# IAEA Safety Standards

**for protecting people and the environment**

# Chemistry Programme for Water Cooled Nuclear Power Plants

## Specific Safety Guide

## No. SSG-13

IAEA
International Atomic Energy Agency

# IAEA SAFETY RELATED PUBLICATIONS

## IAEA SAFETY STANDARDS

Under the terms of Article III of its Statute, the IAEA is authorized to establish or adopt standards of safety for protection of health and minimization of danger to life and property, and to provide for the application of these standards.

The publications by means of which the IAEA establishes standards are issued in the **IAEA Safety Standards Series**. This series covers nuclear safety, radiation safety, transport safety and waste safety. The publication categories in the series are **Safety Fundamentals**, **Safety Requirements** and **Safety Guides**.

Information on the IAEA's safety standards programme is available at the IAEA Internet site

http://www-ns.iaea.org/standards/

The site provides the texts in English of published and draft safety standards. The texts of safety standards issued in Arabic, Chinese, French, Russian and Spanish, the IAEA Safety Glossary and a status report for safety standards under development are also available. For further information, please contact the IAEA at PO Box 100, 1400 Vienna, Austria.

All users of IAEA safety standards are invited to inform the IAEA of experience in their use (e.g. as a basis for national regulations, for safety reviews and for training courses) for the purpose of ensuring that they continue to meet users' needs. Information may be provided via the IAEA Internet site or by post, as above, or by email to Official.Mail@iaea.org.

## OTHER SAFETY RELATED PUBLICATIONS

The IAEA provides for the application of the standards and, under the terms of Articles III and VIII.C of its Statute, makes available and fosters the exchange of information relating to peaceful nuclear activities and serves as an intermediary among its Member States for this purpose.

Reports on safety and protection in nuclear activities are issued as **Safety Reports**, which provide practical examples and detailed methods that can be used in support of the safety standards.

Other safety related IAEA publications are issued as **Radiological Assessment Reports**, the International Nuclear Safety Group's **INSAG Reports**, **Technical Reports** and **TECDOCs**. The IAEA also issues reports on radiological accidents, training manuals and practical manuals, and other special safety related publications. Security related publications are issued in the **IAEA Nuclear Security Series**.

# CHEMISTRY PROGRAMME FOR WATER COOLED NUCLEAR POWER PLANTS

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The Agency's Statute was approved on 23 October 1956 by the Conference on the Statute of the IAEA held at United Nations Headquarters, New York; it entered into force on 29 July 1957. The Headquarters of the Agency are situated in Vienna. Its principal objective is "to accelerate and enlarge the contribution of atomic energy to peace, health and prosperity throughout the world''.

IAEA SAFETY STANDARDS SERIES No. SSG-13

# CHEMISTRY PROGRAMME FOR WATER COOLED NUCLEAR POWER PLANTS

SPECIFIC SAFETY GUIDE

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# FOREWORD

## by Yukiya Amano
## Director General

The IAEA's Statute authorizes the Agency to "establish or adopt… standards of safety for protection of health and minimization of danger to life and property" — standards that the IAEA must use in its own operations, and which States can apply by means of their regulatory provisions for nuclear and radiation safety. The IAEA does this in consultation with the competent organs of the United Nations and with the specialized agencies concerned. A comprehensive set of high quality standards under regular review is a key element of a stable and sustainable global safety regime, as is the IAEA's assistance in their application.

The IAEA commenced its safety standards programme in 1958. The emphasis placed on quality, fitness for purpose and continuous improvement has led to the widespread use of the IAEA standards throughout the world. The Safety Standards Series now includes unified Fundamental Safety Principles, which represent an international consensus on what must constitute a high level of protection and safety. With the strong support of the Commission on Safety Standards, the IAEA is working to promote the global acceptance and use of its standards.

Standards are only effective if they are properly applied in practice. The IAEA's safety services encompass design, siting and engineering safety, operational safety, radiation safety, safe transport of radioactive material and safe management of radioactive waste, as well as governmental organization, regulatory matters and safety culture in organizations. These safety services assist Member States in the application of the standards and enable valuable experience and insights to be shared.

Regulating safety is a national responsibility, and many States have decided to adopt the IAEA's standards for use in their national regulations. For parties to the various international safety conventions, IAEA standards provide a consistent, reliable means of ensuring the effective fulfilment of obligations under the conventions. The standards are also applied by regulatory bodies and operators around the world to enhance safety in nuclear power generation and in nuclear applications in medicine, industry, agriculture and research.

Safety is not an end in itself but a prerequisite for the purpose of the protection of people in all States and of the environment — now and in the future. The risks associated with ionizing radiation must be assessed and controlled without unduly limiting the contribution of nuclear energy to equitable and sustainable development. Governments, regulatory bodies and operators everywhere must ensure that nuclear material and radiation sources are used beneficially, safely and ethically. The IAEA safety standards are designed to facilitate this, and I encourage all Member States to make use of them.

# THE IAEA SAFETY STANDARDS

## BACKGROUND

Radioactivity is a natural phenomenon and natural sources of radiation are features of the environment. Radiation and radioactive substances have many beneficial applications, ranging from power generation to uses in medicine, industry and agriculture. The radiation risks to workers and the public and to the environment that may arise from these applications have to be assessed and, if necessary, controlled.

Activities such as the medical uses of radiation, the operation of nuclear installations, the production, transport and use of radioactive material, and the management of radioactive waste must therefore be subject to standards of safety.

Regulating safety is a national responsibility. However, radiation risks may transcend national borders, and international cooperation serves to promote and enhance safety globally by exchanging experience and by improving capabilities to control hazards, to prevent accidents, to respond to emergencies and to mitigate any harmful consequences.

States have an obligation of diligence and duty of care, and are expected to fulfil their national and international undertakings and obligations.

International safety standards provide support for States in meeting their obligations under general principles of international law, such as those relating to environmental protection. International safety standards also promote and assure confidence in safety and facilitate international commerce and trade.

A global nuclear safety regime is in place and is being continuously improved. IAEA safety standards, which support the implementation of binding international instruments and national safety infrastructures, are a cornerstone of this global regime. The IAEA safety standards constitute a useful tool for contracting parties to assess their performance under these international conventions.

## THE IAEA SAFETY STANDARDS

The status of the IAEA safety standards derives from the IAEA’s Statute, which authorizes the IAEA to establish or adopt, in consultation and, where appropriate, in collaboration with the competent organs of the United Nations and with the specialized agencies concerned, standards of safety for protection of health and minimization of danger to life and property, and to provide for their application.

With a view to ensuring the protection of people and the environment from harmful effects of ionizing radiation, the IAEA safety standards establish fundamental safety principles, requirements and measures to control the radiation exposure of people and the release of radioactive material to the environment, to restrict the likelihood of events that might lead to a loss of control over a nuclear reactor core, nuclear chain reaction, radioactive source or any other source of radiation, and to mitigate the consequences of such events if they were to occur. The standards apply to facilities and activities that give rise to radiation risks, including nuclear installations, the use of radiation and radioactive sources, the transport of radioactive material and the management of radioactive waste.

Safety measures and security measures[1] have in common the aim of protecting human life and health and the environment. Safety measures and security measures must be designed and implemented in an integrated manner so that security measures do not compromise safety and safety measures do not compromise security.

The IAEA safety standards reflect an international consensus on what constitutes a high level of safety for protecting people and the environment from harmful effects of ionizing radiation. They are issued in the IAEA Safety Standards Series, which has three categories (see Fig. 1).

**Safety Fundamentals**

Safety Fundamentals present the fundamental safety objective and principles of protection and safety, and provide the basis for the safety requirements.

**Safety Requirements**

An integrated and consistent set of Safety Requirements establishes the requirements that must be met to ensure the protection of people and the environment, both now and in the future. The requirements are governed by the objective and principles of the Safety Fundamentals. If the requirements are not met, measures must be taken to reach or restore the required level of safety. The format and style of the requirements facilitate their use for the establishment, in a harmonized manner, of a national regulatory framework. Requirements, including numbered 'overarching' requirements, are expressed as 'shall' statements. Many requirements are not addressed to a specific party, the implication being that the appropriate parties are responsible for fulfilling them.

**Safety Guides**

Safety Guides provide recommendations and guidance on how to comply with the safety requirements, indicating an international consensus that it is necessary to take the measures recommended (or equivalent alternative measures). The Safety

[1] See also publications issued in the IAEA Nuclear Security Series.

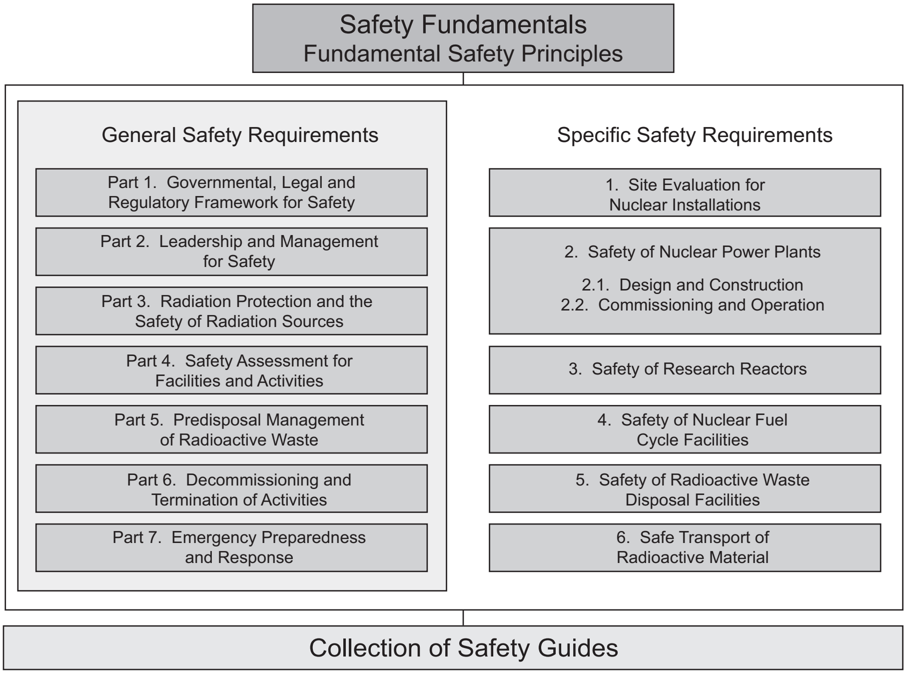


*FIG. 1. The long term structure of the IAEA Safety Standards Series.*

Guides present international good practices, and increasingly they reflect best practices, to help users striving to achieve high levels of safety. The recommendations provided in Safety Guides are expressed as ‘should’ statements.

## APPLICATION OF THE IAEA SAFETY STANDARDS

The principal users of safety standards in IAEA Member States are regulatory bodies and other relevant national authorities. The IAEA safety standards are also used by co-sponsoring organizations and by many organizations that design, construct and operate nuclear facilities, as well as organizations involved in the use of radiation and radioactive sources.

The IAEA safety standards are applicable, as relevant, throughout the entire lifetime of all facilities and activities — existing and new — utilized for peaceful purposes and to protective actions to reduce existing radiation risks. They can be used by States as a reference for their national regulations in respect of facilities and activities.

The IAEA's Statute makes the safety standards binding on the IAEA in relation to its own operations and also on States in relation to IAEA assisted operations.

The IAEA safety standards also form the basis for the IAEA's safety review services, and they are used by the IAEA in support of competence building, including the development of educational curricula and training courses.

International conventions contain requirements similar to those in the IAEA safety standards and make them binding on contracting parties. The IAEA safety standards, supplemented by international conventions, industry standards and detailed national requirements, establish a consistent basis for protecting people and the environment. There will also be some special aspects of safety that need to be assessed at the national level. For example, many of the IAEA safety standards, in particular those addressing aspects of safety in planning or design, are intended to apply primarily to new facilities and activities. The requirements established in the IAEA safety standards might not be fully met at some existing facilities that were built to earlier standards. The way in which IAEA safety standards are to be applied to such facilities is a decision for individual States.

The scientific considerations underlying the IAEA safety standards provide an objective basis for decisions concerning safety; however, decision makers must also make informed judgements and must determine how best to balance the benefits of an action or an activity against the associated radiation risks and any other detrimental impacts to which it gives rise.

## DEVELOPMENT PROCESS FOR THE IAEA SAFETY STANDARDS

The preparation and review of the safety standards involves the IAEA Secretariat and four safety standards committees, for nuclear safety (NUSSC), radiation safety (RASSC), the safety of radioactive waste (WASSC) and the safe transport of radioactive material (TRANSSC), and a Commission on Safety Standards (CSS) which oversees the IAEA safety standards programme (see Fig. 2).

All IAEA Member States may nominate experts for the safety standards committees and may provide comments on draft standards. The membership of the Commission on Safety Standards is appointed by the Director General and includes senior governmental officials having responsibility for establishing national standards.

A management system has been established for the processes of planning, developing, reviewing, revising and establishing the IAEA safety standards. It articulates the mandate of the IAEA, the vision for the future application of the

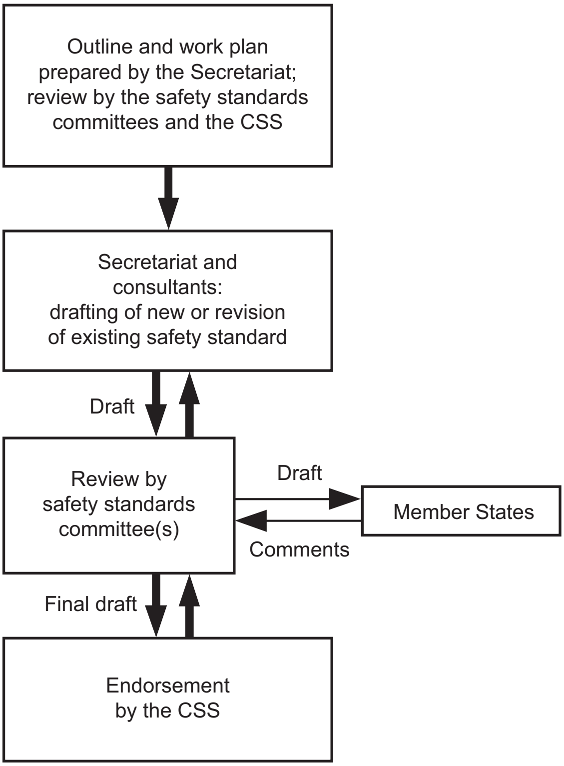


*FIG. 2. The process for developing a new safety standard or revising an existing standard.*

safety standards, policies and strategies, and corresponding functions and responsibilities.

## INTERACTION WITH OTHER INTERNATIONAL ORGANIZATIONS

The findings of the United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR) and the recommendations of international expert bodies, notably the International Commission on Radiological Protection (ICRP), are taken into account in developing the IAEA safety standards. Some safety standards are developed in cooperation with other bodies in the United Nations system or other specialized agencies, including the Food and Agriculture Organization of the United Nations, the United Nations Environment Programme, the International Labour Organization, the OECD Nuclear Energy Agency, the Pan American Health Organization and the World Health Organization.

## INTERPRETATION OF THE TEXT

Safety related terms are to be understood as defined in the IAEA Safety Glossary (see http://www-ns.iaea.org/standards/safety-glossary.htm). Otherwise, words are used with the spellings and meanings assigned to them in the latest edition of The Concise Oxford Dictionary. For Safety Guides, the English version of the text is the authoritative version.

The background and context of each standard in the IAEA Safety Standards Series and its objective, scope and structure are explained in Section 1, Introduction, of each publication.

Material for which there is no appropriate place in the body text (e.g. material that is subsidiary to or separate from the body text, is included in support of statements in the body text, or describes methods of calculation, procedures or limits and conditions) may be presented in appendices or annexes.

An appendix, if included, is considered to form an integral part of the safety standard. Material in an appendix has the same status as the body text, and the IAEA assumes authorship of it. Annexes and footnotes to the main text, if included, are used to provide practical examples or additional information or explanation. Annexes and footnotes are not integral parts of the main text. Annex material published by the IAEA is not necessarily issued under its authorship; material under other authorship may be presented in annexes to the safety standards. Extraneous material presented in annexes is excerpted and adapted as necessary to be generally useful.

# CONTENTS

# 1. INTRODUCTION

## BACKGROUND

1.1. This Safety Guide covers all types of nuclear power plant with water cooled reactors and supports the IAEA Safety Requirements publication on Safety of Nuclear Power Plants: Commissioning and Operation [1].

1.2. A chemistry programme is essential for the safe operation of a nuclear power plant. It ensures the integrity, reliability and availability of the main plant structures, systems and components [2] important to safety, in accordance with the assumptions and intent of the design. A chemistry programme minimizes the harmful effects of chemical impurities and corrosion on plant structures, systems and components. It supports the minimization of buildup of radioactive material and occupational radiation exposure as well as limiting of the release of chemicals and radioactive material to the environment.

1.3. This Safety Guide is intended to be useful to plant personnel for maintaining the quality of existing chemistry programmes at a high level and for identifying opportunities for improvement. It can also be used to develop new chemistry programmes as well as to assist in the development of corrective actions for eliminating known weaknesses in current programmes.

1.4. This Safety Guide is also intended to be of use to managers of operating organizations responsible for oversight of the plant chemistry programme and to regulatory bodies.

## OBJECTIVE

1.5. The objective of this Safety Guide is to provide Member States with assistance for the safe operation of nuclear power plants according to current international best practices for chemistry programmes. The objective is also to provide recommendations on supporting the integrity of various barriers with respect to the potential for corrosion of components, optimizing[1] occupational radiation exposures in the plant and limiting releases of radioactive material and chemicals to the environment.

## SCOPE

1.6. This Safety Guide provides Member States with recommendations and guidance for chemistry activities to ensure that structures, systems and components important to safety are available to perform their functions in accordance with the assumptions and intent of the design.

1.7. This Safety Guide addresses the main activities of the plant chemistry programme for the various types of water cooled reactor and contains recommendations on chemistry and radiochemistry monitoring to ensure compliance with the appropriate plant operational limits and conditions and to allow proper evaluation of the effectiveness of the plant chemistry programme.

1.8. This Safety Guide does not provide detailed technical advice relating to particular chemistry regimes of nuclear power plants. Such details can be found in IAEA TECDOCs, e.g. Ref. [4][2].

## STRUCTURE

1.9. Section 2 provides recommendations on the functions and responsibilities of organizations involved in the chemistry programme and the interfaces between them. General recommendations on the chemistry programme are provided in Section 3. Recommendations on the process of chemistry control are provided in Section 4. Recommendations on chemistry aspects of radiation exposure optimization are provided in Section 5. Chemistry surveillance and radiochemistry surveillance processes are discussed in Section 6. Section 7 provides recommendations on the management of chemistry data and Section 8 provides recommendations on the training and qualification of personnel

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[1] Optimization of protection (and safety) is the process of determining what level of protection and safety makes exposures, and the probability and magnitude of potential exposures, "as low as reasonably achievable, economic and social factors being taken into account" (ALARA) [3].

[2] A report setting out guidelines for water chemistry for WWER nuclear power plants is in preparation as part of the IAEA Nuclear Energy Series.

involved in chemistry activities. Recommendations on quality control of chemicals and other substances are provided in Section 9.

# 2. FUNCTIONS, RESPONSIBILITIES AND INTERFACES

## OPERATING ORGANIZATION

2.1. The operating organization is required to establish and implement a chemistry programme to enhance plant and personnel safety, limit environmental discharges and improve plant reliability by:

(a) Preserving the integrity of structures, systems and components important to safety;
(b) Minimizing the buildup of radioactive material to reduce dose rates at the plant and hence radiation doses to personnel, to reduce the activity of chemical and radioactive waste and to reduce the activity of any planned discharges to the environment;
(c) Preserving the integrity of safety barriers for the fuel;
(d) Controlling the use of soluble poisons.

2.2. The organizational structure of the operating organization should provide for adequate chemistry management at the nuclear power plant [5].

2.3. The operating organization should set challenging goals and objectives for the chemistry programme. The expectations of the management for the implementation of the programme at the plant should be clearly stated. Chemistry staff should understand, support and implement the programme. Feedback on the results of the performance of the chemistry programme should be used to enhance the quality of the chemistry programme and the chemistry regime.

2.4. Information from other utilities and States (e.g. appropriate feedback on operating experience, research results, good practices and standards) should be analysed and incorporated, where considered beneficial, into the chemistry programme. Such information should be made available in the chemistry group and should be kept up to date properly.

2.5. Performance indicators for the chemistry programme should be established to monitor the attainment of goals and objectives and should be promoted and communicated to the staff. Management should periodically reinforce its expectations, monitor and assess performance and correct deviations.

2.6. The operating organization should ensure that the chemistry programme applied to structures, systems and components important to safety is implemented in such a way that the level of reliability and functionality of the structure, system or component remains in accordance with the design assumptions and intent throughout the operating lifetime of the plant.

2.7. The operating organization should provide adequate facilities, sampling and laboratory equipment (including laboratory instruments and on-line instruments) and support for development of methodologies, taking the requirements of the water chemistry programme and appropriate standards into consideration. External contractors and consultants should be made available as necessary to meet analysis needs.

2.8. The operating organization should provide adequate resources, including the requisite number and qualification of chemistry personnel for all levels, such as chemistry staff, supervisors and management, and technical support staff. Planning for continuous improvement should be an established practice among staff in the chemistry group, with account taken of long term operation of the plant.

2.9. Management of the operating organization should periodically evaluate the activities of the chemistry programme by carrying out walkdowns of chemistry facilities and checking plant chemistry equipment. Managers responsible for chemistry programme activities should monitor those indicators of staff behaviour and attitudes that show the development of a strong safety culture (e.g. proper attention to alarms, timely reporting of malfunctions, minimization of backlog of overdue maintenance, adequate labelling, accurate recording of data).

2.10. Managers and supervisors should routinely observe chemistry activities to ensure adherence to plant policies and procedures. Tests after maintenance and modifications should be conducted systematically and thoroughly to ensure that the equipment and systems are ready to return to service. Chemistry performance indicators should be trended, and preventive and/or corrective measures should be undertaken where necessary.

2.11. The plant self-assessment programme should include the chemistry area. In addition, the self-assessment programme should include participation in a recognized analytical certification and intercomparison programme. Audits and other self-assessments and independent reviews of the chemistry programme should be conducted regularly. Non-conformances should be reported and the status of corrective actions should be regularly evaluated [6].

2.12. Management should ensure that any measures to shorten the schedule for planned outage shutdown and to accelerate plant startup will not compromise the full application of chemistry control procedures (e.g. water cleanup during shutdown and startup phases and wet or dry conservation conditions on equipment should be fully respected).

2.13. There should be clear allocation of responsibilities at the plant in accordance with the requirements established in Ref. [7] for all chemistry activities, such as management of resources, chemistry control, dose management, chemistry and radiochemistry surveillance, chemistry and radiochemistry data management, analyses of water chemistry, activity measurement, reviews of results and staff training and qualification.

## CONTRACTORS

2.14. The operating organization should ensure that an effective organizational structure is established for contractors working within the chemistry area. The operating organization may delegate to other organizations the task of implementing the chemistry programme or some part thereof, but the operating organization is required to retain overall responsibility for such delegated work [7].

2.15. The operating organization should provide all the information that contractors need and should ensure that contractors understand instructions important to safety.

2.16. Contractors should be made subject to the same standards as plant staff, particularly with respect to required chemistry skills and competences, adherence to procedures, result reporting, safety culture and performance evaluation. Further recommendations on the management of contractors are provided in Ref. [2].

2.17. The management at the plant should be responsible for all tasks undertaken by contractors at the plant.

## OTHER ORGANIZATIONS, INCLUDING DESIGNERS AND MANUFACTURERS

2.18. The operating organization should have long term access to organizations that have the appropriate competence in laboratory activities, design, manufacturing, engineering and research relating to chemistry. Special commercial arrangements may be necessary to ensure continuity of access to such resources over the long term. When purchasing equipment, the operating organization should ensure that it has a clear understanding of the type of chemistry instrumentation and what it will be used for.

2.19. When plant deficiencies occur or when modifications are required, effective and timely assistance from the designer or manufacturer or from other organizations with sufficient knowledge should be requested as necessary. The operating organization should make chemistry data available to these organizations. On the other hand, changes in organizational structure or in structures, systems and components that could affect the chemistry programme should be brought to the attention of the management of the chemistry programme for their advice, comments or approval if necessary. The scope of such information should be established by means of clear and explicit instructions.

2.20. Requirements and standards for safety systems and safety related systems associated with the water chemistry programme should be established in agreement with the designer and manufacturer of both equipment and fuel.

## INTERFACE CONTROL

2.21. For all chemistry activities, an effective interface control system should be put in place. There should be a clear understanding of the division of responsibilities between all organizational units participating in chemistry activities. Chemistry personnel should have a clear understanding of their authority and responsibilities and the interfaces with other groups.

2.22. Proper interface arrangements should be established between the chemistry group and other groups (operations, maintenance, instrumentation and control, technical support) to ensure that necessary repairs to chemistry systems and equipment are made in a timely manner and that repair backlogs are kept to a minimum.

2.23. A report on water chemistry and radiochemistry parameters should be formulated and shared with other areas in the operating organization and with appropriate external organizations on a regular basis. The report should include water chemistry analysis for safety systems and safety related systems, results of activity measurements, parameter trends, analysis of deviations and corrective actions, as well as their possible consequences, and overviews of quality audits of laboratory performance.

2.24. Interfaces for chemistry related issues should be established between the operating organization and external organizations such as universities, research institutions, equipment and chemical suppliers and the regulatory body. Further recommendations on interfaces with external organizations are provided in Section 4 of Ref. [5].

# 3. CHEMISTRY PROGRAMME

3.1. The chemistry programme should provide the information and support relating to chemistry and radiochemistry necessary to ensure safe operation, long term integrity of structures, systems and components, and minimization of buildup of radioactive material and limiting of radioactive and chemical discharges to the environment.

3.2. The ownership and responsibilities of the operating organization for establishing and implementing the chemistry programme should be defined and communicated to plant personnel. Implementation of the chemistry programme could be organized in various ways, depending on the corporate or organizational structure of the operating organization. For instance, in many nuclear power plants, the chemistry and radiochemistry activities include environmental monitoring, in particular when activities relating to the chemistry programme and to radiation protection are performed by a single group of staff.

3.3. The chemistry programme should include procedures for selection, monitoring and analysis of the chemistry regime, instructions for operations involving chemistry processes and evaluation of operating results, the operation and reference limits for chemistry parameters and action levels and possible remedial actions [1, 8]. In the chemistry regime, account should be taken of feedback from operating experience.

3.4. In the chemistry programme, it should be ensured that:

(a) A suitable chemistry regime exists and is in accordance with the original design and material intent, and account is taken of any structural modifications or operating experience at the plant or at other plants.
(b) The primary water chemistry regime is appropriately selected, with account taken of its potential impact on: (i) uniform corrosion and stress corrosion cracking of circuit materials, (ii) fuel cladding corrosion, (iii) activation and transport of corrosion products, (iv) dose rates, (v) crud induced power shifts and (vi) crud induced localized corrosion.
(c) The secondary side chemistry programme aims to minimize (i) corrosion in the integrated system, (ii) deposits in the steam generators, (iii) concentration of deleterious compounds in crevices of areas with restricted flow and (iv) condenser leaks in both water and air parts, and also aims to increase the effectiveness of the steam generator blowdown purification system and condensate cleaning system (if used).
(d) The chemistry programme for auxiliary systems is in accordance with the material intent to preserve their full integrity and availability.
(e) Appropriate chemistry controls and diagnosis parameters are applied to verify safe and reliable operation.
(f) There is timely reporting of evaluation results to management at the responsible level and to other users of such results (operators, maintenance staff, the system engineering group, technical support organizations, etc.).
(g) There is a timely response to correct any deviations from normal operational status, such as small deficiencies, adverse trends or fast transients of chemistry parameters.
(h) Methodologies for diagnosis and treatment of deviations are utilized and kept up to date.
(i) On-line instruments and equipment in the laboratory are regularly inspected, calibrated, maintained and kept up to date.
(j) Staff from the chemistry department contribute adequately to maintaining the availability of the safety equipment (e.g. by analysis of safety tanks, diesel oil and main pumps oil).
(k) There is support to the plant ageing management programme in order to ensure safe and long term operation of the plant.

(l) Good practices exist in the water chemistry programme, which are in compliance with specifications and consistent with internationally accepted good practices.
(m) Procedures and practices are in place to confirm that water cleanup systems and sampling systems are effectively operated.
(n) Sources of impurities in the water systems are known and actions for minimizing these sources are implemented.
(o) Adequate and reliable on-line systems and laboratory systems for measurement of chemistry parameters are in proper operation.
(p) Modern analytical methods are used to carry out adequate analysis of pollutants, even if chemistry parameters are within their specified range.
(q) The use of substances and reagents that may adversely affect the integrity of equipment is prevented.
(r) Discharges to the environment of radioactive material and chemical pollutants are ALARA and the impact of any changes in the chemistry regime or equipment on radioactive discharges is adequately and accurately analysed and fully understood (e.g. for production of tritium and $^{14}C$).
(s) Hazardous chemicals are managed properly and a set of material safety data sheets (see para. 9.14) is made available.
(t) Adequate support is provided to identify and characterize radioactive waste generated at the nuclear power plant (including waste from decontamination).
(u) Sumps and drains are periodically monitored for radioactivity levels.

## 4. CHEMISTRY CONTROL

4.1. Chemistry control includes the correct application of the appropriate chemistry regimes for safety systems and safety related systems. The appropriate chemistry regime will depend on the design of the system and its construction materials.

4.2. To achieve adequate chemistry control, the chemistry group should apply a graded approach to the various areas of primary circuits, secondary circuits and other significant safety and cooling systems.

4.3. The control parameters selected should be the most important chemistry parameters for monitoring the chemistry regime and monitoring for the presence of deleterious impurities. In addition to control values, expected values may also be specified for internal use by chemistry staff in order to avoid a chemistry parameter inadvertently exceeding its limit value.

4.4. If a control parameter is outside its limit values, degradation of conditions for structures, systems and components may occur in the long term and may result in unavailability of safety systems. Thus, graded action levels should be specified in advance for control parameters; if deviations from these levels occur, corrective actions should be initiated progressively within an acceptable period of time and further corrective actions should continue to be applied until plant shutdown, if necessary.

4.5. In addition, diagnostic parameters should be defined. These provide further information on the chemical status of the plant and can help to identify the reason for any deviation in the chemistry regime.

4.6. The chemistry control programme should be used to confirm, from records, that chemistry control parameters and diagnostic parameters remain within their specified ranges. Records from the chemistry control programme should be controlled and reviewed and any deviations should be analysed in conformance with the management system of the operating organization.

4.7. Limits for chemistry parameters and conditions for operational and safety systems should be defined by the chemistry group for:

(a) Commissioning;
(b) Startup;
(c) Normal operation;
(d) Transients;
(e) Shutdown;
(f) Outages;
(g) Standby;
(h) Decommissioning.

Limits for parameters should not be exceeded; if a parameter exceeds its limit, appropriate actions should be taken to recover its normal operating value within a specified time.

4.8. The corrosion rates of construction materials and the risk of microbiological growth and microbiologically induced corrosion within tertiary systems, particularly when there is a semi-closed cooling system with cooling towers, should be controlled. The risk is dependent on the water characteristics, the materials, the design of the circuit and the temperature. Such microbiological growth could affect plant staff in contact with the circuit and the population in contact with the released water or spray from the cooling tower. Consequently, this risk should be taken into account when deciding if a biocide containing chlorine should be added and at what concentration, or whether other techniques should be implemented.

4.9. Tanks and unventilated spaces containing gases should be strictly monitored and properly maintained to prevent explosions caused by the simultaneous buildup of oxygen and hydrogen. Such monitoring should also be carried out for any tank containing liquids, where radiolysis may induce the presence of explosive mixtures of gases.

4.10. The fuel integrity monitoring programme should include appropriate procedures to ensure that chemistry and radiochemistry data indicative of fuel integrity are systematically analysed for trends and evaluated to detect anomalous behaviour [9].

4.11. The water chemistry regime of active and passive safety systems that contain liquid neutron absorbers (boric acid tanks, containment sprinkler system, bubble stacks, reservoirs containing gadolinium) should be maintained in accordance with design standards, with account taken of the fact that correction of the liquid chemistry within these reservoirs can generally only be made infrequently at specified times (e.g. during a refuelling outage).

4.12. During outages, equipment should be maintained under adequate lay-up conditions (e.g. dry lay-up, wet lay-up with a high pH, or normal operating water conditions) by means of chemicals or nitrogen, depending on the lay-up duration, and in accordance with safety requirements. Lay-up parameters should be monitored and corrective measures for deviations should be implemented.

4.13. The concentrations of the chemical inhibitors that are added to cooling systems should be adequately controlled and monitored. The chemistry parameters that indicate proper treatment and the presence of impurities should be controlled to minimize corrosion of the systems and loss of integrity.

## WATER CHEMISTRY CONTROL AT BWR POWER PLANTS

4.14. During operation, the chemistry control programme at a BWR power plant should be focused on decreasing the impurities in the reactor coolant to the minimum practicable and achievable in order to avoid or minimize intergranular stress corrosion cracking, and on reducing radiation levels.

4.15. To avoid or minimize intergranular stress corrosion cracking, certain agents may be injected. The concentration of these agents should be controlled on the basis of suitable measurements.

4.16. Dissolved hydrogen and oxygen levels as well as impurity levels (e.g. corrosion products, chloride, sulphate and fluoride) should be maintained within specified limits.

4.17. The conductivity and concentrations of chlorides and sulphates should be adequately controlled in the reactor coolant. The concentrations of iron and copper (in the case of components containing copper) should be adequately controlled in the feedwater systems.

4.18. Before shutdown, at those plants where it is possible, the flow rate of the reactor water cleanup system should be increased as much as possible to minimize activated corrosion products in the reactor water.

4.19. The activity of reactor water and the buildup and transport of radioactive material should be minimized. During normal operation, the injection of zinc and iron into the feedwater may be used for this purpose.

4.20. During startup, the oxygen concentration should be controlled adequately and should be maintained at a low enough level to minimize intergranular stress corrosion cracking.

## WATER CHEMISTRY CONTROL AT RBMK POWER PLANTS

4.21. For a Russian built nuclear power plant with graphite moderated nuclear power reactor (RBMK), the neutral water chemistry regime should be applied without the use of any acids or alkalis. The water chemistry should be achieved by the use of high purity feedwater and effective purification systems (for condensate and reactor coolant).

4.22. In the chemistry control programme at an RBMK, it should be ensured that there is:

(a) Minimal deposition on heat exchanging surfaces and piping;
(b) Minimal corrosion and corrosion–erosion (e.g. intergranular stress corrosion cracking, flow accelerated corrosion) of the materials of the main steam–water circuits;
(c) High quality saturated steam, which does not cause droplets to form on the steam flow paths of the turbine, thus ensuring fine water quality and separation.

4.23. The levels of chemistry parameters should be maintained within specified limits.

4.24. Dissolved hydrogen and oxygen levels should be maintained within specified limits. To reduce the risk of corrosion, the concentration of oxygen should be maintained at the minimum possible level.

4.25. To minimize the level of $^{95}Zr$ and other activated corrosion products in deposits on the surfaces, flushing (washing) of the primary circuit should be performed at the beginning of shutdown. Flushing may be conducted without special reagents or by the use of a combined procedure (reagent and non-reagent).

## PRIMARY WATER CHEMISTRY CONTROL AT PWR AND WWER POWER PLANTS

4.26. The presence of variable concentrations of dissolved $^{10}B$ and boric acid in the reactor coolant system for controlling core reactivity should be continuously measured, if possible, and evaluated.

4.27. Addition or removal of alkaline compounds should be used in order to maintain the optimum $pH_T$ value (pH at operating temperature) at all times during operation. In PWRs, generally, lithium hydroxide is added, while in WWERs, potassium hydroxide is added and the total alkali mixture (potassium injected, lithium produced by neutron reaction on boron, and possibly sodium as an impurity) is monitored. The purpose of maintaining this optimum $pH_T$ value is: (i) to minimize rates of uniform corrosion of the circuit materials, mass transfer rates and dose rates; (ii) to prevent materials from undergoing stress corrosion cracking; (iii) to avoid fuel cladding corrosion and (iv) to prevent crud induced power shifts.

4.28. The concentration of hydrogen should be maintained at an optimal level in order to suppress the production of oxygen via radiolysis and to keep the electrochemical potential at a sufficiently low level to prevent the stress corrosion cracking of stainless steel. In addition, make-up water to the primary circuit should be degassed and any remaining oxygen should then be eliminated if its level exceeds specified limits.

4.29. Corrosive impurities should be kept below specified limits to avoid corrosion of the primary system components. The most important constituents of chemical compounds are oxygen, chlorides, fluorides and possibly sulphates.

4.30. The concentrations of chemical compounds with a low solubility (which may deposit on the fuel surface and cause a temperature increase and consequently a fuel cladding failure) should be kept to a minimum. Such chemical compounds include calcium compounds, magnesium compounds, aluminium compounds and, possibly, silicon dioxide (whose ions may form zeolite) and organic compounds.

4.31. Shutdown and startup procedures should be optimized to control the release of corrosion products and remove them using coolant purification system demineralizers, as well as to minimize any risk of intergranular stress corrosion cracking.

## PRIMARY AND MODERATOR WATER CHEMISTRY CONTROL AT PHWR POWER PLANTS

4.32. Chemistry control of the various process systems is necessary to provide support in achieving and maintaining plant availability, safety, and efficient and economic operation by minimization of corrosion, control of reactivity and minimization of impurities that are detrimental to plant operation.

4.33. Corrosion of process systems should be minimized by the careful selection and control of a set of chemistry parameters, which together will reduce the aggressiveness of fluids on the specific materials used in the process systems.

4.34. A management system for heavy water ($D_2O$) should be established to preserve the $D_2O$ inventory and to control the level of tritium activity. Throughout the heavy water management system, $D_2O$ should be segregated on the basis of its tritium and isotopic composition.

4.35. The isotopic composition of heavy water in the heat transport system should not be permitted to decrease below a value that ensures that excessive positive reactivity will be prevented in the event of voiding in the heat transport system. Additionally, the isotopic composition of heavy water in the heat transport system should not be permitted to increase beyond the isotopic composition of the moderator at equilibrium of the fuel cycle.

4.36. When soluble reactivity agents (poisons such as boron and/or gadolinium) are used in the moderator to control the reactivity of the reactor, the requirement for their concentration should be based on the negative reactivity necessary to ensure that the reactor will remain subcritical in the event of a serious process failure. The poison concentration required to achieve an overpoisoned guaranteed shutdown state will be specific to the nuclear power plant and should be documented in the safety analysis. The isotopic concentrations of boron and gadolinium salts intended for use as neutron poisons should be verified prior to their introduction into the reactor system, to ensure that their isotopic concentrations ($^{10}$B, $^{155}$Gd to $^{157}$Gd) are equal to, or higher than, their natural isotopic abundance.

4.37. Action limits for deuterium and hydrogen concentrations in cover gas systems should be adequately established in order to eliminate the possibility of an explosive gas mixture being created.

4.38. The concentration of dissolved deuterium in the primary circuit should be such that radiolysis is suppressed and the system components are protected against hydrogenation.

4.39. Impurity levels, in particular those of corrosion products, chloride ions and fluoride ions, should be kept within specified limits. A good correlation between the concentration, pH and conductivity of the alkaline reagents in the primary circuit should be maintained in order to provide a good indication of the absence of significant concentrations of contaminants.

4.40. During reactor shutdown, normal chemistry specifications should be applied for the primary circuit, except those for dissolved deuterium. Hydrogen should not be added when the reactor is cold and depressurized, and during shutdown maintenance, part of the empty space of the primary system should be filled with nitrogen (nitrogen blanketing) to minimize inward leakage of air.

4.41. During reactor shutdown, normal chemistry specifications should be maintained for the moderator system, except when:

(a) The moderator contains gadolinium as a result of poison injection by the shutdown safety system, as a result of being in a guaranteed shutdown state or as a result of xenon simulation.
(b) The cover gas is being purged.
(c) The moderator is drained.

## SECONDARY WATER CHEMISTRY CONTROL AT PWR, WWER AND PHWR POWER PLANTS

4.42. The secondary circuit should be operated according to an ‘all volatile treatment’ or an ‘all volatile treatment with high pH’. All volatile treatment means the use of only volatile alkaline reagents such as ammonia and/or amines (e.g. morpholine, ethanolamine, dimethylamine). A reducing agent should also be added when necessary.

4.43. Special attention should be paid to the integrity of the various parts of the secondary systems that may be significantly affected by flow accelerated corrosion. Hence the operating organization should establish a periodic inspection programme, especially for secondary side and auxiliary (balance of plant) piping.

4.44. The pH value and the use of ammonia and/or amines and a reducing agent and their concentrations are plant specific and should be such that an appropriate $pH_T$ value is provided in various parts of the secondary system. The values selected should be:

(a) Such that flow accelerated corrosion of carbon steels is avoided or minimized and the amount of corrosion product in the feedwater that will be deposited in the steam generator is minimized;
(b) Compatible with effective purification systems;
(c) Compatible with secondary side materials;
(d) Such that planned releases of liquid waste and solid waste to the environment are minimized.

4.45. The primary to secondary circuit leakage rate in the steam generator tubes should be monitored and strictly controlled within predefined limits for safety reasons. In addition, such leaks should also be limited in order to minimize the production of radioactive waste (e.g. regeneration and flushing solutions, resins, filters, sludge).

4.46. The levels of deleterious impurities (e.g. sodium, chloride and sulphate ions and lead and copper) in the steam generators should be minimized and controlled. Blowdown limits for the steam generator should be established, with action levels for each chemical impurity that may be deleterious for the steam generator tubes and potentially present in the system.

4.47. The influence of chemistry control on the integrity of the steam generator should be evaluated. The main tools for such an evaluation are:

(a) The results of non-destructive testing (in-service inspection) of the integrity of the steam generator tubes, at least for degradation that may be related to the primary and secondary water chemistry programmes;
(b) The evaluation of ‘hideout return’ effects (the levelling of concentrations) during at least some of the shutdowns for refuelling;
(c) Calculation codes or any other relevant method for estimating the chemistry characteristics of the liquid contained in crevices in, and deposits on, the steam generator tube during operation.

4.48. The methods used to control secondary water impurities should be sufficiently effective as to maintain the steam generator blowdown parameters within specified limits.

4.49. If necessary, an effective cleaning procedure should be applied to remove deposits that promote corrosion.

# 5. CHEMISTRY ASPECTS OF RADIATION EXPOSURE OPTIMIZATION

5.1. The optimization of radiation exposures through an appropriate chemistry regime results in:

(a) Continuous reduction, over time, of dose rates in the plant;
(b) Minimization of any releases of radioactive material to the environment;
(c) Minimization of the generation of radioactive waste by means of water chemistry.

## SOURCES OF OCCUPATIONAL RADIATION EXPOSURE AND ENVIRONMENTAL DISCHARGES

5.2. The chemistry programme or radiation protection programme should include control of dose rates from systems and components. Such dose rates should be maintained ALARA. During an outage, and if possible also during operation, dose rates from systems and components should be checked regularly. This makes it possible to monitor the manner in which dose rates develop over time.

5.3. Strict specifications for all important radiochemistry parameters should be established and applied for different operational modes.

5.4. Use of appropriate corrosion resistant materials and a well-defined water chemistry regime are some of the means used to reduce buildup of radioactive material. Various decontamination techniques should be used to optimize occupational doses (with account taken of the recommendations provided in paras 5.22–5.24). Chemical decontamination should be used as the final option if other measures fail to achieve low dose rates.

5.5. The chemistry control programme should support the production of high quality water and should include the following:

(a) The specification and application of a suitable chemical treatment (e.g. pH control for PWRs/WWERs and oxygen control) for the minimization of corrosion processes, and hence reduction of the amounts of corrosion products in the water;
(b) The use of pure make-up water to avoid easily activated chemical contaminants and suspended materials;
(c) The use of effective primary and secondary water cleanup systems for controlling dissolved and suspended radioactive substances;
(d) Quality management of the chemicals used in the coolant systems and hence avoidance of detrimental effects from pollutants.

5.6. The dominant sources of radioactivity during shutdown in the primary circuit are described in para. 5.13. During startup, normal operation, shutdown and standby processes, consideration should be given to all chemistry remedies, and measures should be taken to reduce activity levels and to manage the transport of radioactive contaminants. It is especially important to optimize the chemical aspects of the actual shutdown procedure and planned maintenance activities to reduce the doses to maintenance workers during outages.

5.7. The primary water chemistry programme applied should effectively control and minimize the buildup of radioactive material from the transport and accumulation of fission products and activated corrosion products on the internal surfaces of the systems.

5.8. The operating organization should establish and implement procedures for monitoring and controlling discharges of liquid and gaseous radioactive effluents. Radioactive discharges should be kept ALARA and below the control values.

## SYSTEMS AND MEASURES FOR PREVENTING AND OPTIMIZING OCCUPATIONAL RADIATION EXPOSURES AND ENVIRONMENTAL DISCHARGES

### Fission products

5.9. The activities of fission products in the primary coolant and in other media should be kept below their specified control values. This activity should be checked by continuous monitoring and/or periodic sampling and measurement. The results of the monitoring of activity levels should be analysed and evaluated to monitor the leaktightness of fuel rods.

5.10. The normal level of fission product activity in the primary coolant should be specified during the initial period of reactor operation following startup, in order to provide a reference background level, and this level should be used for trend analysis. This value should be included in the operational limits and conditions or in the radiochemistry technical specifications. This activity is mainly a result of uranium contamination of the cladding surface of the fuel during the manufacturing process and/or a result of fuel failure.

5.11. In the primary water chemistry control programme, all primary circuit materials used should be considered, including fuel cladding, to prevent fuel cladding failure and any detrimental effect on the primary circuit or the environment.

5.12. Dissolved oxygen and/or hydrogen concentration and alkalinity should be strictly controlled to minimize fuel cladding deterioration and thereby optimize occupational radiation exposures and environmental discharges. Zirconium alloy cladding is sensitive to corrosion from oxidation, hydride embrittlement and increased corrosion due to high lithium levels in the coolant or to low pH and low solubility species, which both cause a buildup of deposits on the cladding. Large amounts of deposits can increase the cladding temperature and, as a consequence, increase the risk of fuel cladding failure, which could increase radiation exposure.

**Activated corrosion products**

5.13. Corrosion processes should be monitored, trended and controlled. During shutdown, with little or no failed fuel present, activated corrosion products are responsible for the great majority of out-of-core radiation fields. These corrosion products either come from in-core components or are released from corroding and/or wearing surfaces into the coolant system. The corrosion products are then transported by the primary coolant to the reactor core, where they are deposited on surfaces within the neutron field and become activated. They are subsequently released again into the coolant system, transported out of the core and deposited on out-of-core surfaces.

5.14. The control of corrosion product transport should be established and implemented in order to minimize the release and redeposition of activated corrosion products from the core that may result in very high radiation fields out-of-core. This transport should be minimized by keeping primary water chemistry parameters as constant as possible and as close as possible to the optimal values during normal power operation.

5.15. The use of materials containing cobalt in the primary systems should be minimized as much as possible because the $^{60}$Co radionuclide is the most important contributor to radiation fields. The corrosion rate and the release of cobalt should be controlled through the chemistry regime in order to reduce dose rates due to $^{60}$Co.

5.16. A further important contributor to radiation fields is the $^{58}$Co radionuclide. It is generated from nickel by n–p reaction (where a neutron replaces a proton in the nucleus). As nickel is a substantial constituent of almost all primary system construction materials, the presence of $^{58}$Co cannot be avoided and its activity increases with nickel content in the alloys used. Optimized primary water chemistry control during operation and especially during shutdown is one of the most powerful tools for minimizing radiation fields due to $^{58}$Co.

5.17. The presence of silver and antimony, as easily activated elements, should be minimized in components and, if necessary and if possible, specifically eliminated during the shutdown process by the selection of a proper shutdown chemistry regime. In RBMK units, $^{95}$Zr may also be an important contributor to radiation fields and should be eliminated if possible.

5.18. Once the plant is constructed and is in operation, chemistry control, through an appropriate water chemistry regime, should be the main technique used by the operator to reduce the rate of buildup of radioactive material. Adequate control of water chemistry parameters during normal operation and for shutdown, startup and standby processes should be established and implemented to minimize the release, transport and deposition of activated corrosion products throughout the fuel cycle. During shutdown, the concentration of corrosion products may increase considerably and the directions of transport may also change, resulting in deposition on out-of-core surfaces. This can result in elevated dose rates and occupational radiation exposures during outage and possibly in radioactive hot spots.

**Primary system components**

5.19. During the commissioning phase, surfaces should be preconditioned before and during initial startup in order to produce a protective layer and to ensure appropriate, passivated surfaces in all systems. The protective layer will reduce the subsequent release of corrosion products into the coolant when the plant is at power and hence will reduce the deposition of radioactive material.

5.20. Chemistry control should be applied to avoid detrimental corrosion effects and hence unnecessary dose rate increases due to the deposition of corrosion products. During normal power operation, chemistry control should be ensured by the effective use of built-in (in-line) purification systems.

5.21. When changing equipment and/or parts of equipment in the system, consideration should be given to minimizing the use of materials containing potential contaminants likely to cause corrosion. Programmes for replacement of stellite and antimony should be considered, where practicable.

## DECONTAMINATION PROCESSES

5.22. Effective decontamination techniques (e.g. chemical, electrochemical and mechanical) should be developed and validated for different applications. The cost, the downtime necessary, the risk associated with the use of corrosive reagents and the generation of radioactive waste associated with decontamination mean that the use of decontamination technology should be minimized through effective control of radiation field buildup rates and adequate water chemistry control. The decontamination should result in a net reduction of occupational dose over the entire operating lifetime of the plant.

5.23. In primary circuits, the extensive use of chemical decontamination processes should be avoided in order to minimize deterioration of the protective oxide layer on the surfaces, which then requires time and further passivation to recover, and changes in the surface finish, which increase recontamination and corrosion release rates. Without a uniform and stable protective film on the surface, an extensive corrosion and transport process will start that may induce heavy deposit formation on the fuel surfaces, with increased risk of fuel failure. If chemical decontamination cannot be avoided, then the passive status of the surface should be recovered and controlled following decontamination.

5.24. In the case of the extensive use of chemical decontamination processes, such as chemical decontamination of the steam generator or the full system, detrimental side effects should be evaluated. Other technical measures (e.g. shielding, filling up systems with water, use of robotics, time limitations and training of personnel) should be considered in the optimization of occupational radiation exposure.

## MINIMIZATION OF LIQUID AND GASEOUS RADIOACTIVE WASTE GENERATION AND OF RELEASES

5.25. The generation of radioactive waste should be kept as low as possible in terms of both activity and volume, by appropriate operating and chemistry control practices. Treatment and interim storage of radioactive waste should be strictly controlled in a manner consistent with the requirements for safe disposal of waste [10]. During treatment and interim storage, the requirements defined by waste acceptance criteria should be taken into consideration. Further recommendations on waste management in the operation of nuclear power plants are provided in Ref. [11].

5.26. In order to minimize liquid and gaseous waste and/or activity, consideration should be given to the application of the following methods:

(a) Monitoring and identification of early leakage in the system and immediate corrective actions;
(b) Optimization of the total number of items of equipment and devices as well as optimization of the handling of liquids in the plant in order to reduce the amounts of liquid waste collected;
(c) Segregation of liquids to avoid dilution and mixing of chemically incompatible substances;

(d) Reduction of the amounts of chemicals, recycling of chemical substances (particularly boric acid) if possible and reasonable, or use of chemicals that decompose completely and safely;
(e) Establishment of appropriate chemistry procedures to prevent and control fuel and primary to secondary coolant leakages;
(f) Reduction of the amount of gas introduced into the system to the minimum practicable;
(g) Use of ion exchange resins and selective sorbents;
(h) Use of filters to separate suspended radioactive substances from the liquids;
(i) Use of hold-up tanks and other delay systems (charcoal beds) to allow radioactive decay before material is released;
(j) Use of effective filters to separate aerosols from gaseous discharges;
(k) Use of treatment for volume reduction (recombiners, absorbers, vapour recovery system, pressurized storage), which also serves as a delay system;
(l) Optimization of waste management in order to minimize waste, facilitate disposal and reduce exposure in a cost effective manner.

5.27. Appropriate water chemistry control should be applied to minimize the risk and consequences of a loss of coolant accident resulting in the release of iodine radionuclides to the containment building.

## 6. CHEMISTRY SURVEILLANCE

6.1. The operating organization should establish and implement a chemistry surveillance programme to verify the effectiveness of chemistry control in plant systems. It should also be verified that structures, systems and components important to safety are operated within the specified limit values. Such a surveillance programme should be used to detect trends in parameters and to discover and eliminate undesirable effects and consequences of out-of-range chemistry parameters. The chemistry surveillance programme should reflect chemistry specifications for all stages of the lifetime of a plant, including commissioning, shutdown and startup periods, and when systems are taken out of operation for prolonged periods.

6.2. The objectives of a chemistry surveillance programme are:

(a) To verify compliance with control and diagnostic chemistry limits and conditions;
(b) To maintain the availability of structures, systems and components;
(c) To detect and thus permit early corrective action for any abnormal chemistry condition before it becomes a consequence significant for safety;
(d) To ensure compliance with discharge limits.

6.3. The chemistry surveillance programme should utilize all available sources of information, including chemistry data and other technological data related to chemistry.

6.4. Software for calculations of chemistry processes important to safety should be verified and validated by a third party or another appropriate independent organization or experts before use. For details see Ref. [12].

6.5. Trending should be included in the surveillance programme in order to check if relevant control and diagnostic parameters are within the accepted limits.

6.6. The use of chemistry performance indicators for the most important chemistry parameters should be considered; these indicators should be trended and periodically reported on for evaluation.

6.7. Chemistry surveillance should be accomplished through the use of on-line instruments, analysis of individual, representative samples (‘grab samples’) and subsequent evaluation of results.

## CHEMISTRY MONITORING

6.8. Consideration should be given to the use of on-line monitoring of control parameters as the preferable monitoring method for evaluating chemistry conditions in plant systems.

6.9. Laboratory analysis should be considered a necessary complement in the diagnosis of chemistry problems, to verify the accuracy of on-line monitors and whenever it is either not possible or not reasonable to apply on-line monitoring.

6.10. Written procedures should be developed for all on-line and laboratory analyses and such procedures:

(a) Should describe the intended use of the procedure;
(b) Should reference information sources used for development of the procedure;
(c) Should provide a summary of analytical methods used, indicating possible interference, accuracy, linearity and range of the methods and the precision of the measurements in order to show ways of validation;
(d) Should state equipment, reagents and standards required to perform analysis;
(e) Should provide step by step instructions for performing analysis and calculating the results;
(f) Should indicate quality control requirements and industrial safety and radiological protection measures;
(g) Should provide information on instrument calibration.

6.11. A calibration and maintenance programme should be established and applied to all on-line and laboratory monitoring instrumentation. The responsibilities for calibration and maintenance should be clearly defined.

6.12. Reagents and sources used for calibration should be valid (e.g. all standards applied should be traceable to certified standard solutions or reagents).

6.13. Calibration points should be chosen such that their measurement ranges overlap and that they are as close as possible to the expected measurement value.

**On-line monitoring**

6.14. On-line chemistry monitoring and data acquisition systems should be used that accurately measure and record data and provide alarms for key chemistry parameters. The measurement ranges of analytical instruments should extend beyond the operating ranges and safety limits of the plant.

6.15. As part of the integrated management system for the nuclear power plant [7], a management system should be implemented that ensures that the data collected by on-line monitoring and the data acquisition system are accurate and reliable. Other methods that could be used for this task include:

(a) Timely calibration, performed either on the basis of equipment manufacturers' recommendations and plant experience or by using standard solutions;
(b) Comparison of results from on-line monitors and laboratory equipment;

(c) Comparison of data from different sampling points (e.g. intercomparison of measurements of cation conductivity in the steam generator blowdown system) or comparison of different parameter measurements from the same sampling point for evaluating the plausibility of the data measured.

6.16. Typical physical conditions (e.g. temperature, flow rate) at the measuring location should be taken into account. Although some instruments have temperature compensation, temperature should be controlled for the evaluation of results, as such instruments may have limited accuracy and temperature ranges.

**Laboratory monitoring**

6.17. Laboratory monitoring involves sampling of plant systems and analysing for specific chemistry properties, concentrations of dissolved and suspended impurities and activities of radionuclides. The scope and periodicity of chemistry monitoring activities to be performed should be set out and made available. Sampling points, periodicity of analysis and procedure should be established for each chemistry regime (startup, shutdown, operation at stable power levels, transients).

6.18. 'Check standards' (measurements made at specified time intervals) should be analysed and control charts should be maintained to show that the methods applied continue to give accurate results. The establishment of an interlaboratory comparison programme may be considered.

6.19. In determining the analytical methods to be employed, expected concentration levels should be considered for the chemistry parameter of interest. The method chosen should provide sufficient sensitivity in the expected concentration range. The 'matrix effect' (the effect of other components in the sample) should be determined and corrected if necessary.

## RADIOCHEMISTRY

6.20. Control of radiochemistry is a fundamental part of chemistry activities at a nuclear power plant. Measurement of radiochemistry parameters is important for the safe management of the plant at all stages of its lifetime, from initial operation to decommissioning.

6.21. Radiochemistry measurements should be carried out for systems such as closed cooling water circuits and the primary and secondary sides of PWRs to detect leaks in material barriers. Radiochemistry measurements should be implemented for a wide basis of plant activities, as described below.

6.22. Primary coolant activity monitoring should be carried out in support of the following tasks:

(a) Measurement of fission product activity as a means of evaluating the fuel integrity, identifying fuel cladding leaks and estimating cladding defect type and number:
   - For this purpose, good quality, well-maintained and calibrated gamma spectrometry instrumentation, a sufficient variety of calibrated measurement geometries, and effective and verified radiochemical separation procedures should be applied.
   - Results of such measurements should serve as input data for validated calculations for evaluating fuel leaks. Sufficient sensitivity with respect to activity measurements of key fission products should be ensured as a major condition for the early detection of fuel leaks.
   - Power transients accompanied by 'spiking phenomena'[3] for fission products should be adequately monitored.
   - As part of these actions, and depending on the type of fuel, proper selection of both volatile (e.g. noble gases, iodine) and non-volatile (e.g. caesium, transuranic elements) radionuclides should be made to enable the detection of both small and large cladding defects.
   - Properly selected radionuclide activity ratios should be applied to assess the burnup of leaking fuel rods in order to facilitate their identification during operation or outages, depending on the type of reactor.
(b) Measurement of the activities of corrosion products as a means of monitoring chemistry performance, radioactive material transport processes and potential foreign material ingress. In order to ensure good representative data, appropriate isokinetic sampling methods capable of 'activity fractioning' for liquids and particles (separation of activity into specific fractions) should be implemented if possible.
(c) Measurement of other activated species (e.g. radioisotopes of sodium, potassium and chlorine) as a useful means of verifying or cross-checking

[3] Spiking phenomena occur when fission products that are accumulated in all the spaces in the fuel pin (in fractures in the fuel pellets, in the gap between the fuel pellets and the cladding and in the expansion chamber) are released into the coolant when the pressure is decreased (see Ref. [13]).

the results of chemical analyses and for early warning of low concentrations of possibly unknown impurities.

6.23. Radiochemistry measurements should be part of spent fuel handling operations, starting from reactor pool storage through any transport operations to interim storage facilities, in order to monitor fuel integrity and the possible propagation of defects after removal of fuel from the reactor.

6.24. Radiochemistry measurements should be applied in monitoring the performance of purification systems, especially when removal of radioactive material is the main purpose of operation of the purification system.

6.25. Measurement of the activities of relevant radionuclides should be carried out while monitoring the efficiency of decontamination processes, especially in the decontamination of large components, in order to optimize treatment time and minimize radioactive waste generation. Monitoring practices should be in accordance with ALARA principles and objectives.

6.26. Radiochemistry methods should be applied to provide the results necessary for the characterization of radioactive waste with regard to its treatment, conditioning and disposal:

(a) Effective and validated radiochemical separation methods should be developed for activity measurement of difficult-to-measure radionuclides (e.g. pure alpha or beta emitters and low energy gamma emitters).
(b) For the radionuclides specified for each disposal facility, and as defined in the safety analysis report, the activities should be determined repeatedly in a defined set of waste streams, so that sufficient data are accumulated from which mathematical correlations can be derived between difficult-to-measure radionuclides and key (reference) radionuclides (so-called 'fingerprinting').
(c) Such correlations should then be used for the calculation based characterization of newly generated waste, but periodic checks of their correctness should be carried out by new radiochemical analyses.

6.27. The activities of radioactive effluents, both liquid and gaseous, should be monitored regularly by appropriate activity fractioning and monitoring methods.

6.28. Radiochemical methods that rely on radiochemical separation methods and properly calibrated liquid scintillation counters should also be applied to monitor liquid and gaseous releases of tritium and $^{14}C$ as specific low energy beta emitters.

6.29. Determination of the activity of primary surface deposits serves for the identification of either potential specific radionuclide contaminants (e.g. antimony, silver) or trends and anomalies in occupational radiation exposure. This determination should be made by the use of wipe sampling, corrosion layer scraping or electrochemical sampling, or by in situ gamma spectrometry of appropriately selected parts of the primary circuit, or by other methods.

## CHEMISTRY FACILITIES AND EQUIPMENT

### Laboratory facilities

6.30. Laboratories should be suitably secured and located, and should be provided with adequate space, supplies and equipment, consideration being given to human factors.

6.31. Redundancy or equivalency of laboratory facilities should be provided to ensure analytical services at all times.

6.32. Laboratories should have good general housekeeping, orderliness and cleanness at working areas and sampling points, including satisfying appropriate contamination level criteria, in accordance with procedures at the plant.

6.33. Industrial safety (provision of fume hoods for ventilation, appropriate storage of flammable solvents and hazardous materials, and flammable and other gases, and provision of safety showers for personnel, as well as personal protective equipment and first aid kits) and radiological safety (proper radiation shielding and contamination control facilities) should be ensured. All laboratory and work practices should be carried out in accordance with industrial safety standards and the principle of optimization of protection (and safety) [3, 14].

6.34. Protective measures should be prepared and included in the available procedures for response to unexpected events such as fires, flooding and other internal or external events.

### Laboratory instruments

6.35. All laboratory instruments and equipment should be in good condition in order to provide accurate and reliable analytical data for monitoring purposes. The condition of such instruments and equipment should be ensured by a documented maintenance plan and a regular calibration plan.

6.36. Adequately redundant instrumentation and equipment for performing analyses of given types and frequency should be made available. Instrumentation, equipment and the methods to be applied should be validated.

6.37. Instrumentation manuals, well-maintained logbooks and calibration records should be made available in the laboratory.

### Testing of laboratory performance

6.38. The adequacy and accuracy of procedures should be checked regularly by means of intralaboratory and interlaboratory tests to identify analytical interference and improper calibration, analytical technique and instrument operation. These test results should be evaluated to determine the cause of unexpected differences and deviations, with account taken of both short and long term effects. If necessary, corrective action should be taken to further improve laboratory performance.

### Survey of instrument performance

6.39. Results of the analysis of standards should be used to verify instrument accuracy on the basis of specified acceptance criteria.

6.40. If instrument performance shows significant deviation from expected values, an investigation should be performed to determine the cause of the deviation. Repair or recalibration of an analytical instrument may be necessary to maintain or recover the desired level of accuracy.

### Sampling systems

6.41. Appropriate consideration should be given to the need for correct sampling conditions, as one of the most important factors affecting the accuracy and reliability of measurement results is sampling, which is the first step of every analytical measurement. Account should be taken of delays in obtaining samples (due to, for example, the volume of the ‘sampling line’ for liquid samples) when using data obtained through on-line or laboratory measurements, and of specific sampling issues associated with obtaining representative soluble and particulate corrosion products.

6.42. Representative grab samples should be ensured by appropriate flushing of sampling lines, proper determination of the flow rate, cleanness of containers, and minimization of the risk of chemical contamination and loss of dissolved gases or volatile substances during sampling. A written procedure on sample collection should be made available.

## POST-ACCIDENT SAMPLING SYSTEM

6.43. A post-accident sampling system or other adequate sampling facility should be ready to operate when required by emergency procedures and should also be considered for use in taking regular samples from plant systems. If a post-accident sampling system does not exist, other approaches should be adopted for core damage evaluation and for estimation of the inventory of fission products released into the containment.

6.44. For proper operation of a post-accident sampling system, the following should be provided:

(a) Operating procedures for the post-accident sampling system.
(b) Radiation protection measures for personnel who carry out sampling and analysis; such measures should be evaluated in advance and applied when the post-accident sampling system is used.
(c) A programme for preventive maintenance.
(d) Regular checks of the operability of the post-accident sampling system.
(e) Regular training of personnel designated for operation of the post-accident sampling system (i.e. personnel taking grab samples and performing subsequent activities).
(f) Specification of the chemistry parameters to be monitored (e.g. conductivity in the reactor water cleanup system and gaseous fission products in the main steam system).
(g) Procedures for optimizing occupational radiation exposure.

# 7. MANAGEMENT OF CHEMISTRY DATA

**Data acquisition**

7.1. The results of analytical and quality control measurements should be recorded properly (e.g. laboratory logs, registered data sheets, databases containing periodic on-line measurements). The results should be supplemented with complementary information necessary for their interpretation, assessment and communication.

7.2. The data relating to chemistry should be suitably archived, stored and easily retrievable, in accordance with the provisions of the quality assurance programme at the plant.

**Data review**

7.3. Analytical data should be reviewed to verify their completeness, accuracy and consistency. To identify actual and potential problems, assessment of chemistry data should commence promptly after the data have been recorded, depending on the importance and potential consequences of any deviation.

7.4. In the case of deviations or anomalies in results, these should be checked and verified by a competent individual and proper and prompt corrective action should then be taken and documented.

7.5. The primary responsibility for review of chemistry data should be assigned to the chemistry staff. The chemistry staff should compare the current data with those previously obtained and should investigate situations where the results obtained are outside the expected range of the system operating conditions, should identify recent additions of chemicals and operational changes and should consider the results of laboratory quality control tests.

**Data evaluation and trending**

7.6. Data should be compared with operational limits and the evaluation and trending of data should be carried out to assess the efficiency of chemistry control, to identify inconsistencies in analytical data and adverse trends in chemistry conditions and to help in optimizing chemistry in the plant systems. Particular attention should be given to data that deviate from operational limits.

7.7. Graphical trending of chemistry parameters should be carried out to provide an adequate picture of plant chemistry conditions and to facilitate correlation between related chemistry parameters and the status of systems.

7.8. Trends should be reviewed soon after data have been recorded, in order to identify problems that may need corrective action before a parameter exceeds its specified limit. Trending should also be used to evaluate transients of short duration caused by plant operational changes and slower long term changes occurring under stable plant conditions. Evaluation of slow changes may facilitate the prediction of when a change could become a significant safety problem.

7.9. Significant short and long term chemistry results should be routinely evaluated and reported to the appropriate level of management. Effective communication with other groups should be established when analytical data indicate the need for prompt action to correct chemistry related problems.

### Feedback

7.10. A method for transferring analytical results to other departments (e.g. the operations department) should be established and communicated to, and should be clearly understood by, personnel, to ensure timely correction of any problems identified [15].

## 8. TRAINING AND QUALIFICATION

8.1. Recruitment, training and qualification of the chemistry staff should be organized in accordance with the recommendations provided in Ref. [16].

### Competence and qualifications

8.2. Management of the chemistry programme should ensure that chemistry personnel are qualified and have the necessary knowledge, skills, abilities and level of supervision to perform their job functions properly and are sufficiently motivated to adopt a positive attitude to safety [1, 17].

8.3. The operating organization should ensure that all personnel (not only chemists) involved in the various parts of the chemistry programme are sufficiently skilled.

8.4. In order to achieve and maintain high levels of safety, chemistry staff should be aware of the technical and administrative requirements for safety.

**Training policy**

8.5. A systematic approach to training for chemistry should be applied in accordance with the recommendations provided in Ref. [16]. Basic training (i.e. general training for all personnel), initial training and continuing training should be developed and implemented. Furthermore, certain specific attributes should be enforced regularly owing to the need for chemistry staff to develop adequate and specific skills and to increase their knowledge base.

8.6. Initial training for chemists should include on the job training at the plant (e.g. in chemistry laboratories, sampling areas, chemical handling and storage areas, and injection points of chemicals in operating systems).

8.7. Regular repeated training should also be considered at plants in which there is a large chemistry staff that does not perform certain tasks on a regular basis.

**Training facilities and materials**

8.8. Consideration should be given to training facilities and methods that are widely used and which have been proven to be effective in attaining the training objectives when appropriately chosen. Such proven facilities and methods include the following:

(a) Training should be provided in the laboratory, workshop or other locations where chemistry activities take place, to ensure safe working practices in the actual environment where the work will take place.
(b) On the job training should be conducted in accordance with written operating procedures for activities such as taking samples, controlling of water treatment technologies, using an on-line chemistry station, fixing deficiencies in on-line and off-line equipment, performing regular minor maintenance on on-line equipment and laboratory instruments, and using the post-accident sampling system.

(c) All chemistry activities should be provided by authorized chemistry staff, but trainees may be assigned to carry out chemistry activities while ‘shadowing’ (following) authorized staff.
(d) Training courses should include techniques for recognizing unusual conditions and adverse trends.

8.9. Chemists at a nuclear power plant should be fully trained and sufficiently knowledgeable in their areas of responsibility to be able to communicate effectively with, and support, the operations group.

**Training programme**

8.10. The training programme should include training in new technologies and analytical methods prior to their introduction in the plant.

8.11. All qualified suppliers and contractors involved in chemistry related activities (e.g. production of demineralized water, oil analysis, calibration of measurement equipment, metrology support and certification of chemicals) should be fully trained in, and should adopt, the applicable plant standards while working at the nuclear power plant.

8.12. Chemistry staff should be involved in any training programme or emergency exercise where releases of chemicals and radioactive material are involved. Emergency chemistry procedures, emergency equipment and values for emergency situations should be verified for use in training and exercises to ensure correct responses by emergency staff. This will also allow confirmation of the adequacy of emergency actions and will allow staff to familiarize themselves with the communication methods to be utilized.

8.13. Chemistry staff and other staff who deal with chemicals should be trained in the following specific areas:

(a) The handling of hazardous and flammable chemicals;
(b) The labelling of chemicals stored and used inside and outside the laboratory;
(c) Material safety data sheets;
(d) The use and maintenance of personal protective equipment;
(e) The specific use and storage of poisonous chemicals.

8.14. The operating organization should support attendance of plant chemistry representative(s) at national and international workshops, conferences and meetings, as well as facilitate access to networks or forums for exchange of operating experience relevant to the nuclear industry through which staff might obtain new information on new scientific results, technical developments and operating experience from other nuclear power plants.

# 9. QUALITY CONTROL OF CHEMICALS AND OTHER SUBSTANCES

9.1. A policy should be established to prevent the use of chemicals or other substances that could introduce potentially harmful impurities into plant areas or circuits, thereby affecting the coolant, auxiliary and safety systems, or other external surfaces. The responsibility for coordinating the control of chemicals and other substances on-site should also be clearly established in accordance with the requirements established in Ref. [7].

9.2. The operating organization should be responsible for the use of the proper chemicals and for their correct quality.

9.3. The use of chemicals and other materials at the plant, including those brought to the plant by contractors, should be controlled in accordance with clearly established procedures. The intrusion of non-conforming chemicals or other substances into plant systems can result in deviations in the chemistry regime, leading to component and system damage or increase of dose rates. The use of uncontrolled materials on the surfaces of the components may also induce damage.

9.4. One or more lists of approved chemicals and other substances that are allowed to be used at the nuclear power plant should be made available. These lists should be well known by chemistry, maintenance and procurement staff and contractors.

9.5. The reagents and ion exchange resins used for any safety related system should be within the required specifications with regard to impurities and this should be verified before their use.

9.6. Chemicals and other substances should not be used in systems, structures or components if they contain corrosion inducing components above specified limits.

9.7. Procedures for the procurement, storage, replacement and ordering of chemicals and other substances, including hazardous chemicals, should be made available.

9.8. When receiving chemicals, the specified quality should be verified by chemical analysis and/or by a certificate and a chemical identification test.

9.9. Chemicals and substances should be labelled according to the area in which they are permitted to be used, so that they can be clearly identified. The label should indicate the shelf life of the material.

9.10. When a chemical is transferred from a stock container to a smaller container, the latter should be labelled with the name of the chemical, the date of transfer and pictograms to indicate the risk and application area. The contents of the smaller container should not be transferred back into the stock container. Residues of chemicals and substances should be disposed of in accordance with plant procedures. The quality of chemicals in open stock containers should be checked periodically.

9.11. The replacement of harmful chemicals or other substances (from the point of view of personnel safety, environmental protection and material compatibility) by harmless ones should be encouraged.

9.12. Staff involved in receiving, storing, transporting and using chemical substances should be trained to understand storage compatibility, labelling requirements, handling, safety and impacts on structures, systems and components at the plant (see Section 8).

9.13. Management should periodically carry out walkdowns of the plant to evaluate the effectiveness of the chemistry programme and to check for uncontrolled storage of chemicals.

9.14. Material safety data sheets for all approved chemicals and substances should be made available and easily accessible. These data sheets should include, as a minimum, possible dangers to the health of staff, preventive measures for handling the materials and medical recommendations in case of accidental use.

9.15. Chemicals should only be stored in an appropriate store that is fire protected and captures spillages and which is equipped with a safety shower, as required. Oxidizing and reducing chemicals, flammable solvents and concentrated acid and alkali solutions should be stored separately. Tanks containing chemicals should be appropriately labelled. Reasonably small amounts of chemicals can be stored in other controlled environments in the workshops or operational department.

9.16. In the storage of chemicals, account should be taken of the reduced shelf life of opened containers. Unsealed and partly emptied containers should be stored in such a manner that the remaining product is kept in a satisfactory condition.

9.17. A procedure should be established to define the proper quality of all oils used for each component important to safety and used for the availability of systems important to safety.

9.18. Lubricants and hydraulic oils from systems important to safety and/or the availability of systems important to safety should be regularly analysed to check control parameters that characterize the condition of the lubricant.

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