be selected based on their relevance in ensuring compliance with the chemistry regime. This should include the presence of additives, impurities and radioactive contaminants.

■ Consideration should be given to the ability to diagnose detrimental failures or on-going issues (e.g. fuel leaks).

■ A graded approach is evident for the various areas of the primary circuit, secondary circuit and other significant safety and cooling systems with those most significant to safety occupying the highest importance.

■ Chemistry regimes are plant specific, i.e. they depend on the particular design of the plant and the materials used in its construction. Generally a regime should contain specified values for each sampling point and each plant status mode. The definition of the specific values should comply with the following general points:

(i) Control parameters should be measured reliably at the levels specified using currently available equipment and procedures.

(ii) "Action levels" and associated response times should be based on quantitative information about the effects of the chemistry variables on the plant. In the absence of quantitative data, prudent and achievable action level values should be specified. Action times needed to respond to

chemistry excursions should be based upon the severity and potential consequences of that event.

■   There should be suitable provisions for the chemistry monitoring and data acquisition procedures and systems (ECH.4). These measurements need to provide accurate measuring and recording of chemistry data and shall provide alarms for relevant chemistry parameters. Records shall be kept available and shall be easily retrievable.

■   A balance will need to be found between which parameters are measured on-line and which via laboratory analysis (ECH.4). This balance will depend upon factors such as the importance of the particular parameter, response time requirements, reliability and accuracy of measurement needed and the likely doses accrued from intrusive sampling.

■   Monitoring involves both online and grab sampling and analysis of plant systems for specific chemical parameters, concentrations of dissolved and suspended impurities, and radionuclide concentrations (ECH.4).

Definition of the Chemistry Programme

5.28   The chemistry programme may include procedures for the selection, monitoring and analysis of the chemistry regime. This may also include instructions for operations involving chemistry processes and evaluation of operating results, with determination of the operation and reference limits for chemistry parameters and action levels and possible remedial actions [1, 11]. In the chemistry programme account should be taken of feedback from operating experience and of experimental programmes and activities.

5.29   The chemistry programme should be developed prior to normal operation and should be in place during the commissioning phases of any new build reactor.

5.30   The chemistry programme should provide the necessary information and assistance for chemistry and radiochemistry for ensuring safe operation, long term integrity of structures, systems and components, and minimisation of radiation levels. Thus, a suitably considered chemistry programme will:

■   Control the use of neutron poisons, chemical additives and potential impurities.
■   Preserve the integrity of the fuel and limit the formation of deposits which could contribute to failures or limit the degradation rate to acceptable levels.
■   Preserve the integrity of structures, systems and components important to safety.
■   Minimise the build-up of radioactive material at the plant which will:

(i)   reduce dose rates and hence radiation doses to personnel;
(ii)   reduce the activity of chemical and radioactive waste; and
(iii) reduce the activity of any planned discharges to the environment.

5.31   The inspector may consider if the following factors have been adequately addressed by the Licensee's Chemistry Programme:

■   The safety claims made on the chemistry regime are clear and unambiguous and have been effectively transferred to the chemistry programme.
■   A suitable chemistry regime is defined and is in accordance with the current design and material balance of the plant. This should consider any relevant modifications or operating experience at the plant or at other relevant or similar plants.
■   Evidence of learning from experience is fed into the Chemistry Programme. Relevant good practices, which are in compliance with specifications and

consistent with internationally accepted good practices, are appropriately incorporated.

■ The chemistry programme sets goals and objectives which are challenging, rather than simply tolerable, and feedback on the performance of the chemistry programme is an integral part of continuous improvement.

■ An ALARP approach to the Chemistry Programme has been adopted, including holistically for all the safety aims.

■ The impact of any changes in the chemistry regime or equipment on nuclear safety, including radioactive waste production, is adequately and accurately analysed, understood and appropriately justified at a level commensurate with the potential hazards.

■ The chemistry regime applied to the various circuits takes appropriate consideration of the relevant safety concerns, including;

(i) The primary chemistry regime is appropriately selected, with account taken of its potential impact on:
    a) reactivity control;
    b) uniform and localised corrosion of the circuit materials;
    c) fuel cladding corrosion and deposition;
    d) activation and transport of corrosion products, and;
    e) supporting systems, e.g. purification system performance, especially for existing reactors where the chemistry has evolved from that at the design stage.

(ii) The secondary side chemistry regime is appropriately selected, with account taken of its potential impact on:
    a) corrosion in the whole system;
    b) formation of deposits in the heat transfer components (i.e. boilers or steam generators);
    c) concentration of deleterious compounds in crevices or areas with restricted flow;
    d) condenser leaks in both water and air parts; and
    e) the effectiveness of the purification systems.

(iii) The chemistry programme for auxiliary systems is in accordance with the design and material balance to preserve their integrity, reliability and availability in accordance with the safety case.

■ Appropriate chemistry controls and parameters are applied to verify safe and reliable operation. There is a timely response identified to correct any deviations from normal operational status, such as small deficiencies, adverse trends or fast transients of chemistry parameters. The impact of such deviations is understood and factored into the Chemistry Programme.

■ Methodologies which allow for the diagnosis and treatment of deviations are included within the chemistry programme, and these can be justified.

■ Measures used to control the on-line instruments and equipment in the laboratory are regularly inspected, calibrated, maintained and kept up to date.

■ The impact of chemistry in maintaining the availability of the safety equipment (e.g. by analysis of safety tanks, diesel oil and main pumps oil) is an appropriate part of the Chemistry Programme.

■ There is support and input into the plant ageing management programme in order to ensure safe and long term operation of the plant.

6.   REFERENCES

1   *Safety Assessment Principles for Nuclear Facilities 2014 Edition Revision 0. November 2014. www.onr.org.uk/saps/saps2014.pdf.*

2   *ONR How2 Business Management System. Purpose and Scope of Permissioning. PI/FWD Issue 6. ONR. November 2016. http://www.onr.org.uk/operational/assessment/index.htm.*

3   *Licence condition handbook. Office for Nuclear Regulation. February 2017. www.onr.org.uk/documents/licence-condition-handbook.pdf.*

4   *ONR How2 Business Management System. ONR guidance on the demonstration of ALARP (as low as reasonably practicable). NS-TAST-GD-005 Issue 9. March 2018. www.onr.org.uk/operational/tech_asst_guides/index.htm.*

5   *ONR How2 Business Management System. Integrity of metal components and structures. NS-TAST-GD-016 Issue 5. March 2017. www.onr.org.uk/operational/tech_asst_guides/index.htm.*

6   *ONR How2 Business Management System. The limits and conditions for nuclear plant safety. NS-TAST-GD-035 Issue 5. March 2018. www.onr.org.uk/operational/tech_asst_guides/index.htm.7 ONR How2 Business Management System. Radiological protection. NS-TAST-GD-038 Issue 8. November 2017. www.onr.org.uk/operational/tech_asst_guides/index.htm.*

8   *Western European Nuclear Regulators' Association. Reactor Harmonization Group. WENRA Reactor Reference Safety Levels for Existing Reactors, WENRA. September 2014. www.wenra.org.*

9   *IAEA Safety Standards, Safety of Nuclear Power Plants: Design, Specific Safety Requirements No. SSR-2/1 Revision 1, IAEA. February 2016. www.iaea.org.*

10   *IAEA Safety Standards, Safety of Nuclear Power Plants: Commissioning and Operation, Specific Safety Requirements No. SSR-2/2 Revision 1, IAEA. February 2016. www.iaea.org.*

11   *IAEA Safety Standards, Chemistry Programme for Water Cooled Nuclear Power Plants, Specific Safety Guide No. SSG-13, IAEA. July 2011. www.iaea.org.*

12   *ONR How2 Business Management System. Examination, Inspection, Maintenance and Testing (EIMT). NS-TAST-GD-009. Issue 4. November 2018. www.onr.org.uk/operational/tech_asst_guides/index.htm.*

13   *Davis-Besse Reactor Pressure Vessel Head Degradation, US Nuclear Regulatory Commission, NUREG/BR-0353, Rev. 1, August 2008.*

Note: ONR staff should access the above internal ONR references via the How2 Business Management System.

7. GLOSSARY AND ABBREVIATIONS

AGR	Advanced Gas-cooled Reactor
ALARP	As low as reasonably practicable
AVT	All Volatile Treatment
BoP	Balance of Plant
BWR	Boiling Water Reactor
CCW	Closed Cooling Water
CIPS	Crud Induced Power Shift
COMAH	Control of Major Accident Hazards Regulations
CoSHH	Control of Materials Hazardous to Health
DSEAR	Dangerous Substances and Explosive Atmospheres Regulations
DZO	Depleted Zinc Oxide
EIMT	Examination, Inspection, Maintenance and Testing
ECP	Electrochemical Corrosion Potential
FAC	Flow Accelerated Corrosion
F/D	Filter-demineraliser
HHOR	High Hazard Operating Rule
HSE	Health and Safety Executive
HWC	Hydrogen Water Chemistry
IAEA	International Atomic Energy Agency
IGA	Inter Granular Attack
IRR	Ionising Radiation Regulations
LC	Licence Condition
LHOR	Low Hazard Operating Rule
LWR	Light Water Reactor
MSR	Moisture Separator Reheater
NBA	Nickel-base Alloys
NMCA	Noble Metal Chemical Addition
NWC	Normal Water Chemistry
OEF	Operational Experience Feedback
OG	Off-Gas
ONR	(The) Office for Nuclear Regulation
OTSG	Once Through Steam Generator
ppb	Parts Per Billion
PVCW	Pressure Vessel Cooling Water
PWR	Pressurised Water Reactor
RCS	Reactor Coolant System
RPV	Reactor Pressure Vessel

RSG	Recirculatory Steam Generator
SAP	Safety Assessment Principle(s)
SCC	Stress Corrosion Cracking
SFAIRP	So far as is reasonably practicable
SG	Steam Generator
SSC	Structures, Systems and Components
TAG	Technical Assessment Guide(s)
UK ABWR	UK Advanced Boiling Water Reactor
WENRA	Western European Nuclear Regulators' Association

8. APPENDICES

Appendix 1 summarises the ONR Technical Assessment Guides that may be of relevance to a reactor chemistry assessment.

Appendix 2 summarises the relevant IAEA safety standards and guidance.

Appendices 3 to 8 describe, at a high level, typical operating chemistry regimes used in a number of circuits at UK reactors. These descriptions apply only to power operations and not transient periods such as start-up and shutdown, during which other safety considerations also apply or become more prominent. They are not a complete description, but demonstrate the types of balancing that must be achieved in order to derive a holistic approach to chemistry.

APPENDIX 1: RELEVANT TECHNICAL ASSESSMENT GUIDES

A1.1.   The following Technical Assessment Guides may be relevant to a reactor chemistry assessment:

TAG Reference	TAG Title
NS-TAST-GD-004	Fundamental principles
NS-TAST-GD-005	ONR guidance on the demonstration of ALARP (as low as reasonably practicable
NS-TAST-GD-014	Internal hazards
NS-TAST-GD-016	Integrity of metal components and structures
NS-TAST-GD-020	Containment of reactor plants
NS-TAST-GD-021	Containment of chemical plants
NS-TAST-GD-022	Ventilation
NS-TAST-GD-023	Control of processes involving nuclear matter
NS-TAST-GD-034	Transient analysis for DBAs in nuclear reactors
NS-TAST-GD-035	The limits and conditions for nuclear plant safety
NS-TAST-GD-038	Radiological protection
NS-TAST-GD-042	Validation of computer codes and calculation methods
NS-TAST-GD-051	The purpose, scope and content of nuclear safety cases
NS-TAST-GD-081	Safety aspects specific to the storage of spent nuclear fuel
NS-TAST-GD-094	Categorisation of safety functions and classification of structures and components

APPENDIX 2: IAEA SAFETY STANDARDS

Safety of Nuclear Power Plants: Design [9]

A2.1. Within the Safety Standards series IAEA have produced a report [9], which details the specific safety requirements for a nuclear power plant at the design stage. This standard was prepared for water cooled reactors, but aspects may be transferable to other reactor types. This standard identifies several requirements which are relevant to reactor chemistry. The main one directly relevant to reactor chemistry is Requirement 50 (Cleanup of reactor coolant): "*Adequate facilities shall be provided at the nuclear power plant for the removal from the reactor coolant of radioactive substances, including activated corrosion products and fission products deriving from the fuel, and non-radioactive substances.*"

A2.2. In addition, there are a number of other requirements which contain relevant aspects, including:

- Requirement 28 - Operational limits and conditions for safe operation
- Requirement 43 - Performance of fuel elements and assemblies
- Requirement 47 - Design of the reactor coolant systems
- Requirement 52 - Emergency cooling of the reactor core
- Requirement 58 - Control of containment conditions
- Requirement 69 - Performance of supporting systems and auxiliary systems
- Requirement 71 - Process sampling systems and post-accident sampling systems
- Requirement 78 - Systems for treatment and control of waste
- Requirement 79 - Systems for treatment and control of effluents
- Requirement 80 - Fuel handling and storage system
- Requirement 81 - Design for radiation protection

Safety of Nuclear Power Plants: Commissioning and Operation [10]

A2.3. As described in Para 4.9, this Safety Standard for commissioning and operation [10] introduces the requirement for a "chemistry programme" in Requirement 29: "*Requirement 29: Chemistry programme. The operating organization shall establish and implement a chemistry programme to provide the necessary support for chemistry and radiochemistry.*"

A2.4. IAEA describes the chemistry programme as providing "*the necessary information and assistance for chemistry and radiochemistry for ensuring safe operation, long term integrity of structures, systems and components, and minimization of radiation levels.*" Paras. 7.13 to 7.17 in [10] describe the need for chemistry surveillance and monitoring of specific plant systems for chemical parameters, concentrations of dissolved and suspended impurities, and radionuclide concentrations.

Chemistry Programme for Water Cooled Nuclear Power Plants [11]

A2.5. To support Requirement 29 of reference [10], IAEA have also produced a Safety Standard on Chemistry Programmes [11]. This guidance contains much valuable information on the development, implementation and attributes for a successful chemistry programme. While this standard is only applicable to water cooled nuclear power plants, some of the generic guidance is applicable to other types of reactors.

A2.6. The guide contains sections relation to the chemistry programme, chemistry control, the influence of chemistry on doses and wastes and chemistry surveillance; in addition to matters more suited to chemistry compliance inspections such as functions, responsibilities, data control, training and qualifications.

Design of the Reactor Core for Nuclear Power Plants [14]

A2.7. The Safety Standard on the design of the reactor core [14], contains information on the impact of water chemistry on the corrosion of fuel elements and the formation of deposits on the fuel cladding surfaces. Specifically Para. 3.25 onwards under "coolant" provides details of the coolant properties including minimising activity levels, corrosion and contamination of the reactor coolant system.

Design of Fuel Handling and Storage Systems for Nuclear Power Plants [15]

A2.8. IAEA have also produced a Safety Standard on the Design of Fuel Handling and Storage Systems for Nuclear Power Plants [15]. This guidance does not focus on the reactor chemistry aspects of fuel storage facilities but does include provisions related to the control of pond water chemistry.

References

14 *IAEA Safety Standards, Design of the Reactor Core for Nuclear Power Plants, Safety Guide No. NS-G-1.12, IAEA, April 2005. www.iaea.org*

15 *IAEA Safety Standards, Design of Fuel Handling and Storage Systems for Nuclear Power Plants, Specific Safety Guide No. NS-G-1.4, IAEA, 2003. www.iaea.org*

## APPENDIX 3: MAGNOX AND ADVANCED GAS COOLED REACTOR PRIMARY COOLANT CHEMISTRY

A3.1. Both Magnox and Advanced Gas Cooled Reactors (AGRs) use carbon dioxide as the primary coolant. This choice has implications for the graphite moderator lifetimes, metallic structural components, fuel cladding and carbon deposition. To this end additional minor additions are made to the bulk carbon dioxide coolant to control such detrimental effects and limitations are made on impurities, especially oxygen.

A3.2. In both Magnox and AGRs the chemistry of the primary circuit is determined by the Boudouard reaction ($C + CO_2 \leftrightarrow 2CO$), in which the core structural component material graphite (which is also the neutron moderator) reacts with the coolant carbon dioxide. This process is driven by the pressure, temperatures and irradiation. Because the graphite core structures are not meant to be replaced, corrosion must be kept to a tolerable level, which therefore becomes one of the primary drivers for the coolant chemistry regime. The graphite temperature in a Magnox reactor is < 350 °C. The graphite temperature in an AGR is kept below 500 °C by an extensive system of coolant channels, although the average gas exit temperature is 650 °C. Thermal graphite corrosion is therefore low in both cases.

A3.3. Radiation induced graphite corrosion by carbon dioxide is observed in both types of reactors. Irradiated carbon dioxide forms many reactive species. The detailed understanding of these intermediate processes is complex and is still not completely understood, although the overall reactions are. Overall, the corrosion reaction increases with carbon dioxide pressure and with radiation dose. This reaction is thus much more important for AGRs than for Magnox reactors.

A3.4. As an equilibrium, this reaction can be inhibited by its product carbon monoxide. Hence, the carbon monoxide concentration in Magnox stations is maintained at 1 – 1.5 %. This is achieved by use of a gas purification plant. Much higher concentrations would be necessary for AGRs to achieve a similar effect, which would lead to excessive carbon deposition (from the reverse Boudouard reaction). For this reason a small amount of methane (of several hundred parts per million by volume), is injected continually into the primary circuit of AGRs and small amounts are periodically injected intermittently at Wylfa. Methane is much more efficient for this means than the same concentration of carbon monoxide. Methane is also produced in the core of AGRs by radiolysis. The Methane inhibits the corrosion reaction by reacting with the carbon dioxide complexes formed from radiolysis and by depositing carbon on surfaces, which preferentially react with carbon dioxide (functioning as "sacrificial graphite").

A3.5. The total concentration of carbon monoxide must also be limited to avoid excessive carbon deposition (especially on the fuel or boiler surfaces). A 0.1 mm thick carbon layer on the fuel elements can reduce heat transfer so drastically that the elements undergo damage. Therefore, carbon monoxide is oxidized to carbon dioxide in a bypass catalyst bed. The carbon monoxide and methane concentrations must be kept within limits at which significant carbon deposition cannot occur. The carbon is formed by thermal and radiolytic decomposition of methane ($CH_4 \rightarrow 2H_2 + C$) and the reverse Boudouard reaction ($2CO \rightarrow CO_2 + C$).

A3.6. There is some evidence that carbon deposits are catalysed by transition metals within the steel boiler tubes or fuel cladding at AGRs. At lower temperatures carbon monoxide reacts with nickel, most likely from the structural steels, producing nickel carbonyl ($Ni(CO)_4$), which is transported in the gas circuit and is an efficient catalyst for carbon deposition on the fuel but is rapidly decomposed at typical operating temperatures. During AGR operations a useful corollary was observed between the concentrations of carbonyl sulphide (COS) in the coolant and the rate of carbon deposition, with increased COS levels inhibiting deposition. Several of the AGRs

currently inject COS as a mitigation measure, but this must be balanced against the increased transport of ^{35}S observed.

A3.7. Part of the methane added to the coolant is also oxidized under AGR conditions producing water ($CH_4 + 3CO_2 \rightarrow 4CO + 2H_2O$). Most of the water produced is removed continually by dryers to avoid condensation in cooler areas. This prevents the corrosion of metallic components by water and the increased corrosion of metals by water containing dissolved carbon dioxide. Water also leads to the formation of hydrogen via the water-gas shift reaction ($H_2O + CO \leftrightarrow H_2 + CO_2$). Both water and hydrogen levels need to be controlled to minimise any potential corrosion effects.

A3.8. Corrosion of metallic components can also be caused by the carbon dioxide itself. Since about 1970, the gas exit temperatures in the Magnox stations had to be lowered to combat the carbon dioxide corrosion of mild steels, which was unknown during design of the reactors. This process of "break-away oxidation" is caused by the formation of a porous oxide layer underneath the normally protective outer oxide. Chemical investigation showed that in both cases magnetite was formed ($3Fe + 4CO_2 \rightarrow Fe_3O_4 + 4CO$). Lowering the temperature inhibited the porous metal layer formation in Magnox stations.

A3.9. Austenitic steels form a protective chromium oxide layer on the metal surface. Consequently, austenitic steels were used in those regions of AGRs susceptible to breakaway oxidation. However, it was found during commissioning of the first AGRs that the 9Cr-1Mo steel sections of the boilers potentially remained susceptible. Subsequent test have shown this effect is unlikely in operating AGRs given tight controls on gas chemistry and operating temperatures.

A3.10. The radiolytic reactions in the primary circuit yield a variety of mostly organic compounds (e.g. ethane, ethylene, propane, acetaldehyde). These concentrations are, however, so low that they do not affect reactor operation (< 10 ppm by volume).

A3.11. Coolant composition can affect the rate of production of various radionuclides:

- ^{41}Ar is the principal radioactive impurity in the primary circuit and is formed via a (n, γ) reaction from ^{40}Ar. ^{40}Ar is an impurity in the make-up carbon dioxide or it can result from air leakage. Its very short half-life of 1.8 h means that it has virtually no impact on radiation protection.
- ^{14}C is formed by neutron activation of ^{13}C in the moderator, and from ^{14}N through an (n,p) reaction. Production therefore depends on the coolant concentrations of nitrogen, carbon monoxide and methane.
- ^{3}H is formed by neutron activation of ^{2}H, ^{3}He, ^{6}Li and ^{10}B. The primary source of tritium in reactor graphite is considered to be from ^{6}Li which is present at 7.5% in natural lithium. Tritium is also produced by ternary fission in the fuel, where it diffuses to the coolant through the cladding. It is mainly present as H_2O in the coolant and hence is mainly discharged as tritiated water via the dryers.
- ^{35}S is produced from impurities present in the graphite (via an (n,p) reaction with the ^{35}Cl or through neutron activation of ^{34}S). ^{35}S is transported in the coolant mainly as COS. COS injection affects the amount of ^{35}S in the coolant hence ^{35}S follows the fate of COS, namely deposition on boiler surfaces, removal in the coolant-bypass plant (recombiners and driers) or coolant leakage. This has resulted in elevations in ^{35}S discharges, although these have not currently challenged environmental discharge permits.

A3.12. The fission product concentration is usually close to zero and, when it is not zero, it is very low. All fuel elements are monitored and replaced in the event of damage.

A3.13. Circulator oil which leaks into the gas circuit decomposes at power to form a range of organic species, CO, CH_4, H_2 and H_2O, adding to the concentrations of those species

already present. In addition, the sulphur impurity in oil will lead to a rise in COS that will affect discharges of ^{35}S.

A3.14. As described there are many, often competing, factors in determining a suitable coolant chemistry. Because of the differences in design and operating parameters among the various AGRs (especially the pressure) the optimum carbon monoxide and methane partial pressures differ for each reactor, as do the CO to CH_4 ratios. An extensive research program was necessary to determine the optimum concentrations for each reactor. The overall approach to determining the gas composition is represented schematically below, where:

- Line (1) represents the limit above which too much water is produced in the primary coolant for the gas plant to remove
- Line (2) represents the boundary, above which carbon deposition becomes detrimental
- Line (3) represents the minimum levels of methane that are produced within the coolant for a given CO concentration
- Line (4) represents the boundary, below which graphite oxidation becomes detrimental
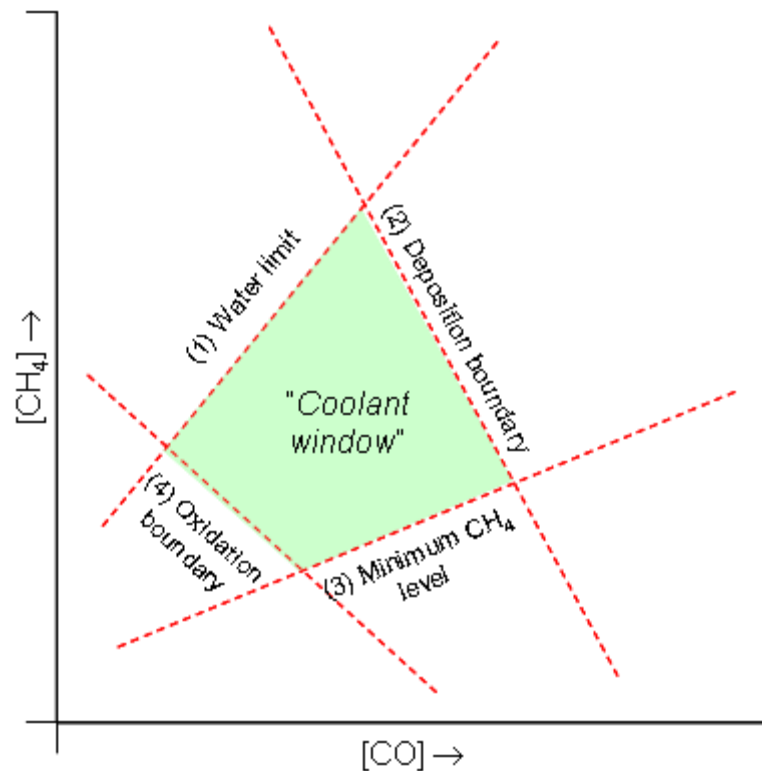
Summary of AGR Primary Coolant Constraints

A3.15. Similarly the effects of the main coolant species is tabulated below, where the effect of an increase in a particular coolant species is shown on the four principal concerns:

Coolant Species	Graphite Oxidation	Carbon Deposition	Corrosion	Radioactivity
CO or CH_4	↓	↑	↑	↓
H_2O	-	-	↑	-
H_2	-	↓	↑	-
COS	-	↓	-	↑
O_2	↑	↓	↑	-
$Ni(CO)_4$	-	↑ (fuel)	-	-
N_2 or Ar	-	-	-	↑

**Effects of Coolant Species**

References

16   *Coolant Chemistry of the Advanced Carbon Dioxide Cooled Reactor, R.L. Fairclough et al, www.iaea.org*

APPENDIX 4: PRESSURISED WATER REACTOR PRIMARY COOLANT CHEMISTRY

A4.1.   In a Pressurised Water Reactor (PWR) the primary coolant water serves as both a moderator and as the medium for transporting heat from the core to the steam generators. It is also a means of controlling the nuclear reaction by dissolving a neutron absorber, boric acid, in the coolant. At high temperature, boric acid influences the pH of pure water only slightly because it tends to undergo reversible polycondensation with increasing temperature. For this reason, the pH value at the operational temperatures of the primary coolant is determined virtually exclusively by the ionisation of water, which depends on both pressure and temperature. Under typical PWR primary coolant conditions (15.7 MPa and 325 °C) the pH of pure water would be around 5.7 or around 5.0 with 1200 mg kg^{-1} of boron as boric acid. This pH, if unchecked, would have a detrimental effect on the corrosion and integrity of metal components in the primary circuit.

A4.2.   To counter the effects of decreased pH the coolant is conditioned by the addition of an alkalising agent. In western PWRs almost isotopically pure ^{7}Li in the form of hydroxide is used. The use of ^{7}LiOH as a pH control agent is advantageous because ^{7}Li is also formed during power operation from boron in the coolant by the nuclear reaction ^{10}B (n,α) ^{7}Li. LiOH containing < 0.01% ^{6}Li (natural abundance 7.4%) ensures that levels of tritium, that would otherwise be produced by the ^{6}Li (n,a) ^{3}H reaction, are minimised. Other alkalising agents are possible, such as ammonia, or sodium and/or potassium hydroxide, but these are not thermally and radiolytically stable leading to the production of hydrogen, ^{24}Na or ^{42}K. Despite these drawback, many Eastern European PWRs (VVERs) operate successfully with a mixed sodium and potassium hydroxide conditioning.

A4.3.   Lithium (and sodium or potassium) has been shown to adversely affect the zirconium based fuel cladding, increasing the rates of corrosion. Fortunately the aqueous concentrations required to do so are much above that required in a PWR. However, any mechanism which causes accumulation of lithium close to the cladding could threaten this margin and fuel manufacturers generally impose restrictive limits on the maximum soluble lithium concentration as a result.

A4.4.   The precise pH$_T$ (pH at temperature T) that the plant operates at influences many other aspects of the chemistry regime. Irrespective of the pH$_T$ chosen some finite amount of corrosion will occur. While this is may not be important to the structural integrity of the circuit, it is the main source of corrosion products in the coolant. The pH$_T$ will also influence the solubility and transport of these around the circuit, particularly through the core where there is typically a 30-40 °C rise in coolant temperature. The optimum approach would be to keep both the absolute solubility and solubility changes around the circuit to a minimum. In reality it is not possible to achieve both of these objectives as they are almost mutually exclusive. The best compromise and hence the approach commonly adopted is to limit the deposition of material in the core. In this way, the most detrimental of the corrosion product issues (namely heat transfer impairment and activation) should be minimised by minimising the mass of deposit in the core and thus the quantity available for activation. To achieve this the pH$_T$ can be chosen such that a "*negative temperature coefficient of solubility*" exist through the core and absolute solubility in the remainder of the circuit is minimised (i.e. at higher pH$_T$ material is more soluble at the core outlet temperature than at the core inlet temperature). Such decisions are complex and depend upon what species is considered in the evaluation, as for example, Ni would require a different pH$_T$ than Fe and different forms of the same element are not identical in this regard.

A4.5.   As the fuel is used throughout the operating cycle the concentration of boric acid needed correspondingly decreases. The concentration of alkalising agent is coordinated with this to achieve the desired pH$_T$. All PWRs operate with this type of "*coordination*". The method of achieving this coordination depends on the factors

described above, leading to a number of different methods of pH control, coordinated, modified and elevated:

A4.6. Coordinated regimes have a constant pH_T, but the limit on lithium means that only lower pH_T values are possible. To overcome this limitation modified regimes were developed. In this regime the lithium is held at the maximum level, until a point in the cycle when the desired pH_T is reached, at which point the coordination is continued. The pH_T in these regimes changes through the cycle, from low to high at the beginning and then constant. Elevated regimes are similar to modified, however the initial lithium level is also raised resulting in a much higher initial pH_T and less time outside the coordinated period.
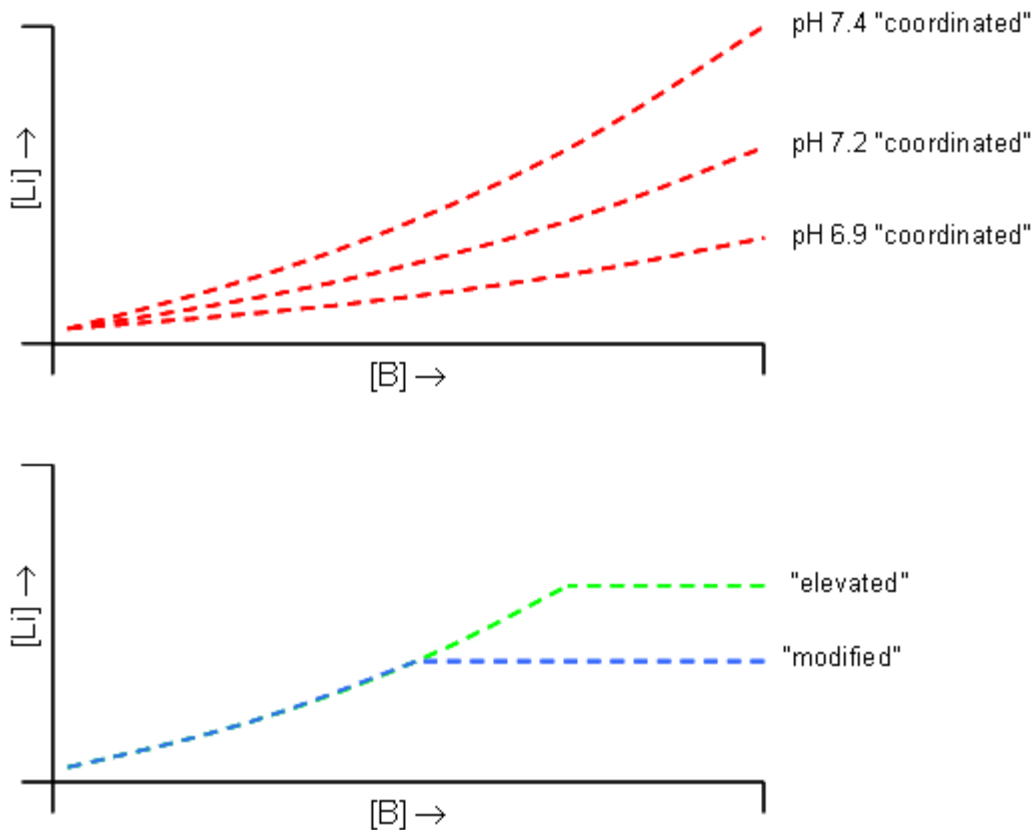
PWR Primary Coolant B:Li Coordination Regimes

A4.7. The radiation field is an important aspect of the PWR design that influences the primary coolant chemistry. The volumes and flow rates around the primary circuit are such that a given mass of coolant (and the species it contains) spends a large proportion of its time within a high intensity radiation environment. Radiolysis of water leads to the production of oxidising species, which increase the rates of damage to fuel and structural materials. Addition of dissolved hydrogen to the coolant suppresses this mechanism.

A4.8. Western PWRs add hydrogen from hydrogen bearing gas, whereas some eastern European PWRs add ammonia which is radiolytically decomposed to hydrogen (and nitrogen leading to ^{14}C). Ammonia is also formed from radiolysis in reactors that add hydrogen by the reverse of this reaction. The precise concentration of hydrogen added can influence other effects; excessive hydrogen levels could potentially lead to hydriding of the fuel cladding or accumulation of combustible gases whereas the concentrations needed to avoid maximising rates of localised corrosion in susceptible materials is currently ambiguous.

A4.9. Other species in the coolant are also subjected to the radiation environment, producing activation products. This is mainly a problem for corrosion products which are released to the coolant from structural materials producing many isotopes, including importantly ^{60}Co, ^{58}Co, ^{54}Mn, ^{59}Fe and ^{51}Cr. Should boiling occur in the core, corrosion product may deposit on the fuel surface, initially producing more active species. However eventually, should thicker deposits develop, they could impair heat transfer or accumulate other species including boron. Such thicker deposits can affect both fuel cladding corrosion and power distributions in extreme cases. Other impurities in the coolant have the potential to exacerbate this accumulation, for example silica.

A4.10. It has been shown that the operating pH_T has an important impact on both the production and transport of corrosion product activity around the primary circuit.

A4.11. This demonstrates the close connection between the choice of materials and water chemistry; the water chemistry conditions specified must fulfill its requirements for all materials which are in contact with the primary coolant including:

- Austenitic stainless steels for components and piping of the primary system
- Zirconium alloys for cladding of fuel assemblies
- Incoloy 800, Inconel 690 or Inconel 600 for steam generator tubes
- High-alloy materials (ferritic stainless steels) of low surface area for internals of the primary system

A4.12. As can be seen form the above descriptions, situations exist where conditions of water chemistry are optimum for achieving one goal but are not at optimum with respect to other goals. Thus, the water chemistry specifications must define parameters to achieve a balance among the various benefits and detriments, taking into account that highest priority is assigned to reactivity control, then materials and fuel integrity. This synergism is illustrated in the diagram below;
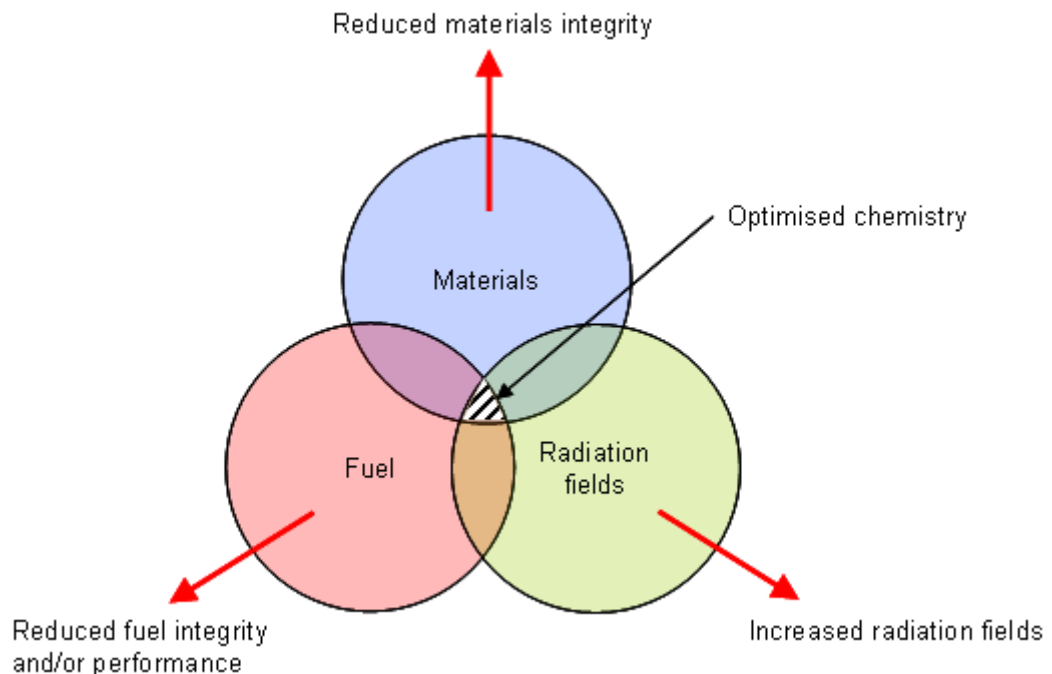
PWR Primary Coolant Chemistry Interactions

A4.13. Thus, aside from the principle nuclear functions defined above (reactivity control and heat removal) the task of the primary water chemistry regime in a PWR can be summarised by the following points:

- Metal release rates (general corrosion) of the structural materials should be minimal
- The occurrence of localized forms of corrosion should be avoided
- The transport and deposition of corrosion products must be influenced in such a manner that contamination of the primary coolant system is kept low and deposition on heat-transfer surfaces, particularly on fuel assemblies, should be prevented as far as possible
- The radiolytic formation of oxidising species should be suppressed
- The formation of activation products in the coolant should be minimised

A4.14. There are many on-going developments in primary coolant chemistry for PWRs which are aimed at having positive effects on one or more of the detriments highlighted above. It is not appropriate to describe each of these in detail here, but they include:

- The use of higher lithium coordinations (up to 6 mg kg^{-1} Lithium)
- The use of zinc for radiation field and stress corrosion cracking control
- The use of Enriched Boric Acid (EBA)
- Changes to the operating limits for dissolved hydrogen

References

17   *Safety Aspects of Water Chemistry in Light Water Reactors, IAEA TECDOC 489, IAEA, 1988. www.iaea.org. While the general principles described in this document remain relevant, some of the technical information is outdated, having been prepared in 1988, and should not be relied upon by the inspector unless confirmed via alternative sources. TRIM ref. 2012/73002.*

18   *EPRI PWR Primary Chemistry Guidelines. The latest version is available only to members, however earlier versions which contain much of the technical background are available at www.epri.com. Many other useful technical reports are also available on the EPRI website. Other guidelines are available, but do not provide the detailed theoretical background found in EPRI reports. (e.g. VGB Guideline for the water in nuclear power stations with light water reactors (PWR), VGB-R 401 J, third edition 2006).*

19   *LCC7 – PWR/VVER Primary Side Coolant Chemistry Volume I - Technical Basis and Recent Discussion, ANT International, 2011. TRIM 2014/440185.*

20   *LCC8 – PWR/VVER Primary Side Coolant Chemistry Volume II - Water Chemistry Tool to Mitigate the Concerns, ANT International, 2012. TRIM 2014/440153.*

21   *Primary circuit chemistry of western PWR and VVER power plants, 02004Ren9653, Unipede, December 1994. TRIM 2012/243709.*

APPENDIX 5: SECONDARY CIRCUIT COOLANT CHEMISTRY

A5.1.   Compared to the primary circuits of power plants, the secondary circuits are often much larger and the materials in contact with the coolant experience a much larger range of environmental conditions, including temperatures and pressures, meaning that the range of materials used is correspondingly larger. This difference has important consequences for the operating chemistries that are, or could be, applied.

A5.2.   The second major influence on secondary circuit chemistry is the purification system design. Impurity ingress to the secondary circuit is much more common, mainly due to the use of seawater or closed loop cooling to the main condenser and it is important that the consequences for such incidents can be tolerated.

A5.3.   The objective of secondary side water chemistry control is to minimise corrosion damage and performance losses for all secondary system components and thereby to maximise the safety, reliability and performance of the secondary system. The operating chemistry applied on the secondary side can influence the behaviour of the:

- ■   Corrosion issues
- ■   Deposition problems
- ■   Thermohydraulic problems

A5.4.   To achieve this objective, the water chemistry has to be compatible with all parts of the secondary system including Steam Generators (SGs)/boilers, turbines, condensers, feedwater heaters, Moisture Separator Reheaters (MSRs), and finally piping. Special emphasis has to be put on SGs/boilers, because they are one of the key components of the plants and may not be replaceable or easily repaired and are a barrier to contain radioactivity. Their degradation or performance loss greatly affects the overall plant performance and safety, especially where they form part of the pressure barrier to the primary circuit. Most of the SG/boiler degradation problems are related to corrosion caused by inappropriate material, design or selection or poor secondary side chemistry control. Many other degradation mechanisms throughout the secondary circuit are also influenced by the operating chemistry (e.g. flow accelerated corrosion).

A5.5.   The secondary coolant chemistry must therefore be balanced to account for all of the factors given above, in addition to ensuring that other constraints or requirements (such as environmental discharge limits) are met. A very brief summary of these considerations as applied to Magnox, AGRs and PWRs is given below.

Magnox

A5.6.   As there is only one operating Magnox reactor, a description of the secondary chemistry of the Magnox reactors is of limited value to this TAG. However the operational chemistry history at Wylfa is described as this provides a useful overview of how chemistry changes can influence and mitigate degradation phenomenon.

A5.7.   At Wylfa each reactor has two pairs of once through steam generators that produce steam at 3.5 MPa and superheated to 315 °C. The serpentine steam generator tubes are made from mild steel and progress from 18 mm diameter in the economizer to 24 mm in the evaporator section and 30 mm in the superheater. The secondary circuit includes a full flow condensate polishing plant.

A5.8.   Initial operation with 0.2 mg kg^{-1} ammonia in the feedwater resulted in flow accelerated corrosion damage at the 18 mm to 24 mm transition region between the economizer and evaporator. The ammonia concentration was increased to 2 mg kg^{-1} in an unsuccessful attempt to decrease the corrosion, but resin regeneration considerations prevented operation above 2 mg kg^{-1}.

A5.9.   A programme was undertaken to find a less volatile, stronger amine that could be dosed at levels compatible with the condensate polishers, yet provide adequate protection from flow accelerated corrosion in the mild steel boilers. As a result amino-

methyl-propanol (AMP) was used for pH control at Wylfa, starting in September, 1983. The concentration of AMP was increased from 5 to 10 mg kg^{-1} in March, 1984. Unfortunately this resulted in a condensate polisher loading that required regeneration every 2 days. While its high base strength and low relative volatility gave the expected improvement, its thermal stability led to unacceptably high after cation conductivity in the high temperature drains that returned to the boiler. This forced the recycle of these drains to the condenser for organic acid clean-up and increased the cation loading on the condensate polishing system.

A5.10. Other amines were then investigated and tested to define a better amine. This led to the use of 5-Aminopentanol (5-AP). A full scale test of 5-AP was undertaken at Wylfa in July, 1991. The success of this test led to routine use at both units.

AGRs

A5.11. The most important design choice in the AGR secondary circuit which affects the operating secondary circuit chemistry is the boiler design. All of the AGRs have non-replaceable once-through boilers located within the concrete pressure vessel of the reactor. The operating steam outlet temperature of the boilers is also high at around 500 °C. The boiler tubes themselves are made from a mixture of carbon or low alloy steel, 9%Cr steel and 316 stainless steel. Ensuring that boiler tube failures are minimised is therefore a key objective for AGR secondary circuit chemistry, in addition to controlling corrosion threats to the rest of the secondary circuit.

A5.12. In addition to the boiler design, all of the AGRs include a deaerator vessel and a full flow condensate polishing plant. These choices mean that the feedwater dissolved oxygen and impurity levels can be reduced to very low levels. The use of full flow condensate polishing does limit the maximum pH_T that can practically be achieved. These are important aspects of the design that contribute to chemistry control and the choice of operating regime.

A5.13. The corrosion threats which could damage the secondary circuit are a function of the materials and environmental conditions, which due to the large range of materials and conditions can include:

■ General corrosion: while general corrosion should not threaten integrity it can contribute to deposition elsewhere which can lead to heat transfer impairment, pressure losses and enhanced solute concentration and corrosion. Maintenance of a high pH_T minimises the general corrosion rate.

■ Localised corrosion: many forms of localised corrosion are possible, but these mainly result from aggressive (often acidic) environments developing as a consequence of solute concentration. These processes can be minimised by removing the factors that lead to accumulation (e.g. deposits or crevices) or by increasing the pH_T.

■ Stress Corrosion Cracking (SCC): the superheater and reheater sections of the AGR boiler are potentially prone to this form of corrosion. To avoid this they are operated "dry" and the impurity levels and redox potential are controlled. Other areas of the secondary circuit may also be prone to this mechanism, particularly where the potential for impurity concentration exists, hence the main chemical mitigations are to minimise impurity levels as far as practical and operate under reducing conditions.

■ Intergranular Attack (IGA): some high Cr steels can be subject to IGA due to sensitisation. In AGRs the superheaters and reheaters may be subject to IGA. The chemical controls that are applied for SCC mitigation (reduced impurities and reducing conditions) are beneficial for IGA as well.

■ Steam Oxidation: this is essentially general corrosion caused by steam rather than water. However, the high steam temperatures in the AGRs means that steam oxidation rates can be significant. This is the main reason for using 9%Cr and 316 stainless steel in the AGR boilers. The rates of steam oxidation

are not directly influenced by the operating chemistry (but are through the influence on redox conditions) and chemistry is not used to control the process.

- <u>Flow Accelerated Corrosion (FAC)</u>: FAC affects carbon and low alloy steels by the effect of flow (turbulence) removing the protective magnetite corrosion film. Temperature is another important variable, with damage potentially seen over a large range (around 50 - 250 ºC) and a maximum at around 150 $\pm$ 25ºC. FAC can be controlled by reducing the solubility of the formed corrosion film, either through pH_T increases or by operating under oxygenated conditions (haematite is formed). Alternatively, use of steels with a small amount of Cr reduce or eliminate this effect.

A5.14. In addition to corrosion, deposition within the AGR boiler is a concern. It has been noted that the helical boilers at Heysham and Hartlepool have experienced high pressure drops, meaning that is difficult to ensure the correct flows within the boilers, increasing the potential to overheat and fail boiler tubes. This is believed to be caused by "rippled" magnetite deposits within the boilers. Chemical mitigation has used boiler chemical cleaning and changes in the operating chemistry to reduce magnetite solubility in the feedwater.

A5.15. These design choices and potential corrosion and degradation threats limit the feedwater chemistry to an All Volatile Treatment (AVT) with redox control and minimised impurity levels. The AGRs therefore operate under two variations on this theme, which differ in a minor but important way:

- Deoxygenated AVT; via ammonia dosing and with hydrazine dosing to remove residual dissolved oxygen,
- "oxygenated" AVT; via ammonia or Dimethylamine (DMA) dosing, however low controlled levels of oxygen are maintained within the final feedwater to mitigate FAC. Hydrazine dosing is still used but is not fully effective until the temperature increases in the boiler, thus still maintaining reducing conditions in the evaporator and reheater sections.

A5.16. Thus the AGR secondary circuit operating chemistry is based upon:

- Dosing with a volatile pH control agent
- Minimisation of feedwater impurity levels
- Control of the dissolved oxygen concentration

PWRs

A5.17. The large number of PWRs worldwide leads to many variations in the materials and design of the secondary circuits. The designs have also evolved over time as lessons are learnt from early plants and different manufacturers and designers adopt different strategies and options. This leads to a large variation in material and design choices for the secondary circuit systems and components, all of which in turn can affect the chemistry that may be applied. A brief history of the evolution in chemistry, materials and design of PWR secondary circuits is given below.

A5.18. Early PWRs were built and designed based on knowledge from conventional fossil power plants of that era. This meant that carbon steels were used for pipe work and components and copper or copper alloys were selected for the tubes of heat exchangers, MSRs and condensers. After a short use of austenitic stainless steel (18% Cr – 10% Ni) in a few PWR plants, Inconel 600 MA (mill annealed), a nickel based alloy, was used as the steam generator tubing material (except for russian designed VVER plants where austenitic stainless steels continue to be used for steam generator tubes). In recirculating steam generators, drilled hole tube support plates made from carbon steel were used to support the tubes against vibration. For impurity control of the feedwater, condensate polishing systems were used especially for the PWRs with seawater cooling and also for the PWRs with once-through steam

generators. To counter impurity build-up in recirculating steam generators a steam generator blowdown (SGBD) capability was included, to remove a small portion of the steam generator fluid for clean-up.

A5.19. Similarly, the original water chemistry selection was again based on the experience of fossil power plant chemistry and resulted in phosphate chemistry for the RSGs combined with an AVT treatment for the secondary side. For OTSGs, AVT chemistry was applied. Unfortunately the use of carbon steel piping, copper based heat exchangers and condensate polishing meant that a sufficiently high pH could not be attained to mitigate FAC in the secondary circuit piping. In addition to piping failures this resulted in high corrosion product deposits in the SGs, which when combined with the tube support plate design which acted as an efficient crevice location, led to severe corrosion problems affecting early PWRs. The well known "combined chemistry" (ammonia with high dissolved oxygen) used in fossil plants to combat this problem could not be used in PWRs due to the known risk of SCC of the Inconel 600 MA SG tubing under oxidizing conditions.

A5.20. When the material, design and chemistry of early PWRs are considered together it can be seen that the approach taken does not allow the selection of an adequate water chemistry to avoid significant corrosion issues. This was effectively the main root cause of the SG and secondary circuit degradation problems seen in early PWRs.

A5.21. The most significant SG degradation problems were experienced from the early 1970s until the end of the 1990s, requiring SG replacement in some cases. During this period of almost 30 years of PWR operation a lot of modifications and improvements to the design, materials and water chemistry were undertaken. The historical evolution of corrosion problems which affect PWR SGs are shown below, and include a wide range of corrosion phenomena as described:
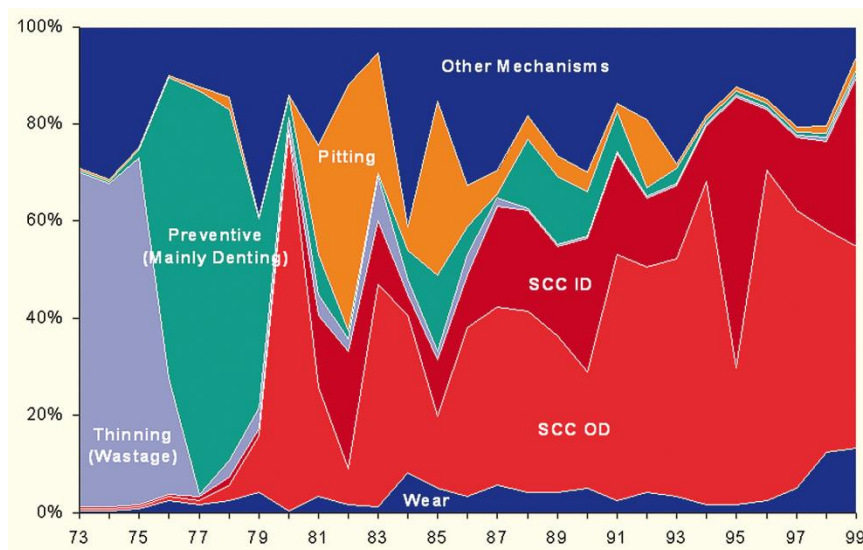
Chronology of PWR SG Corrosion Problems

- <u>Thinning (wastage)</u>: Wastage is tube thinning caused by a build-up of acidic phosphate beneath deposits. As such it was seen only in early PWRs which had high phosphate dosing levels. Early attempts to control the Na:PO$_4$ ratio resulted in SCC. For this reason phosphate treatment of SGs was discontinued and plants switched to AVT.
- <u>Denting</u>: Denting is caused by corrosion of the carbon steel tube support plates. The oxides formed have a higher volume ration than the base metal, filling the tube support gap and ultimately squashing the tube. Denting requires acidic oxidising conditions, which result from impurity accumulation in crevices,

such as in occluded tube support plates. Denting occurred as a consequence of switching from phosphate to AVT chemistry in many instances, as removing the buffering capacity of phosphate allowed this mechanism to become more prevalent. The experience of denting was a significant milestone in PWR secondary chemistry and resulted in:

- Better impurity control management (condenser and air ingress)
- Design changes to SG tube supports from carbon steel drilled holes to stainless steel broached/eggcrate designs

■ Pitting: Pitting requires acidic oxidising conditions. Similar to denting, this occurs due to impurity ingress and concentration behind deposits, but can occur at both high and low temperature (with differing mechanisms). The precise cases can vary by plant, but in many cases it is thought that copper oxides or reduced sulphur species in the deposits acted as the oxidant source. Pitting can also lead to SCC if stresses are also present. Pitting was controlled by reducing impurity ingress and accumulation (via SG cleaning) and avoiding oxidising conditions. Removing copper bearing heat exchangers helped significantly.

■ SCC: SCC is experienced not only on the secondary side of the SG tubes (ODSCC), but also on the primary side (IDSCC or PWSCC). For the secondary side the degradation is due to a combination of material sensitivity, stress level and chemical environment. The chemical conditions needed for SCC are either extreme caustic or extreme acidic (pH_T: > 9 or < 4) or in presence of specific detrimental impurities (lead, sulphur compounds). Stress is responsible for damaging the protective oxide layers on the tube surface, which protects the tubing material against the corrosive environment. Initiation of SCC can also be caused by pitting, which also damages the protective oxide layer. SCC can be either Inter or Trans-granular (IGSCC or TGSCC). As with the other corrosion processes such chemical conditions generally require a concentration mechanism, typically in crevices. The resistance of SG tube material on SCC is important, and generally Inconel 600 MA < 600 TT < 690 TT ~ 800 (although this is dependant upon the precise conditions and mechanism). Mitigation of SCC (mainly PWSCC) was the main driver to change SG tube materials to Inconel 690 TT or Alloy 800, although this contributed to other changes such tube support plate design and materials, heat exchanger tubing (exclusion of copper) and purification systems.

A5.22. As well as acting as concentration sites within the SGs deposits can also cause thermohydraulic problems. For example a number of French PWRs have suffered tube failures caused by wear and vibration, the cause of which is the build-up of insoluble deposits in the tube support plates and consequent changes to flows. Chemistry control is the root cause of these deposits.

A5.23. FAC can also be a significant problem in PWRs, where large parts of the secondary circuit operate in the susceptible temperature and flow regions. In addition to material changes (increased Cr content) chemistry mitigations can be applied, including the use of alternative amines to improve the pH_T of affected areas.

A5.24. Overall, due to the large experience of degradation problems the design, materials and chemistry in the secondary circuit of PWRs are much improved compared to early plants although chemistry controls must still be strictly maintained. Typical PWR secondary circuit operating chemistry is similar to that applied in AGRs, and is based upon:

■ Dosing with a volatile pH control agent
■ Minimisation of feedwater impurity levels

- Maintaining a reducing environment in the steam generators by hydrazine addition

References

21   Primary circuit chemistry of western PWR and VVER power plants, 02004Ren9653, Unipede, December 1994. TRIM 2012/243709.

22   LCC11 – Key Emerging Issues and Recent Progress Related to Plant Chemistry/Corrosion in PWR/VVER/CANDU Reactors, ANT International, 2015. TRIM 2017/31146

23   EPRI PWR Secondary Chemistry Guidelines. The latest version is available only to members, however earlier versions which contain much of the technical background are available at www.epri.com. Many other useful technical reports are also available on the EPRI website. Other guidelines are available, but do not provide the detailed theoretical background found in EPRI reports.

APPENDIX 6: SPENT FUEL POND CHEMISTRY

A6.1. The role of the spent fuel pond is to provide safe storage of irradiated fuel elements discharged from the reactor until their radioactivity and decay heat have reduced sufficiently to allow transport, reprocessing or longer term storage. The pond water itself serves to remove the decay heat from the fuel and provide shielding for the fuel. Depending upon the design of the pond, the criticality controls in place and the fuel, soluble boron may also be added to the pond water to maintain an adequate margin to criticality. In addition pH control additives may be added to minimise corrosion of fuel cladding.

A6.2. Thus pond water chemistry is controlled to avoid criticality incidents, minimise fuel cladding corrosion, minimise pond water radioactivity and to minimise spent resin and pond water discharges. In addition the water clarity is maintained to improve operations and the pond water may be a further water source to other process and equipment on the plant which may introduce additional requirements. Typical pond water treatment systems include filters and ion exchange systems.

A6.3. The typical pond water chemistry in the UK reactor types is described briefly below:

- Magnox: The Magnox fuel cladding must be stored under alkaline conditions in order to minimise cladding degradation. This is achieved by dosing the ponds with Sodium Hydroxide. However, this absorbs carbon dioxide from the atmosphere, lowering the pH, which must also be controlled. Soluble poisons are not necessary due to the low enrichment of Magnox fuel. Impurity controls, especially for chloride are necessary to minimise any degradation of the passive oxide film formed on the fuel. Historically control of radioactive caesium was a problem in the older Magnox fuel storage ponds and specific caesium selective resins were used to manage the build-up.

- AGR: Boric acid is added to the spent fuel ponds at the AGRs in order to provide sufficient margin for criticality control. This decreases the pH to around 5, which would result in enhanced corrosion of the sensitised stainless steel fuel cladding so Sodium Hydroxide is also added to raise the pH back to neutral. Impurities which could accelerate corrosion, particularly of the sensitised or highly oxidised regions, are minimised by treatment of the pond water through ion exchange systems. The main isotopes found in AGR ponds are ^{45}Ca, ^{60}Co, ^{134}Cs, ^{137}Cs and ^{46}Sc, which arise from impurities in the graphite sleeves and ^{54}Mn, ^{51}Cr and ^{58}Co, which arise from the fuel clad. ^{134}Cs and ^{137}Cs would also be released from fuel having clad failures or from the fuel flasks returned from Sellafield. The main radioactive contaminant of the spent fuel ponds is caesium, which accumulates due to its inefficient removal by the ion exchange resins due to the high sodium content of the pond water.

- PWR: The chemistry control in the spent fuel ponds at a PWR are very similar to those found within the primary coolant, due to the mixing of water that occurs during refuelling. This means boric acid is added to the pond at the cold shutdown concentration and impurities are minimised to minimise the potential corrosion of zircalloy fuel cladding or sensitised stainless steel components. Attention is also given to elements which could form tenacious fuel deposits, such as calcium, magnesium and silica. The main radioactivity present within the pool will be ^{3}H from the nuclear reactions of ^{10}B and ^{7}Li; ^{60}Co, ^{58}Co, ^{54}Mn, ^{51}Cr and ^{59}Fe from corrosion product activation; and ^{137}Cs and ^{131}I from fission product contamination.

APPENDIX 7: CLOSED COOLING WATER SYSTEM CHEMISTRY

A7.1.   There are many components or systems within nuclear plants where there is a continuing need to remove excess heat or provide cooling. This is often provided by a Closed Cooling Water (CCW) system. The heat exchangers within these systems can act as a barrier to contain radioactive fluids or can cool components or systems which provide a safety function. Corrosion or fouling of the heat exchange equipment can interfere with its intended function, which is especially important in safety equipment, and hence chemistry control is often employed to mitigate these risks.

A7.2.   The design of such closed cooling water systems can vary significantly in terms of metallurgy, flow rates, capacity, radiation fluxes and chemistry control provisions amongst others. However, the basic design consists of a closed loop where heat is transferred from the component heat exchanger(s) to the heat sink heat exchanger(s). The system is "closed" to minimise evaporation and exposure to the atmosphere. The CCW system therefore functions as an intermediate heat exchange loop.

A7.3.   The materials of construction chosen for nuclear CCW systems are a function of many factors including engineering, economics, water quality and design. In most plants, the piping is typically unlined carbon steel or stainless steel. The heat exchanger tubesheets, channels, and channel heads are typically bare or coated carbon steel or stainless steel. Heat exchanger tube materials include copper alloys (for example, Admiralty brass or copper-nickel), stainless steel or titanium. Other non-metallic materials might be included in a CCW system for gaskets, valve seats, pump seals, packing and sacrificial anodes.

A7.4.   Chemical control provisions in CCW systems vary by design. Some systems may allow the control of dissolved oxygen by deaeration or other means, whereas others may operate fully aerated. Impurity control may also be included in the design by using ion exchange or other systems, whereas other may need to "bleed and feed" to minimise contaminant build-up. The make-up water quality can vary from towns mains to demineralised water.

A7.5.   When taken together these variations in design, materials and chemistry mean that the potential degradation mechanisms in CCW systems can include:

- Corrosion (general, pitting, crevice, stress corrosion cracking, galvanic, flow accelerated corrosion and microbiologically induced corrosion)
- Fouling
- Microbiological growth
- Scaling

A7.6.   To address these concerns some form of chemical control is often employed. This may include some combination of impurity minimisation, pH control or corrosion inhibition, depending upon the specific system:

- A range of corrosion inhibitor chemicals such as chromates, nitrites or molybdates are used which act to form a thin film on the surfaces and inhibit corrosion. Inhibited glycol (ethylene glycol or propylene glycol) is also used in some systems. Both generic chemicals and proprietary blends are used in CCW systems.
- The purpose of pH control is to keep pH in a range where corrosion is minimized and other treatment chemicals (inhibitors) are most effective. Common pH additives include sodium, potassium or lithium hydroxide, sodium bicarbonate, sodium carbonate, sodium tetraborate (borax), amines, and phosphates.
- In addition, some plants achieve satisfactory control by operating with a pure water chemistry.

A7.7. It is important to note that the use of chemical control in CCW systems will not resolve problems originating from poor design or maintenance practices that result in excessive system leaks. Excessive leakage makes consistent chemical control very difficult and offsets the ability of the chemicals to provide adequate protection.

A7.8. A very brief description of some of the most common CCW system corrosion inhibitors is given below:

■ Nitrite: nitrite is a well known corrosion inhibitor for ferrous systems, forming a passivating oxide film which does not require oxygen to form the film. Nitrite is often combined with a pH additive and a copper corrosion inhibitor (such as an azole) is needed if copper components are present. Nitrite is an effective nutrient for microbiological growth if not controlled and may decompose depending upon the pH and aeration. Sulphate is more corrosive than chloride in nitrite dosed systems.

■ Molybdate: Molybdate operates in a similar manner to nitrite, forming a passive film, although in this case there is some absorption into the oxide. Molybdate is applicable to both ferrous and aluminium systems. The effect of oxygen on the effectiveness of molybdate is unclear, with some evidence suggesting that a minimum concentration is needed to ensure inhibition or at least an additional oxidising source. Molybdate requires a pH control agent and a copper corrosion inhibitor may also be needed. Chloride is more aggressive than sulphate for molybdate systems.

■ Nitrite/Molybdate: A mixed nitrite/molybdate inhibitor is a standard mixture which combines the oxidising power of nitrite with molybdate, especially in deaerated or partially deaerated water. The combination of nitrite and molybdate is synergistic in that nitrite maintains the surface oxide film and molybdate protects the surface oxide from sulfate and chloride attack. This combination minimises the required concentration of each component. pH control remains necessary to minimise degradation as does a copper inhibitor, if necessary.

■ Chromate: Chromate is a strong oxidising agent so promote the formation of a thin protective oxide. It is also an effective microbiological control agent, but is toxic. It is applicable to ferrous, copper, zinc and aluminium systems. While effective over a broad pH range a pH additive is often also added.

■ Azoles: Chemicals used for copper corrosion control are nitrogen containing organic compounds (azoles). Azoles react with copper ions to form a thin film that reinforces the oxide film on the copper. They are not used on their own and are an addition to ferrous inhibitors such as nitrite or molybdate.

■ Inhibited/blended glycols: Glycol based systems are generally used when some form of frost protection is required, and are used as either a separate glycol and inhibitor packages or as a proprietary blend. The range of systems is too large to describe here, but may also include pH agents, azoles or antifoaming agents as part of the package.

A7.9. As mentioned above, an alternative approach to chemistry control of CCW systems is to operate without chemical additions. This may be applicable to systems which have low operating temperatures (around 40 °C) and use demineralised water for make-up. While this offers advantages in terms of simplicity, the main disadvantage is the lack of chemical buffering, which requires that system purity and integrity be maintained. The primary impurities of concern are anions that can accelerate corrosion (general and pitting corrosion, as well as stress corrosion cracking of stainless steels). Oxygen control in these systems is a very important parameter as well, particularly for systems which contain copper or copper alloys as the corrosion mechanism take place in two separate oxygen control ranges. In the low range (< 100 μg kg^{-1}) a cuprous oxide film is formed, whereas in the high oxygen range (> 2000 μg kg^{-1}) a cupric oxide film forms. While both of these oxygen control regimes can be used successfully, they must be

used separately as enhanced corrosion rates are observed between these oxygen ranges. This type of approach is applicable to stator water chemistry systems.

A7.10. Of particular note to the UK are the Pressure Vessel Cooling Water (PVCW) systems. The use of a pre-stressed concrete pressure vessel requires a cooling system to preserve the structural integrity of the concrete vessel by maintaining the temperature and temperature gradients of the liner and concrete within acceptable limits. The PVCW systems also cool other safety relevant systems. All of PVCW systems are manufactured from mild steel, in a variety of conditions. The majority of the pipework is buried within the concrete, and is therefore inaccessible, and operates up to around 35°C and 10 bar g. However, small areas of pipework are exposed to the primary coolant gas and hence in-leakage of carbon dioxide to the PVCW system can occur, affecting pH control and increasing the potential for carbonate deposits to impair flows. Currently, all AGRs control the chemistry within the PVCW system by maintaining a high, alkaline pH using LiOH, and minimising the concentrations of dissolved oxygen, total CO_2 and ionic impurities, as does Wylfa.

References

24   *EPRI Closed Cooling Water Chemistry Guidelines. The latest version is available only to members, however earlier versions which contain much of the technical background are available at www.epri.com. Many other useful technical reports are also available on the EPRI website.*

APPENDIX 8: BOILING WATER REACTOR OPERATING CHEMISTRY

Introduction

A8.1.   Whilst there are currently no operating Boiling Water Reactors (BWRs) in the UK, it is of value to capture here aspects of BWR chemistry, with focus on the at power operating chemistry of the Reactor Coolant System (RCS), following the completion of the generic design assessment of the UK Advanced Boiling Water Reactor (UK ABWR).

A8.2.   In a BWR, water serves as both a coolant and neutron moderator. The heat generated from the fission process boils and partially evaporates water within the Reactor Pressure Vessel (RPV), at a pressure of around 7.0 MPa. The resulting steam-water mixture enters steam separators located above the core, where water is removed, and the remaining steam is passed upwards through steam dryers. In a direct cycle, the dry steam is then used to power the turbine after which it is condensed, and this condensate is cleaned, de-aerated, and heated before being returned as feed water to the core. Since boiling occurs on the fuel rods in a BWR, the coolant must be of a high purity to avoid a build-up of crud on the fuel and in the reactor water. Therefore, as well as clean-up of the condensate before return to the RPV, a reactor water clean-up system is required and typically runs at 0.5 to 2 % of the feed water flow rate.

A8.3.   As water flows through the BWR core it is exposed to neutron and gamma radiation, leading to the generation of a wide variety of radiolysis products. For simplicity, the primary species in the BWR environment can be considered to be hydrogen and hydrogen peroxide. Since hydrogen partitions to the steam phase during boiling, and hydrogen peroxide has a relatively low volatility, the reactor water is oxidant rich. Hydrogen peroxide decomposes to form water and oxygen, and the relative proportions of these vary with time and distance away from the core. Expressed as oxygen, pure reactor water in a typical BWR would have several hundred parts per billion (ppb) oxygen and only tens of ppb of hydrogen. Most of the radiolysis gases partition to the steam phase and eventually reach the condenser, where they are exhausted to the Off-gas (OG) system. Radiolysis gases are recombined to water in the OG system to prevent the formation of a flammable atmosphere. A 900 MWe BWR typically produces around 190 m^3 of radiolysis gases for each hour of operation in a stoichiometric mixture, where two thirds of the mixture is hydrogen and the remaining third is oxygen.

A8.4.   The oxygen level in BWR coolant can impact dose levels during operation, since in-core transmutation of oxygen atoms leads to the production of radioactive nitrogen-16, which is the dominant radionuclide for dose during operations. In pure water coolant, referred to as Normal Water Chemistry (NWC), the oxidising conditions result in nitrogen-16 forming nitrate, which remains dissolved in the coolant. Other species also become activated when exposed to the core radiation field, particularly metallic corrosion products. This leads to the production of radioactive species, including cobalt-60, cobalt-58, manganese-54, zinc-65, and chromium-51, which deposit on the RCS pipework and contribute to personnel dose uptake during outages.

A8.5.   All currently operating BWRs were initially run using some form of NWC. However, the full extent of the impact of the oxidising chemical environment on the integrity of the plant components and on dose rates in the longer-term was not fully appreciated. US BWR plants, as shown in Figure 1, and others worldwide, now operate under Hydrogen Water Chemistry (HWC – explained further below), many with addition of noble metals and zinc. However, it should be noted that many European and Japanese BWRs continue to operate under NWC conditions. Overall, the RCS chemistry of operational BWRs is a complex interaction between several variables, some of which are well understood, whereas others can only be empirically followed based on plant experience. There is also no industry-wide consensus on the operating chemistry to be applied for BWRs; it is taken as being design specific.
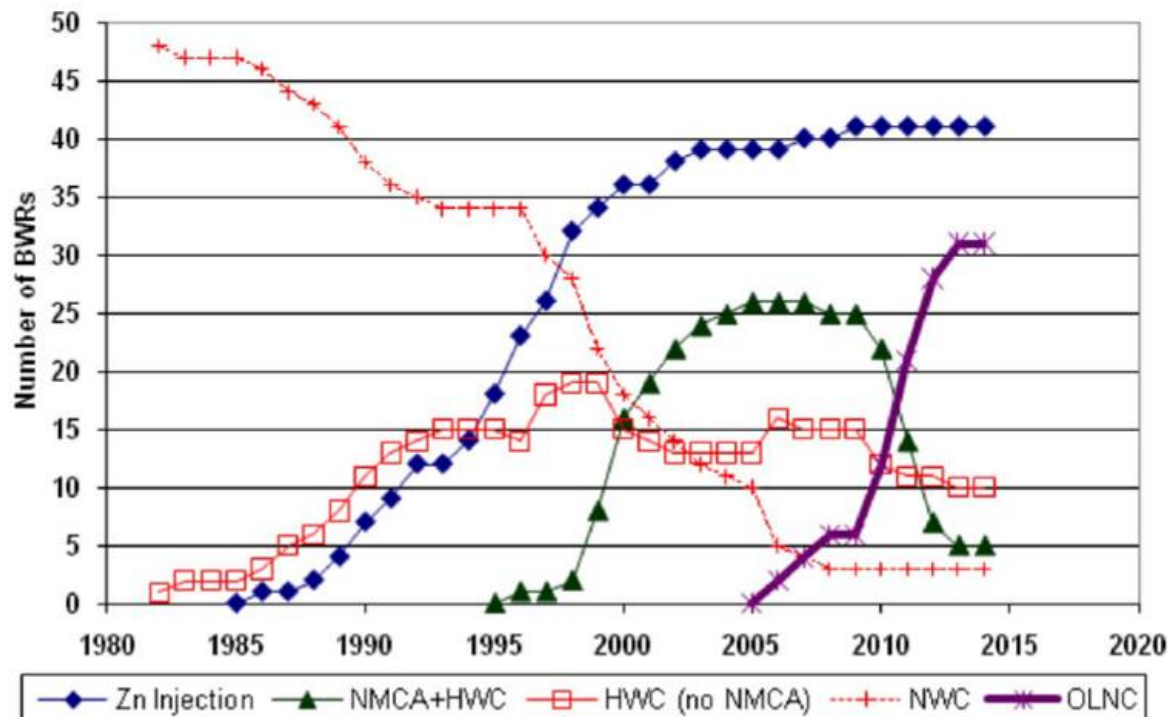
Figure 1 Evolution of BWR chemistry regimes in the US [28]

A8.6.   Over many years of BWR operating experience a large number of materials degradation threats have emerged, attributed to both divergence from chemistry limits and conditions and inadequate materials conditions associated with manufacturing. Such incidents have highlighted the importance of considering BWR materials and operating chemistry choices together; essentially if appropriate materials are selected for structures, systems and components (SSCs), the chemical control requirements needed to mitigate materials degradation mechanisms should be less onerous.

BWR Operating Chemistry

A8.7.   Under NWC, the oxidising environment causes an increase in the electrochemical corrosion potential (ECP) of metallic components, and can lead to issues relating to stress corrosion cracking (SCC) of stainless steel components. SCC of nickel-base alloys (NBA), used in applications where both high strength and corrosion resistance are required, can also be an issue in BWRs. Many plants now opt to modify the operating environment to mitigate SCC by adding dissolved hydrogen to the feedwater.

A8.8.   This regime is commonly referred to as hydrogen water chemistry (HWC). The principal aim is to mitigate the growth rate of existing SCC cracks. Hydrogen recombines with the oxygen and hydrogen peroxide in the coolant to form water; the reaction is catalysed by gamma radiation in the downcomer region of the BWR RPV. When HWC is implemented, the feedwater oxygen concentration can also decrease from several hundred ppb to around 2 ppb or less, depending on the amount of hydrogen added. This can have important impacts on the risk of specific materials degradation threats like flow accelerated corrosion. In terms of the impact on reactor water, as the coolant boils in the RPV, the hydrogen concentration decreases and therefore components exposed to recirculated water are not protected from SCC in the same way. This leads to complex redox conditions in the core, where some regions are oxidising and some reducing. It is also worth noting that the effect of hydrogen addition varies between BWRs. Gamma radiation dose rates in the RPV downcomer vary between reactor designs, which means the rate of the hydrogen + oxidants recombination reaction, and therefore the resulting feedwater hydrogen concentration

required to mitigate SSC, also varies. As explained further below, there are also important factors related to the core design which influence the hydrogen efficiency of BWRs and even variations within the fuel cycle itself, which need to be adequately understood.

A8.9. Adding hydrogen to BWRs can also have a number of detriments. Under the reducing conditions brought about by HWC, nitrogen-16 forms stable NO_x and eventually ammonia, which is volatile and therefore carried over with the steam to the turbine. This can result in unacceptable dose rates around steam cycle components during operation. However, the short half-life of nitogen-16 (7.13 seconds) is such that dose rates in the balance of plant (BoP) reduce rapidly following reactor shut-down. Implementation of HWC can also lead to increases in shutdown dose rates, due to release of cobalt-60. When the feedwater changes from oxidising to reducing, the thick loose haematite (Fe_2O_3) oxides that make up the outer layer of stainless steel corrosion films and fuel deposits under NWC conditions become unstable, and are converted to a more protective spinel form (magnetite, Fe_3O_4). The conversion gives rise to an iron release and an associated release of cobalt-60[1] from the oxide film.

A8.10. The amount of hydrogen that needs to be added to offset the oxidising nature of the coolant can be reduced with the addition of noble metals. Noble Metal Chemical Addition (NMCA) is the original method developed by the industry to enable noble metals to be added to BWRs, and is conducted during reactor shutdown. On-Line NobleChem™ (OLNC), is a more recent variant of the technique and is conducted during at-power operations. A solution of noble metal (typically as the sodium salt $Na_2Pt(OH)_6$), is injected into the feedwater and deposits on wetted surfaces as metallic nanoparticles. These particles have a high catalytic activity for the recombination reaction of hydrogen with oxygen and hydrogen peroxide, and therefore "protection" of the core internals from SCC (and for older BWRs, other components such as the stainless steel external recirculation loop piping), can be achieved at lower feedwater hydrogen concentrations. Part of the justification to add noble metals to BWRs has also extensively considered the impact platinum may have on fuel reliability and integrity. Fuel performance issues have been postulated with the addition of large amounts of noble metals, and fuel deposit spalling in cycles subsequent to noble metal application was observed in a number of plants. It is therefore common practice for BWR operators injecting noble metals to impose specific limits and conditions, based on operating experience (OPEX) of OLNC application in plants that have not experienced adverse effects. Amongst other things, some of the most common restrictions include limits on the total amount of platinum injected and timings for OLNC immediately after the outage once fresh fuel has been loaded into the core. As depicted in Figure 1, OLNC has been rapidly adopted by US BWR operators since its inception in the mid-2000s.

A8.11. As previously noted, the principal reason for adding hydrogen and platinum to the feedwater of a BWR is to mitigate the risk of SCC of austenitic materials. With these additions a reducing environment is created, therefore suppressing the ECP. In BWRs, ECP is a measure of the electrochemical driving force for SCC i.e. the higher the ECP, the greater the thermodynamic tendency for SCC initiation and growth in materials susceptible to SCC. Extensive studies have shown that lowering the ECP of austenitic materials used in BWRs to <-230 mV (vs. the Standard Hydrogen Electrode (SHE)), mitigates SCC. Consequently all BWRs which implement HWC are operated to achieve an ECP of <-230 mV (vs. SHE), which is considered to be the industry standard accepted value. As previously stated, a number of factors, including core design and dose rates in the RPV downcomer region, mean that the responsiveness of BWRs to HWC is plant specific. BWR operators therefore make extensive use of

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[1] The main sources of cobalt-60 in a BWR are stainless steels, nickel base alloys and high-cobalt alloys e.g. Stellite. Cobalt-59 is released to the coolant through corrosion of these materials, and is carried into the core where it can form cobalt-60 by neutron activation.

radiolysis modelling and ECP calculations to determine the levels of feedwater hydrogen required for the plant from cycle-to-cycle, and at different points in the same fuel cycle, to be able to achieve SCC mitigation in the required locations.

A8.12. To mitigate the increased shutdown dose rates seen with HWC due to cobalt-60 release, several plants, including the majority of US BWRs, inject Depleted Zinc Oxide (DZO). As previously noted, the reducing conditions brought about by hydrogen addition result in changes in steel corrosion films from haematite to magnetite spinel forms. Zinc competes with cobalt for the same sites within the spinel structure, and its incorporation is thermodynamically favoured over cobalt. Therefore, less cobalt makes up the spinel structure, meaning that dose rates due to cobalt-60 from piping and other components are reduced. Released cobalt is removed by the reactor water clean-up system; ion exchange media specifically tailored to target cobalt removal are available. It should be noted that there is a balance to be struck in selecting feedwater and reactor water zinc levels, since increased levels have been observed to lead to a change in the nature of fuel crud deposits, which appear to be denser and more adherent; this can be a factor in fuel cladding failures.

A8.13. Fuel deposit spalling has been observed with high concentration zinc injection in the presence of high concentrations of feedwater iron and copper. Iron corrosion products arising from carbon steel and low alloy steel components in the BoP lead to increased feedwater iron concentrations. As mentioned above, feedwater iron plays an important role in the transport of cobalt-60 from stainless steel corrosion films and fuel deposits. The importance of properly controlling feedwater iron to mitigate dose rates has therefore been recognised by all BWR operators. However, much like the choice of implementing HWC, noble metal and/or zinc injection for the RCS operating chemistry, there is no single agreed consensus for one specific approach to adopt for feedwater iron concentration control in BWRs. For example, some plants operate with "ultra-low" feedwater iron, some purposefully add iron into the feedwater (either by direct injection or purposefully bypassing feedwater clean-up provisions), whereas some control other parameters, including the ratio of iron-to-nickel in the feedwater.

A8.14. As well as materials selection, there are specific design features which influence BWR feedwater iron concentrations (and other feedwater impurities). BWR condensate clean-up systems remove most feedwater impurities, including iron. Older BWRs tend to use either a deep bed mixed resin system or a filter-demineraliser (F/D). An F/D is an integral system, which combines a filter screen with a layer of powdered resin flocculated onto the filter holder. In newer BWR plants, dual systems tend to be used in the condensate purification system to remove impurities. These employ a separate pre-filter upstream of the deep bed mixed resin. Several older BWR plants have also back-fitted these systems, as the importance of proper feedwater iron control on dose rates became more apparent. The configuration of the heater drain system also has important consequences for feedwater iron concentrations. For example, in some BWRs, the high temperature heater drains are "forward pumped", thereby bypassing some, or all of, the condensate treatment system. This improves the heat balance of the system and the overall efficiency of the plant. However, depending on the materials selected and specific design of the plant, the heater drain system can make a large contribution to feedwater iron levels in BWRs.

A8.15. Depending on the specific design of the condensate clean-up system, the configuration of the heater drain system (i.e. "forward pumping") and operational practices, the final feedwater iron concentration can range from <0.01 to over 10 ppb.

A8.16. Irrespective of the specific RCS operating chemistry employed in a BWR, the overarching requirement remains to minimise impurities to very low levels in order to avoid a build-up of fuel deposits and to maintain the integrity of the pressure boundary and associated components, amongst other things. During plant operation and outage maintenance activities, the reactor water accumulates impurities due to the ingress of soluble and insoluble metallic and non-metallic species. In terms of materials

degradation threats, the main concern is with soluble non-metallic species, such as chloride and sulphate. These species have a marked impact on both SCC crack initiation and growth rates in stainless steels, and can enhance corrosion rates for carbon steels and low alloy steels. Also of concern is the detrimental impact of copper ingress on the effectiveness of HWC and OLNC, due to the mechanism by which it alters the recombination reaction of oxygen and hydrogen on stainless steel surfaces.

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APPENDIX 9: APPLICATION OF LIMITS AND CONDITIONS OF OPERATION IN CHEMISTRY

Introduction

A9.1.   As defined in LC 23(1), safety cases should "*identify the conditions and limits necessary in the interests of safety*". Limits and conditions (operating rules) are an integral output of any safety case, in defining the boundaries of safe operation. Chemistry is no exception. There are a number of chemistry parameters requiring associated operating rules. In line with the expectations of SAP ECH.1, they should be clearly derived from the safety case and linked to any chemistry claims, with substantiation from operational experience or theoretical analysis. Guidance on ONR's expectations for operating rules is provided in NS-TAST-GD-035 more generally, and specifically for chemistry above in para. 5.24 of this TAG. This Appendix seeks to expand upon both this TAG and NS-TAST-GD-035 for chemistry in operating reactors. Importantly, these should both be read in conjunction with this Appendix. The key objectives of this appendix are therefore to:

    a.   Clarify how the terminology used for LC 23 applies to chemistry;

    b.   Outline ONR's expectations for the identification and characteristics of limits and conditions;

    c.   Explain ONR's expectations with regard to the implementation of limits and conditions.

Terminology

A9.2.   LC23(1) defines "*conditions and limits*" as "*operating rules*". The two terms may therefore be used interchangeably. Different terminology is often used among potential operators and licensees to describe operating rules. They may also be presented at different levels in the hierarchies of safety case documentation. While not exhaustive, this may include terms such as '*technical specifications*', '*environmental specifications*', '*limits and conditions of operation (or LCOs)*' and even '*operating rules*'. 'S*tation operating instructions*' and '*required operating instructions*' may also contain operating rules. There is therefore potential for confusion as to what may constitute the limits and conditions in the interests of safety for chemistry. Importantly, ONR considers all limits and conditions under the definition in LC23, as opposed to any terminology which may be applied by an individual organisation or licensee. For clarity and consistency, the term operating rules is used throughout this TAG.

A9.3.   Additionally, IAEA guidance [10] also introduces the terms '*chemistry control*', '*expected*' and '*limit*' values, while some operators also utilise '*target values*' and '*action levels*'. '*Action levels*' are also presented in various industry guidance documents, including that from the EPRI. '*Expected*' and '*target*' values indicate where a particular parameter may normally be, i.e. it is inside the operating rule or '*limit value*'. '*Action levels*' are the points at which an operator response may be expected in response to breaching these boundaries defined by operating rules, with increasing urgency generally required for breaching higher '*action levels*' due to the quicker degradation mechanisms present.

Identification and Characteristics of Chemistry-Related Operating Rules

What

A9.4.   Chemistry by its nature impacts upon a wide array of plant, structures, systems and components (SSCs). Chemistry parameters and their control may therefore influence reactivity, pressure boundary integrity, fuel and core component integrity, radioactive waste generation and radiological doses to workers and the public. A chemistry programme (as defined in para 5.4 above) should provide the necessary information and assistance for chemistry and radiochemistry for ensuring safe operation, long term

integrity of structures, systems and components, and minimisation of radiation levels. IAEA guide [30] states that "*The control parameters selected should be the most important chemistry parameters for monitoring the chemistry regime and monitoring for the presence of deleterious impurities.*", while Requirement 29 of [10] adds that "*Chemistry surveillance shall be conducted at the plant to verify the effectiveness of chemistry control in plant systems and to verify that structures, systems and components important to safety are operated within the specified chemical limit values*". Appropriate operating rules for chemistry are therefore required to define the boundaries of safe operations of chemistry parameters.

A9.5. There are many sources of industry guidelines of indicative expected ranges and action levels for chemistry related parameters (including EPRI, VGB and EDF – Ref [18]). It is imperative to highlight that these are not always solely derived for safety, nor are these specific for individual reactor designs. ONR considers simply adopting industry guidelines is not sufficient for ensuring safe operations. Importantly, these are not solely derived for safety nor are these specific for individual reactor designs. However, industry guidelines are often authoritative sources of information and may be suitable inputs to deriving appropriate operating rules as part of a plant specific safety case. Importantly, clear distinction should be made where a limit is in the interests of safety or other reasons (i.e. commercial), with prominence given to those important to safety in the safety case to ensure clear visibility and consistency. There may also be instances where operating rules are defined as a result of fuel vendor guarantees which may have an overall safety aim but are particularly conservative. Importantly, inspectors should be aware of the underpinning reasoning for fuel vendor limits to understand the arguments made and importance of limits applied. SAP states that "*A systematic approach should be adopted that identifies the limits and conditions*". Reviewing industry guidelines may therefore form an aspect of such an approach. SAP ECH.3 expands upon this further, presenting ONR's expectation for maintaining chemistry operating rules and setting out some expectations of what chemistry operating rules should cover.

A9.6. It is for the dutyholder to identify operating rules; however, specific examples of chemistry-related operating rules may include:

- minimum concentration of a particular additive in a system;

- maximum concentration of a group of impurities within a system;

- availability of equipment;

- maximum flow rates through a clean-up system.

A9.7. Annex 1 of NS-TAST-GD-035 contains a list of characteristics for operating rules. A selection of those judged to be of most relevance to chemistry is highlighted in Table A9.1 below, with examples of their specific application in chemistry.

Characteristic	Application in chemistry
Operating rules should be a condition or limit, not an instruction	For example: '*reactor water Zn should be <# ppb*', as opposed to: '*cease Zn injection when reactor water Zn is ># ppb*'
Operating rules should be derived from the safety case	For example, minimum levels of zinc purposefully added to control operational radiation exposure should be justified by a plant specific safety case to reduce doses ALARP. Similarly, maximum zinc levels (for example, related to fuel integrity concerns) should also be justified.

Operating rules should be written for the operators, so that compliance can be readily demonstrated	For example, for an additive which may concentrate on fuel surface, it may be more appropriate to place a limit on the total quantities to be injected as opposed to a limit on fuel surface mass loadings. Importantly, the former is directly measureable, therefore compliance can be "controlled", whereas the latter would require fuel to be removed and inspected to ensure the operating rule is adhered to, i.e. after the event.
Operating rules should be specified in directly measurable terms	
Operating rules should be graded, in terms of safety significance	For example, an operating rule for primary water boron concentration in a PWR should have more stringent controls (i.e. it may be a High Hazard Operating Rule (HHOR)) in comparison with an operating rule for "aggressive" anions in a component cooling water system (which may be a Low Hazard Operating Rule (LHOR)). This should be reflected by where the operating rule sits in the safety case hierarchy.
The number of ORs should be minimised	For example, while it may be feasible to measure concentration of specific "aggressive anions", the same means may also be achieved by monitoring higher level, bounding conductivity values.
ORs should cover all modes of operation	As highlighted below, in addition to normal power operation, operating rules should address all modes of operation and transients.
ORs should include operability, settings and availability of SSCs	For example, the availability of clean-up and chemical injection systems.

Table A9.1: Characteristics of ORs

A9.8. It is also important to take cognisance here of SAP ECH.2 (Resolution of conflicting chemical effects). Specifically in regard to these SAPs, chemistry related operating rules should take note of both synergistic and competing effects of chemical parameters. For example, the addition of platinum to complement and reduce the required concentration of hydrogen in a Hydrogen Water Chemistry regime (discussed above in Appendix 8) represents such a synergistic effect. Conversely, balance must be sought between chemistry operating rules which may have competing or negative synergistic effects. Examples here could include operating rules for zinc, which may afford a reduction in dose rate and improved control of primary water stress corrosion cracking at specified concentrations, but may give rise to the formation of tenacious zinc silicate fuel crud at higher levels (for a BWR or PWR).

A9.9. Notably, operators may also identify diagnostic parameters. These may be used to inform trouble shooting or be set on the basis of commercial aims. As above, the definition in LC 23 applies. Where these do not inform maintaining safe operation within prescribed limits and conditions (i.e. they are solely for commercial requirements or to inform trouble shooting), ONR does not consider that these constitute operating rules.

Implementation of Chemistry-Related Operating Rules

When

A9.10. LC 23(3) requires licensees to ensure that their operations "*are at all times controlled and carried out in compliance with [these] operating rules*". Licensees should therefore also consider the temporal nature of any operating rules and transients. Specifically in this regard, [11] highlights that "*Limits for chemistry parameters and conditions for operational and safety systems should be defined by the chemistry group for:*

- *Commissioning;*

- *Startup;*

- *Normal operation;*

- *Transients*

- *Shutdown;*

- *Outages;*

- *Standby;*

- *Decommissioning."*

A9.11. Ref. [11] further adds that where deviations occur outside chemistry limits (operating rules), be it above or below prescribed boundaries, appropriate action(s) should be taken to recover its normal operating value within a specified time. This is consistent with LC 23(3), and expanded upon in para. A9.13 below. Importantly, operating rules represent not only normal safe operating envelope for the facility, but should also include any other limit or condition which needs to be controlled in the interests of safety. This is therefore additional to the expected modes of operation identified in para. A9.10. This is expressed diagrammatically in Figure A9.1 and discussed in more detail below.

How

A9.12. IAEA guidance [11] states "*In addition to control values, expected values may also be specified for internal use by chemistry staff in order to avoid a chemistry parameter inadvertently exceeding its limit value.*" It is therefore clear that IAEA guidance supports a multi-faceted, tiered approach for operating rules and application of expected and limit values as discussed above in para. A9.3. This is presented below in Figure A9.1, utilising reactor water zinc as an example. Here, several operating rules are presented with varying impacts to safety, albeit presented for the same chemical parameter. This includes expected ranges for normal operation (green); administrative limits (amber) and the outermost limits for safe operation (red) as defined by the safety case. Specifically for the Generic Design Assessment of a new reactor, ONR considers that the provision of expected ranges (green) and outermost limits (red) to be sufficient. Importantly, given the definition in LC 23, ONR considers all of these limits presented in Figure A9.1 would constitute operating rules.

A9.13. Ref. [11] also states that "*graded action levels should be specified in advance for control parameters; if deviations from these levels occur, corrective actions should be initiated progressively within an acceptable period of time and further corrective actions should continue to be applied until plant shutdown, if necessary.*" IAEA guidance therefore supports action levels for breaching operating rules being proportionate to the risk presented. Importantly, the action itself and response timeframe should be proportionate to the impact to safety and determined by the safety case. Explicitly, a more rapid and onerous action should be expected where the consequences of not

doing so are greater. For example, the operational response to a deviation of primary water boron concentration in controlling criticality should be greater than that for a deviation in conductivity in an auxiliary cooling water circuit. Similarly, a less onerous response is anticipated for entering an administrative limit (amber region in Figure A9.1) in comparison to breaching an operating rule defining the boundary of safe operations (red region in Figure A9.1). The key difference is in how these are implemented into the safety documentation as indicated in Table A9.1 above. For example, similarly to how a HHOR may be expected to reside further up in a safety case hierarchy (i.e. *'technical specifications'*), a LHOR may reside at a lower level (i.e. *'station operating instructions'*).
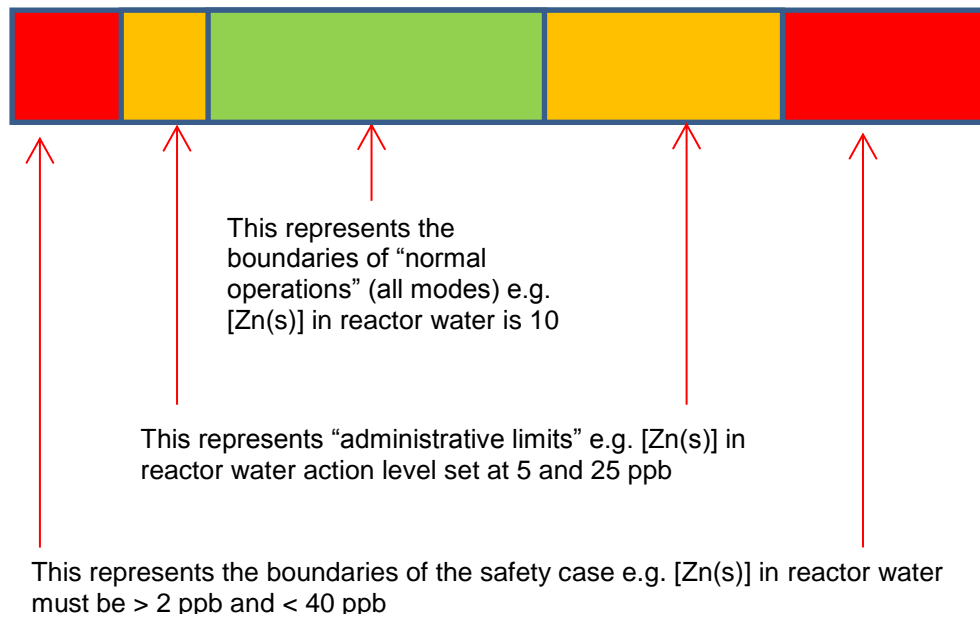
This represents the boundaries of "normal operations" (all modes) e.g. [Zn(s)] in reactor water is 10

This represents "administrative limits" e.g. [Zn(s)] in reactor water action level set at 5 and 25 ppb

This represents the boundaries of the safety case e.g. [Zn(s)] in reactor water must be > 2 ppb and < 40 ppb

Figure A9.1: Pictorial representation of operating rules

References

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