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Chemistry Programme for Water Cooled Nuclear Power Plants

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New Safety Guide

IAEA
International Atomic Energy Agency

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FOREWORD

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Director General

The IAEA's Statute authorizes the Agency to establish safety standards to protect health and minimize danger to life and property – standards which the IAEA must use in its own operations, and which a State can apply to its nuclear and radiation related facilities and activities. A comprehensive body of safety standards under regular review, together with the IAEA's assistance in their application, has become a key element in a global safety regime.

In the mid-1990s, a major overhaul of the IAEA's safety standards programme was initiated, with a revised oversight committee structure and a systematic approach to updating the entire corpus of standards. The new standards that have resulted are of a high calibre and reflect best practices in Member States. With the assistance of the Commission on Safety Standards, the Agency is working to promote the global acceptance and use of its safety standards.

Safety standards are only effective, however, if they are properly applied in practice. The IAEA's safety services – which range in scope from engineering safety, operational safety, and radiation, transport and waste safety to regulatory matters and safety culture in organizations – assist Member States in applying the standards and appraise their effectiveness. These safety services enable valuable insights to be shared and I continue to urge all Member States to make use of them.

Regulating safety in nuclear and radiation related activities is a national responsibility, and many Member States have decided to adopt the IAEA's safety standards for use in their national regulations. For the Contracting 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 used around the world by organizations that design, manufacture and apply nuclear and radiation related technologies in power generation, medicine, industry, agriculture, research and education.

The IAEA takes seriously the enduring challenge for operators and regulators everywhere – of ensuring a high level of safety in the use of nuclear and radioactive materials around the world. Their continuing utilization for the benefit of humankind must be managed in a safe manner, and the IAEA safety standards are designed to facilitate the achievement of that goal.

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1. INTRODUCTION

BACKGROUND

1.1. This Safety Guide covers all types of nuclear power plants with water cooled reactors and supports the IAEA Safety Requirements for Nuclear Power Plants: 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 (SSCs) [2] that have a bearing on 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 systems. It supports the minimization of radiation build-up and exposures in the plant as well as the release of chemicals and radioactivity to the environment.

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

1.4. This Safety Guide is also intended to be useful to operating organizations' corporate members 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. This objective includes supporting the integrity of various barriers due to the potential of corrosion of components, reducing occupational exposures in the plant and limiting releases of radioactivity and chemicals into the environment.

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SCOPE

1.6. To achieve this objective, this Safety Guide provides Member States with recommendations and guidance for chemistry activities to ensure that SSCs important to safety are available to perform their functions in accordance with assumptions and intent of the design.

1.7. This Safety Guide refers to the main activities within the plant chemistry programme of the various types of water cooled reactors and to the chemistry control parameters having impact on their safe operation. These parameters are derived from research and development data as well as operational feedback experience. In addition, diagnostic parameters are defined which are of significant importance to the other objectives, i.e. plant availability, extended component lifetime, chemical and radioactive releases to the environment, and personnel exposure data.

1.8. This Safety Guide contains guidance on chemical monitoring to ensure compliance with the appropriate plant operational limits and conditions (OLCs) and to allow proper evaluation of the effectiveness of the plant chemistry programme.

1.9. This Safety Guide does not give detailed technical advice in relation to particular chemistry regimes of nuclear power plants. These details could be found in IAEA TECDOCs and IAEA Nuclear Energy Series reports, e.g. Refs [3] and [4].

STRUCTURE

1.10. 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. The process of the chemistry control is reviewed in Section 4. Chemistry aspects of exposure minimization are reviewed in Section 5. The chemistry surveillance process is discussed in Section 6. Section 7 deals with the chemistry data management and Section 8 concerns the training and qualification of personnel involved in chemistry activities. All aspects dealing with the quality control of chemicals are addressed in Section 9.

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2. FUNCTIONS, RESPONSIBILITIES AND INTERFACES

OPERATING ORGANIZATION

2.1. The operating organization is required to prepare and implement a chemistry programme to enhance the performance of the plant in the area of plant and personnel safety, environmental emission, and reliability by:

- preserving integrity of the SSCs important to safety;
- minimizing activity build-up to reduce plant dose rates and hence personnel radiation doses, reduce the activity associated with chemical and radioactive wastes, and to reduce the activity of any planned discharges to the environment;
- maximizing fuel integrity and reliability.

2.2. The organizational structure of operating organization should provide adequate chemistry management at their nuclear power plants [5].

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

2.4. Information from other utilities and countries (appropriate operating feedback, research results, good practices, etc.) should be analyzed and incorporated, where considered beneficial, to the chemistry programme. Such information should be available in the laboratories and properly maintained to be up to date.

2.5. Chemistry performance indicators (e.g. content of some chemicals and/or isotopes, in the cooling circuits) should be established to monitor the accomplishment of goals and objectives, and should be promoted and communicated to the staff. The management should periodically reinforce their expectations, monitor and assess performance, and correct deviations.

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2.6. The operating organization should ensure that the chemistry programme applied to the SSCs related to safety is implemented to ensure that the level of reliability and functionality of the SSCs remains in accordance with the design assumptions and intent throughout the plant’s operating lifetime.

2.7. The operating organization should provide adequate facilities, sampling and laboratory equipment and methodological support, taking water chemistry programme requirements and appropriate standards into consideration. Outside analytical contractors and consultants should be made available as necessary to fulfill analytical needs.

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

2.9. The operating organization should periodically evaluate the activities in relation to the chemistry programme by touring the chemistry facilities and plant chemistry equipment. The managers who are responsible for chemistry programme activities should observe that indicators of staff behaviour and attitude which are likely to be helpful to the development of strong safety culture are evident (proper attention to alarms, timely reporting of malfunctions, minimization of backlog of overdue maintenance, adequate labelling, accurate recording system, etc.).

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 (e.g. ion exchanger regeneration or replacement, repair of instruments, etc.). Trending of chemistry indicator deviations should be conducted in order to undertake preventive and/or corrective measures where necessary.

2.11. The plant self-assessment programme should include the chemistry area. In addition, the self assessment should include participation in a recognized analytical certification and inter-comparison program as well as use of internal standards, blanks, and blind samples. Audits and other self-assessment and independent reviews should be regularly conducted. A review

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of non-conformances should be reported and the status of corrective actions should be regularly evaluated [6].

2.12. Plant management should ensure that any measures to shorten the pre-planned outage shut-down schedule and accelerate the plant start-up will not compromise the full application of the chemistry control procedures (e.g. water clean-up during shut-down and start-up phases and the wet or dry conservation conditions on equipment should be fully respected).

2.13. There should be clear allocation of responsibilities at the plant according to the IAEA Safety Requirements for Management System [7] for all chemistry activities such as control of resources, chemistry control, chemistry dose management, chemistry surveillance, chemistry data management, analyses of water chemistry, review of the results and staff training and qualification.

CONTRACTORS

2.14. The operating organization should ensure that an effective organization is established for contractors working within the chemistry area. The management at the plant should remain responsible for all tasks undertaken by contractors.

2.15. A good interaction should be established between plant staff and outside contractors to ensure the contractors are familiar with the plant goals and procedures for a given activity.

2.16. Contractors should be subject to the same standards as plant staff, particularly with respect to chemistry skills and competence, adherence to procedures, result reporting, safety culture, and performance evaluation. Further guidance on the management of contractors is contained in Ref. [2].

2.17. The operating organization may delegate to other organizations the task of implementing the chemistry programme or any part thereof, but operating organization should retain the overall responsibility for such delegated work.

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OTHER BODIES, INCLUDING DESIGNERS AND MANUFACTURERS

2.18. The operating organization should have long term access to organizations that have the appropriate chemistry competence in laboratory activities, design, manufacturing, engineering, and research. Special commercial arrangements may be necessary to ensure continuity of access to these resources over the long term. When purchasing equipment, the operating organization should ensure that they are familiar with the field of chemistry instruments and what they will be used for.

2.19. When plant deficiencies occur or modifications are required, effective and timely assistance from the design/manufacturer or other organization with sufficient knowledge should be requested. The operating organization should make chemistry data available to these organizations. On the other hand changes in organizational structure or in SSCs that could have impact on the chemistry programme should be brought to the attention of chemistry management staff for advice, comments or approval if necessary. The scope of such information should to be regulated by clear and explicit instructions.

2.20. Water chemistry programme requirements and standards for the safety and safety related systems should be in agreement with the designer and manufacturer of such system equipment.

INTERFACE CONTROL

2.21. For all chemistry activities, an effective interface control system should be in place.

2.22. There should be a clear understanding of the division of responsibilities between all organizational units participating in chemistry activities. In particular, the interface between chemistry and other departments should be clearly specified. Chemistry personnel should clearly understand their authority, responsibility and interfaces with other groups.

2.23. Interfaces in Chemistry related issues between plant and off-site organizations such as universities, research institutions, equipment and chemical suppliers, authorities, should be established. For further guidance on interfaces, see Section 4 of Ref. [5].

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2.24. Proper coordination should be established between chemists and other groups (operation, maintenance, I&C, engineering) 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.

2.25. A report on water chemistry parameters should be formulated and shared with the other subdivisions and appropriate organizations on a regular basis. The report should include water chemistry analysis for the safety and safety related systems, parameter trending, analysis of deviations and corrective actions as well as their possible consequences, and overviews of quality audits of laboratory performance.

3. CHEMISTRY PROGRAMME

3.1. The chemistry programme should provide the necessary chemical and radiochemical information and assistance to ensure safe operation, long term integrity of SSCs, and minimization of radiation levels.

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

3.3. The programme should include the procedure for chemistry regime selection, monitoring, analyses, instructions for operations involving chemistry processes and evaluation of operating results.

3.4. There should be included in the programme the operation and reference limits for chemistry parameters as well as action levels [8].

3.5. The chemistry programme should ensure that:

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- a suitable chemistry regime exists and is in accordance with the original design and material concept, following any structural modifications or internal/external operating experience;
- the primary water chemistry regime is selected taking into account its impact on uniform corrosion and stress corrosion cracking of circuit materials, fuel cladding corrosion, corrosion product activation and transport, dose rates, crud induced power shifts (CIPS) or crud induced localized corrosion;
- the safe use of hydrogen and other combustible and/or toxic gases is guaranteed (to prevent deflagration and/or detonation in the presence of oxygen);
- the secondary side chemistry programme should aim 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; (iv) condenser leaks in both water and air parts, and (v) corrosion of the steam generator blowdown purification system;
- appropriate chemistry controls and diagnosis parameters confirm safe and reliable operation ;
- there is timely reporting of the evaluation results to the responsible level of management and other users of such chemistry programme results (operators, maintenance, system engineering group, technical support organizations, etc.);
- there is a timely response to correct any deviations from normal operational status such as small deficiencies, weak trends or quick transients of chemistry parameters;
- diagnostic and treatment methodologies are utilized and are up-to-date;
- the analysis equipment in the laboratory is regularly inspected and is up-to-date;
- there is an adequate contribution from the chemistry department to maintain the availability of the safety equipment (e.g. safety tanks, diesel, and main pump oil analysis);
- there is support to the plant predictive and corrective maintenance, flow accelerated corrosion programme and the life time management programme as requested by maintenance and engineering departments;

- good water chemistry practices exist and include that reagent make-up, raw water treatment and condensate polishing plant relevant procedures are in compliance with specifications and consistent with internationally accepted good practices;
- procedures and practices exist for water clean-up systems (e.g. evaporators, resin beds) and sampling system to confirm that they are efficiently operated;
- sources of impurities in the water systems are known and actions for minimizing these sources are implemented;
- an adequate and reliable online and off-line chemistry measurement system is in proper operation;
- modern chemistry analysis methods are used to permit adequate analysis of pollutants even if the chemistry parameters are within their correct range;
- the use of substances and reagents, that may negatively affect equipment integrity, is prevented;
- the management of hazardous chemicals and availability of a set of material safety data sheets (MSDS) exists.

4. CHEMISTRY CONTROL

4.1. The chemistry control includes the correct application of the appropriate chemistry regimes of safety and safety related systems depending on the design and materials.

GENERAL WATER CHEMISTRY CONTROL CONSIDERATIONS

4.2. The primary water chemistry regime for PWR, WWER and PHWR should be the following:

4.3. The presence of variable concentration of dissolved boron (boric acid from more than 2000 ppm with a new core to less than 10 ppm at the end of the cycle) in the PWR and WWER reactor coolant system to control core reactivity should be continuously measured and evaluated by a boron meter.

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4.4. The addition or removal of alkaline compounds should be used in order to maintain at any time during operation the optimum pH_T (pH at operating temperature). In PWRs generally LiOH is added while in WWER, KOH is added and the mixture of total alkali is monitored (K injected, Li produced by neutronic reaction on boron, and potentially sodium as an impurity). The purpose of this optimum pH_T is (i) to minimize rates of uniform corrosion of the circuit materials, mass transfer and dose rates (ii), to prevent materials from undergoing stress corrosion cracking, (iii) to avoid fuel cladding corrosion, and (iv) to mitigate CIPS sometimes called flux anomalies. Some plants also add small quantities of zinc to the primary coolant. This is an option, if it proves useful to minimize dose rates associated with radioactive corrosion products (mainly ^{60}Co) or reduces risk of the austenitic material stress corrosion cracking.

4.5. The concentration of hydrogen (directly added or produced by decomposition of added ammonia) should be optimal in order to suppress oxygen produced by radiolysis and to keep the electrochemical potential at a sufficiently low level to prevent stress corrosion cracking of stainless steel. In addition, make-up water to the primary circuit except for PHWRs should be degassed and remaining oxygen should then also be eliminated with hydrazine.

4.6. The most corrosive impurities should be kept below the specified limit to avoid corrosion of the primary system components. The most important chemical species are oxygen, chloride, fluoride and potentially sulphate, depending on the specific primary water condition and source of sulphate. The reduced compounds of sulphur that may come from some ion exchange resin fines are particularly detrimental and can remain undetected by traditional analytical chemical methods. Due to the presence of high and variable concentration of the boron (boric acid), at all stages of the operation for neutron (criticality) control, special attention should be paid knowing that this chemical could be a major threat, in case of leak, for the carbon steel equipment.

4.7. The concentration of chemical compounds with a low solubility that may deposit on the fuel surface and cause a temperature increase should be kept at minimum. This includes calcium, magnesium, aluminium and potentially silica, considered as potentially zeolite forming elements.

4.8. The chemical environment at shutdown condition should be defined and applied to avoid component degradation, to minimize the impact of radioactive corrosion products on occupational exposure during maintenance activities and to avoid any risk of explosive gas mixtures (hydrogen + oxygen).

4.9. The secondary water chemistry regime for PWR, WWER and PHWR should be the following:

4.10. The secondary circuit should be operated according to an all volatile treatment (AVT) or an all volatile treatment with high pH (HAVT). This means the use of only volatile alkaline reagents such as ammonia, amines (e.g. morpholine, ethanolamine, dimethylamine) that will not concentrate in the steam generator. A reducing agent (e.g. hydrazine) should also be added when necessary and this will be thermally decomposed into ammonia contributing to the pH adjustment.

4.11. The pH, ammonia/amine and their concentration selections is plant specific. Where utilized, it should provide appropriate pH_T in various parts of the secondary system. It should be:

- able to avoid/minimize flow accelerated corrosion of carbon steels and amount of the corrosion product in the feedwater that will deposit in the steam generator,
- compatible with efficient purification systems,
- compatible with secondary side materials, particularly copper alloys,
- limiting liquid and solid waste purposely released into the environment.

4.11. In some specific cases, other chemicals in limited quantities may be added to keep a controlled environment either on the slightly alkaline or acidic side, based on the materials present. An acidic environment should be avoided for WWER steam generators. At some WWER plants, a small quantity of LiOH is added for this purpose. For PWR with Alloy 600, an alkaline environment should be avoided. At some PWR plants, a small quantity of boric acid or ammonium chloride is added for this purpose.

4.12. 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 the secondary side and balance of plant piping.

4.13. The level of deleterious impurities (e.g. sodium, chloride, sulphate, lead, and potentially copper) in the steam generators should be minimized and controlled. There should be steam generator blowdown limits established with action levels for such chemical impurity that may be deleterious for the steam generator tubes and potentially present in the system (generally sodium, chloride and sulphate and/or cation conductivity).

4.14. The primary to secondary circuit leak rate in the steam generator tubes should be monitored and strictly controlled within predefined limits for safety reasons, which are the most important ones and are not strictly dealing with chemical characteristics (loss of primary coolant, the dissemination of radioactive elements). In addition, such leaks should also be limited for minimizing the production of radioactive wastes e.g. regeneration and washing solutions, resins, filters, sludge.

4.15. The corrosion rate of construction materials and risk of microbiological growth and microbiological induced corrosion within tertiary systems, particularly when there is a semi-closed cooling system with cooling towers should be controlled. The risk is specific to the water characteristics, the materials and design of the circuit, and to the temperature. The risk concerns the 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 a biocide containing chlorine should be added and at which concentration, or if other techniques should be implemented.

4.16. The chemistry regime of auxiliary systems that are important for safety in PWR, WWER, BWR and PHWR should be the following:

4.17. In PWRs the chemical inhibitors in adequate concentration should be added to cooling systems that are important for safety. Chemical cleaning of steam generators should precede such use of corrosion inhibitors. The chemistry parameters to keep the proper treatment and the impurities (mainly chlorides for PWRs and chlorides and sulphate for BWRs) should be controlled to avoid any corrosion of the system and loss of integrity.

4.18. Tanks containing gases should be strictly maintained to prevent an explosion due to the simultaneous presence of oxygen and hydrogen above the recognized limits. Such monitoring should also take place in any tank containing liquids where radiolysis may induce the presence of explosive mixtures of gases.

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4.19. To achieve adequate chemistry control, the chemistry organization should take into account a graded approach in the different areas of chemistry control mainly for the primary and secondary circuits.

4.20. The control parameters should be defined as the most important chemical parameters to monitor the chemistry regime treatment and the presence of deleterious impurities. If a control parameter is out of the limit values, degradation of SSCs conditions may occur on the long term. Thus an evaluation of the situation and a remedial action should be considered for any deviation of a parameter above its limit value. Expected values may be defined in addition to control values for the chemistry staff internal use in order to avoid the chemical parameter going inadvertently above the limit value.

4.21. In case of deviation of some of the most important control parameters, graded action levels should be defined in advance and correction of control parameters should start progressively within acceptable period of time and go up to plant shut-down if necessary, to avoid short term degradation of the materials. Action levels for these most relevant parameters that may be indicative of a risk of corrosion inducing a lack of integrity or other consequences should thus be defined. The number of action levels and associated allowed duration of operation before having the plant shutdown is specific of the design and materials;

4.22. Diagnostic parameters should be additionally defined, that provide supplemental information to have a comprehensive knowledge of the chemistry programme status of the plant and support in identifying the source of chemistry programme deviations.

4.23. Additionally, the chemistry organization should define operational limits and conditions of safety, safety related and auxiliary systems during:

- commissioning,
- startup,
- normal operation,
- shutdown,
- decommissioning.

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These limits of the parameters should not be exceeded and appropriate actions should be taken to recover its normal operating value within the allowed duration;

4.25. The chemistry control programme should confirm, from the records, that chemistry control and diagnostic parameters have been kept within their specified ranges. Records of these chemistry control results should be controlled, reviewed and any deviations should be analysed in conformance with plant abnormal condition procedures.

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

4.27. The water chemistry regime of active and passive safety systems that contain liquid neutron absorber (boric acid tanks, containment sprinkler system, bubble stacks, reservoirs containing gadolinium) should be maintained in accordance with design standards, taking into account that correction of the liquid chemistry within these reservoirs can be generally made in appropriate time (e.g. during a refuelling outage).

WATER CHEMISTRY CONTROL AT PWR AND WWER POWER PLANTS

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

- the results of non destructive testing (in-service inspection) of steam generator tubes integrity at least for degradation potentially related to the primary and secondary water chemistry programme,
- the evaluation of hide out return during at least some of the shutdowns for refuelling,
- the use of calculation codes or any other relevant method for estimating the chemistry characteristics of the liquid contained in the steam generator tube crevices and deposits during operation.

4.29. The various potential sources of impurities entering the secondary system should be limited to minimize the risk of steam generator tube degradation. The limitation of such impurities is controlled by the specified limits of chemical parameters at the steam generator blowdown. This is part of the system where the detection is the most sensitive and where the deleterious compounds may cause corrosion of the steam generator tubes. The main potential sources of pollutants are:

- condenser leaks with raw water or air ingress,
- make up water system,
- the reagents injected in the secondary system (ammonia or amine, hydrazine),
- any of the systems connected to the secondary system, such as auxiliary cooling systems,
- purification systems with resins beds. These include the steam generator blowdown and/or the condensate polishers. High quality resins should be used, carefully regenerated or discarded. Special attention should be given to the regeneration process, when it applies, to avoid the ingress of regeneration chemicals or resin fines into the secondary system, where they may have a particularly detrimental corrosion effect on steam generator tubes. In PWR and WWER plants, whenever possible, and with the exception of start-ups and condenser leak, the operation with tight condenser may be preferred to the use of condensate polishers, if these cannot be safely regenerated and giving a high feedwater quality;
- ion exchange resin degradation products. Proper ion exchangers operation and their status monitoring is important with regard to potential resin degradation caused by operating conditions and reagents used;
- any intake or foreign materials or products in the secondary circuit;
- any oil leaks inside the circuit.

4.30. The purification systems for the secondary water should be available and sufficiently efficient to maintain the steam generator blowdown within the limits of the corresponding control parameters of the technical specifications or other relevant documents.

4.31. During outages the secondary circuit 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 according to the lay up duration, safety requirements with the use of hazardous chemicals or nitrogen, other requirements on the steam generators such as in service inspection, sludge lancing. Lay up parameters should be monitored and corrective measures for deviations should be implemented.

WATER CHEMISTRY CONTROL AT BWR POWER PLANTS

4.32. During operation the chemistry control programme at BWR power plants should focus on decreasing the impurities in the reactor coolant to the practical and achievable minimum in order to avoid/minimize intergranular stress corrosion cracking.

4.33. To avoid/minimize the intergranular stress corrosion cracking the injection of agents with possible catalyst enhancement (hydrogen, noble metals and/or titanium oxide) is used. The reducing agents are controlled based on measurements of hydrogen, oxygen and/or corrosion potential.

4.34. The reactor water should be adequately controlled for the limits of conductivity and the concentration of chlorides and sulphates. The concentration of iron and copper should be adequately controlled in the feedwater systems.

4.35. Dissolved hydrogen and oxygen levels should be within the specifications and impurity levels (e.g. corrosion products, chloride, sulphate and fluoride) should be maintained below the specified limits.

4.36. Before shutdown, the flow rate of the reactor water clean-up system should be increased as much as possible to minimize activated corrosion products in the reactor water and in deposits at those plants where clean-up flow can be increased.

4.37. The radioactivity of reactor water and the radiation build-up on pipes should be minimized. During normal operation, the injection of such as zinc, iron and nickel to the feed water may be used for this purpose.

4.38. During start-up, the oxygen concentration should be controlled adequately and be maintained at a low enough level to minimize intergranular stress corrosion cracking.

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4.39. Those BWRs which may have flow accelerated corrosion problems in their feedwater, main steam or other systems, should apply an appropriate chemistry regime to minimize them.

WATER CHEMISTRY CONTROL AT RBMK POWER PLANTS

4.40. For the Russian 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).

4.41. The chemistry control programme at RBMKs should provide:

- minimal levels of deposition on heat exchanging surfaces and piping;
- minimal corrosion and corrosion-erosion (e.g. intergranular stress corrosion cracking, flow accelerated corrosion) of the materials of the main steam-water circuits;
- high quality saturated steam, which does not cause any droplets on the steam flow-paths of the turbine.

4.42. Levels of conductivity, pH and impurities (iron, copper, chloride, fluoride, sodium and oils) should be maintained below the specified limits.

4.43. Dissolved hydrogen and oxygen levels should be within the specified limits. To reduce the possibility of corrosion, the concentration of oxygen should be maintained at the minimum possible level. Some nuclear power plants, during start-up, use de-aerated water to reduce the possibility of corrosion.

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

4.45. Heavy water isotopic composition for moderator as well as for primary system should be maintained within the specified limits. Additionally, the HTS isotopic should not be higher than the moderator isotopic at fuel cycle equilibrium.

4.46. Tritium analysis instruments and procedures should be available.

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

4.48. The isotopic concentration of boron and gadolinium salts intended for use as neutron poisons should be verified prior to their introduction into any reactor system, to ensure that isotopic concentration (^{10}B, $^{155-157}Gd$) is equal or higher than natural isotopic abundance.

4.49. A good correlation among the primary circuit alkaline reagent concentration, pH and conductivity should be maintained as a good indication of the absence of any significant concentration of a contaminant.

4.50. The primary circuit dissolved hydrogen concentration should be within specified limits to suppress oxygen formation due to radiolysis. Impurity levels, in particular corrosion products, sulphates, chloride and fluoride should also be within the specified limits. However, optimization of protection (and safety) [10] principle should be applied to the impurities.

4.51. The cover gas of the moderator system should have online monitoring for H_2, O_2 and N_2 to minimize the risk of an explosion/deflagration hazard.

5. CHEMISTRY ASPECTS OF EXPOSURE MINIMIZATION

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

- optimization of occupational dose rates in the plant,
- reduction of any releases of radioactivity to the environment.

SOURCES OF OCCUPATIONAL EXPOSURES AND ENVIRONMENTAL DISCHARGES

5.2. The chemistry programme should include control of radiation dose rates coming from systems and components. These dose rates should be maintained as low as reasonably achievable. During outage, and if possible also during operation, the does rate of systems and components should be regularly controlled. Hence it makes possible to monitor the dose rate development over years.

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

5.4. Resistant construction materials with low corrosion product release rates and a well defined water chemistry regime should be used as the main tools for the reduction of radiation build up. Decontamination procedures should only be used if no other method is satisfactory in achieving a low level of dose rate.

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

- the definition and application of a suitable chemical treatment (e.g. pH for PWR/WWER and oxygen control) for minimizing corrosion processes, and hence reduction of the amount of corrosion products in the water,
- the use of pure make-up water to avoid easily activated chemical contaminants and suspended materials,
- the use of effective primary and secondary water clean-up systems for controlling dissolved and suspended radioactive substances,
- the quality management of chemicals used in the coolant systems and hence avoiding any detrimental effects from pollutants.

5.6. The dominant sources of radioactivity during shutdown in the primary circuit are normally the activated corrosion products generated from component materials. During start-up, normal operation, shutdown and stand-by processes, all chemistry remedies and measures should be taken into consideration to reduce the activity level and to optimize transport of

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these radioactive contaminants. It is especially important to take appropriate measures before shutdown to reduce the doses to maintenance workers.

5.7. The applied primary water chemistry programme should effectively control and minimize radiation build-up owing to the transport and accumulation of fission and activated corrosion products on internal system surfaces.

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

SYSTEMS AND MEASURES FOR PREVENTING AND MINIMIZING OCCUPATIONAL EXPOSURES AND ENVIRONMENTAL DISCHARGES

Fission products

5.9. The radioactivity of fission products in the primary coolant and other media should be kept below their defined limit value. This radioactivity should be controlled by continuous monitoring and/or periodic sampling and measurement. The results of the monitoring should be analyzed and evaluated to determine the extent of fuel leakages.

5.10. The normal level of fission product activity in the primary coolant should be specified during the initial period of reactor operation following start-up in order to provide a reference background level and this level should be used for trend analysis. This value should be included in operation limits and conditions (OLCs) or the radiochemistry technical specifications. This radioactivity is mainly produced as a result of the uranium contamination of the cladding surface of the fuel during the manufacturing process and, secondary, from fuel failures.

5.11. The primary water chemistry control programme should consider all the primary circuit materials used, including fuel cladding, to prevent fuel cladding failure and any detrimental effect to the primary circuit and the environment.

5.12. Dissolved oxygen and/or hydrogen concentration and alkalinity should be strictly controlled to minimize fuel cladding deterioration and therefore decrease occupational

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exposures and environmental discharges. Zirconium alloy cladding is sensitive to corrosion/oxidation, hydride embrittlement, alkaline environment, and will enhance the build-up of low solubility product deposits. Much deposits can increase the cladding temperature and, as a consequence, increase the risk of fuel cladding failures and subsequently increase exposures.

Activated corrosion products

5.13. Corrosion processes should be monitored, trended and controlled. During shutdown, with little or no failed fuel, 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. They are then transported by the primary coolant to the reactor core where they become activated and are subsequently deposed 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 re-deposition of activated corrosion products from the core that may results in very high radiation fields in steam generators. This transport should be minimized by maintaining the primary water chemistry parameters as constant and as close as possible to the optimal values during normal power operation.

5.15. One of the dominant radiation field contributors is ^{58}Co radionuclide. It is generated from nickel by (n/p) reaction. As nickel is substantial constituent of almost all primary system construction materials, presence of ^{58}Co cannot be fully avoided and its activity increases with nickel content in the used alloys. Optimized primary water chemistry control during operation and especially during shutdown is one of most powerful tools to minimize radiation fields originated from this radionuclide.

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

5.17. Content of silver (Ag) and antimony (Sb), as easily activated elements, should be minimized in component composition and if necessary and possible specifically eliminated

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during the shutdown process by selecting a proper shutdown chemistry regime. In BWR and RBMK reactors, ^{95}Zr may also be an important radiation field constituent.

5.18. Once the plant is constructed and operated, chemistry control should be the main technique available to the operator to reduce the rate of build-up of radiation fields by use of an appropriate water chemistry regime. Adequate control of water chemistry parameters during normal operation and at shutdown/start-up/stand-by 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 considerably increase and the transport directions may also change resulting in deposition on out-core surfaces. This can result in elevated dose rates and occupational exposures during outage and possibly in radioactive hot spots.

Primary system components

5.19. During the commissioning phase the preconditioning of surfaces before and during initial start-up should be done in order to produce a protective layer and to ensure the correct, passivated surfaces in all systems. This layer reduces the subsequent release of corrosion products into the coolant when the plant is at power and hence reduces the deposition of radioactive materials. This should be achieved by using a passivating solution during pre-start testing, with the plant systems at an elevated temperature for sufficient duration where the release of corrosion products is high and until the protective oxide film forms. These corrosion products should be removed by the purification systems during the commissioning period.

5.20. Filtration processes (ion exchangers, ultra-filtration, mechanical or electromagnetic) should have primary importance in assuring the lowest possible dose rates on surfaces by the effective removal of dissolved and suspended forms of corrosion products from the coolant. The usual way of their application is to use them until a pre-defined value of chemical and/or radiochemical concentration of corrosion products is reached (i.e. ^{58}Co, ^{60}Co). Power production demands should not take priority to influence (i.e. shorten) the time that these operations are required in order to reduce the activity inventory of the primary coolant, especially during shutdown process.

5.21. Chemistry control should avoid any detrimental corrosion effects and hence unnecessary dose rate increases owing to the deposition of corrosion products. This should be ensured by the effective use of built-in (in-line) ion exchanger purification systems during normal power operation.

5.22. When changing equipment and/or parts of them in the system, the minimum use of contaminants susceptible for corrosion processes development should be considered.

DECONTAMINATION PROCESSES

5.23. Effective decontamination techniques (i.e. chemical, electrochemical, mechanical, etc.) should be developed and demonstrated for different applications. The cost, downtime necessary for decontamination, the risk associated with the use of corrosive reagents, and also radioactive waste generation require that the need of decontamination technology should be minimized by efficient control of radiation field build-up rates also through adequate water chemistry control.

5.24. In PWRs the extensive use of chemical decontamination processes should be avoided, in order to minimize the deterioration of the protective oxide layer on the surfaces, which then requires time and a further passivation process to recover. 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 the increase of risk for fuel failures. If the chemical decontamination could not be avoided, the passive status of the surface should be recovered and controlled.

5.25. In case of extensive use of chemical decontamination processes, such as steam generator or full system chemical decontamination, detrimental side effects should be evaluated. Other technical solutions and measures are preferred (shielding, fill-up systems with water, robotics, time limitations, and training) for personnel exposure reduction.

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MINIMIZATION OF LIQUID AND GASEOUS RADIOACTIVE WASTE PRODUCTION AND RELEASES

5.26. The generation of radioactive waste should be kept to the minimum practicable 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 final disposal. During these phases, the requirements defined by waste acceptance criteria should be taken into consideration. More details concerning waste management can be found in Ref. [11].

5.27. In order to minimize liquid and gaseous wastes and/or activity, several of the following methods should be selected:

- optimize the total number of equipments and gadgets as well as handling of liquids in the plant in order to reduce the amounts of liquid waste collected,
- segregate liquids to avoid dilution and mixing of chemically incompatible substances,
- reduce the amounts of chemicals, recycle chemical substances (particularly boric acid) if possible and reasonable or use chemicals that decompose completely,
- establish appropriate chemistry procedures to control and prevent fuel and primary to secondary coolant leakages,
- reduce the amount of gas introduced into the system to the minimum practicable,
- use of ion exchange resins and selective sorbents,
- use filters to separate suspended radioactive substances from the liquids,
- use of hold-up tanks and other delay systems (charcoal beds) to allow radioactivity to decay before its release,
- use of effective filters to separate aerosols from gaseous discharges,
- use of treatment for volume reduction (recombiners, absorbers, vapour recovery system, pressurized storage), which also serves as a delay system.

5.28. Appropriate water chemistry control should minimize the consequences of an accident resulting in the release of iodine radionuclides to the containment building and to the atmosphere. Consequently, in the case of loss of primary coolant water and subsequent boron content release to the containment, an alkaline solution (with some reducing agent if it is possible) should be added (normally via containment spray system) if no other method is applied for iodine elimination.

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 is also essential to verify that SSCs important to safety are operated within the specified limit values. Such a surveillance programme should help to detect trends in parameters, to discover and eliminate undesirable effects and consequences of out-of-range chemistry parameters. The chemistry surveillance programme should reflect chemistry specifications for all phases of plant operation including shutdown and start-up periods and when systems are taken out of operation for prolonged periods.

6.2. The chemistry surveillance programme should utilize all available possibilities resulting from usage of combination of chemistry data together with other technological data. It helps to gain complex knowledge about status of plant technology.

6.3. Software for chemistry calculations which have a nuclear safety impact should have been verified by the developer or any other appropriate organization e.g. software for primary and secondary circuit systems or pH_T calculations etc. For details see Ref. [12].

6.4. The objectives of the chemistry surveillance programme are the following:

- to confirm compliance with control and diagnostic chemistry limits and conditions,
- to maintain the availability of SSCs,
- to detect and thus allow early corrective action for any abnormal chemistry condition before it becomes a significant consequence to safety.

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

6.6. Chemistry surveillance should be accomplished through the use of online instruments, analysis of grab samples and the subsequent evaluation of results.

CHEMISTRY MONITORING

6.7. Online monitoring should be considered as the preferable monitoring method for evaluating the chemistry conditions in the plant systems when a short term corrective actions on any control parameter is applicable.

6.8. The use of chemistry performance indicators for the most important parameters should be considered, these indicators being trended and periodically reported for evaluation.

6.9. Laboratory analyses should be considered as a necessary complement to the diagnosis of chemistry problems, to verify the accuracy of online monitors, and whenever it is not possible or reasonable to have online monitoring.

6.10. Account should be taken of delays in obtaining samples (volume of sampling line) for use of data gained by online as well as by laboratory measurements.

6.11. For on-line and laboratory instruments, there should be a procedure developed which:

- describes the intended use of the procedure;
- references identifying sources used for development of the procedure;
- provides summary of analytical methods indicating possible interferences, accuracy, linearity and range and the precision of the measurement,
- states equipment, reagents and standards required to perform analyses,
- gives step-by-step instructions for performing the analyses and calculation of the results;
- indicates quality control requirements, industrial safety and radiological protection precautions;
- provides information on instrument calibration.

Online monitoring

6.12. Online chemistry monitoring and data acquisition systems should accurately measure and record data and provide alarms for key chemistry parameters. The measuring range of automatic instruments should overlap the range of the operational level.

6.13. A calibration and maintenance programme should be applied to all online monitoring instrumentation.

6.14. For optimization of protection (and safety) purposes the online measurement should be considered for hydrogen in the primary coolant.

Online instruments

6.15. A management system [7] should be implemented, which ensures that data collected by online monitors and data acquisition system are accurate and reliable. Other methods, which could be used for this task, include:

- timely calibrations developed either on the bases of equipment manufacturers' recommendations and plant experience or using standard solutions;
- timely comparison of online monitoring with laboratory results or other well calibrated portable online monitors;
- use of technological data comparison from different sampling points (e.g. intercomparison of steam generator blowdown cation conductivity measurements) or use of comparison of different parameters measurements from the same sampling point for evaluation of measured data plausibility.

6.16. A preventive maintenance programme should be established for online chemistry monitors.

6.17. Sample physical conditions (temperature, flow-rate etc.) should be taken into account. Some instruments have temperature compensation, however control of temperature for results evaluation is recommended.

Laboratory monitoring

6.18. Laboratory monitoring involves sampling and analysing plant systems for specific chemistry properties, dissolved and suspended impurity concentrations, and radionuclide activities. There should be made a list of scope and periodicity of chemistry monitoring. Sampling points, periodicity of analysis, procedure, and responsible individual should be determined for each regime (start-up, shut-down, operation at the stable power level, transients).

6.19. Procedures on analytical processes should be applied to provide guidance for performing analyses. These procedures should describe methods to be employed, equipment or materials to be used, acceptance and rejection criteria, and sequence of the analysis.

6.20. 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 concentration range applied. Matrix effect should be known and corrected if necessary.

6.21. Reagents and calibration sources used for calibration should be valid.

6.22. A schedule of required calibrations should be formulated, controlled and implemented.

6.23. Calibration points should be chosen in such a way as to overlap the measuring range and to be as close as possible to the measuring value.

RADIOCHEMISTRY

6.24. Radiochemistry is a specific, inevitable part of chemistry activities at a nuclear power plant operating any type of reactor. Measurement of radiochemistry activity performed either as a total activity or as spectrometry-based specially focused to particular energy for defining the corresponding radionuclides is substantial for safe management of the plant in all stages of plant life from operation to decommissioning.

6.25. Radiochemical measurements should include systems like closed cooling water circuits, the secondary side of pressurized water reactors and the main cooling water to detect leakages in the material barriers. Radiochemical measurements should be implemented on the wide basis of plant activities as described below.

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6.26. Primary coolant activity monitoring should serve for following tasks:

- Measurement of fission product activity is a tool for fuel integrity evaluation, fuel cladding leak identification, cladding defect type and number estimation.
    - For this purpose good quality of well maintained and calibrated gamma spectrometry instrumentation, sufficient variety of calibrated measurement geometries, efficient and verified radiochemical separation procedures should be available.
    - Results of these measurements should serve as input data for validated fuel leak evaluation calculations. Sufficient sensitivity for key fission product activity measurement should be ensured as substantial condition for early fuel leak detection.
    - Power transients accompanied by fission product activity spiking phenomenon should be adequately monitored.
    - Within these activities a proper selection of volatile radionuclides (e.g. isotopes of noble gases and iodine) representing small cladding defects as well as non volatile radionuclides (e.g. caesium, transuranic elements) characteristics for large open defects should be done with regard to the type of fuel.
    - Properly selected radionuclide activity ratios should be applied to assess burnup of the leaking fuel rod to facilitate its identification during operation/outages depending on type of reactor.
- Measurement of corrosion product activity should be performed to monitor chemistry performance, activity transport processes and potential foreign material ingress. In order to ensure good representativity of these measurement results, proper isokinetic sampling method with capability of soluble and particulate activity fractioning should be implemented.
- Measurement of other activated product activity (e.g. radioisotopes of sodium, potassium, chlorine) should be considered as a useful tool for verification/cross-

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checking of chemical analyses results and should also serve as an early warning of low concentration of possibly unknown impurities.

6.27. Radiochemical measurements should be a necessary 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 possible defect propagation after its discharge from reactor.

6.28. Radiochemical measurements should be applied in the monitoring of purification systems performance, especially in the case when activity removal is the main purpose of purification system operation.

6.29. Measurement of relevant radionuclide activities should be implemented for monitoring of decontamination process efficiency, especially in large components decontamination in order to optimize treatment time and radioactive waste generation. These practices should be in alignment with ALARA principles and objectives.

6.30. Radiochemical methods should be applied to provide result necessary for radioactive waste characterization with regard of their treatment, conditioning and disposal.

- Efficient and validated radiochemical separation methods should be developed for activity measurement of difficult-to measure-radionuclides (e.g. pure alpha-, beta- and low energy gamma emitters).

- For defined scope of radionuclides derived from the safety analysis report for a particular disposal facility, their activity should be analysed in defined range of waste streams to accumulate sufficient number of data sets (so called radionuclide vectors) necessary for construction of mathematical correlations between difficult-to-measure radionuclides and key (reference) radionuclides.

- These correlations should be then used for calculation-based characterization of newly generated waste, but periodical check of plausibility should be performed with new radiochemical analyses.

6.31. Activity of radioactive effluents, both liquid and gaseous should be continuously monitored by appropriate fractioning and monitoring method.

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6.32. Radiochemical methods should be applied also to monitor liquid and gaseous tritium and ^{14}C releases as special low energy beta emitters. Validated radiochemical separation methods and properly calibrated liquid scintillation counters should be applied to ensure compliance with release limits if they are applied based on local regulations.

6.33. Determination of activity of primary surface deposits serves for evaluation either of primary chemistry quality with potential presence of specific contaminants (e.g. Sb, Ag) or for occupational exposure trends and anomalies. This determination should be made by the use of smear samples, corrosion layer scraping or electrochemical sampling or should be effectively performed by the in-situ gamma spectrometry measurements of properly selected parts of primary circuit or other types of methods.

CHEMISTRY FACILITIES AND EQUIPMENT

Laboratory facilities

6.34. Laboratories should be suitably secured and located, and should be provided with adequate space, supplies and equipment taking into consideration human factors.

6.35. Laboratory instrument redundancy or equivalency should be provided to ensure analytical services at all times.

6.36. Procedures for the storage, replacement and ordering of laboratory chemicals and other products for laboratory should be available.

6.37. The laboratories should have a good general housekeeping, orderliness, cleanliness at working areas and sampling points, including contamination levels according to the plant procedure.

6.38. Industrial safety (ventilated fume hoods, storage of flammable solvents and hazardous materials, safety showers, personnel protective equipment and first aid kits) and radiological safety (proper radiation shielding and contamination control facilities) should be ensured, applied and well maintained in laboratories, accordingly to the foreseen risk. The whole laboratory and work practices should be in accordance with good industrial safety and optimization of protection (and safety) principle.

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6.39. Protective measures should be foreseen for unusual events such as fire, flooding, and radiological hazards.

6.40. Limited quantity of gags for containers with stored samples should be presented in the laboratory premises.

Laboratory instruments

6.41. All laboratory instruments and equipment should be in a good condition in order to provide accurate and reliable analytical data for monitoring purposes. This condition should be ensured by a maintenance plan for those instruments and equipment.

6.42. Adequately redundant instrumentation and equipment for performing analyses of given types and frequency should be available and calibrated. Calibration standards and procedures should be available with a calibration plan developed. The instrumentation, the equipment and the applied methods should be authenticated.

6.43. Appropriate and well maintained instrument manuals should be available in the laboratory.

Laboratory performance testing

6.44. The adequacy and accuracy of procedures should be checked regularly by intra- and inter-laboratory tests to identify analytical interferences, improper calibrations, analytical techniques and instrument operation. These tests results should be evaluated to determine the cause of unexpected differences and deviations, taking into account short-term and long-term effects.

6.45. Based on the determined causes, corrective actions should be taken to further improvement of laboratory performance.

Instrument performance survey

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6.46. Results of the analysis of standards should be used to verify instrument accuracy based on specific acceptance criteria.

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

Sampling systems

6.48. One of the most important factor affecting the accuracy and reliability of the measurement results is the sampling, as the first step of every analytical measurement.

6.49. Representativity of grab samples should be ensured by appropriate flushing of sampling lines, well determined flow rate, cleanliness of containers, and minimizing the risk of chemical contamination during sampling.

POST ACCIDENT SAMPLING SYSTEM

6.50. A post accident sampling system (PASS) or another adequate sampling facility should be considered for use in taking regular samples from plant systems or should be ready to operate when required by emergency procedures according to the plant design if no other approaches are adopted for core damage evaluation and for estimation of fission product inventory released into containment.

6.51. For proper PASS operation the following should be provided:

- PASS operation procedures;
- radiation protection measures evaluated in advance and applied;
- a programme for preventive maintenance;
- regular checks of PASS operability;
- regular training for personnel designated for PASS operation (taking grab samples and performing subsequent activities).

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7. CHEMISTRY DATA MANAGEMENT

Data acquisition

7.1. The results of analytical and quality control measurements should be properly recorded in the laboratory logs, or registered data sheets and also in a database. The results should be supplemented with complementary information necessary for interpretation, assessment, and communication.

7.2. The data relating to chemistry should be suitably archived, stored during whole plant life time and easily retrievable.

Data review

7.3. Analytical data should be reviewed to verify completeness, accuracy, and consistency. Chemistry data assessment for the identification of actual and potential problems should commence promptly, depending on the importance and potential consequences of the deviation.

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

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

Data evaluation and trending

7.6. Data evaluation and trending should be used, comparing to the operational limits, to assess chemistry control efficiency, to identify inconsistencies in analytical data and adverse trends in chemistry conditions and to help in optimization of the plant system chemistry. Data that are out of range should be highlighted.

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7.7. Chemistry parameters should be trended graphically to provide an adequate picture of system chemistry conditions and make comparisons between related parameters and system status.

7.8. Trends should be reviewed just after data have been recorded to identify problems that may need corrective actions before the parameter exceeds its specification limits. Trends should also be used to evaluate short duration transients caused by plant operational changes and for slower long term changes occurring under stable plant conditions. By evaluating slow changes, it may be possible to predict when the 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 actions to correct chemistry related problems.

Feedback

7.10. The method for transferring analytical results to other departments (e.g. operations) should be established, communicated and clearly understood and accepted to ensure timely correction of problems identified [13].

8. TRAINING AND QUALIFICATION

8.1. Recruitment, training and qualification of the chemistry staff should be organized according to the IAEA Safety Guide NS-G-2.8 [14].

Competence and qualifications

8.2. Chemistry management should ensure that chemistry personnel have the necessary knowledge, skills, abilities and level of supervision to fulfil their job descriptions and to perform their job functions.

8.3. The operating organization should ensure that chemists involved are sufficiently skilled in the different parts of the programme, especially in radiochemistry.

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8.4. In order to achieve and maintain high levels of safety, the chemistry staff should be aware of the technical and administrative requirements for safety and sufficiently motivated to adopt a positive attitude to safety ([1] and [15]).

Training policy

8.5. The systematic approach to training for chemistry should be in accordance with the relevant Safety Standard [14]. Basic training (general employee training), initial and continuing training should be developed, taking into consideration all job descriptions at different levels of the chemistry group. Furthermore, some specific attributes should be re-enforced due to the need of developing adequate and specific skills and increasing the knowledge base of the chemistry staff.

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

8.7. Regular training should also be considered where there is a large chemistry staff that does not perform specific tasks on a regular basis.

Training facilities and materials

8.8. Training facilities and methods, which are widely used and have been proved as effective in attaining the training objectives when appropriately chosen, should be considered, e.g.:

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

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- all the chemistry activities should be provided by assigned staff but chemistry trainees may be assigned to carry out work while shadowing;
- training courses should include techniques for recognizing unusual conditions and adverse trends.

8.9. Chemists at the nuclear power plant should be fully trained and knowledgeable in their areas of responsibility to be able to understand, communicate 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 demineralised water, oil analysis, calibration of measurement equipment, metrology support, and certification of chemicals) should be trained on and 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 chemical and radioactivity releases are involved. Emergency chemistry procedures, emergency equipment and values used during emergency situations should be confirmed during training and exercises to ensure the correct reaction among emergency staff. This would also allow confirmation regarding the adequacy of the actions and allow familiarization with the communication methods utilized.

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

- handling of hazardous chemicals and flammable solvents;
- labelling of chemicals stored and used in and out of the laboratory;
- material safety data sheets;
- the procurement process for all chemicals;
- use and maintenance of personnel protective equipment used in workshop activities;

- specific use and storage of poisonous chemicals.

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

9. QUALITY CONTROL OF CHEMICALS AND OTHER SUBSTANCES

9.1. The responsibility for coordinating the control of chemicals on-site should be clearly established according to Ref. [7].

9.2. The use of chemicals and materials at the plant, including those brought by contractors, should be controlled according to clearly established procedures. The intrusion of non-conforming chemicals or other substances into plant systems can result in chemistry excursions leading to component and system damage. The use of uncontrolled materials on the surfaces of the components may also induce damage. Some corrosion phenomena (e.g. stress corrosion cracking) are thermally activated, meaning that corrosion kinetics may be higher at operating temperature than at room temperature.

9.3. There should be a list of approved materials (chemicals and other substances like lubricants, tapes, cleaning agents, plastic foils, markers etc.) that are allowed to be used. This list should be well known by chemistry, maintenance and procurement staff.

9.4. The reagents and ion-exchange resins used for any safety related system should be within the required specifications for impurities and verified as so prior to use.

9.5. Chemical substances such as tapes, detergents, plastic foils and insulation materials should not be used in SSCs if they contain corrosion inducing components (e.g. fluorine, chlorine or sulphur) above the specified limits.

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

9.7. When receiving chemicals, the specified quality should be verified by chemical analysis and/or by a certificate and a chemical identity check.

9.8. Chemicals and substances should be labelled according to the system where they can be used, so that they can be clearly identified. The label should indicate the shelf life of the material and the application system of the material.

9.9. When transferring a chemical from a stock container to a smaller container, the latter should be labelled with the name of the chemical, date of transfer and pictograms to indicate the risk and application area. The content of the smaller container should not be transferred back into the stock container. Rests of none needed chemicals and substances should be disposed accordingly to the plant procedure. Quality of chemicals in the open stock containers should be periodically checked.

9.10. The replacement of harmful chemicals (from the point of view of personnel safety, environmental protection, material compatibility) by harmless ones should be considered.

9.11. Staff involved in receiving, storing and using chemical substances should be trained to understand storage compatibility, labelling requirements, handling and impacts on the plant SSCs (see also Section 8).

9.12. Management should periodically tour the plant to evaluate the effectiveness of the chemistry programme and to detect the uncontrolled storage of chemicals.

9.13. Safety data sheets for all approved chemicals and substances should be available and easily accessible. These sheets should include as minimum possible dangers for the staff health, preventive measures for handling and medical recommendations in case of incidental use.

9.14. Chemicals should be stored only in an appropriate warehouse that is fire protected, captures spillages, and is equipped with a safety shower, as required. Tanks with chemicals should be appropriately labelled.

9.15. Reasonable amount of chemicals can be stored in other controlled environments of the workshops or operational department.

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

9.17. The operating organization should be responsible for the use of the proper chemicals and their right quality. The quality of these materials should be rechecked if appropriate (e.g. diesel fuel, oil).

9.18. A plant procedure should define the proper quality of lubricant oil for each component that is essential for safety and availability.

9.19. Lubricant oils from systems, that are important for safety and/or availability should be regularly analysed for control parameters that characterize the condition of the lubricant.

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