



ONR GUIDE			
CHEMISTRY ASSESSMENT			
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1. INTRODUCTION

1.1 The Office for Nuclear Regulation has established its Safety Assessment Principles (SAPs) [1] 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, and provides further advice and guidance on the assessment of chemistry.

2. PURPOSE AND SCOPE

2.1 The ONR has the responsibility for regulating nuclear and conventional safety, safeguards and security of nuclear sites in Great Britain (GB), in addition to the regulation of the transport of class 7 goods (radioactive material) in GB. The SAPs for Nuclear Facilities provide a framework to guide assessment activities, as part of the permissioning process. ONR's inspectors use the SAPs, together with the supporting TAGs, to guide regulatory decision-making. The objective 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 inspectors in the exercise of their regulatory judgment, and to support SAPs ECH.1 - ECH.4; it provides general guidance on the main issues that should be considered by nuclear inspectors in their assessment of the chemistry aspects of safety cases for all types of nuclear plant and nuclear chemical processes. By following this guidance, the inspector will be able to:

- understand the objectives of the chemistry SAPs and their application to chemistry assessment;
- understand where chemistry assessment interfaces with other technical disciplines in ONR or other regulatory bodies, and the breadth and depth of a potential chemistry assessment; and
- access more detailed technical information regarding the influence of chemistry on specific hazards.

2.3 Chemistry assessment is a broad topic. The assessment of the chemistry of operating civil nuclear reactors is a particular specialist application of chemistry, and is therefore dealt with in a separate, but synergistic TAG on the topic - Chemistry of Operating Civil Nuclear Reactors [3]. This TAG aims to provide more generic advice on the assessment of chemistry aspects of safety cases and as such is broader in scope. Chemistry assessment can also have an important underpinning and supporting role to assessments in other specialisms, as discussed further in paragraph 5.4 onwards.

2.4 This TAG is applicable to new and existing nuclear facilities throughout their design, construction, commissioning and eventual decommissioning. Similarly, the principles described in this guide are applicable through all the modes of operation of a nuclear facility, including normal operations, fault conditions and severe accidents.

2.5 The guidance to inspectors given in Section 5 onwards firstly provides general advice, then considers the chemistry SAPs, and finally provides more specific guidance on aspects of:

- chemical reaction hazards;
- the effects of chemistry on radiation exposure and criticality;
- the effects of chemistry on corrosion and material degradation; and

- the effects of chemistry on control of nuclear matter, radioactive material and radioactive waste.

2.6 There are also four appendices, which provide further information:

- **Appendix 1:** Chemistry interfaces, cross-cutting topics and relevant ONR TAGs.
- **Appendix 2:** Physico-chemical phenomena in the assessment of radiological consequences for accident source terms.
- **Appendix 3:** Material, chemical and radiochemical sampling and analysis.
- **Appendix 4:** The influence of chemistry effects on combustible gases.

2.7 Comments on this guide, and suggestions for future revisions, should be recorded as per ONR procedures.

3. RELATIONSHIP TO LICENCE AND OTHER RELEVANT LEGISLATION

Site Licence Conditions

3.1 The standard conditions attached to a nuclear site licence are described in [4]. The majority of Licence Conditions (LCs) are potentially relevant to chemistry and its consequential impact on hazards; however, the following are generally the most relevant:

- **Licence Condition 7: Incidents on the Site** – records should be kept where a loss of chemistry control has led to consequential hazards or risks.
- **Licence Condition 14: Safety Documentation** – to satisfy this condition chemistry should be considered for new plant or processes. Chemistry requirements for all relevant phases of operations should be considered (i.e. design, construction, manufacture, commissioning, maintenance, operation and decommissioning).
- **Licence Condition 15: Periodic Review** – to satisfy this condition chemistry should be considered for both plant and processes. Periodic reviews should consider chemistry as appropriate.
- **Licence Condition 22: Modification or Experiment on Existing Plant** – any modification to, or experiment on an item of existing plant that may impact the chemical environment, or the claims made on chemistry in the safety case, should be adequately considered and justified.
- **Licence Condition 23: Operating Rules** – for all types of plant where control of chemistry is essential for maintaining a safe operating envelope, appropriate controls should be specified. This should include any chemistry-based limits or conditions. Depending on the relative importance of the chemistry-based limits and conditions to maintaining overall nuclear safety for the plant or process; these should feature in the hierarchy of safety case documentation, as appropriate.
- **Licence Condition 25: Operational Records** – operational records of the key chemistry parameters which must be controlled to maintain nuclear safety should be collated and maintained. This should include data from systems which automatically acquire and process data and the requirement to manage information from manual sampling points and the results of laboratory analyses.
- **Licence Condition 28: Examination, Inspection, Maintenance and Testing (EIMT)** – requires that a licensee makes and implements adequate arrangements for the regular and systematic examination, inspection, maintenance and testing of all plant which may affect safety. This may include a number of engineered systems installed to maintain adequate chemistry control, for example, chemical reagent injection skids, clean-up systems or sampling and monitoring equipment.

3.2 Depending on the scope of the assessment, chemistry may also be of relevance when assessing the following areas:

- LC 10: Training
- LC 12: Duly authorised and other suitably qualified persons
- LC 19: Construction or installation of new plant
- LC 21: Commissioning
- LC 24: Operating instructions
- LC 26: Control and supervision of operations
- LC 27: Safety mechanisms, devices and circuits
- LC 30: Periodic shutdown
- LC 32: Accumulation of radioactive waste
- LC 34: Leakage and escape of radioactive waste and radioactive material
- LC 35: Decommissioning

Other Relevant Legislation

3.3 Other legislation which is potentially of relevance to a chemistry assessment, but is not expected to form the primary focus of a nuclear safety assessment, includes:

- Ionising Radiations Regulations (IRRs) 2017
- Control of Major Accident Hazards (COMAH) Regulations 2015
- Control of Substances Hazardous to Health (CoSHH) Regulations 2002
- Dangerous Substances and Explosives Atmospheres Regulations (DSEAR) 2002

3.4 There are aspects of chemistry assessment that may fall outside the immediate vires of ONR, such as those impacting the Environmental Permitting Regulations (EPR) 2016. ONR Inspectors should be cognisant of any such requirements and engage with the appropriate agency, as required.

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

Chemistry Safety Assessment Principles

4.1 The SAPs 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. The SAPs are split into sections relating to different aspects of nuclear safety; there are four SAPs which deal explicitly with chemistry:

- **ECH.1: Safety cases** – this SAP describes ONR’s expectations for the scope of the consideration of chemistry and its effects on nuclear safety in the preparation of safety cases for nuclear facilities; a key output of which should be any identified limits and conditions (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 requires a demonstration that risks have been reduced to As Low As Reasonably Practicable (ALARP) to be made, proportionate to the level of risk and hazard, where there are a number of chemistry options available.

- **ECH.3: Control of chemistry** – this SAP expects that once the chemistry-based limits and conditions (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 people, processes and technology.
 - **ECH.4: Monitoring, sampling and analysis** – this is an important part of demonstrating adequate chemistry control. This SAP requires that adequate provisions are in place (people, processes and technology) 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.
- 4.2 The overall objective of the chemistry SAPs is to ensure that chemistry and its impact on safety is considered when developing and implementing the safety case for a nuclear facility. The intent behind the chemistry SAPs is that the effects of chemistry can be demonstrated not to detrimentally affect the safe operation of a nuclear facility, that relevant aspects of chemistry reduce risks to ALARP, and that any chemistry required for safety can be adequately controlled.
- 4.3 The chemistry SAPs have been structured to reflect this objective, in that the expected approach for the chemistry aspects of the safety case is that it should demonstrate the following:
- A comprehensive and systematic analysis has been undertaken to identify all chemistry effects important to safety. It is imperative that the analysis derives and justifies any chemistry-based limits or conditions (Operating Rules) which need to be applied in the interests of safety.
 - Consideration of all the chemistry effects identified as being important to safety is performed in a holistic manner; and a balanced demonstration is provided to justify that where the effects of different chemical parameters conflict with one another, the overall outcome is that risks have been reduced to ALARP. Further guidance on the demonstration of ALARP can be found in [5].
 - The systems, processes and procedures designed to maintain chemistry parameters within the limits and conditions identified in the safety case are demonstrated to be adequate.
 - Appropriate consideration has been given to the need for chemical monitoring, sampling and analysis, including the adequacy of laboratory facilities chosen to undertake such analysis.

Other Safety Assessment Principles

- 4.4 In addition to the chemistry-specific SAPs, there are numerous others in which chemistry can be directly inferred, see in particular paragraph 510 of the SAPs. Depending on the particular safety case being assessed, chemistry may be of relevance when assessing against the following SAPs:
- **EAD.1 to EAD.4** – the through-life tolerance of materials to the chemical environment in which they are required to operate should be considered. There should be consideration of the effects of radiation chemistry and factors such as degradation rates and the impact of chronic degradation threats, amongst others, assumed in the safety case.
 - **EMC.2, EMC.3, EMC.13, EMC.16, EMC.21, EMC.22 and EMC.25** – safety case claims made on maintaining a suitable chemical environment for metal components important to maintaining nuclear safety should be considered.

- **ENM.1 to ENM.8** – chemistry has a role to play in the control of nuclear matter, including its distribution, generation and/or accumulation around a nuclear facility. Important chemistry-based considerations also include the adequacy of sampling and analysis to gain characterisation data on the physical, chemical and radiochemical properties of nuclear matter.
 - **EHA.13 and EHA.14** – uncontrolled or unplanned chemical reactions can be a cause of fire or explosions. They may also produce hazardous substances such as toxic or corrosive materials and gases. Where relevant, chemistry may therefore be an input into internal hazards assessment.
 - **EPE.1 and EPE.3 to EPE.5** – the thermodynamics and kinetics of chemical reactions are fundamental to the design and operation of nuclear chemical processes and facilities, and to the analysis of fault and accident conditions on such plant.
 - **ECR.1** – chemical reactions, solvent evaporation, solute precipitation and other chemical phenomena can impact on the presence or effectiveness of neutron poisons and/or the control of fissile material, including the quantity and behaviour of moderators present, such as water.
 - **FA.2, FA.7, FA.9, FA.15, FA.16 and AV.1 to AV.8** – physico-chemical processes can play a significant part in the assessment of the radiological consequences of accidents. Sophisticated computer codes and models, which take account of chemistry phenomena, are often used when undertaking accident analysis.
 - **RW.1, RW.2, RW.4, RW.5, RW.6, RW.7 and DC.1, DC.2, DC.5 and DC.6** – in many circumstances, appropriate chemistry control can minimise the generation and accumulation of radioactive waste. Chemical reactivity should either be removed or minimised to be able to claim passive safety during storage. Decommissioning nuclear facilities often involves designing chemical processes to treat or condition radioactive wastes. Chemical and radiochemical sampling and analysis arrangements are also important factors in determining the quality and quantity of data used to inform strategy decisions for radioactive waste management and decommissioning.
- 4.5 Chemistry can also have a role in helping to fulfil the Fundamental Principles, FP.1 to FP.8; the Safety Case Principles, SC.1 to SC.8; and the Key Engineering Principles EKP.1 to EKP.5. In addition, a number of other SAPs may be relevant, including Safety Classification and Standards ECS.1 to ECS.5; Maintenance, Inspection and Testing EMT.1 to EMT.8; Containment and Ventilation ECV.1 to ECV.10; Radiation Protection RP.1 to RP.6; and Accident Management and Emergency Preparedness AM.1.

Technical Assessment Guides

- 4.6 There are a number of TAGs of potential relevance to chemistry assessment. The most relevant will be determined by the nature of the assessment being undertaken and the sample of the SAPs considered relevant by the inspector. Appendix 1 contains a list of TAGs which are most likely to be relevant.

WENRA Reference Levels

- 4.7 This TAG considers the Western European Nuclear Regulators Association (WENRA) Safety Reference Levels for Existing Reactors [6], Decommissioning Safety Reference Levels [7] and Waste and Spent Fuel Safety Reference Levels [8] for specific applicability to chemistry. Section 4 of NS-TAST-GD-005 [5] states that the WENRA Reference Levels are identified as relevant good practice. Several Safety Reference Levels feature control of chemistry as an important element and are linked to the appropriate International Atomic Energy Agency (IAEA) safety standard.

4.8 Notwithstanding the above, there are no WENRA reference levels explicitly relevant to this guide. Depending on the safety case under consideration, chemistry assessment will, however, contribute to meeting the following Safety Reference Levels for Existing Reactors:

- Issue E: Design basis envelope of existing reactors;
- Issue H: Operational limits and conditions;
- Issue I: Ageing management; and
- Issue K: Maintenance, in-service inspection and functional testing.

4.9 However, Decommissioning Safety Reference Levels and Waste and Spent Fuel Safety Reference Levels should be considered as relevant good practice for all types of nuclear facilities and cover all phases of the lifecycle of nuclear facilities.

IAEA Safety Standards

4.10 IAEA publishes safety standards that are applicable to nuclear power plants, nuclear fuel cycle facilities and research reactors. The standards relevant to reactor chemistry assessment and the requirement for a 'chemistry programme' are discussed in Appendix 2 of [3].

4.11 IAEA's Safety Standard for Nuclear Fuel Cycle Facilities [9], describes various considerations that should be made during the design of such plant, and states, "*the control of events initiated by chemical hazards can have a significant bearing on achieving the fundamental safety objective.*" The document requires consideration of chemistry with respect to material selection and ageing, emergency planning, decommissioning, criticality and the design basis of the plant.

4.12 Depending on the safety case under consideration, IAEA has also published a series of General Safety Guides (GSGs), Specific Safety Guides (SSGs) and other documentation which may be relevant, including:

- The Safety Case and Safety Assessment for the Pre-disposal Management of Radioactive Waste – GSG-3 [10]
- Chemistry Programme for Water Cooled Nuclear Power Plants - IAEA SSG-13 [11]
- Safety of Conversion Facilities and Uranium Enrichment Facilities – SSG-5 [12]
- Safety of Uranium Fuel Fabrication Facilities – SSG-6 [13]
- Safety of Uranium and Plutonium Mixed Oxide Fuel Fabrication Facilities – SSG-7 [14]
- Storage of Spent Nuclear Fuel – SSG-15 [15]
- Decommissioning of Nuclear Fuel Cycle Facilities Safety Guide – WS-G-2. [16]
- Design of Fuel Handling and Storage Systems for Nuclear Power Plants – NS-G-1.4 [17]

4.13 These publications do not all focus specifically on chemistry aspects but do include provisions related to chemistry assessment. For example, the integrity of materials used for the processing and storage of nuclear material, and control of fuel storage pool water chemistry. In addition, some documents (SSG-5 and SSG-7) describe chemical hazards commonly encountered at particular nuclear facilities.

4.14 IAEA has also published a Safety Report, number 56, Approaches and Tools for Severe Accident Analysis for Nuclear Power Plants [18]. This report contains some information of relevance to the assessment of accident chemistry.

- 4.15 This guide is consistent with the requirements of the above documentation and the inspector should consider these documents, as appropriate, where they are judged to provide relevant good practice in chemistry.

5. GENERAL ADVICE TO INSPECTORS

- 5.1 This guide forms part of ONR's wider suite of standards and guidance on chemistry and should therefore be read in conjunction with the chemistry SAPs and the TAG on the Chemistry of Operating Civil Nuclear Reactors [3].
- 5.2 The main purpose of this particular TAG is to provide guidance to inspectors when interpreting both the chemistry SAPs, and those SAPs where chemistry has been identified as having a role in satisfying their requirements (paragraph 4.4).

Terminology

- 5.3 The introductory section to the chemistry SAPs states that 'chemistry' should be interpreted to mean chemical or radiochemical parameters, or effects. The term 'chemistry' therefore encompasses aspects of chemistry, radiochemistry and radiation chemistry. All of these areas may therefore be considered by the inspector when deciding upon the strategy for sampling and assessing chemistry aspects of a safety case. To avoid ambiguity each of the terms is defined as:

- **Chemistry** – a physical science concerned with the composition, properties and reactions of substances.
- **Radiochemistry** – the branch of chemistry concerned with the composition, properties and reactions of nuclear matter, radioactive material and radioactive waste.
- **Radiation chemistry** – the branch of chemistry concerned with the chemical effects, including decomposition, of energetic radiation or particles on matter.

Chemistry Interfaces with other Disciplines

- 5.4 The chemistry SAPs also state that the specific section on chemistry is not intended to stand alone. Although chemistry is dealt with explicitly in SAPs ECH.1 – ECH.4, the scope of chemistry assessment in ONR can be broad, and consequently chemistry has a role to play in assessing against the expectations of numerous SAPs, where the significance of chemistry can often be directly inferred. This is reflected in the large number of SAPs referred to in this guide. Consequently, undertaking a chemistry assessment may necessitate interacting with inspectors from one or more technical disciplines, which may include:
- chemical engineering
 - structural integrity
 - radiological protection
 - internal hazards
 - fault studies/probabilistic safety analysis
 - nuclear liabilities regulation
- 5.5 Chemistry assessment often supports and underpins the assessment in these disciplines. The key point is that ONR's scrutiny of safety cases needs to be able to challenge the chemistry-based claims and assumptions therein, and not simply take them at face value.
- 5.6 It is appropriate to make special mention of the interface between chemistry and chemical engineering. Both disciplines are inextricably linked, yet differ in several important ways, which ultimately mean they should be considered technical disciplines

in their own right. This point is often missed, and the differences between chemistry and chemical engineering are sometimes misunderstood by those outside the disciplines. The chemical (process) engineering SAPs state:

“Chemical engineering (commonly known as Process Engineering) links the underpinning science of processes to the engineering that delivers the required plant functionality”.

- 5.7 In this context chemistry is the subject that provides the underpinning physical science. It is this distinction, one of scale, where the main difference between chemistry and chemical engineering lies. More often than not chemistry is concerned with the development and study of processes and materials in small quantities, whereas chemical engineering is concerned with up-scaling and the engineering of processes to handle much larger quantities, and with making appropriate choices at plant scale to apply the fundamental underpinning scientific knowledge and understanding which chemistry provides.
- 5.8 A chemistry assessment may therefore often be needed to feed into and underpin a chemical engineering assessment. For example, chemical engineering SAP EPE.1 states that the thermodynamics and kinetics of chemical reactions (including side reactions) should be analysed for all normal operation and fault conditions identified in the safety case - this is likely to require input from chemistry specialists.
- 5.9 Further information on the interfaces the chemistry discipline has with other ONR specialisms and some of the typical cross-cutting assessment topics which chemistry would interact with other disciplines on, is provided in Appendix 1.

5.1 SAFETY CASES

Engineering principles: Chemistry	Safety cases	ECH.1
Safety cases should, by applying a systematic process, address all chemistry effects important to safety.		

- 5.10 The inspector should refer to principle ECH.1 when reading the following section. In forming a judgement on the adequacy and completeness of the claims made on chemistry in the safety case, the inspector should pay particular attention to the requirements of a nuclear facility to be designed and operated according to the concept of defence in depth. Chemistry effects claimed for safety can span the five levels of defence in depth. A safety case claim made on chemistry should therefore be interpreted as:
- any requirement or constraint placed on the chemistry of the plant or process which must be met to enable the plant or process to be operated safely;
 - any chemistry related functional requirement which must be met to ensure that the plant or process is operated within its design basis; and
 - any chemistry effect or consequence of chemistry which must be controlled in order to ensure safety, including normal operations, under fault conditions or during severe accidents.
- 5.11 The definition given above means the assumed performance of chemical processes such as demineralisation by ion exchange, filtration, evaporation *etc.*, should also be considered to form part of the chemistry claims, wherever such a process is claimed for nuclear safety. These claims may often be implicit in the safety case but should

nevertheless still be considered in the derivation of chemistry-based limits and conditions (Operating Rules).

- 5.12 A fundamental part of an adequate safety case is the presentation of suitable and sufficient evidence to be able to demonstrate the safety claims and arguments presented are valid. The supporting evidence for chemistry may take a number of forms, but typically may be expected to include:
- relevant operating experience and chemistry standards;
 - the results of calculations and theoretical modelling;
 - experimental trials data;
 - data from laboratory experiments;
 - literature reviews; and
 - data from chemistry sampling and analysis regimes.
- 5.13 There is no hierarchy associated with the acceptability of the supporting evidence for chemistry. The general principle is that first and foremost, the evidence should be applicable to the facility, design or operation under consideration. If generic chemistry is presented instead, the safety case should provide a clear demonstration and justification of its applicability. The inspector may consider the following factors when judging the acceptability of supporting evidence for chemistry:
- The quantity and depth of evidence presented should be proportionate to the magnitude of the hazard and risk under consideration.
 - The quantity and depth of evidence should be commensurate with the technological readiness of the facility or design. For example, due account should be taken of factors such as any novel design features and/or whether the facility is first of a kind.
 - It should be considered whether the limits of the applicability of the evidence are clearly stated.

Fault Analysis

- 5.14 The scope of chemistry assessment is broader than just considering normal operations. Chemical phenomena can have an important role to play in the consideration of radiological consequences in fault or accident conditions. Many approaches to accident analyses, most commonly for reactor facilities, can make assumptions and/or specific claims on the relative importance of these phenomena in justifying acceptable levels of safety. This may directly impact the ability to meet some of the relevant numerical targets laid out in the SAPs.
- 5.15 In addition, the expectations of SAP AV.2 are particularly clear from a chemistry assessment standpoint. The physical and chemical form of radioactivity has to be considered, but also the physical and chemical processes assumed to be taking place, need to be representative. The inspector may therefore consider if these two aspects are adequate, as appropriate.
- 5.16 Sophisticated computer codes and theoretical models are tools and techniques used frequently to undertake accident analyses for nuclear reactor facilities. Depending on the nature of the assessment, from the perspective of considering the relative importance of the assumed chemistry phenomena in making the safety case, the inspector might take into account the degree to which SAPs FA.7, FA.9, FA.15, FA.16 and AV.1 to AV.8 are satisfied.
- 5.17 As well as the fault analysis principles, the inspector may also consider the relevance of the requirements of principle EPE.4, on severe accidents.

- 5.18 Further guidance on the potential role of chemistry in the analysis of the radiological consequences for accident source terms is provided in paragraph 6.27 onwards, and in Appendix 2. Clearly though, where applicable and necessary, chemistry specialist inspectors may be needed to inform ONR's regulatory judgements against some of the numerical targets presented in the SAPs.

5.2 RESOLUTION OF CONFLICTING CHEMISTRY EFFECTS

Engineering principles: Chemistry	Resolution of conflicting chemical effects	ECH.2
Where the effects of different chemistry parameters conflict with one another, the safety case should demonstrate that an appropriate balance for safety has been achieved.		

- 5.19 As well as providing a claims, arguments, evidence approach for chemistry (or alternative approach which achieves the same aims), where appropriate, the safety case should also present a holistic commentary and justification for chemistry.
- 5.20 This is because, as inferred by SAP ECH.2, it is rarely the case that the most appropriate choice of chemistry parameter to manage/control one particular safety issue, is the optimum choice for other chemistry parameter(s) implemented to manage/control similar or different safety issues. The most appropriate choice of chemistry may therefore be a holistic balance between all of the relevant, claimed, safety aims. This also implies the importance of providing clear separation and justification of the aspects of chemistry control which are implemented for safety reasons, from those which may be implemented for other reasons. This particular scenario is commonly encountered for reactor facilities; the inspector should therefore refer to [3] for further guidance, as appropriate.

5.3 CONTROL OF CHEMISTRY

Engineering principles: Chemistry	Control of chemistry	ECH.3
Suitable and sufficient systems, processes and procedures should be provided to maintain chemistry parameters within the limits and conditions identified in the safety case.		

- 5.21 The inspector should refer to principle ECH.3 when reading this section. ECH.3 essentially requires that the basis of chemistry control for a nuclear facility is clearly linked to the chemistry-based limits and conditions (Operating Rules) derived from the safety case.
- 5.22 This means chemistry parameters selected for 'control' should be determined by their relative significance to maintaining nuclear safety and be reflective of the claims made in the safety case. The inspector should consider if the chemistry parameters selected for control are those which broadly define the safe operating envelope, from a chemistry perspective, for the facility. Further guidance on the limits and conditions (Operating Rules) for nuclear plant safety is provided in [19].
- 5.23 'Chemistry control' is a broad term. Adequate arrangements for chemistry control can therefore involve people, technology and plant engineering. The inspector may therefore consider if the following factors have been adequately addressed in the design or licensee's arrangements for chemistry control:

- Whether a holistic process has been followed, where the safety case requirements for chemistry control have not been considered in isolation. A nuclear facility should be designed so that the engineered systems are able to deliver any claimed chemistry-related safety function.
- Where the safety case claims on chemistry control require reliable and rapid action to ensure adequate control is maintained, for example during gross impurity ingress events, the requirements of principle ERL.3 should be considered. Automatically initiated safety features may be required.
- Limits and conditions (Operating Rules) for all phases of operation should be considered, including fault and accident conditions.
- Reliance on undertaking modelling or performing calculations to demonstrate adequate chemistry control and compliance with the safety case should be carefully considered, especially the potential limits of applicability of the models used and calculations being performed.

5.4 MONITORING, SAMPLING AND ANALYSIS

Engineering principles: Chemistry	Monitoring, sampling and analysis	ECH.4
Suitable and sufficient systems, processes and procedures should be provided for monitoring, sampling and analysis so that all chemistry parameters important to safety are properly controlled.		

- 5.24 The inspector should refer to principle ECH.4 when reading this section. The results of chemical and radiochemical analyses can be a key part in demonstrating compliance with the safety case and the on-going safe operation of a nuclear facility. There should therefore be suitable and sufficient chemical and radiochemical laboratory infrastructure and arrangements in place to be able to deliver the requirements of the safety case. The inspector may therefore consider whether the following sampling and analysis requirements have been adequately addressed in the design and/or licensee's arrangements:

Sampling Requirements

- 5.25 The overarching requirement for sampling systems, processes and procedures is that representative sample(s) are obtained at an appropriate frequency. To be able to demonstrate representative sampling can be achieved, the following should have been considered:

- sampling location
- sample collection
- sample longevity, pre-treatment and preservation

- 5.26 Personnel competent in chemistry should be involved from an early stage in the design process to provide advice on matters such as the location of sample points, the method of sampling (i.e. online or offline), the design of sampling equipment, and the significance of analytical parameters. Decisions on the options selected should be informed by the significance of the claims being made on chemistry for maintaining nuclear safety.

Analysis Requirements

- 5.27 Any chemistry parameters which constitute limits and conditions important to maintaining nuclear safety should be derived from the safety case. This should include

a consideration of the range and frequency of the analysis required to ensure chemistry is adequately maintained within specified limits. Further guidance is provided in Appendix 3.

6. CHEMICAL REACTION HAZARDS

- 6.1 This section has been structured according to the main hazards which chemistry either has a direct, or an indirect effect on, and which may therefore be considered by the inspector when judging whether the expectations given in the SAPs have been satisfied.
- 6.2 When considering chemistry and its effects on hazards, ultimately the hazard is created by the physico-chemical and chemical properties of the substances and materials under consideration. Physical properties can include boiling point, flashpoint, auto-ignition temperature, flammability, vapour pressure, thermal sensitivity and oxidising potential. Chemical properties can include chemical reactivity, heat of reaction, self-acceleration and deposition temperature.

Exothermic Chemical Reactions

- 6.3 When considering the chemistry principle ECH.1, the inspector should also be aware of the requirements of the internal hazards principles EHA.13 and EHA.14. Exothermic chemical reactions and pyrophoric materials can be a cause of explosions and/or fire ignition sources. To be able to demonstrate chemistry effects important to safety have been considered systematically, where applicable, there should therefore be a demonstration in the safety case that chemistry has provided an input into the internal hazards assessment. Chemistry would typically focus on aspects such as generation mechanisms, rates etc., whereas the internal hazards assessment would build on this information to evaluate the impact/consequences of an explosion on the Structures, Systems and Components (SSCs).
- 6.4 In addition to the relevant SAPs, other relevant regulations and the DSEAR Regulations require adequate risk assessments in areas where dangerous and explosive substances are present.
- 6.5 Exothermic chemical reactions are a source of excess heat and energy. In the event they are justified as being unavoidable, and/or thermal excursion is identified as a possibility, an adequate understanding of the reaction mechanism, rate (kinetics) and extent (thermodynamics) can ensure a facility is suitably designed and operated to manage the consequential risks and hazards.
- 6.6 Some nuclear fuel cycle facilities use chemical separation (by solvent extraction) to either refine fissile material or separate fissile radionuclides (normally uranium and plutonium) from one another. Such processes make use of organic solvents (typically tri-butyl phosphate (TBP)), diluents (odourless kerosene (OK)) and nitric acid in various concentrations. As well as the radiological hazard, incorrect management of these reagents can lead to a number of exothermic chemical reactions taking place, with potentially hazardous consequences:
- Diluents, organic solvents and solvent/diluent mixtures, when exposed to hot concentrated nitric acid may generate reaction product gases at a high enough rate to initiate loss of containment. The product gases and hydrocarbon vapours released may then form explosive mixtures with air.
 - Solvents such as TBP can react exothermically with nitric acid or solutions of uranyl or plutonium nitrate to produce intermediate chemical compounds known as adducts. Where adducts are present in sufficient concentrations, runaway

decomposition reactions could occur (see below for further information on thermal runaway).

- 6.7 Chemically reactive metals such as: uranium, plutonium, zirconium, hafnium and Magnox (a magnesium-based alloy) are commonly encountered at nuclear facilities. When finely divided or in powder form, they can be pyrophoric and particularly hazardous, resulting in vigorous exothermic chemical reactions. These reactions should be prevented.
- 6.8 When considering the design, or licensee's arrangements for managing the effects of exothermic chemical reactions, the inspector may therefore wish to consider if the following factors have been adequately addressed:
- Whether appropriate consideration has been given to chemistry at the design stage for a new facility. There should be a demonstration that all alternative process chemistries which are able to achieve the same operational purpose for a facility / process have been considered – also see principles EKP.1 and EPE.1.
 - Unintentional or uncontrolled chemical reactions should be avoided or minimised, including the decomposition of reactive chemical species. Where exothermic reactions are unavoidable, there should be a demonstration to justify why adopting process chemistries with a lower energy potential is not reasonably practicable and that suitable control measures are in place – also see principles EKP.1 and EPE.1.
 - The safety case should provide adequate information on the chemistry and thermochemistry of the chemical reactions under consideration. The depth and breadth of the information should be proportionate to the complexity of the chemical process under consideration and the magnitude of the hazards and risks being managed. Typical information may include:
 - heats of reaction for all possible chemical reactions, including a comprehensive assessment of the possibility of thermal decomposition of raw materials, reaction intermediates, reaction products and by-products;
 - identification of whether any exothermic runaway reactions can occur, and;
 - rates of reaction and quantities of heat and gas produced.
 - The scale on which a chemical reaction is performed can have a significant effect on the likelihood of thermal excursion conditions developing, making it an important parameter which should be considered as part of the safety case.
 - Adequate consideration should be given to the surface-to-volume ratio of a reaction system. As this ratio increases it may challenge the design basis of cooling systems. However, assessing the capacity and the adequacy of the design of cooling systems is largely a matter for chemical engineering and other relevant specialists.
 - Whether the presence of pyrophoric material has been considered (e.g. finely divided reactive metal, or some corrosion products of uranium and plutonium such as uranium hydride, which may form in damp, anaerobic environments) and eliminated, so far as is reasonably practicable. Where it is judged not reasonably practicable to eliminate, the propensity for pyrophoric material to initiate or propagate a fire should be considered by the safety case and included as an input into the assessment of internal hazards.
 - Whether the identified chemistry phenomena consider the most hazardous or combination of hazardous sequences.

Combustible Gases

- 6.9 Nuclear facilities have to be able to safely manage the potential generation and combustion of flammable gases, which is an exothermic chemical process. These reactions may occur during both normal operation and under fault or accident conditions.
- 6.10 Of all combustible gases, hydrogen is one of the most prevalent at nuclear facilities, either purposely by design in normal operations, or as a consequence of a fault or accident scenario. Hydrogen hazards must be treated with particular care and rigour owing to the potential magnitude of the consequences of a hydrogen explosion.
- 6.11 Depending on the type of nuclear facility and the conditions under consideration, a number of exothermic chemical reactions can be a source of significant amounts of hydrogen, produced at high rates. Conversely, chemistry can also play an important role in some hydrogen control and mitigation measures which make use of exothermic chemical reactions.
- 6.12 The operating chemistry for some nuclear facilities may require that combustible gases are purposely used. For example, the injection of hydrogen into kilns or furnaces which process uranic powders at fuel cycle facilities. Where the operating chemistry requires the purposeful use of a combustible gas, the inspector should consider the requirements of principle ECH.2.
- 6.13 The impact of chemistry effects on combustible gases is therefore a broad and detailed topic. Further technical detail on the relevant phenomena is provided in Appendix 4 at the end of this guide. This means that as a minimum, the assessment of combustible gases may involve inspectors from a range of disciplines.
- 6.14 When considering the design, or licensee's arrangements for managing the effects of chemistry on combustible gases, the inspector may therefore wish to consider if the following factors have been adequately addressed:
- Chemical reactions which produce combustible gases should be avoided or minimised, so far as is reasonably practicable.
 - Where it is demonstrated not to be reasonably practicable to avoid chemical reactions which produce combustible gases, a robust and systematic approach to their identification should be followed, which should consider:
 - the possibility of unintentional or uncontrolled chemical reactions;
 - rate of gas generation;
 - total amount of combustible gas produced;
 - the dependence of volumetric concentration with time; and
 - the distribution within the facility, including local and global concentrations.
 - The degree to which chemistry effects, both desirable (i.e. catalytic activity and efficiency) and undesirable (e.g. poisoning, elevated temperatures), in combustible gas control and mitigation strategies, have been considered. Such strategies may include:
 - inerting;
 - deliberate combustion using igniters;
 - catalytic oxidation, and/or;
 - combinations of the above.
 - The need to measure combustible gas concentrations should be considered.
 - The extent to which analysis or modelling has been used to determine the location and arrangement of any devices or features with a function to mitigate combustible gases.

Thermal Runaway

- 6.15 Thermal runaway commences when the heat produced by an exothermic chemical reaction exceeds the amount of heat that is lost to the 'environment' by the reaction system. The excess heat raises the temperature within the system, which further increases the rate of reaction. This feedback loop propagates and can lead to a loss of control of a chemical reaction and a number of consequential hazards, for example:
- the initiation of secondary, more hazardous runaway reactions or decompositions;
 - explosion as a result of large increases in temperature and pressure and the possibility of consequential blast or missile damage;
 - release of flammable material and consequential explosion and/or fire; and
 - a loss of containment of hot/corrosive liquors and/or toxic, corrosive or radioactive materials.
- 6.16 Conditions which give rise to thermal runaway therefore need to be avoided. Where applicable, the safety case should provide the demonstration that possible fault scenarios resulting from thermal runaway have been adequately addressed.

Generation of Toxic and Corrosive Materials and Gases

- 6.17 Nuclear facilities can make use of substantial quantities of a number of hazardous chemicals including strong acids, alkalis, solvents and asphyxiants, amongst others.
- 6.18 Chemistry can impact on the rate of production, distribution, magnitude and removal mechanisms for toxic or corrosive materials and gases that may be generated. In addition, good chemistry control will form an important part of the arrangements for demonstrating inventories of hazardous toxic and corrosive materials and gases, which are present by design, are managed safely.
- 6.19 Similar to the consideration of the role of chemistry in fires, explosions and combustible gas generation, the inspector should consider the requirements of the internal hazards principles, EHA.13 and EHA.14; and whether the relevant chemistry aspects have formed an input into the assessment of toxic and corrosive materials and gases. Chemistry would typically focus on aspects such as generation mechanisms, rates *etc.*, whereas other parts of the assessment would build on this information to evaluate the impact/consequences of an explosion on SSCs.
- 6.20 The inspector may consider if the following factors have been adequately addressed in the design or licensee's arrangements for managing the effects of chemistry on the generation of toxic and corrosive materials and gases:
- Chemical reactions which produce toxic and corrosive materials or gases should be avoided or minimised, so far as is reasonably practicable. See principle EKP.1.
 - Where the purposeful use of, or generation of toxic and/or corrosive materials or gases cannot be avoided, their amounts should be minimised and measures to prevent their unintentional accumulation considered.
 - In some circumstances, the design of a nuclear facility may purposely select a toxic or corrosive material specifically for its chemical properties. For example, an acid that is more chemically reactive, giving a faster reaction time. In some cases, this may lead to a shift in the balance of risks from radiological to chemotoxic safety considerations. The inspector should consider principle ECH.2 and whether the safety case provides a demonstration that on balance,

the chosen solution reduces all relevant risks to ALARP. The inspector may wish to work with Conventional Health and Safety inspectors.

- The safety case should identify all foreseeable chemical reactions which could produce toxic and corrosive materials or gases, including unintentional or uncontrolled chemical reactions. This should include the consideration of the most hazardous, or hazardous combination of sequences, which in some cases may mean the chemotoxic consequences of a chemical reaction are more significant than the radiological consequences. For example, the decomposition reaction of uranium hexafluoride with moist air, which forms uranyl fluoride, but also stoichiometric quantities of hydrogen fluoride gas. The materials degradation section provides further guidance on some chemical reactions that may give rise to toxic or corrosive materials and gases at some nuclear facilities.
- Where chemical reactions producing toxic and/or corrosive materials and gases have been identified, the safety case should demonstrate the performance of the engineered systems, including SSCs important to maintaining nuclear safety, are tolerant of the prevailing chemical conditions.

6.1 RADIATION EXPOSURE AND CRITICALITY

- 6.21 All nuclear facilities must be operated, inspected, maintained and decommissioned in accordance with the regulations relating to the use of ionising radiations (the IRRs). A fundamental requirement of the IRRs is to restrict radiation exposure to workers and members of the public SFAIRP, which includes minimisation of sources of radiation.
- 6.22 Chemistry control can have a marked influence on the rate of production of radioactivity and upon its subsequent transport. As such, it plays a part in satisfying some aspects of the control of nuclear matter SAPs. Principle ENM.3 states that unnecessary or unintended generation, transfer or accumulation of nuclear matter should be avoided. The following chemistry effects, amongst others, may therefore have an impact in satisfying the requirements of this SAP and should be given adequate consideration in the safety case:
- solute precipitation
 - solvent evaporation
 - chemical reactions
 - physico-chemical interactions
- 6.23 Of particular note are nuclear fuel cycle facilities which reprocess spent nuclear fuel, which rely on carefully controlling the oxidation states of uranium and plutonium, using various chemical reagents, to adjust the prevailing chemical conditions to achieve their safe separation. Poor chemistry control in these facilities therefore has the potential to lead to the unintended accumulation of fissile material. The safety case should therefore demonstrate suitable and sufficient provisions have been made to maintain adequate control over these particular chemical reagents, both in terms of availability and the required chemical specification.
- 6.24 The role of chemistry in satisfying principle ENM.3 is also applicable to the control of criticality hazards:
- by influencing the concentration of fissile material present in a solution; and
 - by influencing the concentration of soluble neutron poisons (for example boron) in solution.
- 6.25 Where the safety case places claims on the above two factors, it should take into account the role of chemistry in specifying the necessary safety measures (SAP ECR.1), including the consequences of incorrect chemistry control.

- 6.26 Further guidance on the influence of chemistry in minimising sources of radioactivity, transport of radionuclides, and on controlling criticality hazards in civil nuclear reactors, is provided in [3]. This guidance may be equally applicable to other scenarios.

Radiological Source Terms and Accident Chemistry

- 6.27 Chemistry also plays an important role in the analysis of the radiological consequences of postulated accident scenarios for a nuclear facility. It can influence the progression of an accident by determining the phases of materials, their physical and chemical properties, and heat transfer processes. In addition, appropriate estimation of radiological consequences is a fundamental part of justifying the safety of any nuclear facility, and therefore the ability to meet some of the relevant numerical targets presented in the SAPs [1].
- 6.28 For reactor facilities, losing the ability to cool the nuclear fuel contained in the core can lead to fuel failure, releasing fission products (FPs) to the Reactor Coolant System (RCS) and for the most severe accident scenarios, eventual loss of FPs from the RCS into the containment, which may then leak to the environment. These accident scenarios could result in potential radiological consequences to workers and to members of the public. Similar effects might also be taken into consideration in other cases.
- 6.29 In safety cases it is common to make assumptions about the chemical and physical processes that may take place. They therefore have a role to play in estimating radiological consequences following accidents, and ultimately in ONR's judgement on their acceptability. This means that for some safety case assessments, consideration of how chemistry effects are dealt with and/or the specific claims being made on chemistry phenomena, may be an important input into the work of fault studies (including severe accidents) and/or PSA inspectors.
- 6.30 The chemical and physical processes which may occur under accident conditions represent a complicated topic. Appendix 2 provides further technical information on some of the main phenomena, which are dependent on facility design and the accident scenario under consideration, and which may be considered in the safety case when assessing such behaviour. The appendix provides specific details on iodine chemistry phenomena. This is because iodine is one of a small number of radioisotopes with the potential to exist in volatile forms at relatively low temperatures, has an appreciable fission yield, and is particularly radio-toxic and biologically active, and as such is a key consideration in estimating radiological consequences to members of the public.
- 6.31 The inspector may consider if the following factors have been adequately addressed in the design or in the licensee's arrangements for addressing radiological source terms and accident chemistry. The inspector should also be mindful of the guidance provided by the fault studies, assurance of validity of data and models (AV), series of SAPs:
- Radionuclides are often grouped together where they have similar chemical properties such as volatility and solubility. Assumptions made on these factors influence their assumed behaviour in accident scenarios. Any such groupings should be justified as being appropriate to the design and accident scenario under consideration.
 - In calculations, the assumed behaviour of radionuclides is often quantified by the use of release fractions (RFs) and decontamination factors (DFs):
 - the RF is the amount of release of a particular radionuclide with time; and
 - the DF is the proportion of the original amount of a released radionuclide that is removed from the local plant/site 'environment' and assumed unavailable for release.

- RFs and DFs are highly specific to the type, and design of, nuclear facility and accident scenario under consideration. There should therefore be a clear justification of their applicability. It should also be noted that chemical processes may lead to radioactivity being displaced or transported, therefore it may be necessary to consider this in terms of plant operability & fault progression.
- Safety analyses often use sophisticated computer codes. The codes incorporate models of chemistry phenomena to a varying degree of sophistication, based on knowledge gained from experimental programmes. Codes also require varying degrees of user-defined inputs. The inspector may consider:
 - The level of sophistication with which the model describes radionuclide behaviour. Different codes attempt to model chemistry phenomena as part of a more detailed study, whereas others treat chemistry using a limited, but representative number of phenomena. A judgement on the significance of each phenomenon will need to be made on a case-by-case basis.
 - Whether any ‘user effects’ for the chemistry phenomena exist - where user defined inputs are required, code users may make use of different experimental values or engineering judgement, which may impact on the overall calculation result.
 - The validation status of the calculation tools used for chemistry phenomena. In particular, whether they are relevant to the analysis under consideration.
- The inspector may consider whether the chemistry phenomena included in the analysis of accident source terms are claimed as being representative of realistic behaviour i.e. best estimate or more conservative. Regardless of what is claimed, there should be an adequate justification that the chemistry phenomena are applicable to the specific facility design and are representative of the postulated accident sequences. Part of this justification may include the provision of adequate sensitivity analyses (SAP AV.6).
- The inspector may consider the degree to which the safety case makes claims on the success of any purposeful (either active or passive) chemistry control measures to mitigate radiological consequences. For example, some reactor facilities aim to purposefully control (buffer) the pH of in-containment water sources to mitigate the long-term release of iodine during some accident scenarios. The inspector may consider:
 - The significance of any claimed chemistry control measures to the overall safety argument and whether additional, reasonably practicable measures, could be implemented.
 - Whether suitable and sufficient evidence is provided to substantiate the role of purposeful chemistry control (i.e. pH modelling) in the overall radiological consequence analysis.
- The performance of any claimed safety systems to remove and retain radionuclides, the assumed chemical and physical forms of radionuclides, and how these might evolve over the course of an accident are key considerations. For example:
 - Sprays may be used in a reactor containment to provide post-accident cooling or to remove radioactive aerosols. Sprays will not remove noble gases or organic forms of iodine.
 - The effects of safety systems or accident management strategies on physico-chemical phenomena, e.g. the effects of hydrogen burns or autocatalytic recombiners on iodine chemistry – see Appendix 2 for more information.

6.32 Further guidance on radiological source terms and accident chemistry in civil nuclear reactors, is provided in [3] and NS-TAST-GD-042 [20].

6.2 CORROSION AND MATERIALS DEGRADATION

6.33 Maintaining a suitable chemical environment can often be a significant factor in demonstrating that numerous corrosion and materials degradation threats can be safely managed over the operating life of a nuclear facility. The specific degradation mechanisms will depend on a number of factors such as the material(s) selected and the tolerance of the SSC to its operating environment, amongst other considerations. Typically, the materials degradation mechanisms where chemistry is implicated to a greater or lesser extent, and where it can have an impact on the nature, severity and likelihood of materials degradation threats are:

- general corrosion
- pitting
- galvanic corrosion
- crevice corrosion
- erosion/corrosion (EC)
- flow assisted/accelerated corrosion (FAC)
- high temperature oxidation of steels
- stress corrosion cracking, including:
 - intergranular (IGSCC);
 - transgranular (TGSCC);
 - irradiation-assisted (IASCC); and
 - associated with strain, cold work or hydrogen embrittlement;
- intergranular attack (IGA)
- microbially-induced corrosion (MIC)
- environmental fatigue
- radiolytic degradation that may influence corrosion (e.g. the production of hydrochloric acid)

6.34 From a chemistry perspective there are some specific effects which arise as a consequence of some of the degradation mechanisms above, which may require particular attention, as appropriate. For example, the impact of material released during general corrosion on the generation and transport of radioactivity (and any resultant radiation dose), or the deposition of this material on heat transfer surfaces (and any resultant heat transfer impairment). In general, dealing with the anticipated loss of material from general corrosion in this way, is normally dealt with by the selection of an appropriate corrosion allowance. For more localised corrosion threats, such as IGSCC, consideration may turn to the role of chemical impurities on integrity threats and whether they are being adequately controlled.

6.35 In undertaking an assessment of the chemistry aspects of corrosion and materials degradation threats, there is an important interface between ONR's chemistry and structural integrity specialisms. ONR TAG-016 – The Integrity of Metal Structures and Components [21] is relevant, and the inspector should be aware of the guidance contained within this TAG, particularly the sections on ageing and degradation and use of proven materials. The inspector should also be aware of SAPs EAD.1 to EAD.4 and the following SAPs from the integrity of metal components and structures series: EMC.2, EMC.3, EMC.13, EMC.16, EMC.21, EMC.22 and EMC.25.

6.36 While there may be overlap between the scope of chemistry and structural integrity assessments of corrosion and materials degradation threats, there are several key differences. The expectations for structural integrity are beyond the scope of this TAG, so the inspector should consult [21] if any further guidance is required. Broadly though,

for structural integrity, the general expectation is the breadth and depth of the justification and evidence provided to substantiate the performance of a component (including the materials selected) is proportionate to its structural integrity classification.

- 6.37 For chemistry, the criteria are broader. For example, for Light Water Reactors (LWRs), there are components/systems in the balance of plant, which may have a lower structural integrity classification, but which can make a significant contribution to maintaining adequate chemistry control i.e. where corrosion rates can significantly impact the generation and transport of radioactivity (and subsequently dose to workers), or where specific and direct safety case claims are made on being able to actively maintain a certain chemistry (operating environment), i.e. oxygen injection, to mitigate certain degradation threats (i.e. FAC). These aspects may not necessarily form a key part of the 'structural integrity safety case'; however, they may be an important aspect of the overall safety case, which a chemistry assessment may therefore consider, as appropriate.
- 6.38 In summary, this means in the broadest sense, the scope of a chemistry assessment of corrosion and materials degradation threats:
- May seek evidence to justify the materials selected for SSCs, which may not always directly align with the structural integrity classification of components.
 - May consider the impact of materials selection and degradation threats on other hazards/risks e.g. radioactivity generation, transport, deposition and dose to workers, and whether on balance, relevant risks are reduced to ALARP.
 - May consider the impact of chronic as well as acute degradation threats.
 - Does not in itself directly consider the consequences of component failure.
- 6.39 In addition to the high-level matters given above, the inspector may also consider if the following factors have been adequately addressed in the design or in the licensee's arrangements for addressing corrosion and materials degradation issues:
- There is a clear demonstration that the starting point for mitigating materials degradation threats is not to place reliance on active chemistry control(s), where it is reasonably practicable not to do so. SAP EKP.1 is particularly pertinent here. Some degradation threats can effectively be 'eliminated' by informed materials selection decisions. For example, FAC in some reactor facility systems constructed from carbon steel, by selecting a material with elevated chromium content. This is just one example; there may also be other relevant factors which require consideration.
 - The impact of chemistry and materials selection decisions has been considered holistically, and an optimised approach is demonstrably reached. This is particularly important at the design stage for a nuclear facility, or where potential changes to materials and/or chemistry control are being considered.
 - Suitable and sufficient evidence is available to demonstrate the safety case claims made on the impact of the operating environment (i.e. chemistry) on corrosion and materials degradation threats (through-life degradation) are justified. This should include appropriate consideration of 'bulk' and 'local' chemistry effects and consideration of all relevant OPEX regarding materials degradation threats, to identify any known problem areas.
 - Where careful control of the operating environment (i.e. chemistry) for an SSC is a particularly important consideration for maintaining nuclear safety, the safety case should provide an adequate justification for the chemistry-based limits and conditions (Operating Rules).

- Whether additional hazards created by the corrosion of metallic components have been adequately considered. For example, the generation and/or accumulation of hydrogen.
 - Whether there are other matters pertinent to the assessment of the chemistry aspects of corrosion and materials degradation which the inspector may choose to consider. For example:
 - surface finishes or materials treatment;
 - use of chemical inhibitors to prevent/mitigate corrosion; and
 - the impact of corrosion on clean-up system performance.
- 6.40 Further specific information on these topics and other matters related to assessing the impact of chemistry on materials integrity, is provided in [3]. The inspector should consider the relevant aspects of the guidance in [3] and its applicability, as appropriate.

Non-metallic Materials

- 6.41 As well as impacting the degradation and through-life integrity of metallic components, the chemical degradation of matter by radiation (radiation chemistry) can also have important consequences for other materials and conditions that may be present at nuclear facilities, examples include:
- the corrosion of graphite in some nuclear reactor cores;
 - the degradation of organic materials;
 - radiation chemistry of nitrate, nitric acid and TBP systems; and
 - radiation chemistry of aqueous systems.
- 6.42 An important degradation mechanism in gas-cooled graphite moderated reactors is the radiation induced oxidation of the graphite core by carbon dioxide, and associated phenomena, such as carbon deposition. Further details are contained in [3].
- 6.43 Organic material may commonly be present in the form of waste oils or solvents. Some ion exchange media are polymeric resins, which if exposed to a high enough radiation dose, can cause spent resins to lose their functionality and release radioactivity. Other commonly encountered materials at nuclear facilities containing organics include cable insulation, often made from Polyvinyl Chloride (PVC). Under certain conditions PVC can degrade over time, resulting in other consequential hazards. For example, the evolution of hydrochloric acid. This can lead to the formation of a corrosive environment, and/or the generation of hydrogen, which may accumulate to form an explosive atmosphere.
- 6.44 Polymeric materials have also been used to encapsulate some radioactive wastes and are being proposed as possible alternatives for the encapsulation of chemically reactive metals. Depending on the type of organic material, radiation type and prevailing chemical conditions, radiolysis of these materials can result in degradation, forming potentially corrosive, toxic or combustible gases including hydrogen, methane, hydrochloric acid, and hydrogen sulphide, amongst others.
- 6.45 For nuclear fuel cycle facilities which either refine or chemically separate fissile material, radiation chemistry of nitrate, nitric acid and TBP systems should also be given adequate consideration in the safety case.
- 6.46 For some aqueous systems water is purposely present to provide a cooling safety function, for example, in a LWR. In these circumstances the presence of water is unavoidable, so the consequences of the coolant undergoing radiolysis, ultimately to form hydrogen and oxygen, amongst other chemical species, on the safe operation of the plant, must be adequately addressed in the safety case. In this instance, the

operating chemistry can directly influence the radiolysis mechanism. Further guidance is presented in [3], see principle ECH.2.

- 6.47 Another circumstance where water may be present and its radiolysis products problematic, is the long-term safe storage of nuclear matter, radioactive materials and radioactive waste. The radiolysis of moist air can result in the formation of acidic nitrogen species including nitric acid. Radiolysis of water and other contaminants can therefore be particularly problematic when storing high dose-rate material such as plutonium. Most forms of plutonium are chemically reactive. Almost all potential problems arise from the chemical interactions of the plutonium with air, moisture, or radiolytic breakdown products.
- 6.48 Section 7 provides further guidance on chemistry considerations that may be important where passive safety is claimed. Some of the guidance is also relevant to the consideration of the impacts of the degradation of non-metallic materials.

7. CONTROL OF NUCLEAR MATTER, RADIOACTIVE MATERIAL AND RADIOACTIVE WASTE

- 7.1 Radioactive waste management is principally concerned with developing and implementing strategies to achieve the safe and efficient processing, storage and eventual disposal of waste. In ONR, these are the activities which nuclear liabilities regulation specialists mostly deal with. It is also important to recognise this is the topic where ONR chemistry specialists may most likely need to interact with regulatory colleagues responsible for regulating discharges to the environment i.e. EA, Natural Resources Wales (NRW) and/or the Scottish Environment Protection Agency (SEPA). Further information related more generally to radioactive waste management issues is provided in the Joint Regulatory Guidance on the Management of Higher Activity Waste (HAW) [22] and ONR's TAG on the Management of Radioactive Materials and Radioactive Waste on Nuclear Licenced Sites [23].
- 7.2 Predominately, chemistry assessment sits a level beneath these activities and may have a role to play in implementing strategies for managing radioactive waste and in the development of the supporting safety case. However, in some instances, it may act as one of the inputs to developing the radioactive waste management strategies themselves. Chemistry can therefore be involved to a greater or lesser extent, in most of the steps involved in radioactive waste management on a nuclear licenced site:
- **Waste generation** – good chemistry control can reduce the radioactivity content and overall volume of wastes. An adequate understanding of the physical and chemical properties of the waste from the outset can minimise secondary wastes and support effective segregation.
 - **Pre-treatment** – may include chemically adjusting waste to stabilise or passivate it or using chemical decontamination techniques to remove radioactivity or other chemical contaminants.
 - **Treatment** – utilising chemical processes to selectively remove radionuclides. For liquid effluents this may include filtration or ion exchange media. Precipitation or flocculation may also be used to selectively partition radionuclides from one phase to another. Chemical processes can also be used for waste volume reduction.
 - **Conditioning** – chemical processes to immobilise waste. Depending on waste type, examples include solidification in cement, encapsulation in polymers and vitrification. Chemistry can be used to develop novel encapsulants.
 - **Storage** – the key principle is achieving passive safety. Removing or suppressing chemical reactivity is fundamental.

7.3 SAPs ENM.6 and RW.5 convey the expectation that nuclear matter and radioactive waste should be stored in a passively safe condition. To achieve passive safety, the radioactivity should be immobilised, and packaged in a form that is physically and chemically stable. Where passive safety is being claimed the inspector may consider the following:

- Whether all reasonably practicable steps have been taken to remove or suppress chemical reactivity. This may include:
 - removing or passivating reactive metals or pyrophoric materials in order to reach thermodynamically stable states;
 - the need to remove moisture to acceptably low levels, to minimise the risk of corrosion and/or gas generation through radiolysis, which may threaten containment; and
 - removing organic materials and contaminants which may degrade over time to form combustible or toxic gases, which may leak or pressurise storage containers.
- Whether adequate consideration has been given to the chemical compatibility of the waste, waste form, nuclear matter, or radioactive material, with its proposed storage container and environment. This may include:
 - minimising the likelihood of deleterious chemical reactions occurring, which may evolve slowly over time, but which may chemically degrade the performance of the storage container;
 - minimising the potential to create conditions in immobilised radioactive waste where gases, liquids or expansive corrosion products are formed;
 - purposely adjusting the chemical environment to mitigate risks and hazards, e.g. microbial control, corrosion inhibition.
- Whether adequate consideration has been given to the physical form of the stored material and the impact on any resultant hazards. For example:
 - where appropriate for the material under consideration, thermal stabilisation, where reasonably practicable, to reduce the specific surface area.
- The safety case may consider venting to mitigate the risk of accumulating corrosive, toxic or flammable gases and materials during storage. In these circumstances, consideration may be given by the inspector to the following:
 - dispersability of the material under fault or accident conditions. For example, loose oxide powders are dispersible, metal is not.
 - some materials may blind filters, reducing their efficiency and hampering the ventilation systems' ability to disperse toxic, corrosive or combustible gases, or in the worst case, the filters may become completely obstructed.
- Whether provisions have been made to undertake representative sampling, as prescribed by the safety case, to confirm passive safety is being maintained.

7.4 Further information and expectations for the passively safe storage of radioactive waste and nuclear matter are available in [22] and [24].

7.5 One of the key success criteria for implementing a strategy to manage nuclear matter, radioactive waste, or radioactive material is having suitable and sufficient information to make informed decisions. Importantly, this involves having and maintaining an adequate understanding of physical, chemical and radiochemical properties; see principles ENM.5 and RW.4. The inspector may consider:

- Whether the quality and quantity of data on the physical, chemical and radiochemical characteristics of nuclear matter, radioactive waste, or

radioactive material is sufficient to support decisions on the selection of preferred options for their management.

- For legacy, or unconditioned ('raw') nuclear matter, radioactive waste or radioactive material, whether consideration has been given to if it is reasonably practicable to undertake more frequent characterisation campaigns to ensure the physical, chemical and radiochemical characteristics evolve as anticipated.
- Where characterisation is required, there should be a demonstration in the safety case of the options considered, and that all relevant risks from undertaking the activity have been reduced to ALARP.

7.6 Where the need to characterise nuclear matter, radioactive waste or radioactive material has been identified, the methods selected to undertake chemical and radiochemical sampling and analysis can have a direct impact on the quality of the information obtained. In addition to discrete sampling and analysis campaigns, maintaining a nuclear facility in a safe operating state may also require much more frequent sampling and analysis to take place. Section 5.4 and Appendix 3 provide more guidance on chemical and radiochemical sampling and analysis.

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GLOSSARY AND ABBREVIATIONS

ACoP	Approved Code of Practice
AGR	Advanced Gas Cooled Reactor
AICC	Adiabatic Isochoric Complete Combustion
ALARP	As Low as Reasonably Practicable
BWR	Boiling Water Reactor
CfA	Conditions for Acceptance
CFD	Computational Fluid Dynamics
C&I	Control and Instrumentation
COMAH	Control of Major Accident Hazards
COSHH	Control of Substances Hazardous to Health
DDT	Deflagration to Detonation Transition
DF	Decontamination Factor
DSEAR	Dangerous Substances and Explosive Atmospheres Regulations
EA	Environment Agency
EC	Erosion/corrosion
EPR	Environmental Permitting Regulations
FAC	Flow Assisted/Accelerated Corrosion
FP	Fission product(s)
HAW	Higher Activity Waste
HSE	Health and Safety Executive
HSWA	The Health and Safety at Work etc. Act 1974
IAEA	International Atomic Energy Agency
IASCC	Irradiation Assisted Stress Corrosion Cracking
IGA	Intergranular Attack
IGSCC	Intergranular Stress Corrosion Cracking
IRRs	Ionising Radiation Regulations
LEL	Lower Explosive Limit
LC	Licence Condition(s)
LFL	Lower Flammability Limit
LoD	Limit of Detection
LoQ	Limit of Quantification
LP	Lumped Parameter
LWR	Light Water Reactor
MIC	Microbially-induced Corrosion
NRW	Natural Resources Wales
OK	Odourless Kerosene

OPEX	Operating Experience Feedback
PAR	Passive Autocatalytic Recombiner
PSA	Probabilistic Safety Analysis
PSR	Periodic Safety Review
PVC	Polyvinyl chloride
PWR	Pressurised Water Reactor
RCS	Reactor Coolant System
RF	Release Fraction
RPV	Reactor Pressure Vessel
SAP	Safety Assessment Principle(s)
SCC	Stress Corrosion Cracking
SFAIRP	So Far as is Reasonably Practicable
SEPA	Scottish Environment Protection Agency
SQEP	Suitably Qualified and Experienced
SSA	Specific Surface Area
SSC	Structures, Systems and Components
SSG	Specific Safety Guide
TAG	Technical Assessment Guide(s)
TBP	Tri-butyl Phosphate
TGSCC	Transgranular Stress Corrosion Cracking
TMI	Three Mile Island
UEL	Upper Explosive Limit
UFL	Upper Flammable Limit
VCT	Volume Control Tank
WENRA	Western European Nuclear Regulators' Association



8. APPENDICES

Appendix 1: Chemistry Interfaces, Cross-Cutting Topics and relevant ONR TAGs.

Appendix 2: Physico-chemical Phenomena in the Assessment of Radiological Consequences for Accident Source Terms for LWRs.

Appendix 3: Material, Chemical and Radiochemical Sampling and Analysis.

Appendix 4: The Influence of Chemistry Effects on Combustible Gases.

APPENDIX 1: CHEMISTRY INTERFACES, CROSS-CUTTING TOPICS AND RELEVANT ONR TAGS

	Interfacing ONR discipline	Cross-cutting topic
Chemistry	Chemical engineering	<ul style="list-style-type: none"> Inherent safety – avoiding uncontrolled or unintentional chemical reactions; Reaction rates, timings and thermodynamics; Exothermic chemical reactions – thermal excursion; Experimental processes; Limits and conditions (Operating Rules);
	Structural integrity	<ul style="list-style-type: none"> Chemical operating environment of metallic components and other materials; Ageing management – through-life degradation of materials and components; Limits and conditions (Operating Rules)
	Radiological protection	<ul style="list-style-type: none"> Minimisation of sources of radioactivity; Reduction in the deposition, accumulation and transport of radioactivity; Criticality control of fissile material.
	Internal hazards	<ul style="list-style-type: none"> Minimisation of hazardous materials; Combustible gas source terms and explosion hazards; Generation, accumulation and distribution of toxic or corrosive gases and materials; Exothermic chemical reactions - thermal runaway, ignition sources.
	Fault studies/PSA	<ul style="list-style-type: none"> Combustible gas source terms and management strategies; Radiological consequence assessment - accident source terms; Limits and conditions (Operating Rules)
	Nuclear liabilities regulation	<ul style="list-style-type: none"> Passive safety; Representative sampling and characterisation; Limits and conditions (Operating Rules); Waste minimisation; Strategies.

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	Civil Engineering Containments for reactor plants
NS-TAST-GD-021	Containment: chemical plants
NS-TAST-GD-023	Control of processes involving nuclear matter
NS-TAST-GD-024	Management of radioactive material and radioactive waste on nuclear licensed sites
NS-TAST-GD-034	Transient analysis for DBAs in nuclear reactors
NS-TAST-GD-035	The limits and conditions for nuclear safety (operating rules)
NS-TAST-GD-038	Radiological protection
NS-TAST-GD-041	Criticality safety
NS-TAST-GD-042	Validation of computer codes and calculation methods
NS-TAST-GD-043	Radiological analysis normal operation
NS-TAST-GD-045	Radiological analysis fault conditions
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-088	Chemistry of operating civil nuclear reactors
NS-TAST-GD-094	Categorisation of safety functions and classification of structures and components

APPENDIX 2: PHYSICO-CHEMICAL PHENOMENA IN THE ASSESSMENT OF RADIOLOGICAL CONSEQUENCES FOR ACCIDENT SOURCE TERMS

- A2.1 This appendix provides more details on some of the physico-chemical phenomena involved in accident analysis source terms, including but not limited to source terms for LWRs. This is a particularly complex topic and consequently large parts of it are both beyond the scope of this TAG and chemistry assessment in general. This appendix, therefore, does not provide a detailed overview of accident progression in LWRs.
- A2.2 The appendix provides a brief description of the topics a chemistry inspector may typically look at when performing an assessment of the chemistry aspects of the radiological consequence analysis presented in some safety cases. The appendix then intentionally focusses on the specific example of iodine phenomena, to exemplify how some of the general topics introduced are specifically addressed, from a chemistry perspective. Therefore, while this appendix refers to LWRs, the topics covered may be equally applicable to other nuclear facilities and/or accident scenarios as appropriate; the caveat being that radioactivity release and transport during accidents tends to be very design specific.
- A2.3 Typical topics that may need to be considered by the chemistry inspector when performing an assessment of the chemistry aspects of the radiological consequence analysis presented in some safety cases are as follows:

Radioactivity Physical and Chemical Form

- A2.4 The chemical and physical form of radioactivity plays an important role in determining the relevant phenomena which govern its long-term post-accident behaviour. Chemically, radioactivity can either be in organic or inorganic forms; this dictates important properties such as volatility and solubility. Physically, radioactivity will either be in the form of gases or particles (aerosols). Overall, designing engineered safety systems capable of mitigating releases of radioactivity following accidents, requires an adequate understanding of the physical and chemical form of the radioactivity expected to be present.

Deposition/Retention Processes and Mechanisms

- A2.5 Several different mechanisms can lead to the natural deposition of aerosols on surfaces during an accident. Natural and purposeful processes (i.e. the action of engineered systems) which occur can decontaminate the atmosphere early in an accident and act as 'sinks' for radioactivity. Natural processes may include gravitational settling, diffusive deposition, thermophoresis and diffusiophoresis.

Re-distribution Processes and Mechanisms

- A2.6 Physico-chemical processes can evolve in the later stages of an accident and may re-volatilise or re-suspend some, or all, of the radioactivity deposited during the earlier phases of the accident scenario. Re-suspension processes typically occur when there is a sharp variation in thermal-hydraulic conditions e.g. differences in pressure, temperature and/or heat transfer characteristics. The impact of radioactive decay and radiation chemistry can also therefore have important effects. For example, decay heat can impact natural convection, relative humidity and condensation phenomena.

Engineered Systems

A2.7 The activation of certain systems or components, whether routine, purposeful, or otherwise, during an accident scenario, can impact the physico-chemical phenomena described above and the progression of the accident. For example:

- the transportation characteristics of fluids and aerosols may be altered by the presence of fans or doors;
- the action of engineered safety systems designed to mitigate the radiological consequences of an accident, including sprays, filtered containment ventilation systems, suppression pools and/or heat removal systems.

A2.8 Further information on the above topics can be found in references: [25], [26] and [27].

EXAMPLE: IODINE PHENOMENA [27], [28], [29]

A2.9 In the early 1960s, safety assessments of reactor accidents assumed the physical form of iodine entering containment was predominately volatile molecular iodine. More recent events in the nuclear industry, namely the reactor accident at Three Mile Island (TMI), sparked intense research efforts to gain a better understanding of iodine behaviour under severe accident conditions. Iodine is particularly important because it is one of a small number of radioisotopes with the potential to exist in volatile forms at relatively low temperatures. In addition, it has an appreciable fission yield and is particularly radio-toxic and biologically active.

A2.10 A much better understanding of the phenomena governing the behaviour of iodine under severe accident conditions has now been established. The analysis of most reactor accidents now assumes, for example, the physical form of iodine released from the RCS during a severe accident is predominately in the form of aerosols of metal iodides e.g. caesium iodide; accompanied by a much smaller fraction of volatile iodine in the gas phase.

A2.11 The majority of the physico-chemical phenomena which dictate the behaviour of iodine have been identified. The sophisticated computer codes used in the analysis of reactor accidents incorporate models to address most of these phenomena. Despite appreciable advances in the field of iodine chemistry over the last several decades, the results of more recent experimental and modelling research programmes suggest the complexity of different iodine phenomena and their interactions are still not fully understood.

A2.12 Iodine exhibits a complex chemistry which determines its chemical form, and which means there are potentially a wide variety of forms of iodine present in a post-accident reactor containment, each with a varying degree of volatility. The major iodine species important in reactor accidents are shown in Table A2.1 below.

Table A2.1: Major iodine species in reactor accidents

Iodine species	Physical form	Volatility
Caesium iodide - CsI	Aerosol	Involatile
Silver iodide - AgI	Solid – insoluble	Involatile
Iodide – I ⁻	Aqueous	Involatile
Molecular iodine – I ₂	Aqueous/gaseous	Volatile
Organic iodides – RI, CH ₃ I	Gaseous	Volatile
Iodate – IO ₃ ⁻	Aqueous	Involatile
Iodine oxides - I _x O _y	Aerosols	Involatile
Hypoiodous acid - HOI	Aqueous/gaseous	Volatile
Hydroiodic acid - HI	Aqueous/gaseous	Volatile

A2.13 Numerous chemical phenomena exist in a post-accident containment, which result in a dynamic process where the released iodine is converted from one chemical (and/or physical) form to another. From a nuclear safety perspective, the most important chemical processes to understand and confidently predict are those which lead to the evolution of gaseous iodine. The main chemical reactions and phenomena which are currently understood to influence this process are:

- the fraction of gaseous iodine entering containment from the RCS;
- radiolytically induced formation of volatile iodine species in containment water sources and their release to the containment atmosphere;
- adsorption and desorption processes of iodine on containment surfaces, surface treatment (i.e. painted or un-painted) and the potential formation of organic iodides; and
- volatile iodine interacting with air radiolysis products and the fate of the resulting oxidation products.

A2.14 The following subsections summarise the main chemical and physical processes and chemistry-based phenomena which are understood to influence the behaviour of iodine under severe reactor accident conditions.

Iodine Behaviour in the RCS [27], [28], [29]

A2.15 Intense research in the field of iodine chemistry in reactor accidents has showed that caesium iodide is not the only likely chemical form. The equal importance of both thermodynamics and kinetics has been realised, as well as the effect of certain structural materials and FPs on the chemical speciation of iodine. Considering the case of a Pressurised Water Reactor (PWR) with silver-indium-cadmium control rods, experiments have shown other possible chemical forms of iodine may include rubidium iodide, indium iodide, cadmium iodide and/or silver iodide. Regardless of the chemical form these initial iodine vapours take, as the RCS cools, iodine-bearing aerosol particles will form.

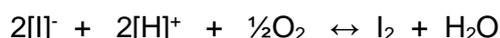
In-containment Iodine Phenomena [27], [28], [29]

A2.16 A large fraction of the core inventory of iodine could eventually reach the containment during an accident. Of this fraction, between 2- 4% of the fuel bundle iodine inventory could be in the gas phase. This means that in the early stages of a severe accident, the in-containment concentration of gaseous iodine is dominated by the fraction initially released from the degrading core.

A2.17 The assumption is though, that the largest fraction of iodine exits the RCS in the form of suspended aerosols composed of metal iodides. The aerosol physics phenomena and deposition mechanisms for FPs previously described above mean that in the short-term, the largest fraction of iodine would be expected to deposit on in-containment surfaces.

Aqueous phase chemistry

A2.18 Most metal-iodides are soluble and will readily dissolve in containment bulk water sources to yield iodide ions. Unfortunately, there are a number of thermal and radiolytic chemical reactions, forming a range of species, that can occur in containment bulk water sources or on surfaces, under accident conditions, which cause the oxidation of iodide to volatile iodine:

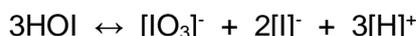


A2.19 This means a fraction of the iodine released from the core and initially dissolved as non-volatile iodide ions can become available for re-release to the containment as the accident progresses. The steady-state fraction of volatile iodine is therefore the net balance of numerous chemical reactions. The extent of volatile iodine production in aqueous conditions depends on:

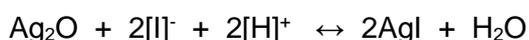
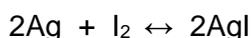
- pH – acidic conditions favour the formation of iodine;
- dose rate – directly influenced by FPs entering the containment following the accident; higher rate promotes radiolytic reactions;
- temperature – low temperatures favour the formation of volatile iodine species; and
- redox potential – the presence of reducing species, for example hydrogen, should decrease the formation of volatile iodine species.

A2.20 There are also a number of competing formation and decomposition hydrolytic and radiolytic reactions which result in a steady-state concentration of organic iodides. In-containment water sources may contain dissolved or suspended organic impurities which iodide ions or iodine may react with. Organic iodine may also be formed from iodine reactions with immersed painted surfaces. Some organic iodides are also volatile, leading to further partitioning of iodine to the containment atmosphere.

A2.21 As well as reacting with impurities which may be present, any iodine formed can also undergo hydrolysis, forming hypoiodous acid as a product. Hypoiodous acid itself may then decompose:



A2.22 For PWRs, if silver is present in the water in excess to the iodine concentration, as a result of control rod melting, experiments have shown it can effectively suppress iodine volatility, precipitating solid silver iodide. This mechanism can occur for both metallic and oxidised forms of silver:



A2.23 The relative success and efficiency of these two reactions is determined by a number of factors, which results in significant uncertainties when determining the degree of silver suppression on iodine volatility. Factors include:

- number of silver particles entering containment;
- whether the silver particles are contaminated by other FPs or structural material degradation products;
- silver oxidation state before entering in-containment water sources;
- radiolytic decomposition of silver iodide in the presence of beta radiation.

Gas-liquid Partitioning

- A2.24 Mass transfer of volatile iodine species between the liquid and gas phase can occur, increasing the iodine concentration in the containment atmosphere. The important thermodynamic parameter to consider is the partition coefficient, which is defined as the ratio of the concentrations of volatile species in the liquid and gas phases. The overall iodine partition coefficient will therefore depend on the concentrations of volatile species in the solution and their individual partition coefficients.
- A2.25 Some safety analyses may claim acceptable partition coefficients as a function of pH. The lower the pH, the greater the concentration of volatile iodine species in solution, which then partition to the atmosphere. The strategy adopted at some plants exploits this tendency by using engineered measures to maintain control of the pH of in-containment water sources.
- A2.26 Where this is not implemented, a calculation may have to be performed to predict the pH profile with time as the accident progresses, to demonstrate an acceptable pH/partition coefficient is maintained. This is a complex calculation and the methodology should consider all potential sources of acidic and basic chemical species which may be present during an accident. These may include:
- soluble sources of neutron poisons, e.g. boric acid;
 - carbon dioxide – present in air and adsorbed by water to produce carbonic acid;
 - caesium hydroxide – strongly basic, introduced during accidents from the degrading core;
 - core-concrete aerosols – produced during the ex-vessel phase of some accident scenarios;
 - dissolved products from the radiolysis of moist air under accident conditions to produce nitric acid;
 - hydrochloric acid – formed during accidents from the radiolysis or burning of chloride-bearing insulation on cables;
 - hydroiodic acid – the chemical form of some of the iodine fraction released from the degrading core during an accident;
 - organic impurities which may react with water radiolysis products to form organic acids.

Gas Phase Chemistry

- A2.27 From a nuclear safety standpoint, developing an adequate understanding of the processes which govern the concentration of gaseous radioiodine (i.e. iodine volatility) in the containment atmosphere of nuclear reactors is fundamental to the demonstration of safety. This is principally because in the event of purposeful venting, leakage or failure of the containment, the gaseous radioiodine contained in the atmosphere may constitute a dominant source of the total radioactivity released to the environment under these scenarios.
- A2.28 The volatile forms of iodine are molecular iodine and organic iodides, the most volatile of which under nuclear reactor accident scenarios tends to be methyl iodide. There are a number of mechanisms responsible for the formation of organic iodides, including reaction of iodine with organic species dissolved in in-containment water sources, or

reaction of any iodine which has partitioned from the liquid to the gas phase, with organic species in the gas phase. The formation of volatile organic iodides can be particularly problematic, as when compared to molecular iodine, they are less easily scrubbed or filtered from the containment atmosphere, which introduces further uncertainty in the estimation of radiological consequences for some reactor accident scenarios.

- A2.29 In addition, there is the added complication of the radiolytic reactions of iodine which may take place in the gas phase. The effect of radiation on the gases present in the containment atmosphere (i.e. oxygen, nitrogen, steam), produces a number of chemically reactive decomposition products. Reaction with these can lead to the decomposition/conversion of organic iodides and iodine into involatile iodine oxides. This may lead to a reduction in the concentration of iodine in the gas phase (and therefore in the amount available for potential release to the environment), as iodine oxides deposit on any in-containment surfaces including walls, pipework etc., aerosols or water droplets, or re-dissolve in water sources. There is still considerable uncertainty, however, as to the dominance of this mechanism in reducing iodine volatility. Iodine oxide solids are hygroscopic and the impact of radiation in post-accident reactor containments, means further conversion into other physical and chemical forms is likely.
- A2.30 Iodine contained in the containment atmosphere will undergo adsorption and desorption from a number of in-containment surfaces, each of which will have a different affinity for iodine depending on a number of factors i.e. material type, moisture content etc. Each of these can therefore impact iodine volatility in different ways. Painted surfaces are commonly encountered in the containments of nuclear reactors, mainly to mitigate corrosion phenomena. Consequently, the action of painted surfaces on iodine behaviour may also be an important factor and has therefore been explored by a number of experimental programmes, to seek to gain a better understanding of the relative importance of this phenomenon in determining the behaviour of iodine.
- A2.31 The action of painted surfaces on iodine behaviour generally has two countering effects: they can act as both a 'sink' for iodine and/or a source of volatile organic iodine. Although painted surfaces may adsorb iodine from the containment atmosphere and therefore reduce the inventory of gaseous iodine available in the containment for potential release to the environment, the concern comes with the action of some painted surfaces on iodine, which can convert iodine into organic iodides, which as stated above, are more difficult to scrub/filter from the containment atmosphere and may therefore lead to an increase in the inventory of radioiodine available for release.
- A2.32 A common design feature of LWR containments is to include a spray system(s) which reduces pressure in the containment during some accident scenarios. As well as performing this function, sprays may also wash-out aerosols and volatile iodine from the containment atmosphere and/or which are adsorbed on various in-containment surfaces. Unsurprisingly, therefore, these phenomena have been the focus of numerous experimental programmes. The general conclusions are that the removal efficiency of aerosols by sprays is generally governed by thermal hydraulics, whereas the prevailing chemistry conditions play a more significant role in the removal of volatile iodine i.e. by the addition of additives to the spray water, and/or pH buffering (similar to control of the pH of in-containment water sources), to promote iodine hydrolysis.
- A2.33 In summary, understanding iodine phenomena is a complex topic and it is clear that there are numerous competing processes which give rise to different physical and chemical forms of iodine in a post-accident reactor containment. This means that understanding the iodine source term is one of the numerous uncertainties inherent in undertaking accident analysis for nuclear facilities.

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APPENDIX 3: MATERIAL, CHEMICAL AND RADIOCHEMICAL SAMPLING AND ANALYSIS

- A3.1 This appendix provides further guidance and information in relation to SAP ECH.4.
- A3.2 The overarching requirement for sampling systems, processes and procedures is that representative sample(s) are obtained. The sampling systems, processes and procedures can be used to ensure the facility is operating within its Limits and Conditions for Operation (LCOs), to monitor the material integrity of SSCs and hence to maintain plant safety.
- A3.3 The sampling and analysis requirements can depend on the type of nuclear facility. Therefore, the inspector should consider the type of nuclear facility when assessing the adequacy of the licensee's sampling and analysis arrangements. For civil nuclear reactor sampling and analysis, the inspector should be aware of the guidance in NS-TAST-GD-088 – The Chemistry of Civil Nuclear Reactors. Guidance on assessing the characterisation of nuclear matter and radioactive waste may also be relevant here (see SAPs ENM.5 and RW.4).
- A3.4 Typical topics that may need to be considered by the chemistry inspector when performing an assessment of the chemistry aspects of the material, chemical and radiological sampling and analysis presented in some safety cases are as follows:

Sampling and Analysis Programme

- A3.5 A chemistry sampling and analysis programme can be used to verify the effectiveness of chemistry control in plant systems. The programme may be used to provide assurance that the structures, systems and components are operating within the Limits and Conditions for Operation.
- A3.6 The chemistry sampling and analysis programme usually reflects the chemistry requirements for all stages of the lifetime of a plant, including commissioning, shutdown and start-up periods and when systems are taken out of operation for prolonged periods.
- A3.7 The sampling and analysis programme can be used to detect trends in the chemistry parameters and eliminate undesirable effects and consequences of out-of-range chemistry parameters. Dependent on the chemistry parameter, there may be a requirement to respond in a timely manner to correct any deviations from normal operational status, such as small deficiencies, adverse trends or fast transients of chemistry parameters.
- A3.8 The nuclear facility will usually have some sampling equipment and/or laboratories to enable representative sampling and analysis of the chemistry parameters. The type and extent of the sampling and analysis equipment will be dependent on the type of nuclear facility.
- A3.9 To be able to demonstrate representative sampling can be achieved, some of the requirements outlined below should have been considered:

Species sampled

- A3.10 Chemistry parameters important to maintaining nuclear safety should be derived from the safety case. This should include consideration of the range and frequency of analysis required to ensure chemistry is adequately maintained within specified limits. Some examples of the types of chemical species which may be sampled include:

- Soluble chemical species (e.g. hydrazine, ammonia, chlorides, oxygen)
 - Fission products (e.g. I-131, Cs-137, H-3 etc.)
 - Insoluble corrosion products
 - Soluble corrosion products (e.g. chromium iron, nickel)
 - Steam
 - Gases (e.g. hydrogen)
- A3.11 The sampling and analysis chemistry programme should provide an adequate understanding of the chemical species which are important to the safe operation of the facility (sometimes referred to as ‘control parameters’) and those which provide additional information on the operation of the facility (sometimes referred to as ‘diagnostic parameters’).
- A3.12 The programme should consider the potential challenges associated with the analysis of different types of chemical species and how this informs the sampling system design; for example, the solubility of a corrosion product over a temperature range. Further information can be found in [30].
- A3.13 Failure to collect a sample correctly (i.e. a non-representative sample) should be considered in the safety case.

Sampling System

- A3.14 Sampling and analysis programmes may combine on-line monitoring of plant operating parameters and results obtained from manual grab samples which are analysed in the laboratory.
- A3.15 The type of sampling system may differ depending on the species being sampled, sample location and frequency. In addition, an existing facility may have further restrictions on the sampling and monitoring system, whereas a new facility in the design stage may have greater flexibility in the type of sampling system which can be installed [31].
- A3.16 The accuracy of the chemical analyses from either online monitoring equipment or grab samples is dependent on the sampling procedure. Guidelines for sampling have been reported by the Electric Power Research Institute (EPRI) [32]. The American Society for Testing and Materials (ASTM) standards D3864 and D2777 [33] [34] also give sampling practices and sampling system design. Factors to consider when assessing the adequacy of a sampling system include:
- Solubility of species to be sampled – the solubility of chemical species can vary depending on pH, temperature or pressure. If samples need to be cooled or depressurised to ambient conditions, consideration should be given to how this could affect the solubility of the species.
 - Temperature of system to be sampled – if the system normally operates at an elevated temperature the sample may be cooled. Careful consideration should be given to the specific location of cooling equipment in a sampling system. There should be consideration as to how the temperature of the sample may impact the solubility of key species which are required to be measured.
 - Pressure of system to be sampled – if the system normally operates at an elevated pressure the sample pressure may be conditioned to almost ambient conditions. This can be reduced by pressure reducing valves, pressure regulation and relief valves.
 - Length of sample line and flow rate – samples collected via long sample lines may become less representative of the bulk, as material can deposit; this can be mitigated by high (turbulent) flow rates. In addition, long sample lines may

result in the sample stagnating and therefore may not reflect the current operating conditions.

- Decomposition of samples – for volatile species it may be necessary to employ sample stabilisation or pre-treatment, to ensure the species remains in the correct physical form.
- Generation of secondary waste volumes - the impact of sampling location on secondary waste volumes.

The sampling systems should include safety features to protect the operators collecting samples from hazards; these can include exposure to potentially highly active samples, high temperatures or pressures. Ref. [31] provides some examples of sampling system safety features.

Sample Location and Frequency

- A3.17 The chemistry sampling and analysis programme should include a justification for the sample location, number of sample points and frequency of sampling. The design of the sampling system should be considered at a sufficiently early point in the design process, such that it does not foreclose sampling options.
- A3.18 To ensure a representative sample, there may be a single sample location or multiple locations depending on the facility and importance of the parameter to maintain safety. The sampling frequency should be determined in the safety case Ref. [30] and [31]. This should consider the time taken for a system to deviate from its expected range.
- A3.19 Consideration should be given to the sampling system design; the location of system components needs to allow access for maintenance and calibration during plant operation. Where frequent sampling and lab-based analysis is required or frequent calibration and maintenance of online instrumentation is necessary, instrument and sample point locations should cater for safe, reliable access, which minimises risks to workers Ref. [30] and [31].

Sample Transportation

- A3.20 Suitable and sufficient means of sample transportation should be provided when collecting samples from locations remote to the analytical laboratory Ref. [30] and [31]. The following may be considered:
- The method used to transport samples should consider the requirement to contain radioactive material and minimise the risk of its leakage or escape.
 - The designated route to transport samples containing radioactive material should be designed to avoid radiological hazards and minimise the risk of leakage or escape of radioactive material.
 - Where analyses for 'difficult' or volatile chemical species are required, it may be necessary to employ sample stabilisation or pre-treatment, to ensure the species remains in the correct physical form.

Analysis Requirements

- A3.21 This section provides an overview of the analytical techniques used to aid monitoring and control of the chemistry parameters. The evaluation of the results should be considered; these results may be trended and periodically reported.

Analytical technique

- A3.22 The analytical technique(s) selected to report chemistry parameters should take full account of the safety significance of the parameter being measured and the phase of

facility operations during which the analytical result is required, i.e. normal operations, accident or fault conditions Ref. [30] and [31].

A3.23 The analytical technique should consider a range of requirements, these may include sample availability, sample type, sample size and transit time requirements. It should be noted that the methods for sampling and analysis need to be complementary, for example the size of the sample may depend on the analytical technique available and vice versa. Analysis approaches can be classified as:

- In-situ, this is typically for material and corrosion monitoring.
- Ex-situ, this is typically for soluble species whereby samples are diverted to the analytical equipment.

A3.24 The analytical techniques can include, but are not limited to, ion chromatography, colourimetry, light spectrometry and mass spectrometry Ref. [30] and [31]. The typical analysis range should also be defined for each sample analysis.

A3.25 There should be adequate quality control processes for chemical and radiochemical analyses in place, which give suitable consideration to factors such as Ref. [30] and [31]:

- relevant errors and uncertainties;
- limits of detection (LoD) and quantification (LoQ);
- quality assurance arrangements such as appropriate chemical standards and calibration of equipment and instrumentation; and
- regular inspection and maintenance of on-line instruments and equipment in the laboratory.

Trending and Reporting of Analytical Results

A3.26 Once the analysis is complete, the results should be recorded. It is important to record the correct units for the analytical measurement, for example ppb or ppm. The results should be compared with an expected value. If the sample analysis shows a deviation from normal operational status, such as small deficiencies, adverse trends or fast transients of chemistry parameters, the safety case should identify the timescales for action if required. The methodologies for diagnosis and treatment of deviations should be utilised and kept up to date.

A3.27 The chemistry parameters should be trended and periodically reported on for evaluation.

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APPENDIX 4: THE INFLUENCE OF CHEMISTRY EFFECTS ON COMBUSTIBLE GASES

A4.1 This appendix provides more details on combustible gases in nuclear facilities. It is not intended to be a complete description of all possible phenomena or hazards but provides examples of the type of information that may need to be considered by the inspector when considering a nuclear safety case that involves combustible gas hazards. Typical topics that may need to be considered in such a safety case may include:

- combustible gas sources;
- combustible gas distribution;
- relevant combustion phenomena;
- consequences of combustion;
- measurement and detection of combustible gases; and
- mitigation of combustible gases.

A4.2 This appendix therefore provides some brief background information and then intentionally concentrates on aspects where the chemistry inspector's involvement is expected to be greatest under each of these topics. It also provides some additional information on the modelling approach for such phenomena, rather than the full scope of a particular assessment. In totality, combustible gases in nuclear facilities often require consideration by specialists in disciplines other than chemistry, and may include specialists from: fault studies, internal hazards, civil engineering and/or PSA.

A4.3 While this appendix refers to combustible gases, many of the concepts would also apply to other dispersed combustible mixtures such as gaseous or vaporised fuels, or some dusts.

General Combustible Gas Behaviour

A4.4 Combustible gases are those which will burn (or oxidise) when mixed with air (or an oxidant) and ignited. This a chemical process, releasing heat and often light. In this context the combustible gas is the fuel. Such mixtures will only burn if the fuel concentration lies within defined limits, referred to as the lower flammability limit (LFL) and upper flammability limit (UFL). Outside of these limits the mixture is not capable of sustaining combustion even if an ignition source is present. Such limits are commonly quoted as volume percentage of fuel in air at room temperature and pressure. Understanding these limits is important in terms of both avoiding and mitigating hazards posed by combustible gases. Such limits are experimentally determined and readily available [35]. A typical example is given in below:

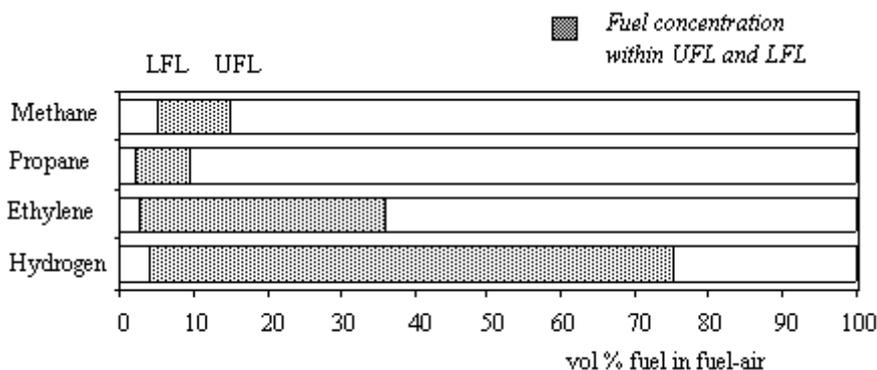


Figure A4.1: Lower and Upper Flammability Limits of some common gases

A4.5 As shown above, the values for these limits vary from gas-to-gas but are also influenced by other factors such as the temperature, pressure or gas mixture composition. For example, increasing the temperature, pressure or oxidiser concentration lowers the LFL and increases the UFL, increasing the range over which the gas mixture will combust. Conversely, the opposite is true, and importantly for preventing flammable atmospheres developing, reducing the concentration of oxidiser (for example by increasing the fraction of inert gas) raises the LFL and decreases the UFL. This type of behaviour is shown schematically below:

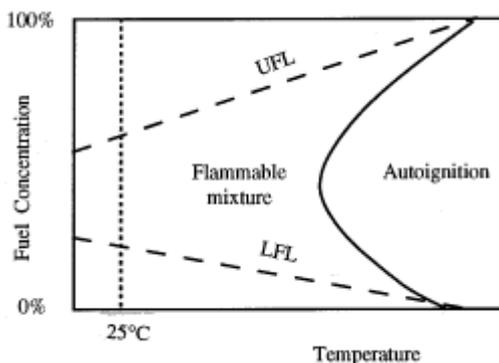


Figure A4.2: Effect of temperature on Lower and Upper Flammability Limit

A4.6 The above figure also introduces the concept of auto-ignition. The combustible gas mixture will spontaneously ignite, without an external ignition source at this temperature. This value also varies with the mixture composition, with the minimum being close to the stoichiometric composition.

Combustible Gas Sources

A4.7 Combustible gases such as: hydrogen, propane, acetylene, and methane are used for various purposes during normal operations of nuclear facilities. Hydrogen is the most common combustible gas used. For example, it is used as a coolant for the main electrical generator in both advanced gas cooled reactors (AGRs) and PWRs. In the majority of PWRs, it is also fed to the volume control tank (VCT) in the chemical volume and control system to control the dissolved oxygen concentration in the RCS. It is also used as a process gas for uranium fuel production. Other combustible gas may be used. For example, the gas chemistry of an AGR includes additions of methane and carbon monoxide. In these cases, the combustible gas is a purposeful addition to the process.

A4.8 In other cases, combustible gases can be a product of the process, either purposefully or by accident, although the former is not common and should be avoided if possible. As above, hydrogen is the most common combustible gas, but this depends on the particular situation under consideration. Such sources could include:

- **Radiolysis of water, producing essentially stoichiometric hydrogen and oxygen.** The rate is a function of the radiation energy, the fraction absorbed by the water and the rate of dissociation. Other solutes in the water can increase or decrease the yields. Different equilibrium conditions can be reached, depending on whether the system is 'closed' or 'open' and whether a gas phase exists above the water. Radiolysis of water can be a significant source of combustible gases, particularly for high dose rate conditions.
- **Corrosion reactions, producing hydrogen.** While metals corrode in all pH conditions, the yield of hydrogen from these reactions may become significant particularly if the pH is high or low, the surface area is large, or the timescales

are long. Aluminium and zinc are typical metals prone to this type of degradation, as is Magnox fuel cladding during long-term storage.

- **Zirconium oxidation, producing hydrogen.** In LWR accidents which involve exposure of high temperature fuel to steam, the zirconium fuel cladding will oxidise producing hydrogen: $\text{Zr} + 2\text{H}_2\text{O} \rightarrow \text{ZrO}_2 + 2\text{H}_2 + \text{heat}$. The actual process is complex, and at low and moderate temperatures it is kinetically limited by diffusion through the outer oxide layer on intact fuel rods but becomes more complex at higher temperatures (and may no longer be chemically limited). In such accidents, this is the major source of combustible gases and the rate and quantity of hydrogen generated in this way therefore has a large impact on the potential accident progression.
- **Steel oxidation, producing hydrogen.** In a similar manner to zirconium, stainless steels may be oxidised by high temperature steam, but the rates are much slower and the reaction exotherm is several orders of magnitude lower.
- **Uranium oxidation, producing hydrogen.** Uranium and uranium oxides will oxidise with steam producing hydrogen. Uranium metal will oxidise completely to uranium dioxide. Some uranium dioxide will oxidise further to triuranium octoxide, but the amount is very small with only small amounts of hydrogen present. The rate of oxidation of ceramic uranium dioxide is negligible.
- **Molten core – concrete interactions, producing hydrogen and carbon monoxide.** In a severe accident in a LWR, molten core debris in contact with concrete will produce combustible gases either through direct chemical reaction or through thermal degradation. Such sources may become significant for the most severe LWR accidents, particularly in the longer term.

A4.9 In addition to the origin of combustible gases, the rate and timings of release are important in determining any potential consequences. These are often chemically driven. Any assumptions used in determining these parameters could be important, particularly at higher temperatures where rates are higher but also uncertainties are greater. In such cases the expectations of the relevant SAPs should be considered, including EKP.1, EHA.13 and ECH.1.

Combustible Gas Distribution

A4.10 Combustible gas mixtures can vary from fully homogeneous fuel-oxidant mixtures to inhomogeneous clouds. The combustion behaviour in the former case is relatively easy to predict. However, such situations seldom arise, particularly during accidents where a combustible gas is often released in some manner and mixes with air or other gases and the latter case results. Understanding the mixing and distribution of combustible gases is part of determining the potential consequences, including how this distribution evolves and changes over time.

A4.11 To do this the form of the combustible gas release is important and can be broadly categorised as either a jet (i.e. through a nozzle), or diffuse release (i.e. an evaporating pool). These have very different characteristics:

- A jet release has a high momentum and establishes a strong flow field due to additional air entrainment and zones may be generated where the gas concentration can reach a combustible level, particularly within building or confined spaces where large combustible clouds can be generated. Conversely such releases into a confined space may lead to more homogenous mixtures (in the absence of ignition sources), given the intense mixing effects.
- A diffuse release source is much gentler and slower, and wind forces and buoyancy will control the dispersion process. If the diffuse gas is notably denser or lighter, a stratified layer of combustible gas may be formed, leading to a very inhomogeneous mixture, even within the cloud itself.

- A4.12 If the gas cloud formed from the release is not within the flammability limits, or if the ignition source is lacking, the gas cloud may be diluted and disappear. Ignition may occur immediately or may be delayed, all depending on the circumstances. In the case of an immediate ignition (i.e. before mixing of the fuel and oxidiser has occurred), a fire will occur (i.e. a diffusion flame). Generally, the most dangerous situations occur if a large combustible premixed fuel-air cloud is formed and ignites.
- A4.13 Understanding the mixing behaviour of gases in such situations is therefore an important aspect of being able to predict the likely consequences of any subsequent combustion event. More general information on combustible gas behaviour can be found in [36].

Relevant Combustion Phenomena

- A4.14 How the combustion proceeds will directly affect the consequences. When a combustible gas ignites, the flame can propagate in two different modes through the flammable parts of the cloud. From the point of view of nuclear safety, the combustion regimes can be broadly classified as deflagrations or detonations:
- **Deflagration** – this is the most ‘common’ type of combustion. In a deflagration the flame propagates at subsonic speed relative to the unburned gas. For a fuel-air cloud (ignited by a spark) the flame will normally start out as a slow laminar flame. If the cloud is truly unconfined and unobstructed the flame is not likely to accelerate significantly, and the resultant pressure may be negligible. However, fast deflagrations, and even slow deflagrations in a closed vessel, can generate appreciable pressures. Deflagrations are therefore not necessarily benign, as the flame speed, therefore the degree of confinement and geometry become important.
 - **Detonation** - a detonation wave is a supersonic (relative to the speed of sound in the unburned gas ahead of the wave) combustion wave. The shock wave and the combustion wave are in this case coupled. High ignition energies are commonly required to directly initiate detonations, although the energy is minimised close to stoichiometry. In a typical fuel-air detonation the shock wave may propagate at thousands of m s^{-1} , generating very significant peak pressures. Detonation events are therefore often the most damaging.
- A4.15 In certain circumstances, it is possible for a deflagration to accelerate to such an extent that it turns into a detonation. In a building or within process equipment, the flame may accelerate significantly. As the gas undergoes combustion the temperature will increase, and the gas will expand. The unburned gas is therefore compressed and pushed ahead of the flame front and a turbulent condition is generated. When the flame propagates into a turbulent flow, the effective burning rate may increase causing the flow velocity and turbulence ahead of the flame to increase further. This strong positive feedback mechanism causes further flame acceleration and high pressures, and in some cases transition to detonation. This process is known as deflagration to detonation transition (DDT) and is one of the most difficult aspects to predict.
- A4.16 Diffusion flames are a special case of combustions which are stabilised at the source of a jet of fuel into oxidant (or vice-versa). They are unique in terms of accident analysis since they do not lead to significant pressure loadings (spatially non-uniform), but can affect equipment survivability due to high, localized heat fluxes.

Consequences of Combustion

- A4.17 As stated in the main body of the relevant sections of this TAG, the chemistry inspector should be aware that the task of assessing the adequacy of a nuclear safety case with

respect to the consequences of combustion is predominately a matter for other ONR specialisms, namely internal hazards and/or fault studies etc.; chemistry may provide an input into the overall assessment.

A4.18 Estimating the consequences of a given gas combustion is often not a simple task as it can depend on numerous factors, many of which can have a large effect on the results, including:

- type of fuel and oxidiser;
- size and fuel concentration of the combustible cloud;
- location of ignition point;
- strength of ignition source;
- size, location and type of vent areas;
- location and size of structural elements and equipment; and
- mitigation schemes.

A4.19 However, once it is established that a given mixture is in the flammable region, the question then becomes how fast the resultant combustion is and does it have the potential to accelerate or even detonate. Thus, there are three basic steps for identifying the combustion regime [37], which in turn will determine the potential consequences:

- 1) Determine the flammability of the mixture (flammability criterion). The location of a given combustible gas mixture on the Shapiro ternary diagram (Figure A4.3) is a simple measure of determining whether a given gas mixture is flammable or even potentially detonable. The latter mode is less well defined in this approach, as there is some effect of scale on determining this boundary. In this diagram, the flammability and detonation zones are, respectively, delimited by the exterior (blue) and interior (red) curves.

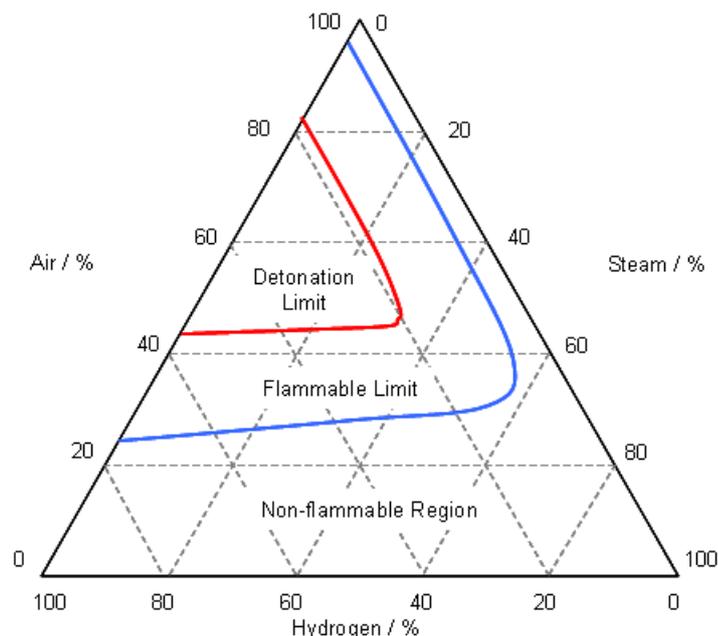


Figure A4.3: Typical Shapiro ternary diagram for hydrogen-air-steam

Figure A4.3 shows that below around 4% vol. and above 75% vol. hydrogen the mixtures are not flammable, no matter what proportions of steam or air are also present. In between these boundaries the mixture could be non-flammable, flammable or even detonable dependent upon the other

components present. For example, air-hydrogen mixtures above 4% vol. will combust provided they are not inerted by steam and are mixed with sufficient oxygen, but not completely. Above 8% vol. combustion will be complete. Above 10% vol. there is the possibility that the combustion can accelerate and become a detonation. Above 16% vol. direct detonation is possible, given a sufficient energy input. The Shapiro diagram also demonstrates the important effect of steam on inerting what would otherwise be a flammable mixture. The determination of where a given gas mixture resides in such diagrams is therefore an important indicator for the potential hazards that are possible.

- 2) Determine the possibility of flame acceleration.
- 3) Determine the possibility of DDT.

A4.20 Importantly, these last two can be established based on criteria which are conservative prerequisites based on experimental results, that is, it is unlikely that flame acceleration or DDT would occur without fulfilling these criteria (i.e. they are useful at predicting when flame acceleration or DDT will not occur rather than when it will).

A4.21 Ultimately, the consequences of such combustions can all be related back to the increase in temperature and pressure that results from the reaction. The strength and form of these can impact on structures, systems and components important to safety. These can only be described in general terms here as they are very much sequence and plant design related:

- The pressure generated by the combustion depends on how fast the flame propagates and how the pressure can expand away from the gas cloud. For slow deflagrations pressure can be considered to be uniform in the region involved in the combustion and the rate of pressure rise will be quite slow and the pressure loading can be considered to be approximately static, assuming adiabatic isochoric complete combustion (AICC) will bound pressure loads from such deflagrations in closed volumes. For very fast deflagrations and for detonations, pressure and shock waves can generate dynamic loadings, and the AICC pressure is no longer bounding. Diffusion flames create almost no pressure.
- Temperature increases can be accurately determined provided the rate of combustion is known (although this in itself may not be straightforward). In general deflagration and detonation temperature increases are modest in terms of impact on other structures, given the volumes and heat transfer mechanisms involved but transient temperatures can be significant. Diffusion flames are a special case given the localised and sustained nature of the heat transfer and can impact on close equipment.

A4.22 More information can be found in [36].

Detection and Measurement of Combustible Gases

A4.23 Management of a combustible gas hazard may necessitate the need to detect or measure the concentration of combustible gases, firstly as a means of ensuring combustible conditions are not generated, and secondly to monitor the progression of an accident to ensure timely and appropriate corrective action is taken. This can take the form of sampling systems or direct sensors. Further information is provided in [38]. Consideration should therefore be given to the need and means of detecting or measuring combustible gases. This requirement is further outlined in SAP ECH.4.

Mitigation of Combustible Gases

A4.24 If possible, the use or generation of combustible gases should be avoided, as per SAP EKP.1. If this is not possible then the use, storage or generation should be minimised, controlled and appropriately located, as per SAP EHA.13. In practical terms the control of combustible gas hazards is usually achieved by applying sufficient natural or mechanical ventilation to limit the concentration of combustible gases to a maximum level of 25% of their LFL, or in some cases, 50% of their LFL, as per the DSEAR ACoP [39].

A4.25 If the possibility of combustion cannot be excluded, including during accident conditions, appropriate mitigation measures need to be considered. There are a number of mitigation options available, the adoption of which will depend on the nature and potential severity of the hazard. Such measures include the following, either in isolation or combination, which are discussed briefly below:

- **Mixing and dilution** – mixing (and hence dilution) can prevent the generation of combustible mixtures. This can include both passive (e.g. jet releases) and active mixing (e.g. fans). Active mixing may also be induced by devices not specific to this purpose, for example spray systems in LWRs. Mixing may also be initiated by addition of inert gas, though not in sufficient quantities to affect inertion but rather to disperse a localised cloud.
- **Inerting** – inerting schemes control combustion by limiting the supply of oxidant, usually by adding inert or combustion suppressing gases. This includes pre-inerting, post-inerting and partial-inerting. Inerting may also occur as part of an accident sequence. For example, if large quantities of steam are released before or alongside the combustible gas.
- **Venting** – venting schemes tend not to be for combustible gas control, but pressure relief, but do represent an effective means of removing combustible gases from a given volume. Consideration does need to be given to the resultant gas concentrations in the downstream environment (for example a non-combustible mixture that is vented may no longer be so).
- **Recombination** – both thermal and catalytic recombination of hydrogen and oxygen is possible. The advantage of this approach is that such devices can be passive and can remove combustible gases over a wide range of gas compositions, including levels below the LFL. The disadvantage is that they may have side-effects such as acting as ignition sources. Careful consideration needs to be given to factors such as: efficiency, capacity, location, poisoning and side-reactions.
- **Deliberate ignition** – such schemes initiate combustion at levels as close to the LFL as possible, thus avoiding the potential for more damaging modes of combustion. As with recombiners, the: location, number and side-effects of deliberate ignition systems need to be carefully considered, as do the supplies needed to operate them.
- **Water fogs and foams** – such systems do not stop combustion occurring but can be beneficial in reducing the pressure and temperature transients, mainly via cooling of the atmosphere. The effect of such systems on other aspects, such as flame acceleration, is less clear.

A4.26 Clearly each of these brings its own potential benefits and/or detriments. These should be appropriately considered in order to select an overall “ALARP solution”.

Prediction of Combustion Events

A4.27 In order to predict combustion events, it is often necessary to use computer codes to model the various steps described above. Reference [37] suggests an overall ‘roadmap’ for evaluating the combustion risks to a given plant. This roadmap consists

on several distinct sequential steps. Clearly not all of these would be relevant to every possible situation and the approach adopted needs to be proportional. These include:

- Definition of a set of accident sequences of relevance to the nuclear plant design.
- Evaluation of the combustible gas and other release source terms for the postulated accident and release scenarios.
- Evaluation of the gas distribution and mixing, on the basis of the defined source terms, including consideration of any mitigation measures.
- Evaluation of the flammability of the mixture in each area and application of flame acceleration and DDT criteria for a quantitative measure of the possibility of these events.
- In some cases, and despite the use of mitigation techniques, a risk for flame acceleration or DDT may still exist during some part of the transient considered. In those cases, a more detailed investigation with dedicated simulations of flames or detonations may be needed.
- Determination of the thermal and mechanical loads of the combustion processes (slow deflagration, fast deflagration or detonation) on relevant structures, systems or components.
- Finally, evaluation of the consequences on the basis of the results of the previous steps. If fast combustion modes cannot be excluded despite the risk mitigation system present, a detailed investigation of the structural response is needed, along with further consideration of any additional measures which reduce the risks to ALARP.

A4.28 In order to cover these different requirements, it is often necessary to use different analysis codes. Large scale effects over the long timescales of accident sequences are better suited to simplified lumped parameter (LP) codes. Conversely, these do not offer the required accuracy to analyse the phenomena which occur on small time and spatial scales, such as local stratifications and fast combustions. These can be simulated in detail by more sophisticated computational fluid dynamics (CFD) codes. This in itself requires careful consideration, in particular the expectations given in TAG-42 [40] and exemplified in [36] and [41] are particularly pertinent. From a chemistry perspective, it is important that the expectations of SAP AV.2 are met. Namely, that chemical processes are appropriately and adequately represented by such codes, models and methods.

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