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Good Practices for Water Quality Management in Research Reactors and Spent Fuel Storage Facilities

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GOOD PRACTICES FOR
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IN RESEARCH REACTORS
AND SPENT FUEL STORAGE FACILITIES

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IAEA NUCLEAR ENERGY SERIES No. NP-T-5.2

GOOD PRACTICES FOR WATER QUALITY MANAGEMENT IN RESEARCH REACTORS AND SPENT FUEL STORAGE FACILITIES

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FOREWORD

Water is the most common fluid used to remove the heat produced in a research reactor (RR). It is also the most common media used to store spent fuel elements after being removed from the reactor core. Spent fuel is stored either in the at-reactor pool or in away-from-reactor wet facilities, where the fuel elements are maintained until submission to final disposal, or until the decay heat is low enough to allow migration to a dry storage facility.

Maintaining high quality water is the most important factor in preventing degradation of aluminium clad fuel elements, and other structural components in water cooled research reactors. Excellent water quality in spent fuel wet storage facilities is essential to achieve optimum storage performance. Experience shows the remarkable success of many research reactors where the water chemistry has been well controlled. In these cases, aluminium clad fuel elements and aluminium pool liners show few, if any, signs of either localized or general corrosion, even after more than 30 years of exposure to research reactor water. In contrast, when water quality was allowed to degrade, the fuel clad and the structural parts of the reactor have been seriously corroded.

The driving force to prepare this publication was the recognition that, even though a great deal of information on research reactor water quality is available in the open literature, no comprehensive report addressing the rationale of water quality management in research reactors has been published to date.

This report is designed to provide a comprehensive catalogue of good practices for the management of water quality in research reactors. It also presents a brief description of the corrosion process that affects the components of a research reactor. Further, the report provides a basic understanding of water chemistry and its influence on the corrosion process; specifies requirements and operational limits for water purification systems of RRs; describes good practices for water chemistry control in research reactors; defines parameters recommended, techniques applicable, sampling procedures and sampling frequency to monitor water quality in RRs, and describes the importance of a quality assurance programme, and the implementation of a corrosion surveillance programme (CSP) as part of the water management programme. Whenever applicable, considerations are made for primary cooling system, spent fuel storage basins, secondary cooling system, emergency cooling systems, make-up systems and water reservoirs of RRs.

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EDITORIAL NOTE

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1. INTRODUCTION

For over 60 years, research and test reactors (hereinafter referred to as ‘research reactors’[1]) have made valuable contributions to the development of nuclear power, basic science, materials development, education, training, and radioisotope production for medicine and industry. In total, 660 research reactors have been built since the Chicago graphite pile CP-1 went critical in December 1942. From these, 239 are operational and 236 are in permanent shutdown, without having been decommissioned [1]. Considering that the majority of shutdown reactors still have nuclear fuel elements within the facility, they require, for safety reasons, a continuous maintenance programme, especially to avoid corrosion of fuel elements to maintain fuel integrity, prevent release of radioactivity, and ensure safe handling throughout the storage period.

Because research reactors have a variety of applications, such as validation of reactor physics codes, training, neutron activation analysis and radioisotope production, several types were built. Some reactors are pressurized; others are open pool type. Some use heavy water but most use light water as the neutron moderator. The various reactors’ cores are loaded with fuels of very different designs, such as single fuel rods, fuel bundles, or plates assembled in fuel elements or sometimes termed ‘fuel assemblies’. The reactors also have a variety of fuel compositions, core configurations and power levels, ranging from ‘zero power’, also known as critical facilities, to hundreds of megawatts.

Regardless of the reactor type, its application, composition or power level, in the majority of them, water is used as the core cooling fluid, moderator and biological shielding. As the cooling fluid, water removes the heat produced by the fission reaction and transports it to the heat exchanger system; as moderator, the water slows down the high energy neutrons produced in the fission process, making them energetically favourable for new fission reactions required to sustain the reaction chain; and as radiological shielding, it attenuates the radiation emitted in the reactor core in order to assure a safe environment for the reactor operators. Being an efficient agent for all three purposes, it can produce undesirable conditions if its quality[2] is poor. Dispersed impurities may become activated by the neutron flux as the water circulates through the reactor core, and if their concentration is too high, it can result in unwanted high radiation levels. Also, low quality water can lead to crud accumulation, decreasing thermal conductivity, with a consequent fuel temperature increase, which accelerates oxidation of the cladding and causes further decrease of thermal conductivity, in a vicious loop that may result in fuel failure. On the other hand, if the water chemical purity is assured, no elements other than the water components (e.g. deuterium in heavy water) will be available for activation, heat transfer from the fuel to the coolant will be high, and electrical conductivity of the coolant will be low, resulting in an environment with a very low corrosion rate for both the fuel and structural materials in the reactor system.

Because water is the main substance in contact with the fuel elements, maintenance of very high quality water is the most important factor to prevent degradation of the fuel clad and structural components of the reactor. In a research reactor, water deterioration can occur for various reasons: use of a poor quality water source for water make-up, incorporation of environmental dirt, biological activity and primary circuit corrosion. Because water quality can deteriorate, maintenance of good water quality is a key feature of the reactor maintenance programme, and it is essential to achieve optimum fuel performance, either in the reactor core during reactor operation, or in the spent fuel storage pool, after the fuel reaches its maximum burnup level.

Fuel elements used in research reactors are made primarily of aluminium alloy claddings. Stainless steel and zirconium alloys (e.g. Zircaloy) are also used as cladding materials for the fuel, but they represent a very small percentage of the total fuel elements produced worldwide. The oxidation levels of these alloys in normal operating conditions (with fuel/water interface temperatures below 100ºC) in general pose no limiting operating condition for the reactor. However, stainless steel and Zircaloy have some disadvantages when compared to aluminium. Stainless steel constituents have higher absorption cross sections and production of activation products with higher half-lives compared to aluminium cladding alloys and Zircaloy. In particular, cobalt-60, produced from activation of cobalt as an impurity, and by capture reactions with nickel in austenitic stainless steels, causes a significant radiation dose

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[1] In this publication, the term ‘research reactor’ also includes critical and sub-critical assemblies.

[2] Water quality is defined by a set of parameters used to characterize the water physical and chemical conditions. It includes pH, conductivity, dissolved impurity species, undissolved solids, colloids, organic substances, biological organisms and temperature.

due to its high energy gamma decay. In addition, Zircaloy is more expensive than aluminium, and aluminium based fuel core materials with aluminium cladding are readily fabricated. The challenges and higher costs for fabrication, disassembling and decommissioning operations for stainless steel and Zircaloy compared with aluminium are the primary reason that most of the fuel used in research reactors, in both eastern and western countries, is fabricated with a core consisting of uranium–aluminium alloys or dispersion and protected by an aluminium alloy cladding. There are important considerations, however, in the use of aluminium and aluminium alloy claddings for reactor fuel during reactor operation and in post-reactor fuel storage in water. Aluminium alloys show very different oxidation behaviour from fuels produced with stainless steel and Zircaloy claddings. During reactor operation in an aqueous environment, aluminium claddings can develop relatively thick oxide layers. Oxide layer thicknesses of up to 61 µm have been reported under high heat flux conditions [2]. Depending on the reactor operating condition, there is the risk of high corrosion, oxide spalling, blistering and intergranular attack of the aluminium fuel clad materials when the thicknesses of the oxide layer reaches about 25 µm [3, 4]. Spalling can also occur with oxide layers on the order of 10 µm [5]. Therefore, it is important to consider the conditions of reactor operation for aluminium clad fuels to avoid excessive oxide layer buildup that leads to a high metal/oxide interface temperature, especially when the reactor operates under high heat flux conditions.

Water is also the most common media used to store spent fuel elements[3] from research reactors after being removed from the reactor core. Spent fuel is stored either in the reactor pool or in some away-from-reactor (AFR) wet facilities, where the fuel elements are safely maintained until they can be moved to a dry storage facility, or until they are retrieved for final disposal or reprocessing. There are some documented cases of aluminium clad spent fuels that have been in water storage for more than 40 years and remain in pristine condition, while others are severely degraded by pitting corrosion after a few years of exposition to low quality water, causing serious concerns, since pitting corrosion can eventually lead to breach of the cladding material and release of radioactivity to the storage basin [6]. Not surprisingly, in a survey conducted by the IAEA in 2002, addressing the concerns expressed by research reactor operators over their spent fuel management programmes, research reactor materials degradation was one of the main concerns, together with final disposal of the spent fuel and limited spent fuel storage capacity. Information gathered in this survey is part of the IAEA's restricted access Research Reactor Spent Fuel Database (RRSFDB).

The IAEA recognizes that, although a great deal of information on reactor water quality is available in the open literature, only a few publications address the rationale of water quality management in research reactors. The IAEA also understands that such a document can help research reactor operators in implementing water quality management programmes in their facilities, and with this objective the IAEA supported the production of these guidelines to provide a comprehensive catalogue of good practices in water quality management for research reactors. The report was produced with the main purpose to give research reactor operators and managers insight into basic principles of aluminium corrosion, water chemistry and current good practices in the reactor ageing/safety management adopted in a number of Member States, thus helping them manage their own problems associated with reactor ageing, in particular, corrosion problems that can arise by an inadequate water quality maintenance programme.

The publication is mainly intended for operators and managers of facilities dealing with aluminium clad fuel and aluminium structural components in the reactor pool, and in the spent fuel storage pool. It emphasizes requirements for open pool reactors, mainly Material Test Reactors (MTRs) and TRIGA type reactors using ordinary water as the surrounding environment for the reactor core. The report does not include procedures or good practices for water quality management in reactors that use heavy water as the surrounding environment for the reactor core. However, this report can be used by operators and managers from other reactors, especially those in which stainless steel is used. In this case, it is important to recognize that stainless steel is more resistant to water corrosion than aluminium, and therefore, the requirements for stainless steel structures and fuel cladding may be relaxed.

It is also important to mention that an important part of this report is based on knowledge gained during a co-ordinated research project (CRP) on Corrosion of Research Reactor Aluminium Clad Spent Fuel in Water — Phases I and II, organized by the IAEA from 1996 to 2005; findings of the CRP have been published [7, 8].

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[3] Fuel is regarded as spent nuclear fuel, regardless of burnup level, when it is discharged from the reactor core for the final time, and put in a certain place, in the reactor pool, or in a pool away from the reactor, for removal of the residual heat.

Finally, considering that practices for maintaining integrity of the fuel and structural components of research reactors are part of the overall strategy for safe operation of a research reactor, it is necessary to mention that the recommendations and practices described in this report comply with IAEA Safety Standards Series No. NS-G-4.2 (Maintenance, Periodic Testing and Inspection of Research Reactors), NS-G-4.3 (Core Management and Fuel Handling for Research Reactors) and NS-G-4.4 (Operational Limits and Conditions and Operational Procedures for Research Reactors).

2. WATER CHEMISTRY

2.1. IMPORTANCE OF WATER QUALITY IN RESEARCH REACTOR SYSTEMS

As any other chemical substance, water has a certain potential to interact with the materials of components within the water. The type and extent of interaction is, inter alia, determined by the physical state and composition of the water and its parameters such as temperature and pressure to which the materials under consideration are exposed. Careful selection of suitable materials for any functional, water bearing, component is of utmost importance, as interaction between the water and this component may affect the chemical and mechanical properties of the latter. Prolonged reaction may lead to degradation (corrosion) and loss of the structural integrity of the component. Selection is therefore restricted to materials known to show very limited interaction with water during prolonged exposure under a range of conditions. An example of such a material is aluminium. Under certain conditions, the properties of aluminium are hardly influenced by constant exposure to water. This and other favourable properties such as its density, mechanical properties, ease of fabrication and neutronic properties make aluminium a widely used construction material for research reactors.

The actual situation is complicated because water commonly contains a wide range of dissolved and non-dissolved species in various concentrations: metal ions, colloids, gasses and dust particles. Some of these species have a profound influence on the interaction between water and materials. Under certain conditions, the corrosion resistant character of a material like aluminium is even undermined.

In this section, a brief overview of the chemistry of water is presented with a focus on the prime parameters and processes that are relevant for the interaction between water and aluminium. The focus is on the processes that take place or could take place in the primary cooling system. However, it should be noted that these processes apply to all other water-bearing systems in a research reactor such as storage basins, decay tanks, the secondary cooling circuit and water make-up systems.

2.2. CHEMICAL COMPOSITION OF WATER

The chemical compound water is almost entirely made up of H_2O molecules, with the exceptions that approximately one atom in 6500 is deuterium, and that water in the liquid state is dissociated (ionized) into H^+ and OH^- that is dependent on temperature. However, the same term ‘water’ is also commonly used for aqueous solutions such as tap water and impure cooling water. Such solutions consist of more than 99% water, the remainder consists in a wide range of compounds other than H_2O. Although present in only small amounts, some of these compounds may have a profound influence on the properties of the medium water present in a research reactor.

The nature and concentration of non-pure H_2O compounds is the product of reactions and interactions between the medium water and its environment. On circuits with forced circulation, the kinetic energy of the water stream causes erosion of pipes and components of the circuit. During erosion, very small fractions of these components are mechanically released in the form of particles that are transported downstream, to be deposited as sediments, or dissolved in the form of charged particles: cations (e.g. Na^+, Ca^{2+}, K^+) and anions (e.g. Cl^-, CO_3^{2-}, SO_4^{2-}). The capacity of water for dissolved species in a solution is limited: if the amount of dissolved species exceeds the ‘solubility product’ of a certain compound, this compound will precipitate from the water in the form of salts.

Additionally, there is a continuous interaction between the water and the atmosphere in contact with it. Components from the atmosphere such as O_2 and CO_2 will — to a certain limit — dissolve in water. These dissolved gaseous species will also exert influence on the composition and the reactions that take place in water. Another factor of great importance is the temperature. Most chemical reactions are temperature controlled as heat provides the energy necessary for the reactions to occur. An increase of temperature generally tends to accelerate reactions and increase the capacity of water for dissolved species.

The cooling system of a research reactor is not a very complex one. In this system, the number of variables involved is very restricted. This, and the restricted size of the cooling system, make the composition of the (cooling) water less prone to variations, allowing the establishment of very simple water management programmes, with countermeasures to keep the original composition, such as, for instance, water purification. Management of cooling water aims at keeping the water as ‘pure’ as possible, i.e. keeping the amount of non-H_2O species as low as technically possible. Yet, interactions between the water and the contacted material (aluminium) and the atmosphere cannot be avoided. Using the basic principles of water chemistry, it is possible to model these interactions and to quantify their contributions to the composition of the cooling water. In the next sections, some of these principles will be highlighted in the light of the aluminium-water system. The specific limits and recommended ranges for water quality parameters for each reactor water system are discussed in Section 6 and are reproduced in Appendix I.

2.3. pH

In the management of water cooled systems, the pH together with conductivity are two of the foremost parameters used in characterizing the quality of the water. The reason for this is that the interaction of water with metals is heavily controlled by the pH of the water. Accurate determination and registration of the pH is therefore of utmost importance. In this section, some of the background behind the pH parameter is highlighted.

Pure water is a poor electrical conductor, yet the observation that it weakly conducts electric current indicates that pure water contains ions (charged particles). It appears that part of the water is dissociated (ionized) into H^+ and OH^-. In reaction form:

$$H_2O \leftrightarrows H^+ + OH^- \tag{1}$$

The $\leftrightarrows$ symbol indicates that this reaction is an equilibrium reaction, i.e. the reaction is reversible. The tendency for the reverse reaction (to the left) to occur, however, is more likely than the ionization reaction (to the right), that is, only a very small part of the H_2O is ionized. At 25°C, 10^{-5} % of the water molecules are ionized, i.e. the concentration of H^+ ions, and thus also of OH^- ions (denoted as $[H^+]$ and $[OH^-]$), in pure water amounts 10^{-7} mol/L. As for any equilibrium reaction, an ‘equilibrium constant’ K is defined, and for this specific reaction K is:

$$K_w = [H^+] * [OH^-] \tag{2}$$

K is, therefore, the mathematical product of $[H^+]$ and $[OH^-]$. At T = 25°C K_w is 10^{-14}, a constant for any aqueous solution at 25°C. As with any equilibrium reaction, the dissociation reaction of water is temperature dependent. At 60°C, K_w is $9.62*10^{-14}$, corresponding to H^+ and OH^- concentrations of $3.1*10^{-7}$ mol/L; at 100°C the concentrations of H^+ and OH^- in pure water amount to $7.42*10^{-7}$ mol/L. In general, an increase of the temperature will result in higher H^+, and OH^-, concentrations.

Mathematically, the value of pH is defined as the negative ‘log’ of the H^+ concentration when expressed in moles per litre:

$$pH = -\log[H^+] \tag{3}$$

Therefore, an H^+ concentration of 10^{-7} mol/L corresponds to a pH value of 7. Similarly, a pH of 5 means that the H^+ concentration is 10^{-5} mol/L, still very low, yet 100 times higher than in a solution with pH 7.

A solution with a pH value of 7 is ‘neutral’; solutions with a pH value less than 7 are termed ‘acidic’; and those with pH between 7 and 14, ‘basic’. In acidic solutions, H^+ is dominant over OH^-, whereas in basic solutions, the opposite is the case. However, for a given temperature, the equilibrium constant K_w, product of $[H^+]$ and $[OH^-]$ remains the same. Therefore, assume an aqueous solution with an H^+ concentration of 10^{-1} mol/L at T = 25°C. For this temperature, K_w is 10^{-14}, then the concentration of OH^- can be calculated as $[OH^-] = 10^{-13}$ mol/L.

Perfectly pure water has a pH value of 7. However, this is only the case for an entirely isolated volume of water. In most cases, water is exposed to an atmosphere with a certain composition like air. As explained in Section 2.2, components from the atmosphere will be taken up (dissolved) in the water and subsequently react with it. A prominent air component is CO_2, which dissolves and reacts with water according to the reactions:

CO_2 (g) = CO_2 (l) (the equilibrium between dissolved CO_2 in water and air)

$$CO_2\ (l) + H_2O\ (l) = H_2CO_3\ (l) \tag{4}$$

$$H_2CO_3 + H_2O = H_3O^+ + HCO_3^- \tag{5}$$

$$HCO_3^- + H_2O = H_3O^+ + CO_3^{2-} \tag{6}$$

The ultimate effect of CO_2 uptake by the water from the atmosphere is formation of more H^+, with consequent lowering of the pH.

The pH also depends on the partial CO_2 pressure: the higher the CO_2 pressure, the more CO_2 is dissolved and thus the lower the pH becomes. Pure water at 25°C in equilibrium with air with a CO_2 concentration of 338 ppm has a pH of 5.7, assuming that the air is in equilibrium with the water, i.e. that the CO_2 uptake has reached its maximum and is perfectly mixed with the water.

The case of CO_2 uptake is a good illustration of an interaction between water and its environment which has a significant impact on its composition. Most natural systems have a tendency to restore equilibrium after a disturbance. In more complex systems, lowering the pH may therefore trigger counter reactions, resulting at an increase of the pH in order to restore the former equilibrium. The ultimate pH is then the product of a series of reactions, the number of the reactions being a function of the number of species present. The capacity of a system to restore equilibrium is commonly referred to as the ‘buffering capacity’.

2.4. CONDUCTIVITY

Conductivity is a very important parameter related to corrosion of metals in an aqueous medium. By definition, conductivity is simply a measure of the ability of a medium to carry an electric current. As stated, conductivity is an index of how easy it is for electricity to flow in the medium. In water it is caused by the presence of some dissolved ionic species. Ions pass electric charge from one ion to the next. This means that the more anions and cations contained in water, the more electricity is carried, and the higher the conductivity. Therefore, pure water has a very low conductivity, and seawater has a very high conductivity. The conductivity of water is expressed in S/cm (S = siemens), or more usually, in μS/cm, where siemens is the inverse of the resistance; 1 S = 1/ohm. At room temperature, the conductivity of pure water at 25°C is 0.0548 μS/cm. Seawater, on the other hand, has a conductivity of about 40 000 μS/cm.

It is understood that even in purified water it is impossible to avoid some degree of impurities. Important sources of impurities are corrosion of components of the cooling system including the dissolution of (metallic) impurities in the piping, dust that falls into the pool, the air in contact with the water in the pool surface, aerosols and detergents. Typical dominant impurities are Al^{3+}, Fe^{2+}, NO_2^-, HSO_3^-, NO_3^-, SO_4^{2-} and Cl^-. Each ion makes a contribution to the total conductivity of the aqueous solution. One parameter used to estimate the overall conductivity of an aqueous solution with ions present in it, is the molar conductivity, Λ, defined as the conductivity (in S/cm) divided by the molar concentration of the ion in the solution, expressed in mol/cm^3. Table 1 [9] gives the molar conductivity for some ions important for water quality control in research reactors. By using this table, it is possible to estimate the contribution of these ions to the conductivity of an aqueous solution.

TABLE 1. MOLAR CONDUCTIVITY[a] FOR VARIOUS COMMON IONS [9]

Ion	Λ [(S/cm)/(mol/cm^3)]
Cl^-	76.3
NO_2^-	71.8
NO_3^-	71.4
HSO_3^-	58
SO_4^{2-}	80
HCO_3^-	44.5
OH^-	198
H^+	349.6
K^+	73.5
Na^+	50.1

[a] Considering infinite dilution and temperature equal to 25°C.

Frequent element specific analyses of water samples are one option to monitor its quality. They provide detailed information about the concentrations of all elements present. However, this is time consuming and not a practical solution for an on-line measurement system. Instead, the overall conductivity of the water is measured. Continuous or frequent measurement of the conductivity is a good method to detect sudden or gradual increase in the bulk concentration of ionic species. Element specific analyses are then required to determine the cause (origin) for the increase.

The conductivity of water is reduced by adding, to the original bulk, water with lower concentrations of non-H_2O ionic species, or circulating the water through a water purification system, in which these ionic species are removed from the water. In a research reactor, it is not recommended to add any chemical solution to the reactor cooling water, to avoid eventual activation with consequent increase in radiation dose. Therefore, the only recommended alternative is to circulate the water through the water purification system, keeping the purification system (see Section 4) as required to maintain water quality limits.

Considering that pH and conductivity are based on ion concentrations, as expected, there is a correspondence between the two values. Figure 1 shows the relation between conductivity and pH, considering the presence of hydrochloric acid in pure water. The values for other acids will be comparable.

Although the pH value of water is an indication of the quality of water, a low conductivity is a more reliable indication for low corrosion potential. A solution of 0.01 molar KCl will have a pH value comparable to ultrapure water, but will have a conductivity of about 15 mS cm^{-1}.

With a pH value between 4.5 and 7 and conductivity below 1 μS.cm^{-1} corrosion of most metals is minimal.

2.5. ACTIVATION PRODUCTS IN REACTOR PRIMARY COOLANT WATER

There are numerous water activation products and activated water impurities in the reactor primary water. The species that are significant include: ^{3}H, ^{13}N, ^{16}N, ^{18}F, ^{24}Na and ^{38}Cl.

2.6. FORMATION OF IONS IN WATER, OXIDATION-REDUCTION

Oxidation-reduction reactions are among the most prominent type of reactions in chemistry. The basic principle behind these reactions is that most elements have a tendency to donate part of their electrons to elements with a larger affinity to accept electrons. The potential (tendency) of a metal to donate electrons largely depends on the distribution of the electrons in the metal atom. Magnesium and aluminium are examples of metals with a great tendency to donate electrons in electrochemical reactions. In contrast, nickel and titanium are more resistant to

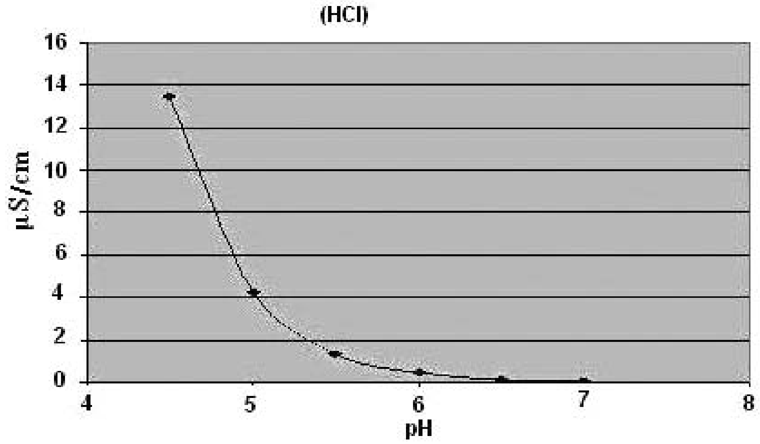

FIG. 1. Relation between conductivity and pH for an aqueous solution with HCl.

oxidation; their tendency to act as an electron donor is much less. Platinum and gold are noble metals; they are the least susceptible to oxidation.

Most metals do not occur as metallic species in nature. For example, Fe and Al are found as oxides (e.g. Al_2O_3), sulphides (e.g. FeS_2) and carbonates (e.g. $FeCO_3$), etc. Formation of these compounds involves oxidation-reduction reactions, with the metals donating part of their electrons. For instance, Al_2O_3 may be written as $Al_2^{3+}O_3^{2-}$. The process of metal oxidation is also known as corrosion, the result of a chemical reaction, with consequent deterioration of the properties of the metal.

A well known example of metal oxidation is the corrosion of iron (rust formation) by water in the presence of oxygen.

$$Fe \leftrightarrows Fe^{2+} + 2e^- \tag{7}$$

+

$$H_2O + 1/2O_2 + 2e^- \leftrightarrows 2OH^- \tag{8}$$

$$\overline{Fe + H_2O + 1/2O_2 \leftrightarrows Fe(OH)_2} \tag{9}$$

In this case, iron donates electrons to oxygen, resulting in the formation of iron oxide. The reaction (9) is a summation of two half-reactions: an oxidation (7) and a reduction (8) reaction. The oxidation and reduction reactions are also referred to as the anodic and cathodic reactions, respectively. Reactions (7)–(9) are an example of an electrochemical reaction. Note that the presence of water is vital. This is the reason that iron hardly corrodes when exposed to air with low humidity.

In aqueous environments, oxidation-reduction reactions are a common feature. Dissolution of metals occurs by means of oxidation-reduction reactions. For aluminium in water, the aluminium will donate three electrons:

$$Al \leftrightarrows Al^{3+} + 3e^- \tag{10}$$

In this case, the acceptor is H^+:

$$2H^+ + 2e^- \leftrightarrows H_2\ (g) \tag{11}$$

Therefore, oxidation of aluminium promotes the formation of (small) amounts of hydrogen at the expense of H^+. This example illustrates the close connection between pH and oxidation-reaction. In an acidic environment ($pH < 7$), there are relatively many H^+ ions that combine to H_2 by accepting electrons. More H^+ ions means that more electrons are required, and they have to be donated by the Al. This increasing need can only be met with more dissolution of Al; i.e. the lower the pH, the more aluminium will be dissolved.

Thermodynamic models provide insight to the reactions that are likely to occur in a system. However, the results do not provide a clue on the speed with which a reaction will proceed. The results are time independent. At any moment in time, the reaction will occur as each reaction has its own ‘kinetics’. Also, the physical form of the reaction products may be decisive for the progress of the reaction. In case of the corrosion of aluminium, $Al(OH)_3$ is formed. In nature, several varieties of $Al(OH)_3$ are known to occur dependant on the conditions that aluminium is exposed to. In case of reactor fuel at high temperature, the oxidation product has a very dense structure, which makes the underlying aluminium inaccessible for the cooling water, i.e. the oxidation process comes to an end. Consequently, the oxidation product protects the bulk of the aluminium from further corrosion. This process is also referred to as passivation.

The rate of metal corrosion in a water environment can be strongly affected if the metal is in contact with another metal, resulting in a special type of electrochemical reaction known as ‘galvanic corrosion’. Galvanic corrosion is a process that occurs in a water environment, involving two coupled metals with different potentials. Assuming the difference between their potentials is large enough, the metal with the highest potential will donate electrons, whereas the other metal will act as an acceptor; i.e. one metal may cause corrosion of the other. The role of water in electrochemical reactions is essential. It acts as the medium by which the aqueous species involved in the reactions are transported. In addition, it plays a key role in the flow of the electric current (electrons).

Table 2 [10] shows a typical galvanic series for some metals and alloys in seawater. It is based on corrosion potential measurements in seawater, and shows the relative potential/nobility of the metal/alloy. According to this table, metal/alloys of a lower position in the table have their corrosion rate increased when placed in seawater and in contact with metal/alloys of an upper position. The relative position can be different for other environments. Metallic species more noble (i.e. higher position in the table) than a reactor material would tend to cause oxidation of the material and its dissolution. For example, copper ions in water are detrimental to aluminium. Mercury is forbidden in aluminium systems for this same reason.

2.7. EFFECT OF DISSOLVED ANIONS IN ALUMINIUM STRUCTURES

For systems with components and structures made of aluminium, dissolved anions such as Cl^-, HCO_3^- and SO_4^{2-} are of special interest because of their capacity to influence the breakdown of the passivation layer that protects the underlying aluminium from corrosion. Corrosion attack preferentially takes place at weak spots or regions of loosely adherent oxides. The breakdown of the passivation layer facilitates rapid corrosion at these spots, which may result in the formation of holes (‘pits’) in the aluminium metal.

Cl^- is by far the most aggressive agent. Once Cl^- has broken down the passivation layer and has reached the metal surface, further corrosion takes place according to the reactions:

At the anode:

$$Al \leftrightarrows Al^{3+} + 3e^- \tag{12}$$

Followed by:

$$Al^{3+} + 3Cl^- \leftrightarrows AlCl_3 \tag{13}$$

And at the cathode (Cl^--free zone):

$$H_2O + 1/2O_2 + 2e^- \leftrightarrows 2OH^- \tag{14}$$

The resultant of these reactions is:

$$AlCl_3 + 3OH^- \leftrightarrows Al(OH)_3 + 3Cl^- \tag{15}$$

Reaction (15) makes it clear that Cl^- is not consumed during corrosion; rather, it remains available for further corrosion. It is therefore of utmost importance to keep the Cl^- concentration of the cooling water as low as possible. Sufficient flow of the cooling water has also a positive effect. The generation of Al^{3+} ions in the pit attracts Cl^-, and by keeping the water in motion, the buildup of local concentrations of Cl^- and other species is avoided.

TABLE 2. TYPICAL GALVANIC SERIES FOR METAL/ALLOYS IN SEAWATER [10]

Platinum (most cathodic, noble, or resistant to corrosion)
Gold
Graphite
Titanium
Silver
Hastelloy C
18-8 stainless steel (passive)
Chromium steel >11% Cr (passive)
Inconel (passive)
Nickel (passive)
Monel
Bronzes
Copper
Brasses
Hastelloy B
Inconel (active)
Nickel (active)
Tin
Lead
18-8 stainless steel (active)
Ni-resist
Chromium steel >11% Cr (active)
Cast iron
Steel or iron
2024 aluminium
Cadmium
Commercially pure aluminium
Zinc
Magnesium and its alloys (most anodic or easy to corrode)

2.8. ORGANIC COMPOUNDS

The contribution of organic compounds to corrosion effects is in most cases of minor importance; only the presence of strong organic acids and complexing agents should be avoided. Possible sources of organic compounds are: detergents, organic material leached from seals, traces organics from ion exchangers, organic traces in dust and dissolved volatile organic compounds (small aliphatic acids, alcohols, at trace level present in outdoor air).

Good practice is to keep the dissolved organic compound (DOC) concentration at subppm levels. Usually, an active carbon filter is present in the water cleaning system, a very effective tool for keeping the amount of organics in water at a low level. The measurement of DOC gives information on the amount of organic materials present in the water. Section 6 provides the recommended limits for DOC concentrations for the various reactor systems.

2.9. ALGAE

The control of algae formation in water systems is by avoidance of light, circulation of water, and avoidance of nutrients in the water.

3. DEGRADATION OF MATERIALS IN WATER

3.1. INTRODUCTION

The degradation of materials immersed in water is a very complex process. Depending on the material and the water composition, several chemical reactions can occur to form soluble or insoluble compounds. In case of metals, they can dissolve electrochemically (corrode) or can accumulate hydrogen as a result of high hydrogen fugacity at the material surface, and thereby become embrittled. The modes of attack can be thinning, pitting, and cracking by stress corrosion mechanisms (metals). Hydrogen embrittlement can also lead to cracking of metals.

Since water is a strong polar solvent, metallic materials tend to dissolve (corrode) in water and water solutions through mechanisms involving electrochemical reactions. The reactions typically involve other commonly dissolved species, namely: hydrogen ions (H^+ = protons), which comes from water dissociation; oxygen, which originates from the air and dissolves in the water as O_2; and dissolved impurity ions.

Various metallic materials are commonly used in experimental or research reactors. Particularly, in the primary circuit, stainless steels are used for structural components and fuel cladding and aluminium alloys are also used for various types of fuel cladding and structural components. Zirconium alloys are also used for fuel cladding and structural materials, and nickel-based alloys are used for heat exchangers and other minor applications. In the secondary circuit, carbon steel, and copper-based alloys are typically used. Concrete is also an important structural material that may be in contact with water storage basins. Due to the various working and environmental conditions that they are subjected to, different degradation mechanisms can occur, some of an electrochemical nature and some not (e.g. leaching), which have to be individually considered in water systems [11].

Table 3 provides a list of the important mechanisms that can degrade reactor materials in water systems.

TABLE 3. MECHANISMS OF DEGRADATION FOR REACTOR MATERIALS IN WATER

General corrosion
Pitting corrosion
Crevice corrosion
Galvanic corrosion
Intergranular corrosion
Stress corrosion cracking
End-grain attack
Erosion-corrosion
Blister formation
Microbial corrosion
Sediment induced corrosion
Leaching of calcium and silicon from concrete
Carbonation and rebar corrosion in concrete

Other degradation mechanisms of reactor components that are not related to water quality conditions (e.g. irradiation induced loss of compressive strength of concrete) are not considered in this section.

This section describes the modes and mechanisms of attack on research reactor fuel and structural materials in reactor water systems. The basic concepts of water chemistry and its affect on materials, which were introduced in Section 2, are extended in detail for specific material systems to identify specific water quality conditions that can cause degradation. The first system considered is aluminium in Section 3.2.

3.2. ALUMINIUM AND ITS ALLOYS

3.2.1. Overview of aluminium corrosion and corresponding oxyhydroxide film formation

Aluminium is one of the most thermodynamically reactive metals, which in normal room conditions rapidly forms a thin and dense stable oxide layer (Al_2O_3) on the surface. On fresh metal, this dense oxide layer measures about 2.5 nm, and increases gradually with time. This protective oxide barrier film is strongly bonded to the surface, relatively inert, and tends to prevent further oxidation, making aluminium a metal durable for many applications, especially when exposed to air. However, when placed in a wet environment, aluminium may be strongly affected by corrosion. Aluminium oxyhydroxide (also known as aluminium hydroxide, or simply, aluminium oxide) films form and grow in wet environments. From an engineering standpoint, the kinetics or rate of corrosion of a metal is usually of primary importance. Corroding metals are not in equilibrium and therefore thermodynamic calculations cannot be applied. For metal corrosion to occur, an oxidation reaction (generally metal dissolution or oxide formation) and a cathodic reduction reaction (such as oxygen reduction) must proceed simultaneously. In most normal water environments, the overall reaction for aluminium corrosion is a reaction with water to form aluminium hydroxide and hydrogen. Within a certain pH range, the aluminium hydroxide has very low solubility in water and precipitates as bayerite or boehmite, depending on the temperature of the water [11, 12]. At low temperatures (<~80°C), the following is the predominant corrosion reaction:

$$2Al + 6H_2O \rightarrow 2Al(OH)_3 + 3H_2 \qquad (16)$$

The oxidation (anodic) reaction is given by:

$$Al \rightarrow Al^{3+} + 3e^- \qquad (17)$$

The reduction (cathodic) reaction is given by:

$$2H^+ + 2e^- \rightarrow H_2 \qquad (18)$$

In the electrochemical reaction, the positively charged ions leave the surface of the anode and enter the electrolyte solution, leaving electrons behind to flow through the metal to the cathode. At the cathode, the electrons are consumed by the hydrogen ions at the surface, and hydrogen gas is liberated. The oxidation and deterioration of the anode surface causes corrosion (i.e. loss of the aluminium metal).

As stated, aluminium oxyhydroxides may form and adhere to the aluminium surface; the specific type of oxyhydroxide formed depends on the temperature and pH conditions of the water [12–15]. Furthermore, aluminium is amphoteric; its oxyhydroxides are not stable and will dissolve more readily at pH levels below about 4 and above about 10 at 25°C, when compared to pH levels within that range.

The protective film (i.e. the film formed with pH in the range of 4 to 10) can also be attacked in the presence of some chemicals, which this can lead to dissolution of the metal. When the film is mechanically damaged or chemically weakened, localized corrosion in the form of pitting attack can occur because normal ‘self-healing’ or re-formation of the oxyhydroxide does not occur due to local aggressive water chemistry [16]. Additional discussion of general and pitting corrosion can be found in Ref. [17, 18] and in Section 3.2.3.

As with any diffusion controlled process, as the oxide film increases in thickness, the growth rate becomes slower with the growth kinetics tending to be parabolic. Investigations have shown that the formation of a protective oxide film on the aluminium surface at moderate temperatures occurs in three distinct stages [19], which are a function of time and temperature. The chemical precursor of the crystalline oxyhydroxide film structures is a gelatinous pseudo-boehmite [14]. The gelatinous film ages to form a tri-hydroxide with the structure of Gibbsite (hydrargillite) [γ-$Al(OH)_3$] if the pH is lower than 5.8 or higher than 9, and Bayerite [α-$Al(OH)_3$] if the pH is between 5.8 and 9 at temperatures below about 70–80°C. Boehmite, a monohydroxide, [γ-AlOOH], forms at temperatures above about 70–80°C.

Gibbsite formation and release as turbidity may occur in the reactor system where the high temperature water and circulation promote the formation and release of the oxide. In this case, a tight limit on the range of pH would control the Gibbsite formation. Specifically, a pH of 5.2 is the value to limit Gibbsite formation on aluminium at 25°C [20, 21].

These passive films are stable, showing limited oxide dissolution for waters with pH levels between 4 and 10. For all aluminium oxides, the minimum solubility is reached at approximately pH 5.2 [21]. However, normal water pH in open pool research reactors is 5.7, a value well accepted, which corresponds to the CO_2 concentration in water at 25°C in equilibrium with air with 338 ppm CO_2. This value is also within the range for recommended water quality of the primary system and the fuel storage system listed in the tables in Section 6.

It is not uncommon for thick layers to turn porous or crack and hold some water at a microscopic level; then, the migration can proceed through other mechanisms than diffusion. Movements along pores, oxide cracks and grain boundaries permit a higher transport rate of oxygen or aggressive species, which can lead to a higher corrosion rate. Bayerite films tend to be porous and thicker, whereas Boehmite is thinner and compact. Thus, Boehmite provides high resistance to continued corrosion. Autoclave treatment to form a passive, adherent Boehmite film on the surfaces of the clad fuel assemblies has been used prior to reactor irradiation at several sites. Boehmite films on the cladding over the high temperature fuel regions during reactor operation can also form if no pre-treatment is applied. Aluminium clad fuel is subjected to different environmental conditions in the reactor during irradiation and in basin storage. In the reactor, water is normally maintained using high quality standards, whereas water purity in decay or storage basins may vary. Basins located inside reactor facilities, which are kept by the same reactor crew, tend to be kept in a much better condition than away-from-reactor installations. For this reason, when evaluating degradation of fuel in reactor operation, corrosion mechanisms involving aggressive species dissolved in the water are not generally considered; the main concern, rather, is the metal oxidation taking place under heat transfer conditions, which could affect fuel operation. The situation during long interim spent fuel storage is exactly opposite: electrochemical forms of low temperature corrosion are much more relevant than oxide growth under high temperature conditions.

High temperature aluminium corrosion relevant to fuel cladding during reactor operation and low temperature aluminium corrosion relevant to fuel in storage are discussed in the next two subsections, respectively.

3.2.2. High temperature aluminium fuel element corrosion under reactor operation

Figure 2 shows the oxide film produced as a corrosion product through general corrosion on an outer fuel plate for an MTR assembly that occurred under the heat flux condition during reactor operation.

Aluminium alloys oxide growth in water depends on many variables, including fuel plate temperature, pH, conductivity, dissolved species, heat flux and coolant flow rate. There is no comprehensive predictive model taking into account all these parameters. Only mechanistically based empirical regressions are available, which are valid only for the conditions of the experiments used to develop them. Those by Griess [5], Kritz, as described by Ondrejcin [22], Pawel, in the ‘Correlation II’ model [23] and a recent one by Soo Kim et al. [4, 24] are available to provide an estimate of the oxide film growth on aluminium during high temperature, high heat flux conditions that are relevant to reactor operation.

In order to sustain the corrosion reaction with an adherent oxide film, oxygen ions, aluminium ions or both must diffuse through the oxide film; then, the reaction controlling temperature should be some value between the metal/oxide and the oxide/water interface. The higher the heat transfer rate, the greater the temperature variation across the oxide, which in some cases have been estimated at 100ºC or more for thick layers; this results in a greater amount of uncertainty on the reaction temperature value. In static tests, with no temperature gradient, intergranular attack on the aluminium substrate has been observed at 200ºC and above, a temperature that could eventually be reached at the metal/oxide interface, depending on the inlet temperature (temperature of the coolant water when entering the reactor core).

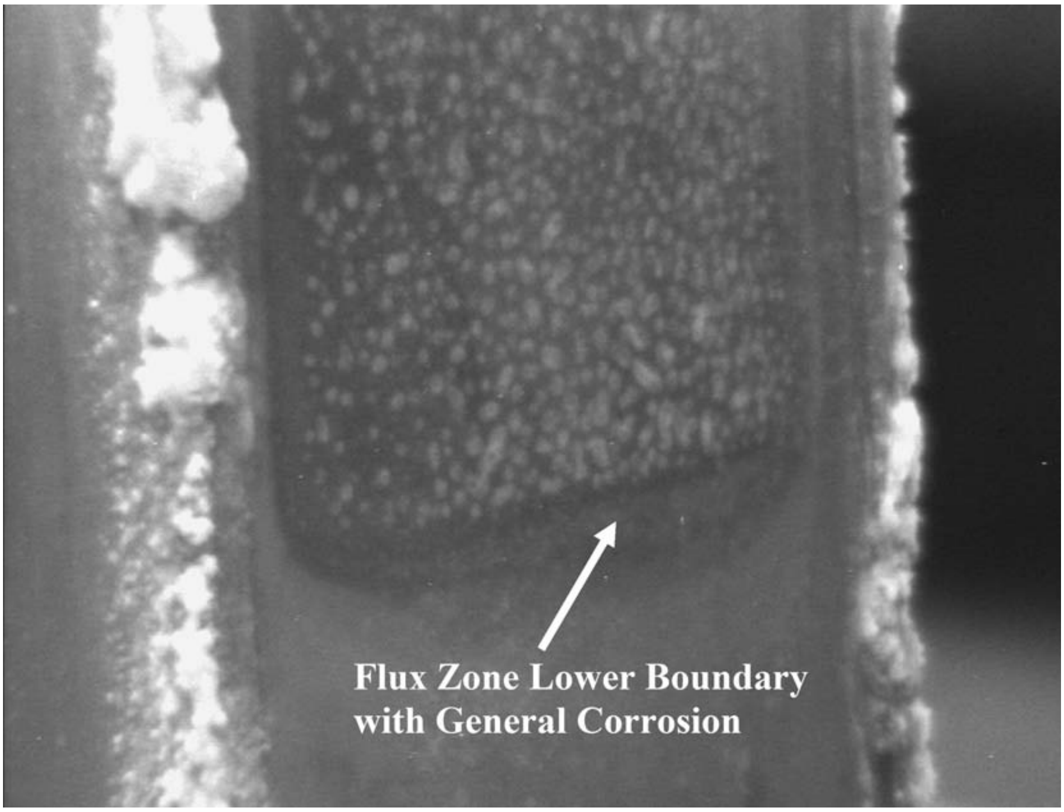

FIG. 2. Oxide film on an aluminium fuel plate in a high heat flux region, produced during reactor operation.

The effect of heat flux under the oxide film growth is obvious. For greater values of heat transfer, the barrier characteristics of the oxide layer become critical. Any increase in film thickness will cause a decrease in the overall heat transfer coefficient, causing the metal temperature to reach higher values, eventually reaching temperatures near 200°C where intergranular attack can occur. Increasing the coolant flow rate is one way to reduce fuel plate temperature; the risk of erosion is not likely since the high temperature oxyhydroxide (boehmite) deposit tends to be relatively hard.

3.2.3. Low temperature modes of corrosion of aluminium in wet environments

Aluminium and its alloys are subject to the possibility of various forms of corrosion during mid to long term exposure (one month to several decades of years) to aqueous environments. This aqueous exposure may affect fuel elements that are used in low power research reactors, sustaining burnup periods that can last for many years, as well as those which are sent to water basins for long term interim storage. The factors promoting corrosion of aluminium alloys are complex and interrelated, and are believed to operate synergistically, making prediction of corrosion difficult. There are several types of corrosion, which are classified according to the corrosion mechanisms involved. The main types of corrosion of aluminium alloys in water at low temperatures, existing conditions in low power reactors, decay pools and spent fuel storage basins are listed in Table 3: general corrosion, galvanic corrosion, pitting corrosion, crevice corrosion, intergranular corrosion, microbiologically induced corrosion and stress corrosion cracking. These types of corrosion are discussed in the subsections below.

3.2.3.1. General corrosion

The general corrosion resistance of aluminium in high purity water is very good. There is no significant general corrosion or gradual thinning of aluminium. General corrosion has not been a problem in research reactors that have operational water purification systems to control the water quality. As previously stated, the protective oxide film on aluminium is very stable in aqueous solutions in the pH range of 4 to 10, or even more stable in the range of 4.5 to 7 [25]; therefore, maintaining the pH within this interval is an assurance that the protective oxide layer on the aluminium surface remains intact.

3.2.3.2. Galvanic corrosion

Galvanic corrosion occurs when dissimilar metals or alloys are electrically coupled to one another in the same electrolyte. Cases of galvanic corrosion have been verified both in research reactor aluminium components and in spent fuel basins. During galvanic coupling, the rate of corrosion of the less corrosion resistant metal increases. This metal becomes the anode, while the rate of corrosion of the more corrosion resistant metal decreases and this metal becomes the cathode. The driving force for the corrosion or current flow is the potential that develops between the dissimilar metals. According to Table 2, shown in Section 2.6, when two metals/alloys are put in contact in a conductive solution, the most cathodic element causes galvanic corrosion on the most anodic element.

Some other factors that affect galvanic corrosion are surface area ratios, distance from the connection of the metals and the geometric shapes of the metals. Galvanic corrosion of the anodic metal takes the form of general or localized corrosion, depending on the configuration of the couple, the nature of the protective films formed and the nature of the metals.

Aluminium and its alloys occupy active positions in the galvanic series and are therefore highly susceptible to galvanic attack [16–19]. In solutions containing chloride ions, aluminium alloys are susceptible to galvanically induced localized corrosion, especially in dissimilar metal crevices. Severe attack is often seen when the aluminium alloys are coupled with more noble metals. The galvanic corrosion behaviour of stainless steels is difficult to predict because of the influence of passivity of the protective oxide film. Stainless steel is a more noble metal than the aluminium in the galvanic series and, depending on the environment and other factors, promotes corrosion of the aluminium. There are some registered cases in which research reactor fuel tubes were fabricated from different aluminium alloys joined together by a weld or mechanically bonded. In this case, galvanic effects promoting corrosion between the two alloys were noted in corrosion tests [26]. In addition, underwater photographs of bundled 1100 alloy fuel tubes in contact with 6061 alloy spent fuel storage racks have shown the tubes to remain free of corrosion while the storage racks appear to corrode sacrificially.

Galvanic effects between an aluminium clad material (Al 8001) and a surrogate fuel material (Al-10% U) were investigated [27]. The corrosion potential of the clad and fuel specimens in solutions at conductivities of 100 and 200 µS/cm and in distilled water were measured. In each case, the difference in the potential was no greater than approximately 75 mV. Separate testing was performed to measure the galvanic current between these specimens in the 100 and 200 µS/cm solutions. The current between the disk specimens of Al 8001 and Al-10% uranium alloy was less than approximately 5 µA. This current would correspond to a corrosion rate of approximately 25.4 µm/y, which is on the order of magnitude for general corrosion rate of aluminium alloys in these waters. These results suggest that no significant galvanic couple would exist between the fuel and cladding in the case of breached cladding.

Galvanic effects can also occur in the contact of aluminium alloys with graphite. This is not a metallic material; nevertheless, it provides a large specific surface area available for cathodic reactions, enhancing the corrosion attack. This has been the case in the corrosion of aluminium thermal columns [28, 29].

Galvanic corrosion of spent nuclear fuels in storage basins is active and can be reduced considerably by removing the couple whenever possible and by lowering the basin water conductivity to below 10 µS/cm.

Figure 3 shows an example of galvanic attack at the location in a fuel assembly where stainless steel screws joined both aluminium end plates and fuel plates to the fuel assembly. The fuel had been in high conductivity water storage conditions for seven years [30].

3.2.3.3. Crevice corrosion

Crevice corrosion is a highly localized form of corrosion and occurs on closely fitted surfaces with water in the crevice [16]. Chloride ions are drawn into the crevice as metal dissolution occurs and the conditions inside of the crevice become acidic. Metals like aluminium, which depend on oxide films or passive layers for corrosion resistance, are particularly susceptible to crevice corrosion.

Crevices can exist in many locations in storage basins where nuclear fuel is supported by hangers and storage racks. Interfaces where fuel elements are supported on hangers or resting on storage racks, or between storage racks

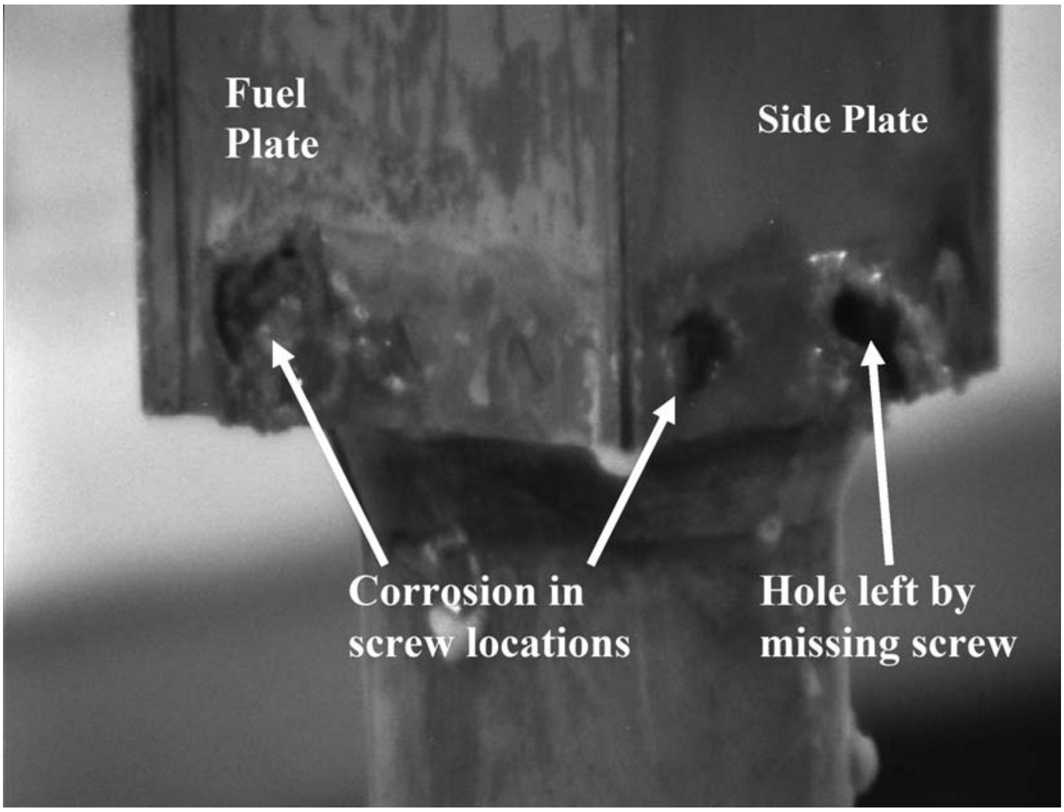

FIG. 3. Galvanic corrosion in an aluminium fuel element assembled with stainless steel screws, after several years of storage in poor quality water.

and metal pool liners may be configurations present in some fuel storage basins and provide the necessary environment for localized corrosion to occur. A crevice corrosion condition can occur with an aggressive species (chloride ion) migrating into the crevice or because of stagnant areas promoting the set-up of differential oxygen cells. One example is the slug bucket storage, which had been used at Savannah River Site for the storage of aluminium clad Mark 31A target slugs. In this situation, the stacking of slugs, combined with the sludge and corrosion product accumulation within the bucket, created conditions for crevice corrosion.

The means available to minimize crevices are usually limited. Much of the work needs to be done up front, in the initial design and construction stage of the facility. Storage racks and storage bucket designs should minimize crevices between the aluminium cladding and the storage surface, and permit flow of water across the fuel elements.

Figure 4 shows an example of crevice corrosion at the location where a fuel plate (1100 aluminium) joined a side plate (6061 aluminium). The assembly had been in aggressive water storage with a conductivity ranging from 70 to 80 μS/cm for more than ten years [30].

3.2.3.4. Stress corrosion cracking (SCC)

Stress corrosion cracking is a highly localized effect that occurs when the material is under the simultaneous action of tensile stress and an aggressive environment, favourable to corrosion. Stress corrosion cracking is usually caused by some residual stress remaining after fabrication, combined with some localized corrosion effect. Because the alloys used in research reactors are mainly made of pure aluminium — 1100, 6061 and 6063 — which are not susceptible to this mechanism, SCC has not played a major role in the corrosion of the aluminium fuel and aluminium structures of research reactors.

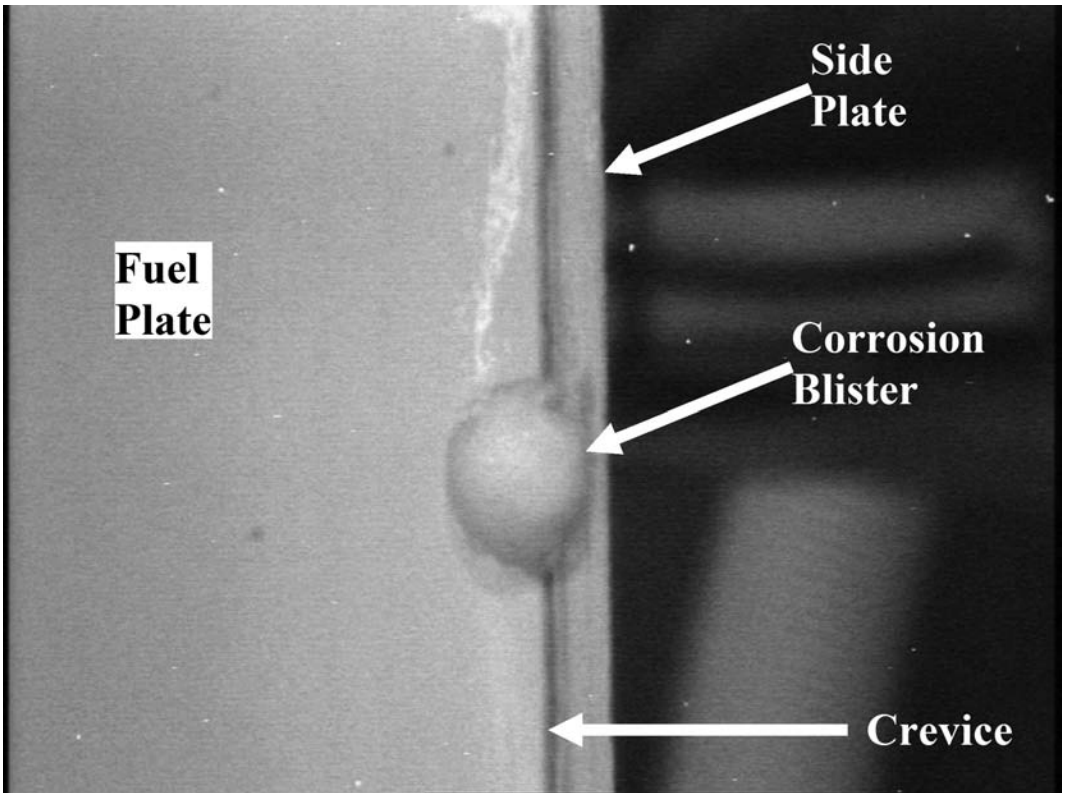

FIG. 4. Crevice corrosion in the joint between fuel and side plate of an aluminium fuel element stored for several years in poor quality water.

3.2.3.5. Blister formation

Blister formation or raised areas in the cladding of spent nuclear fuel can lead to breach of the aluminium cladding and subsequent corrosion of the fuel core. This blistering is a manifestation of internal gas pressurization and/or internal oxide formation. Blisters can be formed by several mechanisms:

- ***Blisters formed during manufacturing.*** Trapped air, inclusions or intermetallic particles formed during the fabrication process.
- ***Blisters formed from agglomeration of fission gas products.*** Fission gases can agglomerate at local unbounded regions at the fuel clad interface during irradiation. Higher than normal temperatures in the reactor or heat buildup in the shipping cask can result in blistering.
- ***Blisters formed due to corrosion.*** This is the most common form of blistering seen on the surface of spent fuel elements and is caused by hydrogen gas formation from normal corrosion reactions of aluminium in the cladding and the fuel core with water. Alloying elements in the aluminium alloy, such as nickel, or impurities trapped in the surface can act as cathodes for hydrogen evolution. If a local unbounded area is located in the proximity of the corrosion pit, hydrogen and/or voluminous corrosion products can be trapped and result in blister-like morphology in this region. Blistering is facilitated under coatings and oxides because hydrogen has low diffusion rates in aluminium oxide, and therefore trapped hydrogen disperses slowly. An example of blister formation is shown in Figure 5 [30].

3.2.3.6. Pitting corrosion

Pitting of the aluminium clad fuel and target materials in wet basin storage is the main mechanism of corrosion in basins around the world [6]. Pitting is an extremely localized form of corrosion in which metal is removed preferentially over very small areas on the surface to develop small cavities, or ‘pits’. The attack is

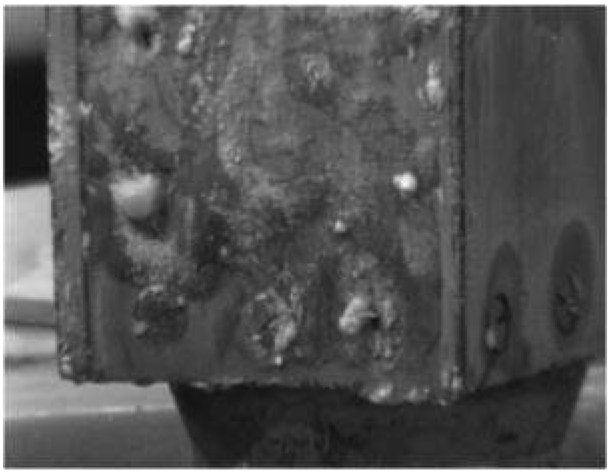

FIG. 5. Blister formation observed in corroded fuel element.

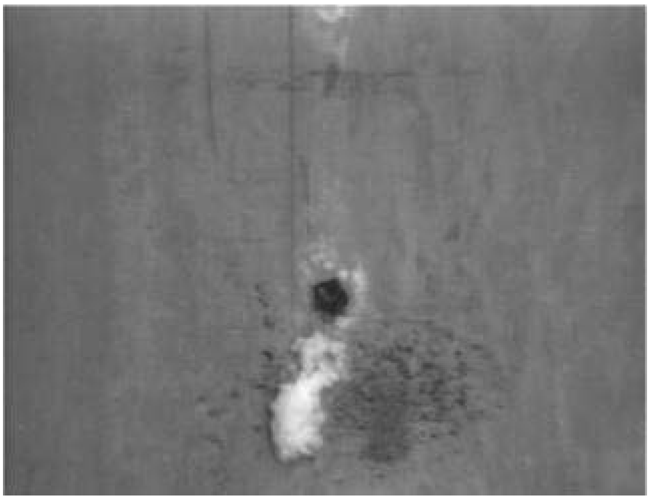

FIG. 6. Through-clad hole from pitting attack on a fuel plate stored for several years in conductive water (nodule removed). Size of hole: about 1 cm.

generally limited to extremely small areas, while the remaining surface is relatively unaffected. The pits usually start at small points on the surface and enlarge with time. This enlargement of the surface area of a pit is usually small in comparison with its increase in depth and volume [31]. Pitting requires the presence of an electrolyte, and in the case of most storage basins, even low conductivity water can serve this purpose. While many pits are hemispherical or conical, the shapes vary considerably. The shape of the cavity at the metal surface tends to be round, but the pit walls tend to be very irregular. They are often hard to detect, as corrosion products usually cover them. The hydrated aluminium oxide (corrosion product) produced during pitting has a much larger volume than the metal corroded. Pitted aluminium cladding surfaces therefore often reveal small white nodules.

In structures, the occurrence of pits is not always detrimental, since the amount of metal removed is usually small and the rate of penetration decreases with time in most cases. On the other hand, under aggressive conditions, the rate of pitting can be rapid [32]. Penetration of the aluminium cladding results in corrosion of the uranium or uranium-aluminium alloy fuel core and the release of fuel and fission products to the storage pool water.

Pitting is most common on metals covered with an adherent surface film. The pits tend to develop at defects or flaws in the surface film and at sites where the film has been mechanically damaged and does not self-heal. A case of pitting produced in fuel plates where the protective oxide film had been damaged by fretting with the stainless steel storage rack is reported in Ref. [33].

Figure 6 shows pitting attack during water storage under aggressive conditions. The attack has led to the formation of a through-clad hole in over the fuel meat region [30].

Considering that not all spent fuel cladding is initially in pristine condition, pits can already exist on some fuel when it enters a storage basin. A more severe environment may exist in the pit beneath the nodule or crusted oxide corrosion product, and corrosion may continue beneath the nodular oxide. However, high quality basin water would minimize or eliminate any new corrosion. In addition, high quality water could slow pit growth by dilution of the severe environment within the pit.

Pitting, like general corrosion, has also been shown to proceed by an electrochemical mechanism. The pitting is caused by electrochemical differences at two adjacent locations on the surface. An individual pit is therefore a local cell with its own anode and cathode. Electrical current flows through the liquid medium from the local anode (the site of metal removal) to the adjacent local cathode. Pitting may also be caused by current entering a solution from the metal surface owing to an external cause, such as an impressed electromotive force or galvanic corrosion produced by contact with a dissimilar metal.

The pitting of aluminium in the presence of aggression anion species can be described as an autocatalytic process. In a situation where a metal is being pitted by aerated water with chloride ions, rapid dissolution occurs within the pit, while oxygen reduction takes place on the adjacent surfaces. The rapid dissolution of aluminium within the pits tends to produce excess positive charge in this area and results in the migration of chloride ions into the pit to maintain neutrality. The reactions for chloride assisted pitting were shown in Section 2.7. Thus, there is a high concentration of metal chloride and of hydrogen ions in the pit. As a result, the pits become more acidic, reaching low pH levels, thus making the oxide unstable. This process stimulates metal dissolution. The depth of a pit can increase with time and progress through the metal thickness.

The distribution of pits in aluminium exposed to aggressive water has been observed to follow an extreme value statistical distribution in which, after initiation and development of the pit distribution, only a small percentage (~1%) continues to propagate [34]. The growth rate (pitting rate) of these deepest pits has been reported by the authors [31] to follow a power law given by:

$$\text{Maximum pit depth} = A\,(\text{time})^{1/3} \tag{19}$$

where A is a parameter that depends on the alloy composition, water quality and temperature.

The depths of pits in water pipe sections were measured at various time intervals, and the maximum pit depths at specific times in the future were calculated using the cube root law. Actual pit depth measurements verified the validity and accuracy of the equation. From the equation, it can be seen that doubling the wall thickness can increase the time for perforation by a factor of 8.

Pitting Rate Index: Although the prediction of the corrosivity of natural and other waters from the values of specific compositional parameters has proven to be extremely difficult, Pathak and Godard developed an empirical relationship for predicting the corrosivity of natural fresh waters to aluminium in 1967 [32]. Using 67 natural waters at room temperature where analyses were available and 3003 alloy, they conducted tests to determine the maximum pit depth as a function of exposure time. From the data, the time required to develop a 1 mm pit was extrapolated, and based on these tests, the pitting rate index (PRI) is defined as the number of weeks needed to obtain a maximum pit depth of 1 mm. An empirical equation for the PRI is as follows:

$$\log \text{PRI} = 2.5 - 0.28 \log (SO_4^{-2}) + 0.18 \log (Cl^-) - 0.20 \log [(pH\text{-}7)^2 \times 100] - 0.42 \log (30\,000/R) - 0.064 \log [(Cu^{+2}) \times 10^3] \tag{20}$$

where R is the resistivity, in ohm-cm, and SO_4^{-2}, Cl^- and Cu^{+2} are the respective ion concentrations in ppm. A PRI of less than 25 weeks is indicative of aggressive water.

Precaution must be used when applying Eq. (20), because this is an empirical equation that was proposed in the late 1960s to predict the aggressiveness of **natural waters** with respect to pitting corrosion of Al alloys. Validity of this equation in pure waters can be found at times, but it cannot be generalized. Even the authors recognize the limitations of the equation. They state that the agreement of the equation with performance is only fair and hoped that others would be stimulated to develop a better equation.

Information from service experience including corrosion surveillance of research reactor fuel in water such as provided in Refs [35, 36] is more directly applicable to evalution of the impact of water composition on the pitting incidence on fuel.

3.2.3.7. Sediment induced corrosion

The fall and accumulation of dust and other particles on aluminium surfaces can cause a stochastic incidence of pitting not directly related to water chemistry. The origin or sources of these solids are mainly airborne dust, corrosion products and precipitated salts. Other sources are the movement of cranes in the reactor room to shift components, opening of doors that lead to less controlled areas, and immersion of inadequately dusted components into reactor pool for experiments or other purposes

Airborne dust in the reactor hall or in the spent fuel storage facility settles on reactor pool or spent fuel basin surfaces. The amount and nature of this dust varies depending on the extent of control of the environment in the building and the nature of activities in the vicinity of the pools. The dust (fine solid particles) on the pool/basin surface floats until wetted by the water. Surface skimmers in reactor pools remove most of the floating dust. However, depending on properties of the solid, mainly density, it settles at the bottom of the pool or on any surface that it encounters as it descends through the pool or basin water. Solids settle faster in stagnant regions of the pool. Fine solid particles also have a tendency to agglomerate to form larger particles that settle faster. This tendency varies with the composition and density of the particles. These solids settle on all surfaces inside pools or basins. Most of these solids eventually settle at the bottom of the pool or basin and are the main constituents of sludge. Air filters in the reactor basin room would help limit dust.

It is well known that sedimentation of particles in suspension in dilute solutions follows Stokes law:

$$U = 2gr^2/9\eta\ (\rho - \rho_o) \tag{21}$$

where U is the sedimentation rate of the particles, g is the gravity constant, r is the radius of the particle in suspension, ρ is the density of the particles, ρ_o is the density of water and η is the viscosity of the fluid.

It can be seen from this equation that the sedimentation rate is directly proportional to the square of the radius of the particles in suspension. It is clear that smaller the particle size, the higher its tendency to remain in suspension.

The effect of settled solids on aluminium has been largely documented during the progress of corrosion surveillance programmes organized by the IAEA using aluminium corrosion coupons [7, 35]. In addition to the known strong influence of chemical water parameters on the corrosion behaviour, the effect of dust and other particles (mainly fragments of iron oxide) that settle on the fuel as sediments has been established. One of the most important documented features has been the fact that these debris particles can produce attack on the aluminium alloys even in quite pure water. However, this effect is more noticeable with higher water conductivities. Also, in these studies, aluminium coupons coupled with stainless steel coupons suffered the strongest attack.

A laboratory programme [8, 36] carried out in order to study the mechanisms by which the corrosion can proceed in nuclear grade waters, including the influence of ion concentration and galvanic potential, proved that iron oxide and other particles that settle as sediments on spent fuel aluminium alloy surfaces can produce pitting corrosion in waters with low amounts of chlorides, such as 4 ppm, even when the corrosion potential is lower than the pitting potential in that environment. Also, galvanic contact with steel strongly influences corrosion susceptibility by increasing the corrosion potential of aluminium to a point in which the pitting process is triggered under the sediments, which would not happen otherwise. Figures 7–10 show examples of the studied cases.

Chemical composition, electrical conductivity and equilibrium potential are factors that may determine the electrochemical behaviour of the different compounds present in particles in contact with the fuel clad material. Among the various types of materials surveyed [37], hematite particles have been shown to be particularly active from the electrochemical point of view, capable of enhancing the oxygen reduction reaction on aluminium samples in pure water, thus producing alkaline attack in the surrounding area. This indicates that they can induce under-deposit corrosion in aluminium alloys.

The occurrence of under-deposit attack has only been verified when the samples were combined with stainless steel in order to bring the corrosion potential near but below the pitting potential in the corresponding solution. In addition, the lack of corrosion in isolated samples immersed up to 60 days in solutions containing 40 ppm of chloride ions without sediments or galvanic couples clearly demonstrate the deleterious synergistic effect of galvanic contacts and sediments.

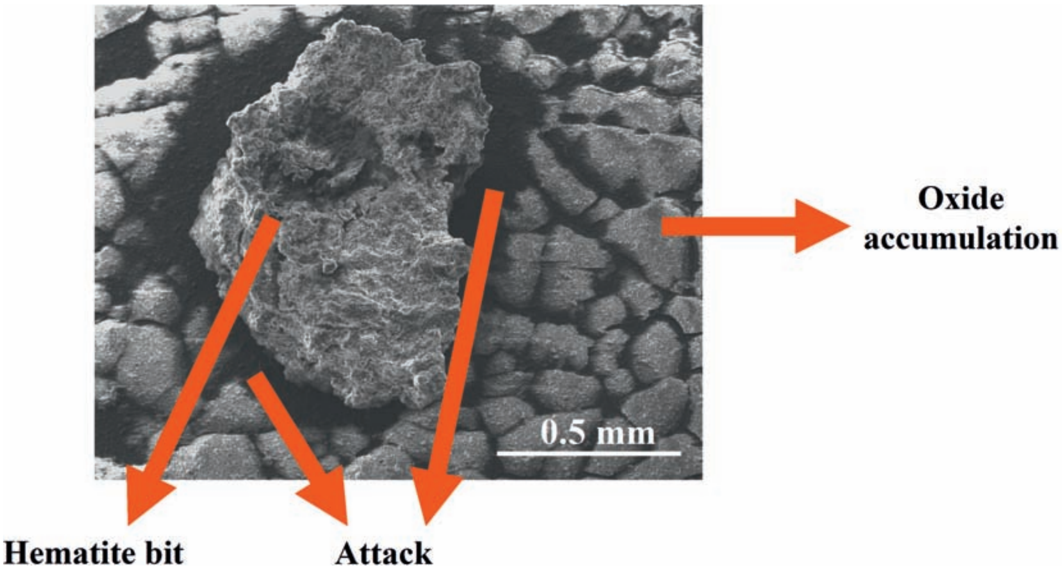

FIG. 7. Attack around a hematite particle after 40 days of immersion in distilled water.

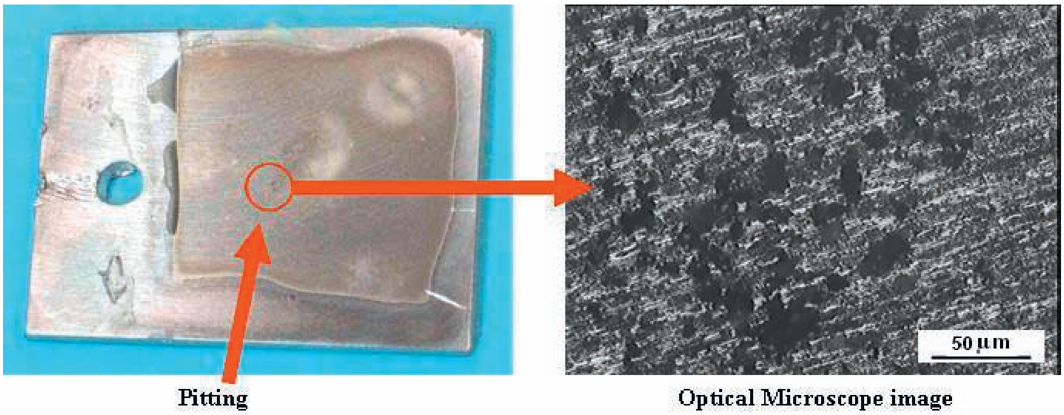

FIG. 8. Seven days in 0.0001M NaCl (equivalent to ~4 ppm). Pitting is produced only underneath the sediment.

This condition of sediments, high concentrations of aggressive species and galvanic couples facilitates the corrosion process, which in bulk good water quality environments takes place only beneath the deposits. This exactly reproduces the situation in some spent fuel storage sites, in which the bundles are positioned inside steel structures, with no provision for electrical insulation [8]. The chloride content of a 0.0001N solution is about 3.5 ppm, a concentration that may be reached in localized regions underneath the particles in a basin.

These results explain the occurrence of pitting in aluminium coupons immersed in some basins for periods of approximately two months [36] as well as the degradation of the actual fuel itself. In a particular case, the fuel in stainless steel tubes had particles of iron oxide, produced by corrosion of carbon steel components present in the facility, lodge onto the stored fuel.

Taking into account the relatively short experiment time in the laboratory studies, only seven days, it becomes clear that spent fuel elements stored for periods of decades can easily undergo this kind of environmental assisted degradation. It is probable that with enough time, corrosion may proceed even in less aggressive conditions.

A more detailed description of sediments induced effects verified in research reactor installations can be found in Sections 9.3 and 9.5, and in Ref. [8].

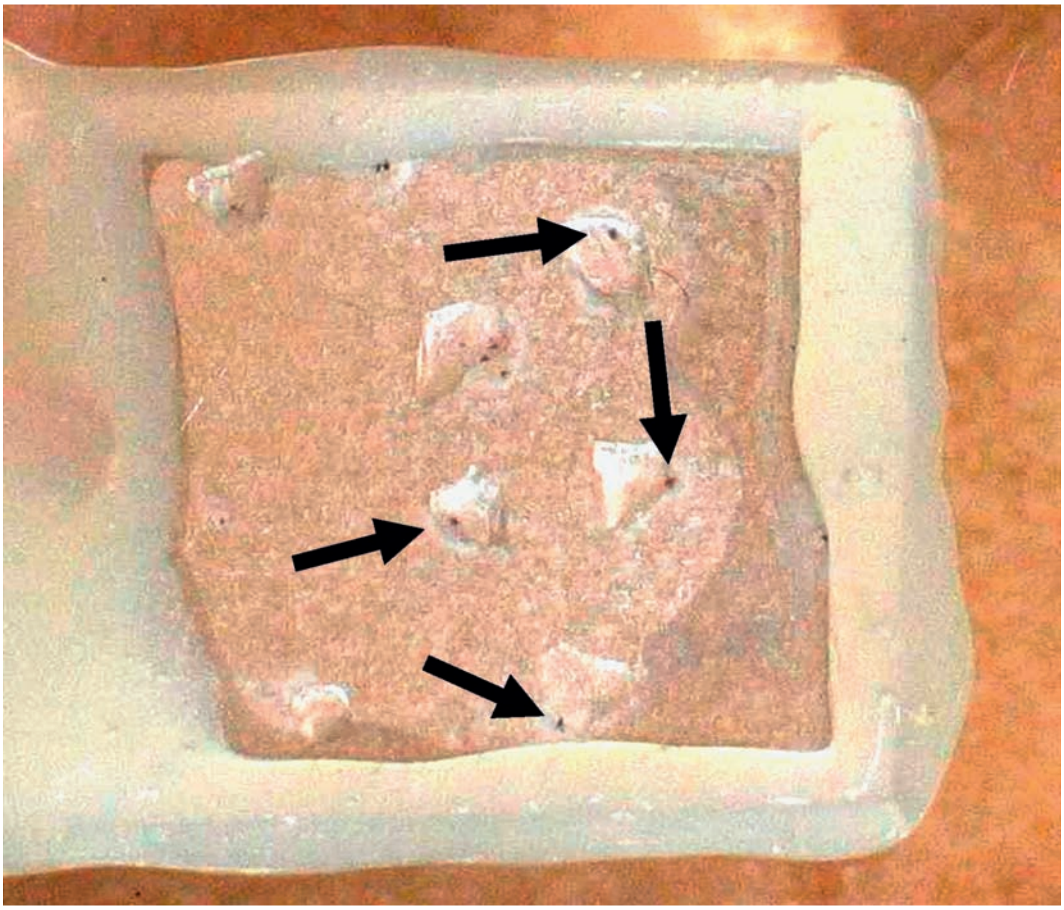

FIG. 9. *Effect of glass bits: seven days in 0.001M NaCl (equivalent to ~60 ppm). Pitting is produced only underneath the sediment and can be seen through the fragments (marked by arrows).*

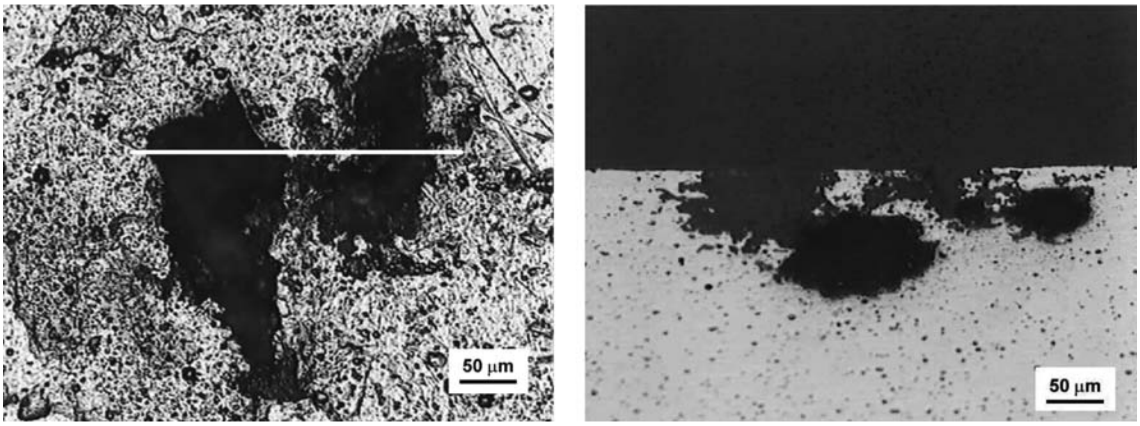

FIG. 10. *Left: Detail of a pit in Fig. 9; Right: metallographic cross-section along the line marked on the left picture.*

3.2.3.8. *Biochemical corrosion*

Biochemical corrosion, or microbiologically-influenced corrosion (MIC), emerges when the environment has contaminants that favour bacterial growth, resulting in biofilms over the metallic surface, and as a consequence, local environments that are aggressive to corrosion. In this case, microbial colonies on the metal surface cause severe change in the local ions concentration, with consequent change in behaviour of the metal substratum and its corrosion products, as well as the electrochemical variables [38]. Different species of bacteria can participate actively to form the aggressive environment. For instance, anaerobe bacteria depolarize the cathodical zones from the metal surface, leading to the disappearance of the anticorrosive protection and the appearance of an anodic dissolution. In a research reactor, if not properly treated, the water can contain organic substances that can support and eventually favour the growth of some microorganisms, resulting in unwanted consequences to the main structural materials, including the fuel cladding. Because radiation is an efficient way to sterilize the environment, biochemical corrosion is usually not a problem for the components of the primary system of the reactor; however, on other systems, the bacteria colonies and cultures can attack the materials, including austenitic steels, by anodic dissolution. The avoidance of the biochemical corrosion generated by the sulphuricus bacteria (active on ferrous materials) is done by filtrating with active charcoal.

3.2.4. Conclusions on corrosion of aluminium and its alloys

Depending on the operation regime, the corrosion processes that can impact aluminium can appear independently or simultaneously, and some precautions and good practices can be taken to stop them, as follows:

- During reactor operation, avoid entering a heat transfer regime that generates an excessive temperature gradient across the fuel cladding, because this situation can lead to an accelerated oxide growth that may lead to oxide blistering, spalling and metal penetration.
- For the reactor pool, eliminate the reducing environments, by eliminating the hydrogen content formed by radiolysis. The continuous contact of water with the air from the atmosphere and the circulation of the water in the pool ensure the stability of the oxide protecting layers.
- Avoid contact of dissimilar materials, especially with aluminium. If necessary, use alumina reels such as those used in TRIGA type reactors, where every aluminium-stainless steel combination is protected by dismountable alumina reels.
- Continuous filtration is the only recommended activity to eliminate impurities from the water, especially the Cl^- ions, and maintain conductivity low.
- Avoid regeneration of the resins using hydrochloric acid in order to avoid inadvertent additions of Cl^- ions; use nitric or sulphuric acid instead.
- Avoid pollution of pool water diminishing the production of ambient dust. If necessary, skim poll surfaces to take floating elements out. When possible, protect the pools with covers manufactured with inert materials.

Recommendations for water chemistry limits to reduce the potential for corrosion attack of aluminium in research reactor systems are given in Sections 6.1 and 6.2.

3.3. CARBON STEELS

3.3.1. Introduction

Ordinary or mild steels are essentially alloys of iron and carbon with small additions of elements such as manganese and silicon to provide the desired mechanical properties. These steels are also referred to as ‘carbon steels’. In research reactor installations, these steels are usually used for pipelines and valves of the secondary circuit.

The different forms of degradation of carbon or mild steels in natural or industrial waters, similar to that used in the secondary systems of research reactors, include corrosion, erosion or wear and cracking due to cyclic stresses or high mechanical loads. Among these, corrosion is the main form of degradation. The many types of aqueous corrosion of carbon steels include uniform or general corrosion, crevice corrosion, pitting corrosion, galvanic corrosion, under deposit corrosion, erosion-corrosion, impingement attack, cavitation and corrosion fatigue. The corrosion of steel in industrial waters is a complicated and many-sided phenomenon, which cannot be fully addressed in the space available in this section. The difficulty arises from the fact that, of the three main considerations involved — the composition and surface condition of the steel, the quality of the water, and the operating conditions — the last is generally the most important. Moreover, in a research reactor, depending on the power of the reactor, the operating conditions of the secondary circuit vary and require individual study.

Consequently, only general aspects and principles of carbon steel corrosion will be presented. For more detailed treatment of the different forms of corrosion, the reader is referred to recognized textbooks [39–41].

This section describes in overview the mechanisms of degradation of carbon steels in water. Section 6.3.3 provides recommendations for water quality limits and controls to minimize the occurrence of these degradation mechanisms.

3.3.2. Mechanism of rusting

In pure dry air at normal temperatures, a thin protective oxide film forms on the surface of polished mild steel. Unlike that formed on stainless steels, it is not protective in the presence of electrolytes and usually breaks down in air, water and soil. The anodic reaction is:

$$\mathrm{Fe} \rightarrow \mathrm{Fe}^{2+} + 2\mathrm{e}^{-} \tag{22}$$

In the presence of oxygen, the following reaction occurs in slightly alkaline and neutral solutions:

$$\mathrm{O_2} + 2\mathrm{H_2O} + 4\mathrm{e}^{-} \rightarrow 4\mathrm{OH}^{-} \tag{23}$$

This is the common form of cathodic reaction in most environments. The OH^- ions react with Fe^{2+} ions to form ferrous hydroxide:

$$\mathrm{Fe}^{2+} + 2\mathrm{OH}^{-} \rightarrow \mathrm{Fe(OH)_2} \tag{24}$$

This is oxidized to ferric hydroxide $Fe(OH)_3$, which is the simple form of rust. The final product is the familiar reddish brown rust $Fe_2O_3.H_2O$, of which there are a number of varieties, the most common being the α form (geothite) and the γ form (lepidocrocite). In situations where the supply of oxygen is restricted, Fe_3O_4 (magnetite) or γ-Fe_2O_3 may be formed.

This is a simplified treatment, but it serves to illustrate the electrochemical nature of rusting and the essential parts played by water and oxygen. The kinetics of the process is influenced by many factors, such as steel composition, surface condition, water composition and temperature.

3.3.2.1. Steel composition

All ordinary ferrous structural materials, mild steels, low alloyed steels and wrought irons corrode at virtually the same rate when totally immersed in natural waters. Generally over 3% of alloying additions such as chromium are necessary to obtain any marked improvement in the corrosion resistance of steel in waters.

3.3.2.2. Steel surface condition

The surface condition of the steel at the time of exposure is of great importance. The presence of mill scale (scale formed during hot processing of steel) on the surface is more dangerous. Hence, it is important to remove mill scale prior to use of steel that is expected to be constantly in contact with water.

3.3.2.3. Influence of water composition on steel

Since saline and acidic waters are particularly aggressive to mild steel, the composition of the water is clearly important in determining the rate of rusting of steel exposed to it. Some of the main factors here are the nature and amount of the dissolved salts (which greatly influences the electrical conductivity), pH value, water hardness, carbon dioxide and oxygen contents and the presence of organic matter.

The effect of dissolved solids is complex. The presence of inorganic salts, notably chlorides and sulphates, promote corrosion because they increase conductivity of the water, thereby facilitating electrochemical processes. Chlorides may be also detrimental to the development of protective films. Alkaline waters tend to be less aggressive than acidic or neutral waters, and rusting rate can be decreased by making the water alkaline.

The most important property of dissolved solids in natural waters is whether or not they lead to the deposition of a protective film on the steel that to some extent will impede rusting. This is determined mainly by the amount of carbon dioxide dissolved in the water. Hence, the equilibrium between calcium carbonate, calcium bicarbonate and carbon dioxide is of fundamental significance. Hard waters are more likely to deposit a protective calcareous scale than soft waters, and are therefore in this respect less aggressive.

Oxygen and carbon dioxide are the most important dissolved gases in water. Oxygen is an effective cathodic depolarizer, and the cathodic reaction in water is generally oxygen reduction. At ordinary temperatures in neutral or near neutral water, dissolved oxygen is necessary for any appreciable corrosion of steel. Increasing the oxygen concentration results in an increase in the rate of corrosion of steel until the oxide thickness reaches a certain value. Beyond this point, the rate of corrosion decreases. Carbon dioxide affects the acidity of the water, as shown in the equation below, and as mentioned earlier, influences the formation of a carbonate scale:

$$CO_2 + H_2O \rightarrow H_2CO_3 \tag{25}$$

Suspended materials such as dust or other solid particles enter the circulating water in cooling systems either from the dusty environment surrounding a cooling tower or from the make-up water. These solids often sediment forming porous deposits in certain sections of the cooling system and quickly establish differential aeration cells, which increase further the corrosion.

The organic matter often found in fresh waters is algae. The waters could also have different strains of bacteria, such as sulphate reducing bacteria that can influence the rusting process. More details on these strains and how to combat it are described in Section 4.4.

3.3.2.4. Influence of water conditions on steel

Operating system parameters such as temperature, flow rate and design features can also influence the corrosion of mild steels. These parameters could influence corrosion individually or synergistically. Temperature affects the rate of rusting in several ways. First, the corrosion process shares the general tendency of chemical reactions to increase in speed with rising temperature. More important are the effects of temperature on the nature and solubility of the corrosion products. For example, a rise in temperature increases the amount of carbonate scale due to increase in the rate of diffusion of oxygen through the water, but decreases its solubility. Some of these effects are conflicting.

The flow rate of water determines the supply of oxygen to the rusting surface and it may also remove corrosion products that would otherwise stifle rusting. An abundant supply of oxygen to the cathodic areas stimulates corrosion, and reduced supplies at slow flow rates lead to the formation of differential aeration cells. At very high flow rates of natural waters, enough oxygen may reach the steel surface to cause partial passivation, and thereby reduce the corrosion rate.

There are two categories of water flow: laminar and turbulent. Laminar flow occurs at low velocities, which may not be constant on all the surfaces in contact with water. Turbulent flow occurs beyond a certain velocity. Even under turbulent flow conditions there is a thin laminar layer of water close to the steel surface and the thickness of this layer decreases with increase in flow rate. Although dissolved oxygen is supplied faster at increasing flow rates under turbulent flow conditions, it does not easily penetrate the thin laminar layer. Thus, corrosion tends to increase only at very high velocities because the oxygen manages to penetrate the ever thinner laminar film of water on the steel surface.

Component design is important and contributes to various forms of localized corrosion such as erosion-corrosion, cavitation, impingement attack, galvanic corrosion and corrosion fatigue.

3.3.3. Forms of corrosion to which mild steel is susceptible

3.3.3.1. Uniform attack (general or uniform corrosion)

This form of corrosion gives the simplest result. Metal is removed at an even rate throughout the pipeline or component surface, whether interior or exterior. Many of the above mentioned factors such as temperature, dissolved oxygen, solids, pH and velocity influence the rate of attack. In addition to thinning of the metal component, uniform attack leads to large increase in iron ion concentration in the flowing water. In systems carrying circulating water, this could cause trouble to equipment further downstream, such as heat exchangers.

3.3.3.2. Pitting corrosion

This is a form of localized corrosion or selective attack at a specific region. The location of attack is hard to predict from tests in the laboratory or even field tests. Once initiated, the pitting process continues rapidly in the pit itself, with the cathodic oxygen reduction reaction taking place on surfaces adjacent to the pit, as shown in Figure 11 [43]. If chloride ions are present, the pit often contains a solution of ferric chloride, which could be strong enough to prevent oxygen from entering and dissolving in the stagnant solution within the pit. Pitting can begin by itself without deposits or similar coverings on the metal surface. This form of corrosion could lead to penetration of thin walled steel pipes.

Pitting corrosion products often cover the pits and may form ‘chimneys’ [42]. Pitting is considered more dangerous than uniform corrosion damage because it is more difficult to detect, predict and prevent. A small, narrow pit with minimal overall metal loss can lead to the failure of an entire engineering system.

3.3.3.3. Crevice corrosion

Crevice corrosion takes place not only in actual crevices, but also in shielded areas retaining a small volume of stagnant solution, such as gaskets, seals and surface deposits. Dirt, scale and corrosion products may be also the site of this form of selective attack, and is also often referred to as ‘under-deposit corrosion’. In theory, crevice corrosion can be prevented if there are no crevices. However, this calls for great care in component design and

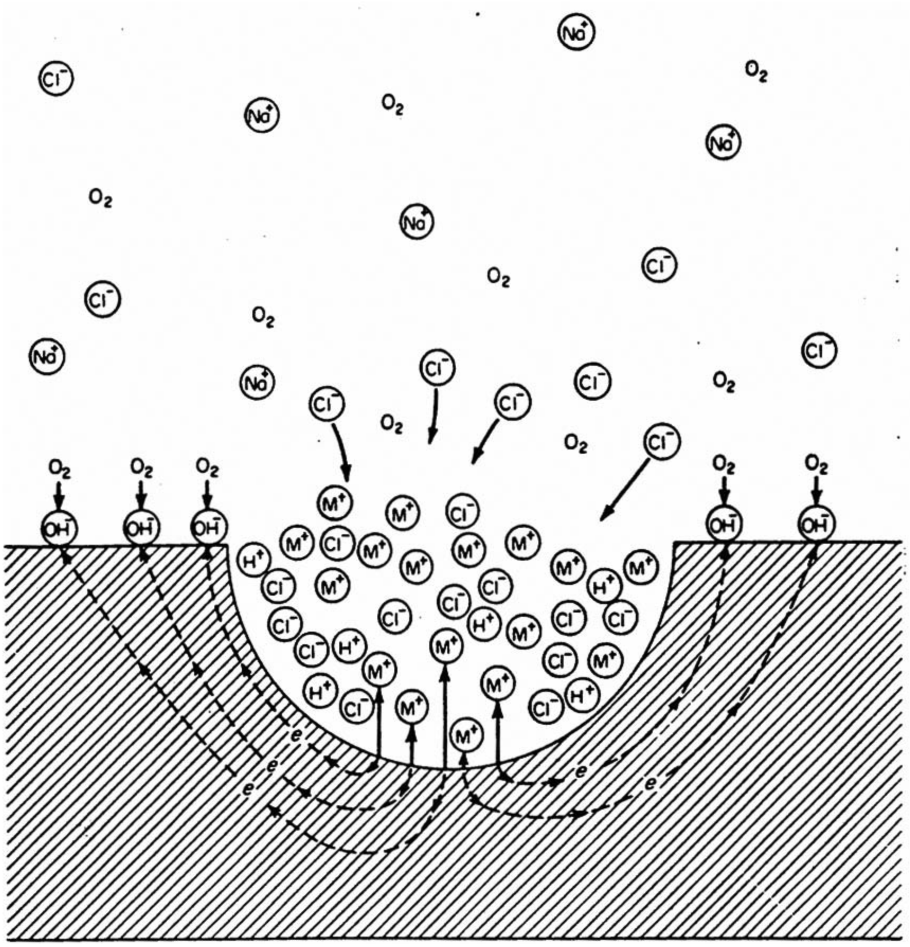

FIG. 11. Schematic illustration of a pit [43].

installation, as well as an adequate maintenance programme to clean the system during operation. In some cases, the materials used for the pipes and components can be selected that are less prone to this form of attack. Pitting and crevice corrosion are similar in many aspects. Once initiated, both crevice and pitting corrosion can be explained by differential concentration cells and cathodic reactions, i.e. oxygen reduction or hydrogen evolution may start in the crevice or in the pits. Large surface areas become cathodic, and pits or crevices become anodic and corrode. Metal dissolution takes place in small areas and proceeds at much higher rates. Large crevices are less likely to corrode because water movement causes mixing and replenishes oxygen, hydrogen ions, bicarbonate or hydrogen sulphide. The chloride ion acts as a catalyst in pitting and crevice corrosion; i.e. chloride ions increase the corrosion rate but are not used up in the reaction. It has the ability to absorb on the metal surface or the passive films and polarize the metal, initializing localized corrosion.

Crevice corrosion can occur at washers, under applied protective films and at pockets formed by threaded joints.

3.3.3.4. Galvanic corrosion

When dissimilar metals such as mild steel and copper alloy in contact are immersed in a conducting solution, there is a flow of current between steel (the metal with the lower potential) to copper (with a higher potential) due to the difference in the open circuit potentials between the metals. The corrosion of steel increases, while the corrosion of copper decreases, in contrast to the situation when both metals are not in contact in the same aqueous environment. Many factors affect galvanic corrosion, including: (a) the corrosion potentials of the two metals, (b) the cathodic reactions and their kinetics on copper, (c) the anodic reactions and its kinetics on steel, (d) the surface areas of the two metals, and (e) the conductivity of the liquid [43].

In galvanic corrosion, the extent of current flow between the two metals is obviously a key factor in the destruction of one of the two metals. The metals involved must be dissimilar in composition or in other ways. The listing of metals and alloys in the galvanic series shown in Table 2 of Section 2.6, indicates the order of tendency to be anodic or cathodic. Metals or alloys close to each other in the series give less trouble than those that are widely separated in the series. Anode metals with large areas are desirable. This reduces metal thickness loss by distributing the weight loss over a large area. The cathode, on the other hand, can be small without significantly worsening matters. This form of corrosion is recognizable by the presence of corrosion products or corroded regions at the joint of dissimilar metals.

Control of galvanic corrosion is achieved by using metals closer to each other in the galvanic series or by electrically isolating metals from each other. Cathodic protection can also be used to control galvanic corrosion effects.

3.3.3.5. Erosion–corrosion

Erosion–corrosion (EC) is associated with flow induced mechanical removal of the protective surface film and results in a subsequent increase in corrosion rate via either electrochemical or chemical processes. It is often accepted that in order to start the EC process in a given material, a critical fluid velocity must be exceeded. The mechanical damage by the impacting fluid imposes disruptive shear stresses or pressure variations on the material surface and/or the protective surface film. EC may be enhanced by particles (solids or gas bubbles) and impacted by multi-phase flows. EC is characterized by surface features with a directional pattern, which are a direct result of the flowing media. In mild steel pipelines carrying natural waters, the attack is sometimes restricted to small areas. Changes in flow patterns tend to promote this form of attack. In piping, where bends, elbows, tees and valves, etc., abound, the damage is often localized near such flow disturbers. Almost all alloys or metals are susceptible to some type of EC depending on the fluid. Alloys that form a surface film in a corrosive environment commonly show a limiting velocity above, which corrosion rapidly accelerates.

Other factors such as turbulence, cavitation, impingement or galvanic effects can add to the severity of attack. EC of mild steels can be controlled by coating the surface with harder alloys (by flame-spraying or welded hard facings). Alterations in fluid velocity and changes in flow patterns can also reduce the effects of EC. Other forms of corrosion control include: re-design of the system to reduce the flow velocity, turbulence, cavitation or impingement of the environment; reduction in the corrosive severity of the environment; use of corrosion resistant and/or abrasion resistant coatings; and cathodic protection.

EC takes the form of grooves, waves, gullies, teardrop shaped pits, and horseshoe-shaped undercutting in the surface. The effects of the hydrodynamic are not well understood. Undercutting may occur in either upstream or downstream directions. As described in the schematic in Fig. 12, turbulent eddies thin the protective film locally to produce undercutting, which is seen in Fig. 13 [44].

3.3.3.6. *Cavitation*

Cavitation is sometimes considered a special case of EC and is caused by the formation and collapse of vapour bubbles in a liquid near a metal surface. Most metals, including mild steels, are susceptible to cavitation damage. Cavitation removes protective surface scales by the implosion of gas bubbles in a fluid. Calculations have shown that the implosions can produce shock waves with pressures approaching 60 ksi (413 MPa). The subsequent corrosion attack is the result of hydro-mechanical effects from liquids in regions of low pressure where flow velocity changes, disruptions or alterations in flow direction have occurred. Cavitation damage often appears as a collection of closely spaced, sharp edged pits or craters on the surface [45].

Some prevention methods for cavitation include improving the flow lines within the pipeline, by deburring (smoothing out irregularities), allowing bends to have larger angles, and changing pipe diameters gradually rather than abrupt changes. Other methods include slowing the flow rate (reducing turbulence), reducing the amount of dissolved oxygen, changing the pH, and changing the pipe material to a different metal or alloy.

3.3.3.7. *Impingement corrosion*

Impingement corrosion is caused by the impingement action of water carrying entrained gas bubbles and striking the metal surface at an angle. It is not the result of mechanical erosion of the metal itself but, rather, of

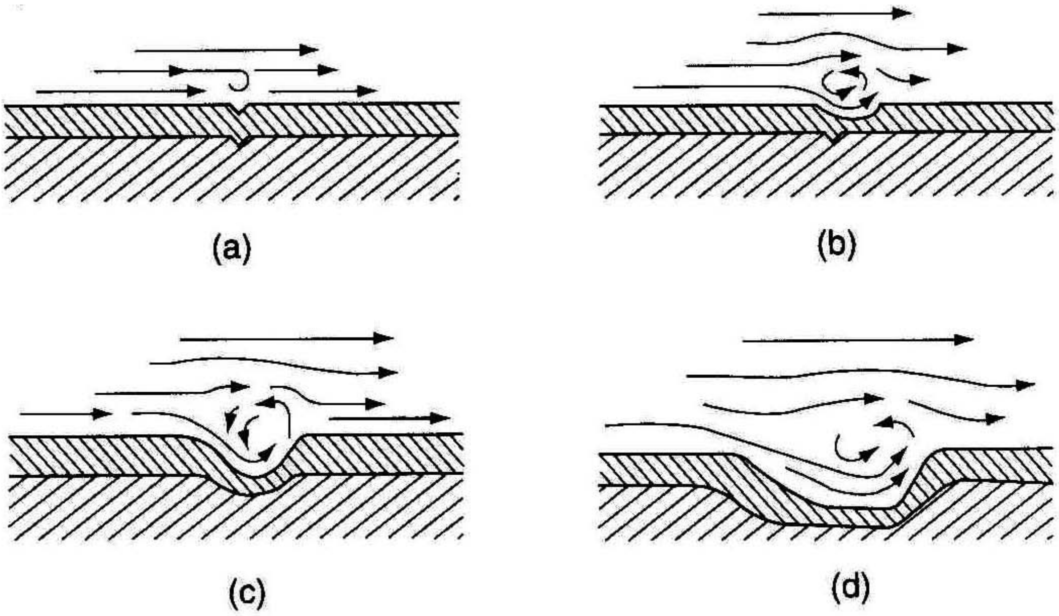

FIG. 12. Schematic illustration of turbulent eddy mechanism for downstream undercutting of EC pits.

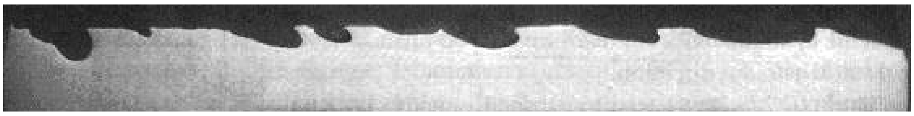

FIG. 13. Photograph of EC showing individual teardrop shaped pits with undercutting in the downstream direction.

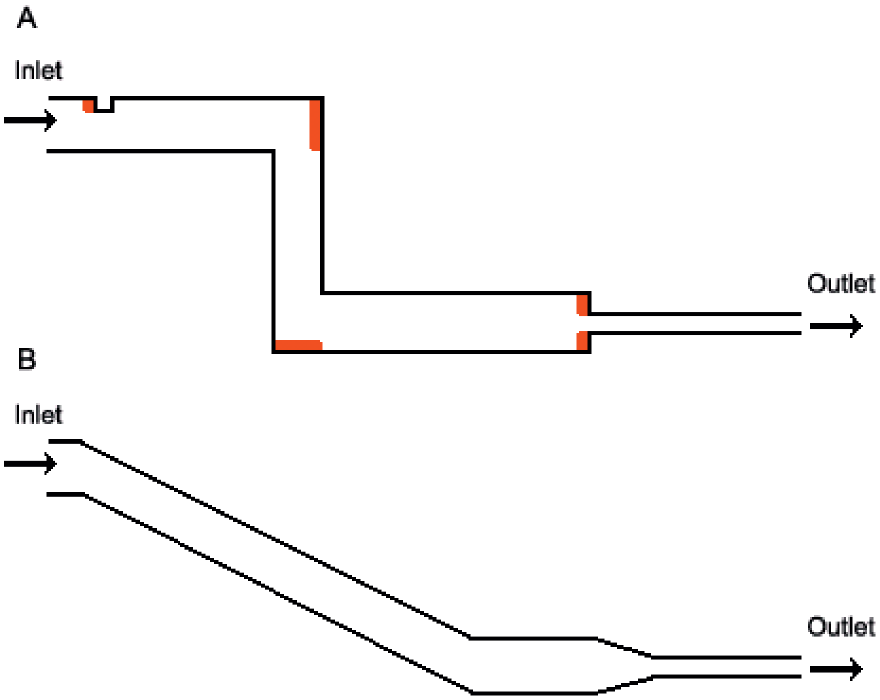

FIG. 14. (A) Schematic illustration of regions (in red) susceptible to impingement attack; (B) change in design to avoid it.

removal by erosion of the film of corrosion products, which is ordinarily protective at lower velocities. Impingement corrosion is usually encountered at or near the entrance to the tubes, the exact location depending upon the angle of impingement. It takes the form of pitting or grooving, and eventual perforation of the wall at that location while the remainder of the tube shows no sign of corrosion. Similar attack may occur in the vicinity of an object lodged in a pipe. Impingement attack can be reduced or minimized by proper component design, as shown in Fig. 14.

3.3.3.8. Microbial corrosion

Microbial corrosion (also called microbiologically influenced corrosion, or MIC) is corrosion caused by the presence and activities of microbes. It can take many forms of which a number of mechanisms are associated. Most MIC takes the form of pits that form underneath colonies of living organic matter and mineral and bio-deposits. This bio-film creates a protective environment where conditions can become quite corrosive and corrosion is accelerated. Bio-films can allow corrosive chemicals to collect within and under the films and cause corrosion. Thus, the corrosive conditions under a biofilm can be very aggressive, even in locations where the bulk environment is non-corrosive. MIC can be controlled by biocides or by conventional corrosion control methods.

MIC can be a serious problem in stagnant water systems. In steel pipelines of secondary circuits, the use of biocides and mechanical cleaning methods reduces MIC. As mentioned earlier, corrosion only occurs if there is some species that can be reduced. In most environments, the species reduced is either dissolved oxygen or hydrogen ions in acids. In anaerobic conditions (no oxygen or air present), some bacteria (anaerobic bacteria) can thrive. These bacteria can provide the reducible chemicals that allow corrosion to occur.

3.3.4. Corrosion of joined pipelines

Pipes can be joined by welding, using special mechanical joints or with flanged connections. Welding gives a leak free joint, but in some instances the weld filler material may be more prone to corrosion than the pipe itself. The inner surfaces of pipe welds often protrude into the flow stream causing flow disturbance. This could worsen EC. If mechanical joints are used, rings are used that may have crevices and at these regions crevice corrosion or pitting can start. Pipe joining methods that do not involve welding include screwed couplings, compression couplings and grooved couplings. In all of these joints, water could penetrate into confined spaces or crevices to initiate crevice or pitting corrosion. Special measures are required to prevent this and include the use of impervious fillers.

Severe corrosion of steel pipes close to weld joints has been attributed to galvanic effects between the weld metal and the steel plate.

3.4. STAINLESS STEEL

Stainless steels are normally passive at all water temperature and pH conditions in reactor service. This passive behaviour is due to the formation of a thin, adherent layer of chromium (III) oxide (Cr_2O_3) when exposed to oxygen [46]. A minimum chromium content of 13 wt% in the stainless steel will normally provide high resistance to corrosion. Other primary constituents in austenitic stainless steel such as nickel and small additives of molybdenum and vanadium, contribute to passivation of the stainless steel.

The chromium oxide layer provides a tenacious barrier against continued oxidation and corrosion of the stainless steel. Therefore, uniform corrosion rates of stainless steel in reactor systems are negligible [47]. For example, in water with 7.5 ppm chloride and under a radiation field of 3×10^5 R/h, a corrosion rate of 0.3 μm/a has been reported [48, 49]; i.e. although the chloride ion is deleterious to pitting, general or uniform corrosion of the stainless steel is low [49].

The breakdown of the passivation layer on the stainless steel surface can occur by a chemical species (e.g. chloride ion), by loss of oxygen, or by chromium depletion at grain boundaries through sensitization that is precipitation of chromium carbides ($Cr_{23}C_6$).

The mechanisms causing irradiated assisted stress corrosion cracking (IASCC) [50], a phenomenon observed in the stainless steel core internals of boiling water reactors, are highly dependent on impurity levels of carbon and sulphur in the steel. The mechanisms causing IASCC are not expected to influence research reactor systems since the conditions of moderate dose (three displacements per atom or dpa) and high irradiation temperature (288°C) are needed to exhibit this threshold phenomenon [50].

The modes of corrosion relevant to stainless steel fuel claddings and reactor system structural materials are briefly described below. Considering that the limits for control of corrosion are much more restrictive for aluminium than for stainless steel, including pH, chloride ion, and other impurities, no specific limits or recommendations to protect stainless steel against corrosion are provided in Section 6.

3.4.1. Pitting corrosion

Pitting corrosion of stainless steel can occur when an ion (the most important of which is chloride) competes for a site and degrades the oxide film on the stainless steel. Once a pit is established, oxygen depletion in the bottom of the pitting can limit repassivation of the stainless steel and pitting can continue.

Since deep, sharp pits can also be an initiator of cracking in steels, pitting conditions should be avoided in systems. Pitting can be prevented by ensuring that chlorides are avoided and that the stainless steel is the material exposed to oxygen. No pitting has been observed in stainless steel immersed in solutions with chloride concentration up to 1000 ppm in aerated water, and this degradation mechanism is readily controlled in research reactor systems.

3.4.2. Crevice corrosion

Crevices are the result of poor design rather than a water quality condition in reactor systems. The mechanism of crevice attack is similar to pitting under oxygen depletion conditions. This corrosion is controlled through design.

3.4.3. Transgranular stress corrosion cracking

Transgranular stress corrosion cracking (TGSCC) in stainless steel can be a severe form of stainless steel corrosion. TGSCC can occur when stainless steel is subjected to tensile stress in a chloride-rich environment, especially at high temperatures. The stresses can be from service loads, fabrication (fit-up or cold working), or from weld joining that creates a residual stress.

Deformation that causes dislocation pile-up along slip planes that can jog the surface of the steel and break the passive film, in conjunction with a weakening of the film by chloride ions, can lead to local corrosion. If the film does not re-heal, cracking at that location will probably continue. Stainless steel placed in an environment where its corrosion potential is near the active/passive transition may be particularly susceptible to TGSCC; i.e. if electrochemical conditions do not drive repassivation, cracking is likely to occur.

Type 300 series stainless steel should not be used in water with higher than a few ppm of chloride if subjected to temperatures at or above approximately 50°C.

3.4.4. Intergranular stress corrosion cracking

Intergranular stress corrosion cracking (IGSCC) in stainless steel can occur as a result of three coincident factors [47]:

- A sensitized microstructure (chromium carbide precipitation at grain boundaries);
- An aggressive water environment; and
- Tensile stresses.

A sensitized microstructure with weld residual stresses typically can occur at the heat affected zone adjacent to welds in austenitic stainless steel. If this condition exists in a system, then the water environment is the only factor that can be easily changed.

IGSCC can occur even in high purity water [47, 51], and at low temperatures, as it was observed in the primary coolant piping of the Savannah River Site production reactors, that operated historically at a low temperature of 35–45°C (cold leg) up to the maximum coolant temperature of 95–105°C (hot leg) [52]. The Savannah River Site reactors were permanently shut down in 1993.

The cooling water in stainless steel piping in most research reactors is at low temperatures (< 100°C). A comprehensive study was conducted in the late 1980s to evaluate the susceptibility of Type 304 stainless steel to water chemistry conditions in environments spanning the reactor and thermal shield water environments of the low temperature Savannah River Site reactors [53]. Special water circulation loops were built to provide controlled environments and perform constant extension rate tests (CERTs) with sensitized stainless steel. The following variables were controlled and measured in real time: T at 40–120°C, Cl- at 2–100 ppb, SO_4^{2-} at 7–500 ppb, O_2 at 100–8000 ppb, H_2O_2 at 400– 5000 ppb, and CO_2 at 20–1000 ppb. Nitric acid was added to maintain pH at 5.1 +/– 0.2. In the tests with H_2O_2, controlled, and not O_2, the following equation with statistically significant coefficients was developed by multiple regression analyses:

$$\begin{aligned}\mathrm{LATMS} = &-0.1553\,(\mathrm{Cl}^-)^{0.43815} - 0.03646\,(T) - 1.799\,(\mathrm{SO}_4^{2-})^{-0.18508}\\ &+ 0.04071\,(T)(\mathrm{SO}_4^{2-})^{-0.18508} - 0.3285(\mathrm{Cl}^-)^{0.43815}(\mathrm{SO}_4^{2-})^{-0.18508}\\ &+0.02149[(\mathrm{Cl}^-)^{0.43815}]^2 + 4.993 \qquad (26)\end{aligned}$$

where LATMS is the logarithm (base 10) of the adjusted time (in hours) to maximum stress in a CERT specimen; Cl^- and SO_4^{2-} are in ppb; and T is temperature in °C.

The LATMS involved a construction to include ductility (sum of per cent elongation and per cent reduction of area) and the maximum stress in the evaluation of the CERT response. An adjusted time to maximum stress >400 hours is a water condition where no IGSCC would be expected to occur in sensitized Type 304 stainless steel.

The results of the testing showed that the variables that decrease IGSCC in order of decreasing importance are T > Cl^- > SO_4^{-2}. The presence of H_2O_2 over the range studied (400 — 5000 ppb) had no impact on cracking susceptibility [53, 54].

In summary, IGSSC can be avoided by avoiding or controlling any of the three main factors, including the water chemistry environment. Temperature, chloride ions, and sulphate ions should be minimized to the extent practicable in a system susceptible to IGSCC [54].

3.4.5. Discoloration of stainless steel

At high temperature (> 250°C) and high oxygen contents in pure reactor waters, the stainless steels may acquire a dark tarnish film, which may develop into loose powdery red rust [55]. It is caused by the pull of metal ions of the passive stainless steel surface into the pure water since the pure water has a strong affinity for the ions. Iron ions do not dissolve at neutral pH and will precipitate as an iron hydroxide film, which has a reddish colour. This phenomenon may result in buildup and may affect coolant flow and heat transfer characteristics of the fuel.

3.5. CONCRETE

A good discussion of aspects of concrete, its formulation and material properties, and ageing topics is provided in Ref. [47]. A brief summary of the ageing mechanisms relevant to basin structures in contact with water in reactor systems follows below.

3.5.1. Thermal degradation

High temperatures (> 200°C) can cause evaporation of the free water in concrete before it is fully hydrated, a process that may take several years. On the other hand, freezing temperatures and large thermal gradients that cause movement of water within the concrete monolith may also be deleterious. Therefore, immediate exposure to these extreme temperatures in service should be avoided.

3.5.2. Carbonation and reinforcement steel bar corrosion

Carbonation is the incorporation of carbon dioxide from the air into the concrete. Carbonic acid, from the reaction of carbon dioxide and water, can form and reduce the alkalinity present in the as-fabricated concrete. The reduction of alkalinity removes the protection of carbon steel, the reinforcement bar material in concrete, from corrosion. The iron corrosion products can stress and crack the concrete, leading to further attack of the carbon steel and cracking of the concrete.

Carbonation is a slow process; nevertheless concrete should be protected from contact with air or water to avoid this degradation mechanism. This can be accomplished with a sound coating or a liner.

3.5.3. Leaching

The components of concrete are not insoluble. A leaching study of bare concrete for the Hanford site reactor basins was performed in 1976 by United Nuclear Industries [56]. Areas in an existing 23 000 gallon seal-coated well were sandblasted and exposed to demineralized water. The first test consisted of recirculating a purification stream of 33 gal./min. The results showed that 1 ft^3 of cation resin could treat 0.45 million gallons throughput before depletion. This test indicated that concrete leaching rates are very low in demineralized water. A second test with recirculated water, with no deionization with resins, was run for 99 days. The trend of the data showed very low leach rates after the first 20–30 days. The maximum leach rate occurred during the first few days and was calculated as 40 milliequivalents of cations per 1000 gallons per day.

Visual examination of the walls after a total of 214 days of testing showed no corrosion or pitting of the exposed concrete surfaces. A light tan film, identified by X ray analysis, as α-SiO_2, which is insoluble in water, was formed.

Another study to determine the extent of leaching and microstructural changes in concrete exposed to flowing deionized water through a simulated crack was reported in Ref. [57]. Depletion of calcium hydroxide and leaching of calcium from calcium silicate increased the porosity to a depth of several millimetres.

In conclusion, to avoid degradation by leaching, the concrete should be protected from contact with water, and as explained above, this can be accomplished with a sound coating or a liner.

3.5.4. Radiation effects

In principle, neutron irradiation can cause swelling through displacement damage to concrete, and gamma irradiation can lead to gas evolution through radiolysis of water [58]. A fluence level of 10^{17} n/cm^2 and an exposure level of 10^{10} rads are cited as threshold levels needed to cause deterioration of concrete [59, 60].

3.5.5. Monitoring and inspection for structural integrity assessment

The primary safety function of concrete basins is to provide a leak barrier while maintaining structural integrity against large failure for design-basis loads. Activities to monitor and inspect basins (e.g. core sampling) are recommended to ensure that these functions are maintained throughout the desired service life of a basin [47, 60].

3.6. COPPER ALLOYS

3.6.1. Introduction

Copper corrodes at negligible rates in unpolluted air, water and de-aerated non-oxidizing acids. Copper and its alloys are unique among the corrosion-resistant alloys in that they do not form a truly passive corrosion product film. In aqueous environments at ambient temperatures, the corrosion product predominantly responsible for protection is cuprous oxide (Cu_2O). This Cu_2O film is adherent and its growth follows parabolic kinetics. Cuprous oxide is a p-type semiconductor formed by the electrochemical processes:

$$4Cu + 2H_2O \rightarrow 2Cu_2O + 4H^+ + 4e^- \text{ (anode)} \tag{27}$$

and

$$O_2 + 2H_2O + 4e^- \rightarrow 4(OH)^- \text{ (cathode)} \tag{28}$$

with the net reaction:

$$4Cu + O_2 \rightarrow 2Cu_2O \tag{29}$$

For the corrosion reaction to proceed, copper ions and electrons must migrate through the Cu_2O film. Consequently, by reducing the ionic or electronic conductivity of the film with the addition of divalent or trivalent cations, the corrosion resistance of the alloy is improved. In practice, alloying additions of aluminium, zinc, tin, iron and nickel are used to dope the corrosion product films and generally reduce corrosion rates significantly. Although corrosion of copper alloys in waters with composition similar to that used in the secondary circuits of research reactors is negligible, further information about the corrosion of copper alloys in other environments is considered relevant [61].

3.6.2. Effect of copper alloy composition on corrosion

3.6.2.1. High copper alloys

High copper containing alloys have excellent resistance to seawater corrosion and bio-fouling, but are susceptible to EC at high water velocities. The high copper alloys are primarily used in applications that require enhanced mechanical performance, often at slightly elevated temperature, with good thermal or electrical conductivity. Processing high copper alloys for increased strength generally improves their resistance to EC.

3.6.3. Heat exchanger service alerts

In research reactor secondary circuit heat exchangers, on-line tube cleaning effectively controls deposit film formation while maintaining acceptable heat transfer efficiency. Water velocities must be sufficient to provide aerated water continuously and to prevent the settling of deposits, but not high enough to strip away the protective film. Generally, the design velocity is in the range of 1.2–2.5 m/s, depending on the alloy. Maximum velocities in clean water service for the widely used condenser tube alloys range from 1.8–4.5 m/s. Excessive turbulence is an additional factor that influences the corrosion behaviour of copper alloys and can influence maximum service velocities.

3.7. OTHER MATERIALS IN CONTACT WITH WATER IN A RESEARCH REACTOR

A variety of different materials is normally present in research reactors, forming part of systems with various purposes. There are graphite thermal columns, beryllium reflectors, control rods that may contain silver, indium and cadmium, zirconium alloys components, etc. In general, these elements are clad in aluminium, stainless steel or zirconium alloys. However, there are reactors in which some of them are in contact with the primary water. It is therefore important to take into account their possible interaction with water and how this can affect the overall reactor performance.

3.7.1. Graphite

Graphite, used to moderate neutrons, is an inert non-metallic material. It is nevertheless a conductor of electricity; it can therefore provide a surface suitable for the charge exchange needed for electrochemical reactions. When in contact with water, all the electrochemical dissolved species can react on graphite, producing anodic or cathodic reactions. This will not affect its integrity; however, if it is in contact with other metal, it will produce a galvanic couple, enhancing the corrosion of this other material. This situation will affect mainly aluminium components, due the reactivity of aluminium alloys. Physical contact between graphite and aluminium in water must be avoided by all means. If the seal fails to isolate the graphite from the water, rapid metallic dissolution will occur. This has been the case of an improper seal of the thermal column assembly in a reactor [28].

Even if unclad graphite is not in contact with other metal, there is always the possibility of having bits of released material circulating with the reactor water. If they become stuck in a fuel channel, for example, corrosion will take place immediately at that point, due to the galvanic effect. Perforation of the fuel plate will occur shortly afterwards. Cases of aluminium corrosion induced by graphite particles have been verified in the vicinity of the naked external reflector of a research reactor [29].

3.7.2. Reactivity control materials

Silver, from Ag-In-Cd control elements, is a very noble metal. Therefore, it will tend to deposit electrochemically on the much less noble aluminium surface, producing localized galvanic couples. The presence of silver, copper or any other noble metal dissolved in the reactor water must be ruled out. Cases in which the control materials envelop degraded, allowing silver to go into the system, are suspected to have led to pitting corrosion in aluminium fuel plates [7].

3.7.3. Zirconium alloys

Many reactors use zirconium alloys in their construction. Due to their permeation to neutrons, these alloys are very convenient for fuel cladding, irradiation channels, structural parts, etc. Zirconium alloys are very stable materials, due to the outstanding protective capacity of the zirconium oxide layers. The only concerns with respect to corrosion possibilities are oxidation and hydriding, which essentially occur at power reactors temperature range.

In most research reactors' low temperature environments, there is no preventive action on the water that should be exerted in either case. Oxidation and hydriding possibilities depend essentially of metallurgical characteristics, such as alloy composition, thermo-mechanical treatments, microstructure, texture, welds and residual stresses. Once hydrogen has been incorporated into the metal, a process called delayed hydride cracking can produce structural failure of zirconium alloys components in a wide temperature range, if the right conditions (hydrogen content and susceptible material) are present [62]. Crack propagation is even possible at room temperature with the marginal amount of hydrogen incorporated during fabrication. Nevertheless, keeping the conductivity low will minimize the intensity of electrochemical reactions that could generate active hydrogen as part of the metal oxidation process.

Other forms of localized corrosion are possible in extreme conditions, as working temperatures above 250ºC or aggressive chemistry, not likely to be found in research reactors.

4. WATER TREATMENT AND PURIFICATION

4.1. WATER TREATMENT AND PURIFICATION: GENERAL CONCEPTS

Treatment and purification of water for a reactor system may involve combinations of the following processes:

- Removal of particulates;
- Removal of dissolved impurity chemical species;
- Additions of chemicals as corrosion inhibitors;
- Destruction of microbial species.

In the following sections, the term 'water treatment' is used to cover any or all of these processes in a system for water treatment and purification.

Design of a water treatment system for a reactor water system considers the water quality of the water source, requirements for water quality of the reactor system, and operation/maintenance of the system. Water filtration and deionization systems are always needed at the reactor site to provide water treatment to meet the water quality requirements set by the site for each of the reactor systems. Usually they are on-line systems; alternatively, portable systems may be brought in periodically to treat the water when the condition of the water deteriorates.

The following subsections in this overview section give a summary of the types of filtration and deionization systems available for water treatment. Section 4.2 provides a design concept for a reactor primary coolant water treatment system. Section 4.3 provides a design concept for a fuel storage basin water treatment system. Section 4.4 provides a detailed summary of water treatment methods for raw water with much sediment, hardness, and impurities to be removed. Section 4.4 also describes water treatment and purification design concepts for reactor secondary cooling systems. For additional information of water treatment and purification methods starting with raw water, Ref. [63] provides a comprehensive description.

4.1.1. Water source

The water source for reactor systems may be a municipal water, well water, or river water supply on the reactor site. Before filling a reactor system, water from the fill source should be analysed to provide information to determine the extent of treatment needed to purify the water for the specific reactor water system.

4.1.2. Water filtration

A variety of types of filters are available for water treatment. The primary purpose of filters is to remove insoluble contaminants by physical adsorption or entrapment. Another feature available in water treatment filters is chemical filtration or binding. Because filters hold undesired materials, they can saturate; therefore, care must be taken to regenerate (clean) or replace filters if the pressure drop across it indicates the onset of plugging.

Since exposure dose, caused by the radioactive particulates trapped in the filters and resin beds, significantly increases as particles accumulate, filter systems that would trap radioactivity needs to have provisions for radiation exposure detection, and the filtering system should be shielded as necessary to allow the necessary maintenance or replacement.

4.1.2.1. Sand filters

Sand filters are granular media that remove particulates by physical entrapment. Sand filters rely on a flow of water through the filter bed to trap the particles. There are a variety of sand filters commercially available with the basic media being silica and anthracite (coal). The size of the sand media is typically between 0.15 and 0.3 mm.

4.1.2.2. Mechanical filters

Mechanical filters are metal foams that are available in a range of pore sizes to provide filtration of particulates.

4.1.2.3. Activated charcoal

Activated charcoal is a highly porous material with a large surface area that attracts and binds impurities through adsorption. It is a black, solid substance that looks like powdered charcoal. Many organic compounds can be adsorbed by activated charcoal. It is also effective for removal of chlorine and moderately effective for removal of some heavy metals. Fluoride, chloride, nitrate, hardness (calcium and magnesium) and most metal ions are not removed by activated charcoal.

4.1.2.4. Ultraviolet filters

Ultraviolet (UV) filters are sources of ultraviolet light used to kill bacteria and microbes. An effective system incorporates UV radiation typically at the 254 nm wavelength with intensity of 5 mW/cm^2. The radiation is absorbed in the DNA of the microbes' nucleus, causing cross-linking mutations. If the absorbed dose is sufficient, DNA replication and transcription is inhibited. Cell functions are diminished, and cell death can occur.

A UV filter system is typically comprised of parallel flow-through columns with the lamps protected by quartz tubes in the system. UV filters are used close to the water to be disinfected since micro-organism colonies can quickly grow in water.

4.1.2.5. Reverse osmosis

Reverse osmosis filters water under pressure through a semi-permeable membrane. This type of filtration is effective at rejecting particles such as bacteria greater than 150 amu (atomic mass unit), where 1 amu = 1.66054e-24 grams. This process typically enables only 10–15% of water flow to be filtered at a time.

4.1.3. Ion exchange resins

An ion exchange resin is an insoluble media (e.g. small beads of polymeric material) with functional or active group ions that are loosely attached to the backbone polymeric structure of the resin. The functional group is readily replaced with ions present in the water; i.e. the impurity ions removed from water are trapped with the release of ions from the ion exchange media. Ion exchange resin systems are ideal for removing dilute impurities from the water in the primary and spent fuel basin systems.

A typical ion exchange resin is an organic co-polymer matrix. The ion exchange resin may occasionally be referred to as 'zeolite', a natural substance that functions similarly to an ion exchange resin.

A typical co-polymer matrix is the polystyrene polymer with the divinyl benzene polymer added to crosslink the polystyrene to provide structural stability. Functional groups are added to the resin and are replaced in the resin by the ions from the water in the ion exchange process.

The resin is in the form of small beads, typically 1 to 2 mm in diameter. A small diameter bead provides a high surface area and overall capacity in a given volume. However, they provide a greater resistance to flow in a bed or column system. The beads are retained in their containers with screens above and below the resin beds in the container. Normal fluid flow is top down to keep from fluidizing the resin beads and thereby decrease their effectiveness.

There are different types of ion exchange resins, which are fabricated to selectively prefer one or several different types of ions. There are four main types of the functional groups, two for cation exchange, and two for anion exchange:

- Strong Acid Cation Resin — Uses sulfonic acid groups;
- Strong Basic Anion Resin — Uses trimethylammonium groups;
- Weak Acid Cation Resin — Uses carboxylic acid groups;
- Weak Basic Anion Resin — Uses amino groups.

The ion exchange resin can be further designed to selectively remove specific ions from the water. For example, perchlorate anion can be selectively removed from drinking water.

In general, resin beds are mixed, formed by a combination of cation and anion resins. The ratio for mixed bed resin depends on the application or ratio of cations and anions to be removed, and the equivalency (see description below) of the cation and anion resins.

Several parameters of a resin must be considered in the design of an ion exchange resin column system for a reactor water system. Important design parameters are:

- Species and amount of species to be removed;
- Flow rate per volume of resin;
- Minimum height of resin bed;
- Equivalency (capacity) of the resin media;
- Allowable temperature range of operation of the resin media;
- Allowable pH range of operation of the resin.

In addition, the selection of a resin must consider operations to regenerate the resin or disposal of the resin without regeneration. A separate processing system would be needed for the regeneration process. For example, the flow of an acid solution through the resin media would be used to regenerate a cation resin to replace the captured impurity ions with the hydrogen ion.

Ion exchange resins have an equivalency that defines their capacity to incorporate ions from the water. Most resins have capacities that are equivalent to an equal volume of caustic or acid at a solution concentration of 5 to 10 per cent. It is noted that cross-linking decreases the ion exchange capacity; however cross-linking is needed to stabilize the resin structure. Tables 4 and 5 list some of the many commercially available anion and cation resins, respectively, and their equivalencies.

4.1.4. Evaluation of resin capacity

The following outlines a calculation method, using an example, to determine the amount of resin needed to remove an inventory of ions from a water volume.

Inputs:

- Ion exchange capacity of resin — assume a resin with a capacity of 1.85 equivalents/litre (eq/L);
- Conductivity — assume water with a conductivity of 200 µS/cm;
- Water volume — assume a volume of 10 000 litres (L).

TABLE 4. SOME COMMERCIALLY AVAILABLE CATION RESINS AND THEIR PROPERTIES[a]

CATION EXCHANGE RESINS — RESINTECH INC.

PRODUCT	TYPE	IONIC FORM	APPROX SHIP WT *lb/cuft*	SCREEN SIZE *US mesh per cent*	WATER RETENTION *Per cent*	TOTAL CAPACITY *meq/mL (kgr./cu.ft.)*	MAX. TEMP. *degrees F*	SWELLING *Per cent*	RECOMMENDED USES
CG8	Strong acid gel 8% DVB	Na	52	+16 <2 –50 <1	45–49	1.95 (42.6)	280	Na to H 5–9	Premium grade gel type strong acid cation resin suitable for softening, and demineralization, including mixed beds, dealkalization. Supplied in the hydrogen form as CG8-H. Available in black colour for easy visual separation in mixed beds.
CG8-H	Strong acid gel 8% DVB	H	50	+16 <2 –50 <1	49–54	1.85 (40.4)	265	—	
CG8-C	Strong acid gel 8% DVB	Na	52	+16 <2 –45 <1	45–49	1.95 (42.6)	280	Na to H 5–9	CG8 with coarse bead size, intended for high flow rate applications and chemical process.
CG8-F	Strong acid gel 8% DVB	Na	52	+16 <2 –50 <1	45–49	1.95 (42.6)	280	Na to H 5–9	CG8 with fine mesh size, intended for softening and iron removal.
CGS-BL	Strong acid gel (black colour)	Na	51	+16 <2 –50 <1	49–53	1.9 (41.5)	280	Na to H 5–12	Strong acid cation resin for use in domestic softening. Specially processed to be free of colour, taste and odour.
CGS	Strong acid gel	Na	51	+16 <2 –50 <1	49–53	1.9 (41.5)	280	Na to H 5–12	
CG10	Strong acid gel 10% DVB	Na	54	+16 <2 –50 <1	40–45	2.2 (48.0)	280	Na to H 4–8	Premium grade 10% DVB gel type strong acid cation resin. More resistant to oxidation than CG8. Excellent for high temperature applications, softening, deionization, and chemical processes. Particularly well suited for use in mixed beds. Also supplied in the hydrogen form as CG10-H. Available in black colour for easy visual separation in mixed beds.
CG10-H	Strong acid gel 10% DVB	H	52	+16 <2 –50 <1	46–53	2.1 (45.9)	265	—	
SACMP	Strong acid Macroporous	Na	50	+16 <2 –50 <1	47–52	1.70 (37.2)	300	Ca or Na to H 4–7	Macroporous structure and high DVB level gives this strong acid cation resin the best resistance to oxidative, thermal and osmotic stresses. Also supplied in the hydrogen form as SACMP-H.
SACMP-H	Strong acid macroporous	H	48	+16 <2 –50 <1	50–56	51.6 (35.0)	300	—	

TABLE 4. SOME COMMERCIALLY AVAILABLE CATION RESINS AND THEIR PROPERTIES[a] (cont.)

CATION EXCHANGE RESINS — RESINTECH INC.

PRODUCT	TYPE	IONIC FORM	APPROX SHIP WT *lb/cuft*	SCREEN SIZE *US mesh per cent*	WATER RETENTION *Per cent*	TOTAL CAPACITY *meq/mL (kgr./cu.ft.)*	MAX. TEMP. *degrees F*	SWELLING *Per cent*	RECOMMENDED USES
WACG	Weak acid gel (Carboxylic)	H	47	+16 <2 –50 <1	42–49	4.0 (87.4)	300	H to Na 100	This gel type weak acid cation resin has nearly 100% regeneration efficiency (Carboxylic) and an extraordinary total capacity, of over 85 kilograins/cu.ft. Useful in dealkalization and chemical processing applications. Also available in the sodium form for use in high TDS softening applications.
WACG- Na	Weak acid gel (Carboxylic)	Na	50	+16 <2 –50 <1	Approx. 75	2.6 (43.7)	300	—	
WACMP	Weak acid macro (carboxylic)	H	47	+16 <2 –50 <1	53–58	3.8 (83.0)	250	H to Ca 27	High capacity macroporous weak acid cation resin with nearly 100% regeneration efficiency for dealkalization, deionization, etc., with improved physical stability. This resin is also available in the sodium form for use in high TDS softening applications.
WACMP-Na	Weak acid macro (carboxylic)	Na	50	+16 <2 –50 <1	Approx.75	2.1 (45.9)	250	H to Na 80	
WACMA	Weak acid macro (methacrylic)	H	41	+16 <2 –50 <1	43–53	3.9 (85.2)	250	—	Recommended for industrial and domestic softening. Has lower pH than WACMP and WACG.
WACMA-Na	Weak acid macro (methacrylic)	Na	43	+16 <2 –50 <1	Approx.67	2.5 (54.6)	250	H to Na 75–100	Product purification, buffering, etc.

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[a] Table courtesy of Resin Tech, Inc.

TABLE 5. SOME COMMERCIALLY AVAILABLE ANION RESINS AND THEIR PROPERTIES[a]

ANION EXCHANGE RESINS — RESINTECH INC.

PRODUCT	TYPE	IONIC FORM	APPROX SHIP WT *lb/cuft*	SCREEN SIZE *US mesh per cent*	WATER RETENTION *Per cent*	TOTAL CAPACITY *meq/mL (kg/cuft)*	MAX. TEMP. *Degrees F*	TOT. REV. SWELLING *Per cent*	RECOMMENDED USES
SBG1	Strong base gel Type 1	Cl	44	+16 <2 –50 <1	43–47	1.45 (31.7)	170	Cl to OH 18–22	Standard gel Type 1 anion resin for use in condensate deionization and single use mixed beds. Has the highest *total* capacity of Type 1 gel anion resins. Superior physical strength and resistance to oxidation.
SBG1- OH	Strong Base Gel Type 1	OH	42	+16 <2 –50 <1	53–60	1.2 (26.2)	140	—	Standard gel Type 1 anion resin supplied in the OH form for use in condensate deionization or single use mixed beds (radwaste), cartridges or single use separate beds (anion complexed metals).
SBG1P	Strong base gel Type 1 Porous	Cl	43	+16 <2 –50 <1	51–57	1.25 (27.3)	170	Cl to OH 20–27	Porous gel Type 1 anion resin, superior kinetics to SBG1, for use in deionization and mixed beds. Has the highest regenerable *operating* capacity of the Type 1 anion resins. Especially recommended for regenerable systems. Good resistance to organic fouling.
SBG1P- OH	Strong base gel Type 1 porous	OH	41	+16 <2 –50 <1	65–70	1.0 (21.9)	140	—	
SBG2	Strong base gel Type 2	Cl	44	+16 <2 –50 <1	38–44	1.45 (31.7)	170	Cl to OH 10–15	Standard gel Type 2 anion resin, featuring very high capacity and regeneration efficiency. Greater resistance to organics than Type 1 resins. Excellent for two bed service. Its good regeneration efficiency and high capacity can help minimize caustic consumption and save operating costs.
SBG2- OH	Strong base gel Type 2	OH	42	+16 <2 –50 <1	43–50	1.3 (28.4)	95	—	
SBMP1	Strong base Type 1 macro	Cl	42	+16 <2 –50 <1	50–60	1.15 (25.1)	170	Cl to OH 15–20	Type 1 macroporous anion resin featuring high exchange capacity, porous gel matrix and superior elution of large organic molecules. Also offered in hydroxide form for immediate use.
SBMP1- OH	Strong base Type 1 macro	OH	40	+16 <2 –50 <1	64–73	.95 (20.8)	140	—	
SBMP2	Strong base Type 2 macro	C1	43	+16 <2 –50 <1	52–58	1.2 (26.2)	170	Cl to OH 10-–15	Type 2 macroporous anion resin featuring high exchange capacity and superior elution of large organic molecules. Suitable for high salt content waters. Also offered in hydroxide form for immediate use.
SBMP2- OH	Strong base Type 2 macro	OH	41	+16 <2 –50 <1	62–71	1.0 (21.9)	140	—	

TABLE 5. SOME COMMERCIALLY AVAILABLE ANION RESINS AND THEIR PROPERTIES[a] (cont.)

ANION EXCHANGE RESINS — RESINTECH INC.

PRODUCT	TYPE	IONIC FORM	APPROX SHIP WT *lb/cuft*	SCREEN SIZE *US mesh per cent*	WATER RETENTION *Per cent*	TOTAL CAPACITY *meq/mL* *(kg/cuft)*	MAX. TEMP. *Degrees F*	TOT. REV. SWELLING *Per cent*	RECOMMENDED USES
SBACR1	Strong base gel (Acrylic)	Cl	45	+16 <2 –50 <1	57–62	1.2 (26.2)	95	Cl to OH 10–15	Acrylic structure allows operating capacity and fouling resistance in applications with a high level of organics. This resin should not be used when service water temp exceeds 85 degrees F.
SBACR2	Strong base gel (Acrylic)	Cl FB	43	+16 <2 –50 <1	57–63	1.4 (30.6)	95	—	Acrylic resin containing a mixture of strongly basic and weakly basic exchange groups. High total capacity and resistance to organic fouling.
WBG30	Weak base (epoxy polyamine)	CI FB	38	+16 <2 –50 <1	52–62	3.0 (65.6)	110	FB to Cl 5	High capacity granular intermediate base resin for use in applications requiring extremely high throughput capacity or nearly 100 per cent regeneration efficiency.
WBMP	Weak base macroporous	Free Base	40	+16 <2 –50 <1	48–54	1.6 (35.0)	212	FB to Cl 10–15	Macroporous weakly basic anion resin, with excellent physical strength and high throughput capacity. Nearly 100 per cent regeneration efficiency and high resistance to organic fouling.
WBACR1	Weak base (acrylic)	Free Base	44	+16 <2 –50 <1	60–65	1.7 (37.2)	250	FB to Cl 10–15	Weakly basic acrylic resin with high total capacity, throughput capacity and regeneration efficiency. Organic substances sorbed during service are easily removed during regeneration.

[a] Table courtesy of Resin Tech, Inc.

First, determine the amount of equivalents of impurities to be removed in the water at 200 µS/cm conductivity. To do so, the total equivalent impurities (TEI) that needs to be removed are calculated, by using bicarbonate, HCO_3^- as reference, a mobile ion that is typically used to represent the equivalency of both anions and cations, and that presents conductivity equal to 1.72 µS/cm at concentration of 1 ppm. Using the 'input' information, TEI is calculated as:

$$\text{TEI} = \frac{\text{Water volume (10 000 Litres)} \times \text{Water Conductivity}\left(200\,\frac{\mu S}{\text{cm}}\right)}{\frac{1.72\frac{\mu S}{\text{cm}}}{\text{1 ppm HCO3}^-}\times\frac{\text{1 ppm HCO3}^-}{\frac{\text{1 mg HCO3}^-}{\text{Litre}}}\times\frac{\text{1000 mg HCO3}^-}{\text{g HCO3}^-}\times\frac{\text{61g HCO3}^-}{\text{mol HCO3}^-}\times\frac{\text{mol HCO3}^-}{\text{eq HCO3}^-}} \tag{30}$$

which gives TEI = 19.06 equivalents of HCO3^- (eq HCO3^-).

Since the ion exchange capacity of the resin is 1.85 eq/L, the resin volume required (RVR) is:

$$\text{RVR} = 19.06\text{ eq}/(1.85\text{ eq/L}) = 10.3\text{ L} \tag{31}$$

For a more accurate calculation, instead of using HCO_3^-, the actual equivalency of the species to be removed from the water can be used in the calculation.

A deionization system using cation and anion ion exchange resins should remove essentially 100% of the ionic impurity species from the inlet water; i.e. the outlet conductivity should ideally be that of pure water at the ambient temperature. The outlet conductivity can be used as an indicator of a resin that is approaching its capacity. When the outlet conductivity climbs to a target value (e.g. 0.3 µS/cm) above that of pure water at ambient conditions (e.g. at room temperature, the conductivity of pure water is 0.0548 µS/cm), the resin from a deionizer system should be changed out or regenerated.

4.1.5. Water cleanup — analysis of transient

The startup of the water treatment system will require a period of time before a concentration of an impurity specie is reduced in the water. The impurity specie will ultimately reach a steady state concentration that is a function of its release rate into the system, and the removal rate of the system.

For the transient period before steady state, the following analysis is performed. A differential equation is set up to describe the change in impurity species content in a water system, that is:

Change in amount of impurity species = amount entering — amount leaving (32)

As an example, consider the change in the amount radioactivity in the water due to Cs-137 as it is removed by an ion exchange resin (e.g. Cs-137 is removed by a cation resin).

For a closed loop system, equation (31) becomes:

$$A'(t) = R - \varepsilon * Q * C(t) = R + Q*(1 - \varepsilon)*C(t) - Q*C(t) \tag{33}$$

where:

A(t)	is the total activity in Bq, for example, in a volume of water V, at time t;
A'(t)	is the change in the total activity in Bq/s, in a volume of water at time t;
C(t)	is the concentration of activity in Bq/L in a volume of water at time t;
R	is the total activity released into a volume of water in Bq/s (e.g. from all leaking fuel);
Q	is the volumetric flow rate in L/s into and out of a closed loop deionization system;
V	is the volume of water in the pool; and
ε	is the efficiency of the deionizer system.

The term $Q*(1 – \varepsilon)*C(t)$ on the right is the activity re-entering the basin after the water has passed through a deionization system with volumetric flow rate Q. The term $Q*C(t)$ on the right is the activity removed from the basin to pass through a deionization system with volumetric flow rate Q.

Note that we are considering a well mixed model, i.e. we are assuming that C(t) is homogenous, therefore $A(t) = V*C(t)$, and equation (32) becomes:

$$C'(t) = R/V + (Q/V)*(1 – \varepsilon)*C(t) – (Q/V)*C(t) \tag{34}$$

With $C'(t) = dC(t)/dt$, and solving the differential equation for an initial condition of $C = C_0$ at $t = t_0$, it can be shown that:

$$C(t) = R/(Q\ \varepsilon) + [C_0 – R/(Q\ \varepsilon)]e^{–(Q*\varepsilon/V)t} \tag{35}$$

This method can be applied to any species of interest in a reactor water system. However, one must be aware that the solution considers the efficiency of the resin (ε) as a constant value. This is valid for most deionization systems, in which the efficiency is 100% ($\varepsilon = 1$) until the resin has reached its capacity.

4.1.6. Water cleanup — analysis of steady state

The impurity species will ultimately reach a steady state concentration in a water system that has a constant source of impurity specie addition, or release rate, into the water system; i.e. at t = infinity, $C(t) = C_{SS}$. As can be seen from Eq. (34), for a closed loop system, the steady state concentration of radioactivity in the water, C (in Bq/L), is given by:

$$C_{SS} = R/(Q\ \varepsilon) \tag{36}$$

where Q is the volumetric flow rate in L/s into and out of a closed loop deionization system, R is the total release rate of radioactivity into the water in Bq/s, ε is the efficiency of the deionizer system and C_{SS} is the activity of the water in Bq/L at steady state.

Once again, this method can be applied to any species of interest in a reactor water system, recalling that the efficiency of most deionization systems is 100% ($\varepsilon = 1$) until the resin has reached its capacity.

4.1.7. On-line chemical analysis

Continuous cleanup of the water by deionizers makes it difficult to follow real time changes in the system with occasional grab samples for offline analyses. An on-line analyser can be used to determine real time trends in impurity species at low (ppb) levels. For example, trends of impurities and additives can be acquired during reactor startup, operation, shutdown and deionizer change-out.

For ionic content, a high performance liquid chromatograph using ion exchange resin columns may be used; i.e. an ion chromatograph is capable of quantifying atomic or molecular ions based on their interaction with the resin to provide custom analysis.

4.2. PRIMARY COOLANT WATER TREATMENT SYSTEM

Active maintenance of the water quality is needed for the primary coolant water. Impurities in the water of the primary coolant can have several consequences. Aggressive ionic species, undissolved particulates (if settled on the fuel cladding) and several microorganisms: cause an increase in the fuel corrosion rate; add to water radioactivity; and cloud the water. Therefore, in order to maintain the integrity of the fuel, and safe operation of the reactor, it is necessary to have very good quality water in the primary coolant system.

Figures 15–17 show sketches of conceptual filter–deionizer (F–D) systems for a primary coolant water treatment system within the primary coolant system. The sketches are conceptual designs for low, intermediate and high power research reactors, respectively. Depending on the design, a high power research reactor may require: a

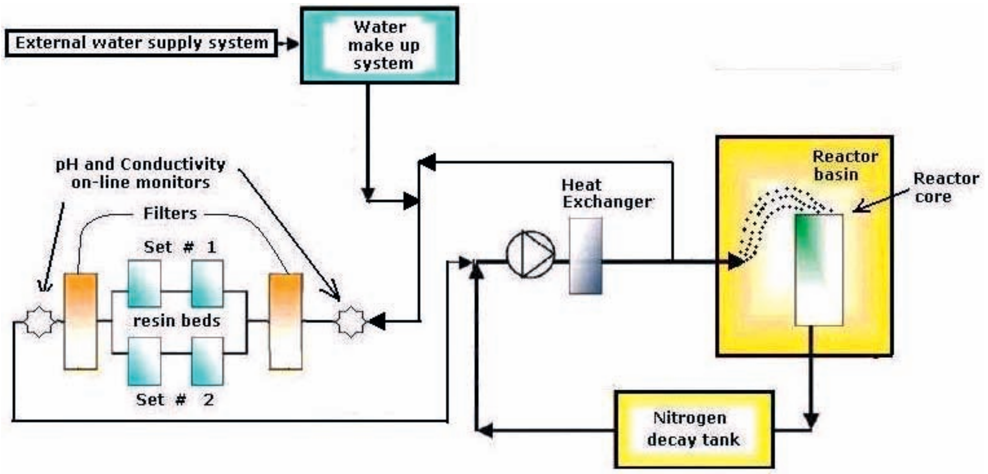

FIG. 15. Water treatment system (filter-deionizer system) concept for low power research reactors. For a non-pressurized reactor, a pool skimmer may serve as the inlet to the treatment system.

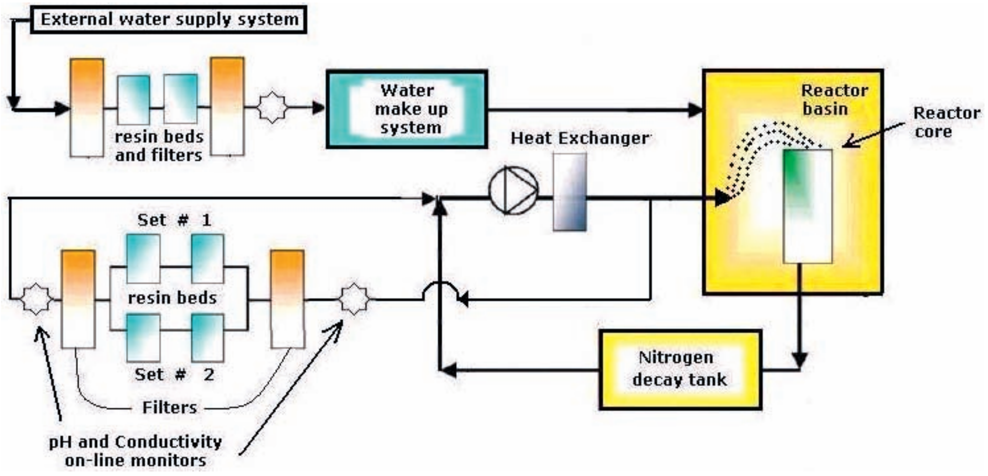

FIG. 16. Water treatment system (filter-deionizer system) concept for intermediate power research reactors. For a non-pressurized reactor, a pool skimmer may serve as the inlet to the treatment system.

closed F–D system to remove impurities from the specific reactor core cooling system; a second system for purification of the water in the reactor pool; and a third system to purify the water from the external water supply system. In a low-power research reactor, only one F–D system may be sufficient to accomplish the necessary treatment to purify the water from the reactor core, the water in the reactor basin, and the water from the external supply system. The F–D systems are not typically designed to be in line with the coolant circulation, but rather operate by drawing a side stream from the coolant loop and returning the purified water to the system. The concepts described in Sections 4.1.5–4.1.6 are applicable to analyse all three configurations.

Primary coolant water is typically continuously treated in the F-D system. The filter subsystem may have a pre-filter before the deionization sub-system, and another filter after the deionization sub-system. For the treatment process, it is recommended to use a physical configuration, as shown in Figs 15–17, with a mechanical filter to retain solids of micro proportions (with sizes greater than 5 μm) followed by the resin beds, for total demineralization, and another mechanical filter at the end. Depending on the reactor power and volume of water to be purified, two or more sets of resin beds may be necessary, especially to allow maintenance of one set while the other is being used so as to avoid shutdown of the rector for long periods due unavailability of the system.

Other minor components that are part of the water treatment system include piping lines with electronic or mechanical detectors to indicate pressure, temperature, flow rate and radiation at various locations, as well as water quality parameters. Leak detection systems from each of the components of the water treatment system can also be considered part of the treatment system. The measurement and detection of water quality parameters such as pH

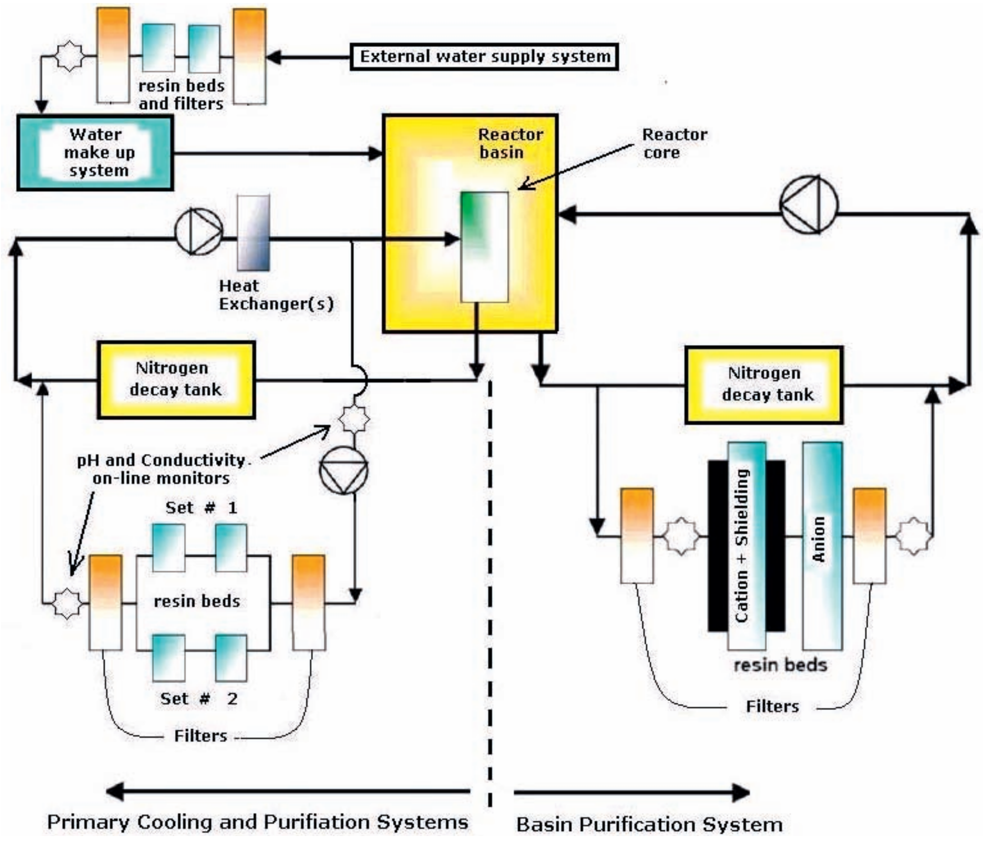

FIG. 17. Concept of a water treatment system (filter-deionizer system) for high power research reactors.

and dissolved impurity species in on-line systems is discussed in Section 5. These detector systems can include electronic alarms with set points.

The design of a primary coolant water treatment system must consider the concepts for filtration and deionization discussed in Section 4.1. The hydraulic impedances of the filters, deionizers and other components to be used in the water treatment system would be considered in the design to ensure that pumps provide sufficient flow rate, Q, to achieve water cleanup.

4.3. FUEL DECAY POOL/FUEL STORAGE BASIN WATER TREATMENT SYSTEM

Fuel taken out of the reactor may be placed in a fuel decay pool for removal of decay heat prior to placement in a dry storage system, or the fuel may be placed in a water basin for interim storage where the water continues to provide cooling and radiation shielding. Concerns for water quality in a decay pool or in a fuel storage basin are similar to those for the primary system. Typically fuel is kept in the storage basin for many years, which would exacerbate the concern for corrosion attack in poor water quality. Therefore, in order to maintain the integrity of the fuel and a safe operation of the storage basin throughout the desired storage life of the fuel in the water, it is necessary to have very good quality water in the system. This requires active water quality management.

In most cases, the fuel decay pool is an extension of the rector pool; in this case, the facility uses the same purification system to purify the water in reactor pool and the water in the decay pool.

The water treatment system for an independent fuel decay pool and fuel storage basin would be a filter-deionizer system for the removal of particulates and dissolved impurity species. A microbial control system is typically an optional subsystem in the water treatment system. Figure 18 shows a sketch of the components needed in a water treatment system for a decay pool or storage basin. Except for the heat exchanger, which depends on the need to remove the decay heat produced by the fuel element, all other components of this system are similar to those for the reactor primary coolant water treatment system because the water quality requirements are nearly identical (see Fig. 16 and the previous discussion in Section 4.2).

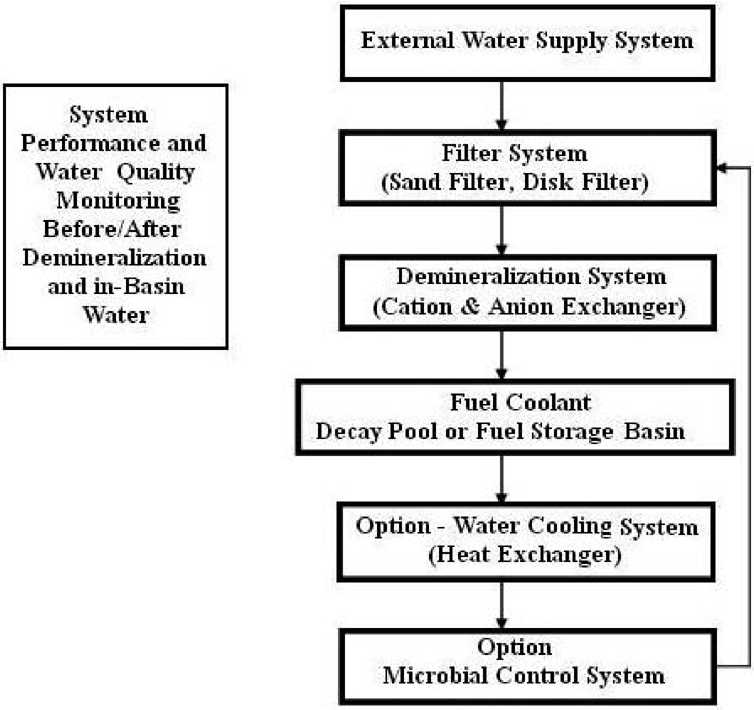

FIG. 18. Sketch of components for a decay pool/fuel storage basin water treatment system.

The treatment of water in a storage only pool may be periodic, using portable filter-deionizer systems, or an on-line filter-deionizer system may be installed. The decision to use a portable vs. an on-line system depends on how rapidly the basin water quality would deteriorate if left untreated. For example, a specific basin may have operating characteristics such that a rise in conductivity from 1 to 10 μS/cm occurs in six months without active deionization (untreated). In this case, a portable water treatment system may be the most economical method to provide periodic treatment. Alternatively, in this case, an installed water treatment system may be operated intermittently.

The fuel storage basin may be physical covered or uncovered to the atmosphere. An important consideration for the water quality in fuel storage basins that are always open to atmosphere is that they can quickly be contaminated with debris from inorganic and organic materials, and micro-organisms that tend to accumulate on all exposed surfaces inside of the storage basin. In these cases, it the use of skimmers is recommended to remove surface debris. It is also recommended to periodically aspirate the surfaces of all structures and the bottom of the basin. The aspired water may be directed to an independent active filter system with a charcoal bed. Also, a water jet, combined with a vacuum system may be used. This ‘aspiration-and-filtration’ operation is recommended to be done at least once at every six months, or when accumulation of dust or debris is evident.

Considering that most reactor pools are also open to the atmosphere, this procedure, i.e. to aspirate the surfaces of all structures and the bottom of the pool, is also recommended for the reactor pool.

4.4. SECONDARY CIRCUIT TREATMENT SYSTEM

4.4.1. Introduction

The source of the water used in the secondary system of a research reactor is usually municipal supplies or any major body of water, such as a reservoir, lake or river in the vicinity. Municipal waters are generally potable. Table 6 shows the typical composition for ideal potable water (drinking water) and Table 7 shows the maximum tolerable levels of specific impurity constituents in it. Water from municipal supplies is always treated for use in the primary system and seldom treated for use in the secondary system of a research reactor. In some cases, municipal waters may require treatment prior to use in the secondary system, mainly to reduce turbidity and/or chlorine levels. Waters from other natural sources require treatment and could consist of a variety of steps [64–66].

TABLE 6. PARAMETERS OF TYPICAL IDEAL POTABLE WATER [64]

Property or constituent	Concentration (ppm)
Turbidity	5 (max) in NTU
Colour	0
Odour	None
Iron (Fe^{2+})	0
Manganese (Mn^{2+})	0
Sulphates (SO_4^{2-})	250 (max)
Chlorides (Cl^-)	250 (max)
Bicarbonates (HCO_3^-)	250 (max)
Hardness ($CaCO_3$)	85 (max)
Fluorides (F^-)	0.8
pH	7.0
MPN coli/100 mL	0
Aggressiveness of iron	Minimum

Note: This is *not* a recommendation for water quality in the secondary system.

TABLE 7. MAXIMUM TOLERABLE LEVELS OF SPECIFIC CONSTITUENTS IN POTABLE WATER, IN mg/L [64]

Constituent	Amount (mg/l)
Phenols	0.001
Arsenic	0.01
Cadmium	0.01
Selenium	0.01
Cyanide	0.01
Chromium	0.05
Lead	0.05
Manganese	0.05
Silver	0.05
Carbon extracted from coliforms	0.2
Iron	0.3
Alkyl sulphonated benzene	0.5
Copper	1.0
Barium	1.0
Fluoride	1.5
Zinc	5.0
Nitrate	45.0
Chloride	250.0
Sulphate	250.0
Total solids dissolved	500.0

Note: These values are *not* recommended limits for water in the secondary circuit.

4.4.2. Clarification of waters and removal of undesirable constituents

Clarification is defined as the removal of finely divided materials in suspension in water. Clarification, if necessary, is the first step in any water treatment. It is often followed by other more sophisticated treatments such as the removal of iron, manganese, ammonia, and the reduction of hardness, alkalinity, dissolved oxygen and dissolved carbon dioxide. Depending of the water quality requirements, other processes like distillation and deionization may be necessary.

Clarification of waters often involves four steps: coagulation (consisting of mixing chemicals with the water and flocculation), sedimentation, chlorination and filtration. Coagulants that are very effective in water treatment are aluminium sulphate, ferric sulphate, ferrous sulphate, ferric chloride, sodium aluminate and polyelectrolytes.

Natural coagulants are those that are present in natural waters, for example, magnesium. If natural coagulants are present in sufficient quantities, the water flocculates (suspended solids are formed in the water) when its pH is adjusted. The ‘right pH’ for coagulation of water is that at which it occurs quickly upon addition of the coagulant. When aluminium sulphate is used as the coagulant, the right pH is in the range of 5 to 6. The right pH varies with the type of coagulant [64]. For coagulation, it is determined experimentally by carrying out the Jar test [65].

Auxiliary additives are often used during coagulation and include alkaline products such as CaO, Na_2CO_3 and NaOH. These are used to adjust the pH and/or to raise the total alkalinity of the water, if low. Other auxiliary agents include those that aid in flocculation and are used when the turbidity of the water is too low, for example, bentonite. Bentonite is a hydrated aluminium silicate and remains in suspension in water in the form of colloids. When used jointly with aluminium sulphate for clarifying water, the bentonite helps to form large and dense flocks which sediments or settles quite rapidly. Bentonite is effective in a wide range of pH (2–12) and its use often eliminates the need to adjust the pH. Activated sodium silicate is also used as an auxiliary additive for coagulation because it accelerates the formation of flocks and their sedimentation.

The term ‘polyelectrolyte’ refers to all water soluble organic polymers used for clarification, whether they function as coagulants or flocculants. In general, polymeric flocculants or coagulants may be anionic, cationic, or non-ionic. Their molecular weights may be as high as 50 000 000. For any given particle, there is an ideal molecular weight and an ideal charge density for optimum coagulation. Because suspensions are normally non-uniform, specific testing is necessary to find the coagulants and flocculants with the broadest range of performance.

Polymeric primary coagulants are cationic materials with relatively low molecular weights (under 500 000). The cationic charge density (available positively charged sites) is very high. The cationic polyelectrolytes commonly used as primary coagulants are polyamines and poly-DADMACS. When used as primary coagulants, they adsorb on particle surfaces, reducing the repelling negative charges. These polymers may also bridge, to some extent, from one particle to another, but are not particularly effective flocculants. The pH of the treated water is unaffected.

4.4.3. Suspended materials in water

Some of the insoluble materials in water sediment mix easily if the water is not agitated or disturbed. However, the finely divided materials remain in suspension and result in turbidity. These materials remain in suspension because their negative electric charges repel one suspended particle from another. The repelling forces and fine size of the particles keep them in suspension. The size of the particle contributes towards its remaining in suspension.

4.4.4. Water quality and its effects in secondary systems

Recommended water quality limits for the water systems for research reactors are discussed in Section 6; the impact of water quality on the components of a secondary system that provide the basis for the water quality limits are discussed in this Section.

Water quality requirements for the secondary circuit are similar to those used in any other industry, where heat from operating systems is removed with the aid of a cooling circuit. The water circulating in the secondary circuit flows through carbon steel pipelines, the heat exchanger (usually made of carbon steel shell with copper tubes) and the cooling towers. Consequently, in this water, heavily oxygenated in the cooling tower, the carbon steel corrodes. As a result, the concentration of dissolved iron ions and the amount of detached corrosion products in the circulating water increase with continued circulation. The ratio of secondary circuit water volume to total area of metallic surfaces is an important factor to be considered. The smaller the volume of secondary coolant, the greater the number of times the same water circulates in a given time. Consequently, the water becomes quickly saturated with contaminants.

Corrosion is one of the two main problems that need to be managed in water cooling systems; the other is formation of deposits, which can lead to obstruction of water flow and also to the formation of concentration and/or aeration cells that could exacerbate the extent of corrosion.

Dissolved inorganic salts precipitate when exceeding their solubility limits. In untreated water, these salts form agglomerates and/or deposit on all surfaces forming scales, as shown in Figure 19 [65]. The low thermal conductivity of the scales results in loss of efficiency of heat exchangers. Other problems also occur, such as localized corrosion under the deposits (under-deposit corrosion or attack). The scale deposits are usually iron oxides, calcium carbonate, calcium sulphates, phosphates, oils or clays. In addition to decreasing heat transfer coefficient, these deposits often restrict passage of water by decreasing the diameter of tubes in heat exchangers, and cause loss of efficiency. In general most heat exchangers are periodically cleaned to remove the deposits to prevent system shut down. Hence, it is important to treat the secondary system water and maintain its quality within specified limits to prevent or reduce corrosion, formation of deposits and the effects of microbial growth.

Most secondary cooling circuits also have to deal with problems caused by airborne bacteria and other microorganisms that get entrained in the water, proliferate and cause blockage and/or further corrosion. Consequently, it is important to chemically treat the secondary circuit coolant to prevent corrosion, formation of scale deposits, and control microbial growth. The chemicals added to the water to inhibit corrosion, deposit formation and microbial growth are referred to as corrosion inhibitors, deposit inhibitors and anti-microbial, respectively.

In the secondary system, the metals in contact with circulating water are typically mild steel and copper. Copper is often used as tubing in tube-shell type of heat exchangers (see Fig. 20). Depending on the design, the secondary circuit water may flow either through the tube or on the shell side (outside of the tube).

4.4.5. Corrosion of iron in aerated water

In the presence of water, even if it is pure, iron ionizes as shown in Eq. (37):

$$\mathrm{Fe} \rightarrow \mathrm{Fe}^{2+} + 2e^- \quad (37)$$

and water dissociates as:

$$2\mathrm{H_2O} \leftrightarrow 2\mathrm{H}^+ + 2\mathrm{OH}^- \quad (38)$$

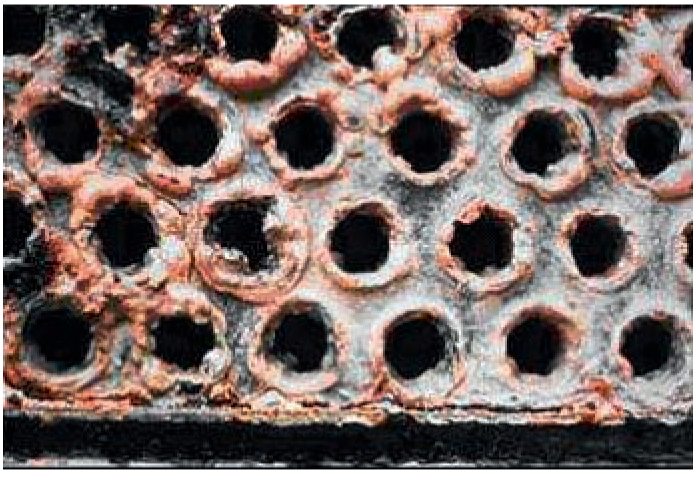

FIG. 19. Scale on heat exchanger plate [65].

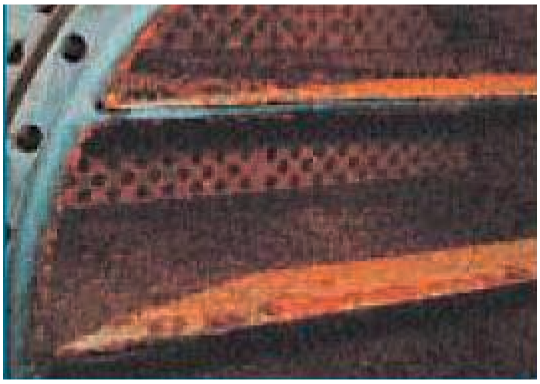

FIG. 20. A tube shell type of heat exchanger.

The iron reacts with the OH^- ion, and the H^+ absorbs the electrons:

$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2 \qquad (39)$$

$$2H^+ + 2e^- \rightarrow 2[H] \qquad (40)$$

The compound ferrous hydroxide or iron (II) hydroxide, $Fe(OH)_2$, passivates the metal and the corrosion ceases.

However, in the presence of oxygen, this layer of $Fe(OH)_2$ is destroyed.

$$4\ Fe(OH)_2 + O_2 + 2H_2O \rightarrow 4\ Fe(OH)_3 \text{ or } 4\ FeO(OH){\cdot}H2O. \qquad (41)$$

Some authors consider that $Fe_2O_3.H_2O$ forms at temperatures above 170ºC. Below this temperature, the film formed is α-FeOOH (goethite) or 2FeOOH ($Fe_2O_3.H_2O$) according to:

$$2Fe + 2H_2O + O_2 \rightarrow 2FeOOH\ (Fe_2O_3.H_2O) \qquad (42)$$

The $Fe_2O_3.H_2O$ that forms is a porous film. It is non-adherent and easily spalls, exposing the metal underneath for further corrosion as per Eq. (37).

A reaction between [H] of Eq. (40) and the dissolved oxygen in the water could also occur, which implies further ionization of iron according to Eq. (37).

$$2[H] + ½\ O_2 \rightarrow H_2O \qquad (43)$$

If CO_2 is present, then the following reactions can also take place:

$$CO_2 + H_2O \leftrightarrow H_2CO_3 \qquad (44)$$

$$H_2CO_3 \leftrightarrow 2H^+ + CO_3^{2-} \qquad (45)$$

The H^+ of Eq. (45) enters the system, due to the presence of CO_2 and absorbs electrons of Eq. (37), causing more Fe^{2+} ions to go into solution, until a new equilibrium is established.

4.4.6. Corrosion inhibitors: General

A corrosion inhibitor is any substance that effectively decreases the corrosion rate when added to an environment. An inhibitor can be identified most accurately in relation to its function: removal of the corrosive substance, passivation, precipitation or adsorption. Passivating (anodic) inhibitors form a protective oxide film on the metal surface. For example, the ferrous ions formed due to dissolution of iron in the anodic reaction

$Fe \rightarrow Fe^{2+} + 2e$ are oxidized to ferric ions or react with anions such as OH^-, present in solution, to form oxides such as Fe_2O_3 and protect the metal. These inhibitors are the best inhibitors because they can be used in economical concentrations, and their protective films are tenacious and tend to be rapidly repaired if damaged. Precipitating (cathodic) inhibitors are simply chemicals that form insoluble precipitates that can coat and protect the surface. Precipitated films are not as tenacious as passive films and take longer to repair after an upset. Chemical adsorption of the inhibitor specie on the metal surface can distinctly alter the corrosion susceptibility of the metal. A small film of the inhibitor provides the protection by effectively forming an inert film. Removal of the inhibitor by precipitation of it from water is straightforward.

Examples of passivation inhibitors (anodic inhibitors) include chromate, nitrite, molybdate, and orthophosphate. All are oxidizers and promote passivation by increasing the electrical potential of the iron. Chromate and nitrite do not require oxygen and can therefore be the most effective. Chromate is an excellent aqueous corrosion inhibitor, particularly from a cost perspective. However, due to health and environmental concerns, use of chromates has been outlawed in many countries, *and it is not recommended***.** Nitrite is also an effective inhibitor, but in open systems it tends to be oxidized to nitrate. Both molybdate and orthophosphate are excellent passivators in the presence of oxygen. Molybdate can be a very effective inhibitor, especially when combined with other chemicals. Its main drawback is its high cost. Orthophosphate is not an oxidizer per se, but becomes one in the presence of oxygen. A negative attribute of orthophosphate is its tendency to precipitate with calcium hardness found in natural waters. In recent years, deposit control agents that prevent this deposition have been developed. Due to its relatively low cost, orthophosphate is widely used as an industrial corrosion inhibitor [65].

The local pH at the cathode of the corrosion cell is elevated due to the generation of hydroxide ions. Precipitating inhibitors form complexes which are insoluble at this high pH (1–2 pH units above bulk water), but whose deposition can be controlled at the bulk water pH (typically pH7–9). A good example is zinc, which can precipitate as hydroxide, carbonate or phosphate.

$$2H_2O + O_2 + 4e^- \rightarrow 4OH^- \qquad (46)$$

$$2Zn^{2+} + 4OH^- \rightarrow 2Zn(OH)_2 \qquad (47)$$

Calcium carbonate and calcium orthophosphate are also precipitating inhibitors. Orthophosphate thus exhibits a dual mechanism, acting as both an anodic passivator and a cathodic precipitator.

4.4.6.1. Chromates and zinc-chromate inhibitors

Sodium and potassium chromates and dichromates have been widely used in the past as corrosion inhibitors in cooling water systems. Chromates were probably the most efficient corrosion inhibitors, but since the late 1990s, increased concerns about health and environmental effects related to chromates have severely restricted or prohibited its use in most industrialized countries. Therefore, *the use of chromates is not recommended*; the following is scientific information on its chemistry, for the reader's reference**.**

Chromates help to form oxides that inhibit corrosion according to:

$$2Fe + 2Na_2CrO_4 + 2H_2O \rightarrow Fe_2O_3 + Cr_2O_3 + 4NaOH \qquad (48)$$

In order to be used as the only inhibitor compound, chromates need a minimum concentration (in the water) of 300 ppm. The normal concentration level is 500 to 1000 ppm in cooling waters with pH in the range of 7.5–8.5. However, some cases with very high concentrations, on the order of even 10 000 ppm, have been documented. It was demonstrated that the use of chromates along with zinc salts is more effective in combating corrosion in cooling water systems, using much lower concentrations of both compounds, 50 ppm of chromate and 10 ppm of zinc. The pH of the water in this case can be between 5.8 and 7.0. It should be pointed out that using only chromate with concentrations below 200 ppm (without zinc) could lead to corrosion instead of preventing it [64].

In closed cooling water systems, where different metals could be in contact with the circulating water, chromate concentrations of the order of 10 000 ppm inhibits galvanic corrosion. Very high chromate concentrations protect steels, cast iron, zinc, brass etc., but in systems where the water contains H_2S, chromate treatments become ineffective due to reduction of chromium, according to Eq. (49):

$$2CrO_4^{2-} + 3H_2S + 10H^+ \rightarrow 2Cr^{3+} + 3S + 8\ H_2O \qquad (49)$$

4.4.6.2. Phosphate/phosphonate inhibitors

Many early corrosion treatment programmes used polyphosphate at relatively high levels. In water, polyphosphate undergoes a process of hydrolysis, commonly called ‘reversion’, which returns it to its orthophosphate state. In early programmes, this process often resulted in calcium orthophosphate deposition. Later improvements used combinations of ortho-, poly-, and organic phosphates. The general treatment ranges were: orthophosphate, polyphosphate and phosphonate with concentrations in the range 2–10 ppm and pH of 6.5–8.5.

A more specific set of control limits within these ranges was developed, based on individual water characteristics and system operating conditions. Where low calcium waters were used (i.e. less than 75 ppm), zinc was often added to provide the desired corrosion protection. With close control of phosphate levels, pH and cycles, it was possible to achieve satisfactory corrosion protection with minimal deposition. However, there was little margin for error, and calcium phosphate deposition was frequently a problem.

The Dianodic II is a trademark treatment system from General Electric that was introduced in the market in 1979. This is a very efficient programme that uses relatively high levels of orthophosphate to promote a protective oxide film on mild steel surfaces, providing superior corrosion inhibition. The use of high phosphate levels was made possible by the development of superior acrylate based copolymers. These polymers are capable of keeping high levels of orthophosphate in solution under typical cooling water conditions, eliminating the problem of calcium phosphate deposition encountered with previous programmes. Dianodic II is an industry standard in non-chromate treatment. The general control ranges for Dianodic II are: total inorganic phosphate 10–25 ppm; calcium as $CaCO_3$ 75–1200 ppm and pH 6.8–7.8. A recent upgrade in performance and capability has been made with the introduction of Dianodic III, the new halogen stable neutral pH treatment programme of General Electric Water and Process Technologies.

4.4.6.3. Alkaline treatment

There are several advantages when operating a cooling system in an alkaline pH range of 8.0–9.2. First, the water is inherently less corrosive than at lower pH. Second, feed of sulphuric acid (to adjust pH) can be minimized or even eliminated, depending on the make-up water chemistry and desired cycles. A system using this make-up could run an alkaline treatment programme in the 4–10 cycle range with no acid feed. This eliminates the high cost of properly maintaining an acid feed system, along with the safety hazards and handling problems associated with acid. Even if acid cannot be eliminated, there is still an advantage to alkaline operation. A pH of 8.0–9.0 corresponds to an alkalinity range more than twice that of pH7.0–8.0. Therefore, pH is more easily controlled at higher pH, and the higher alkalinity provides more buffering capacity in the event of acid overfeed. A disadvantage of alkaline operation is the increased potential to form calcium carbonate and other calcium and magnesium based scales. This can limit cycles of concentration and require the utilization of deposit control agents.

Alkaline zinc programmes are very effective programmes and rely on a combination of zinc and organic phosphate (phosphonate) for corrosion inhibition. Zinc is an excellent cathodic inhibitor that allows operation at lower calcium and alkalinity levels than other alkaline treatments. However, discharge of cooling tower blow down containing zinc may be severely limited due to its aquatic toxicity. Zinc based programmes are most applicable in plants where zinc can be removed in the waste treatment process.

Alkaline phosphate programmes using organic and inorganic phosphates also inhibit corrosion at alkaline pH. Superior synthetic polymer technology has been applied to eliminate many of the fouling problems encountered with early phosphate/phosphonate programmes. Because of the higher pH and alkalinity, the required phosphate levels are lower than in Dianodic II treatments. General treatment ranges are: inorganic phosphate, 2–10 ppm; organic phosphate, 3–8 ppm; calcium (as $CaCO_3$), 75–1200 ppm; and pH8.0–9.2.

All-organic programmes use no inorganic phosphates or zinc. Corrosion protection is provided by phosphonates and organic film-forming inhibitors. These programmes typically require a pH range of 8.7–9.2 to take advantage of calcium carbonate as a cathodic inhibitor.

4.4.6.4. Nitrites

Nitrites are excellent for passivating steels and other iron based alloys. When used to treat distilled cooling waters, 50 ppm of nitrites is sufficient to inhibit corrosion. However, in the presence of high concentrations of sodium chloride, about 5000 ppm of sodium nitrite is recommended and the pH maintained around 6.5–8.0. Protection of the metal is through formation of oxides according to:

$$2Fe + NaNO_2 + 2H_2O \rightarrow Fe_2O_3 + NaOH + NH_3 \qquad (50)$$

4.4.6.5. Quaternary salts of ammonia

Quaternary salts of ammonia protect metals in cooling systems by forming films on the metal surfaces. The use of 10–15 ppm of these salts in cooling water systems has been found to be effective to protect metals from corrosion.

4.4.6.6. Molybdate based treatment

In order to be effective, molybdate alone treatment requires very high concentrations. Therefore, it is usually applied at lower levels (e.g. 2–20 ppm) and combined with other inhibitors, such as inorganic and organic phosphates. Many investigators believe that molybdate, at the mentioned levels, is effective in controlling pitting on mild steel. Because molybdate is more expensive than most conventional corrosion inhibitors on a parts per million basis, the benefit of molybdate addition must be weighed against the incremental cost. Use of molybdate may be most appropriate where phosphate and/or zinc discharge is limited.

4.4.7. Formation of deposits and its control

Deposit accumulations in cooling water systems reduce the efficiency of heat transfer and the carrying capacity of the water distribution system. In addition, the deposits cause oxygen concentration cells to form, which accelerate corrosion that could lead to process equipment failure. Deposits range from thin, tightly adherent films to thick, gelatinous masses, depending on the depositing species and the mechanism responsible for deposition. Deposit formation is influenced strongly by system parameters, such as water and metal surface temperatures, water velocity, residence time and the nature of metallic materials. The most severe deposition is encountered in process equipment operating with high surface temperatures and/or low water velocities. Deposits are broadly categorized as scale or foulants [65].

4.4.7.1. Scale formation and its control

Scale deposits are formed by precipitation and crystal growth at a surface in contact with water. Precipitation occurs when the solid solubility of inorganic compounds either in the bulk water or at the metal surface are exceeded. The most common scale forming salts that deposit on heat transfer surfaces are those that exhibit retrograde solubility with temperature. Scale formation is not always related to temperature. Calcium carbonate and calcium sulphate scaling occurs on unheated surfaces when their concentration saturates, exceeding solubility limits in the bulk water. Metallic surfaces are ideal sites for crystal nucleation because of their rough surfaces and the low velocities adjacent to the surface. Corrosion cells on the metal surface produce areas of high pH, which further promote the precipitation of many cooling water salts. Once formed, scale deposits initiate additional nucleation, and crystal growth proceeds at an accelerated rate.

Scale formation can be controlled through operation of the cooling system at sub-saturated conditions or through the use of chemical additives or anti-scaling compounds.

The most direct method of inhibiting formation of scale deposits is operation at sub-saturation conditions, where scale forming salts are soluble. For some salts, it is sufficient to operate at low cycles of concentration and/or control pH. However, in most cases, high blow down rates and low pH are required so that solubility limits are not exceeded at the heat transfer surface. In addition, it is necessary to maintain precise control of pH and concentration cycles. Minor variations in water chemistry or heat load can result in scaling.

4.4.7.2. Chemical additives to control scale formation

Scaling can be chemically and effectively controlled by the use of sequestering agents and chelates, which are capable of forming soluble complexes with metal ions. The precipitation properties of these complexes are not the same as those of the metal ions. Classic examples of these materials are ethylenediaminetetraacetic acid (EDTA) for chelating calcium hardness, and polyphosphates for iron. Since this approach requires stoichiometric chemical quantities, its use is limited to waters containing low concentrations of the metal. Deposit control additives that inhibit precipitation at dosages far below the stoichiometric level required for sequestration or chelation are called ‘threshold inhibitors’. These materials affect the kinetics of the nucleation and crystal growth of scale-forming salts and permit super-saturation without scale formation. Threshold inhibitors function by an adsorption mechanismwhich delays or retards the rate of precipitation. Crystals eventually form, depending on the degree of super-saturation and system retention time. After stable crystals appear, their continued growth is retarded by adsorption of inhibitor. The inhibitor blocks much of the crystal surface, causing distortions in the crystal lattice as growth continues. The distortions (defects in the crystal lattice) create internal stresses, making the crystal fragile. Tightly adherent scale deposits do not form because crystals that form on surfaces in contact with flowing water cannot withstand the mechanical force exerted by the water. The adsorbed inhibitor also disperses particles due to its electrostatic charge and prevents the formation of strongly bound agglomerates.

The most commonly used scale inhibitors are low molecular weight acrylate polymers and organophosphorus compounds (phosphonates). Both classes of materials function as threshold inhibitors; however, the polymeric materials are more effective dispersants. Selection of a scale control agent depends on the precipitating species and its degree of super-saturation. The most effective scale control programmes use both a precipitation inhibitor and a dispersant. In some cases, this can be achieved with a single component (e.g. polymers used to inhibit calcium phosphate at near neutral pH).

4.4.7.3. Langelier saturation index

The Langelier Saturation Index (LSI) is defined as the difference between the actual pH (as measured with a potentiometer) and the pH at which the water is saturated. It is calculated as a function of hardness due to calcium (in terms of calcium carbonate), total alkalinity of the water (also in terms of $CaCO_3$), total dissolved solids in ppm and the temperature in °F. This index is a qualitative indication of the tendency of calcium carbonate to deposit or dissolve. If the LSI is positive, calcium carbonate tends to deposit: if it is negative, calcium carbonate tends to dissolve. If it is zero, the water is at equilibrium. The LSI measures only the directional tendency or driving force for calcium carbonate to precipitate or dissolve. It cannot be used as a quantitative measure. Two different waters, one of low hardness (corrosive) and the other of high hardness (scale-forming), can have the same LSI.

The Stability Index developed by Ryzner makes it possible to distinguish between two such waters. This index is based on a study of actual operating results with waters having various LSI, and is defined as:

$$\text{RSI} = \text{Ryzner's Stability Index} = 2(\text{pHs}) - \text{pHa} \qquad (51)$$

where pHs is the saturated pH, as defined by Ryzner [65] and pHa is the actual pH of the water solution.

In waters with a RSI of 6.0 or less, scaling increases and the tendency to corrode decreases. In waters where the RSI exceeds 7.0, scaling may not occur at all. As the RSI rises above 7.5 or 8.0, the probability of corrosion increases. Use of the LSI together with the RSI contributes to more accurate prediction of the scaling or corrosive tendencies of the water.

4.4.7.4. Fouling and its control

Fouling occurs when insoluble particulates suspended in recirculating water form deposits on a surface. Fouling mechanisms are dominated by particle-particle interactions that lead to the formation of agglomerates. At low water velocities, particle settling occurs under the influence of gravity. Parameters that affect the rate of settling are particle size, relative liquid and particle densities, and liquid viscosity. The relationships of these variables are expressed by Stokes’ Law. The most important factor affecting the settling rate is the size of the particle. As a result, the control of fouling by preventing agglomeration is one of the most fundamental aspects of deposition control.

Foulants enter a cooling system with make-up water, airborne contamination, process leaks, and as corrosion products. Most potential foulants enter with make-up water as particulate matter, such as clay, silt and iron oxides. The amount of particulate entering a cooling system with the make-up water can be reduced by filtration and/or sedimentation processes. However, pre-treatment operations of make-up water can introduce insoluble aluminium and iron hydroxides into the system.

Airborne contaminants usually consist of clay and dirt particles but can include gases such as hydrogen sulphide, which forms insoluble precipitates with many metal ions. Particles settle when the energy imparted by fluid velocity no longer suspends the particle. After the particles have settled, the nature of the deposit depends on the strength of the attractive forces between the particles themselves (agglomerate strength) and forces between the particles and the surface they contact. If attractive forces between particles are strong and the particles are not highly hydrated, deposits are dense and well structured; if the forces are weak, the deposits are soft and pliable. Deposition continues as long as the shear strength of the deposit exceeds the shear stress of the flowing water.

4.4.7.5. Removing the particulate matter

Fouling can be controlled using a variety of methods [65]. The most common are filtration and sedimentation processes, which can be done with the make-up water, and with the circulating cooling water. However, these methods do not remove all of the suspended matter from the cooling water, and other methods may be necessary. Particle removal depends on the method used, the water velocity and the cycles of concentration maintained in the cooling tower.

4.4.7.6. Influence of high water velocities in fouling

The ability of high water velocities to minimize fouling depends on the nature of the foulant. Clay and silt deposits are more effectively removed by high water velocities than aluminium and iron deposits, which form interlocking networks with other precipitates. Operation at high water velocities is not always a viable solution to clay and silt deposition because of design limitations, economic considerations, and the potential for EC.

4.4.7.7. Use of dispersants to inhibit fouling

Dispersants are materials that suspend particulate matter by adsorbing onto the surface of the particles and imparting a high charge. Electrostatic repulsion between like-charged particles prevents agglomeration, which reduces particle growth. The presence of a dispersant on the surface of a particle also inhibits the bridging of particles by precipitates that form in the bulk water. The adsorption of the dispersant makes particles more hydrophilic and less likely to adhere to surfaces. Thus, dispersants affect both particle-to-particle and particle-to-surface interactions. The most effective and widely used dispersants are low molecular weight anionic polymers. Dispersion technology has advanced to the point at which polymers are designed for specific classes of foulants or for a broad spectrum of materials. Acrylate based polymers are widely used as dispersants; they have advanced from simple homopolymers of acrylic acid to more advanced copolymers and terpolymers. The performance characteristics of the acrylate polymers are a function of their molecular weight and structure, together with the types of monomeric units incorporated into the polymer backbone.

4.4.7.8. Use of surfactants to prevent fouling

Surface-active or wetting agents are used to prevent fouling by insoluble hydrocarbons. They function by emulsifying the hydrocarbon through the formation of micro-droplets containing the surfactant. The hydrophobic (‘water-hating’) portion of the surfactant is dissolved within the oil drop, while the hydrophilic (‘water-loving’) portion is at the surface of the droplet. The electrostatic charge imparted by hydrophilic groups causes the droplets to repel each other, preventing coalescence. Through a similar process, surfactants also assist in the removal of hydrocarbon containing deposits.

4.4.7.9. *Cycles of concentration*

Water circulates through the heat exchangers and the cooling tower at a rate referred to as the ‘recirculation rate’. Water is lost from the system through evaporation and blow down. For calculation purposes, blow down is defined as all non-evaporative water losses (windage, drift, leaks and intentional blow down). Make-up is added to the system to replace evaporation and blow down. As pure water is evaporated, minerals are left behind in the circulating water, making it more concentrated than the make-up water. ‘Cycles of concentration (or ‘cycles’) are a comparison of the dissolved solids level of the blow down with the make-up water. At three cycles of concentration, blow down has three times the solids concentration of the make-up. Cycles of concentration are calculated by comparing the concentrations of a soluble component in the make-up and blow down streams, as follows:

$$\text{Cycles (of concentration)} = \text{Concentration in Blow down}/\text{Concentration in Make-up} \tag{52}$$

If no other technique is used for particle removal, a ‘cycle of concentration’ limit of 3 is recommended for open cooling circuits of research reactors, to prevent precipitation of certain dissolved constituents and consequent formation of deposits [66]. Cooling systems in general can be operated at higher cycles of concentration and/or higher pH when appropriate scale and deposits inhibitors are used. These scale or deposit inhibitors, which belong to one of the four types, namely flocculants, dispersants, chelates and phosphonates (or polyphosphonates), are chemicals added in small quantities to inhibit the formation of deposits. Because chloride and sulphate are soluble even at very high concentrations, they are good choices for measurement. However, the calculation results could be invalid if either chlorine or sulphuric acid is fed to the system as part of a water treatment programme.

Cycles based on conductivity are often used as an easy way to automate blow down. However, cycles based on conductivity can be slightly higher than cycles based on individual species, due to the addition of chlorine, sulphuric acid and treatment chemicals.

To manage the quality of water in the system keeping control on the limit on concentration of dissolved solids, a simple equation is developed:

$$MU = BD + E = \text{Cycles} * BD \tag{53}$$

where:

BD is the blow down rate;
MU is the make-up rate, which includes evaporation (E) plus BD.

From this equation, we obtain that: BD = E/(cycles-1), a very useful equation in cooling water treatment. After the cycles of concentration have been established, based on make-up and blow down concentrations, the actual blow down required to maintain the system at the desired number of cycles, can be calculated. Because treatment chemicals are not lost through evaporation, only treatment chemicals lost through blow down (all non-evaporative water loss) must be replaced. Thus, calculation of blow down is critical in determining treatment feed rates and costs.

As the concentration of dissolved solids increases, corrosion and deposition tendencies also increase. Because corrosion is an electrochemical reaction, higher conductivity due to higher dissolved solids increases the corrosion rate. It becomes progressively more difficult and expensive to inhibit corrosion as the specific conductance approaches and exceeds 10 000 µS/cm. Some salts have inverse temperature solubility; i.e. they are less soluble at higher temperature and thus tend to form deposits on heat exchanger tubes. Many salts also are less soluble at higher pH. As cooling tower water is concentrated and pH increases, the tendency to precipitate scale-forming salts increases. Because it is one of the least soluble salts, calcium carbonate is a common scale former in open recirculating cooling systems. As explained, calcium carbonate can precipitate as a result of decomposition of bicarbonates, which are usually present in natural waters. The solubility of calcium sulphate decreases drastically at temperatures above 45ºC. This compound precipitates when the water temperature increases, forming hard deposits on heat exchanger surfaces. Calcium and magnesium silicates formed by reaction between these cations and silica present in the water also precipitate and form hard deposits in cooling circuit components. Corrosion products such

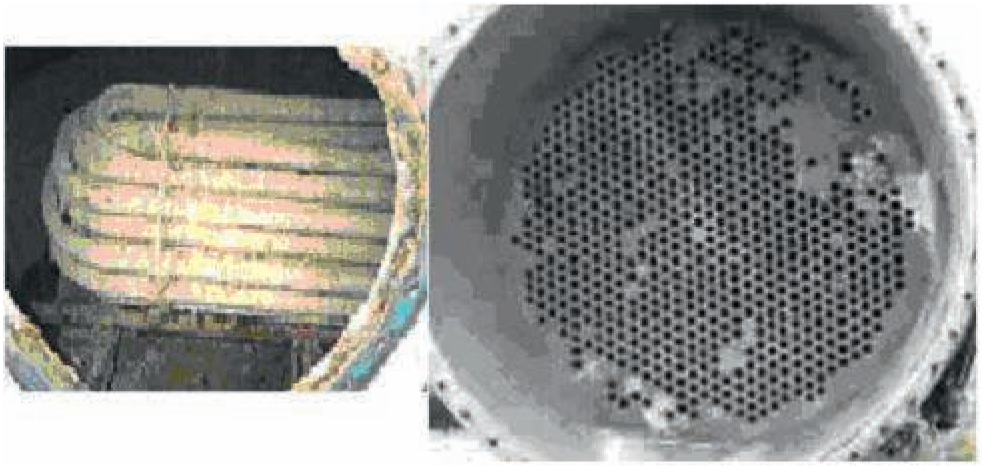

FIG. 21. Scale formation in and on heat exchanger tubes.

as iron oxides form voluminous deposits that often restrict the passage of water through heat exchanger tubes and reduce overall process efficiency, as illustrated in Fig. 21.

The following reactions show how the above-mentioned compounds form:

$$Ca(HCO_3)_2 \rightarrow CaCO_3 + CO_2 + H_2O \quad (54)$$

$$CaSO_4 + 2H_2O \rightarrow CaSO_4.2H_2O \quad (55)$$

$$Mg^{2+} + SIO_2 + H_2O \rightarrow MgSiO_3 + 2\ H^+ \quad (56)$$

$$Ca^{2+} + SIO_2 + H_2O \rightarrow CaSiO_3 + 2H^+ \quad (57)$$

$$2Fe^{2+} + 4OH^- + H_2O + ½\ O_2 \rightarrow Fe_2O_3.\ H_2O + 2H2O \quad (58)$$

4.4.8. Microbiological growth or biofouling in secondary cooling systems and their control

Microbiological fouling in cooling systems is the result of growth of microbes, algae, fungi, and bacteria on surfaces. Such fouling is more extensive in open recirculating systems which scrub microbes from the air and, through evaporation, concentrate nutrients present in make-up water. As a result, microbe growth is more rapid. In addition to the availability of nutrients, factors such as temperature, pH range, and continuous aeration of the cooling water contribute to an ideal environment for microbial growth, as shown in Fig. 22. Sunlight necessary for growth of algae may also be present. As a result, large, varied microbial populations may develop. The outcome of uncontrolled microbial growth on surfaces is ‘slime’ formation. Slimes are typically aggregates of biological and non-biological materials. Slimes can form throughout once-through and circulating systems. Microbial activity under deposits or within slimes can accelerate corrosion rates. Figure 23 illustrates a failure due to microbial accelerated corrosion.

Biofilms develop slowly at first because only a few organisms can attach, survive, grow and multiply. As populations increase exponentially, the depth of the biofilm increases rapidly. Biofilm polymers are sticky and aid in the attachment of new cells to the colonized surface as well as the accumulation of non-living debris from the bulk water. Such debris may consist of various inorganic chemical precipitates, organic flocs and dead cell masses. Fouling results from these accumulative processes, together with the growth and replication of cells already on the surface and the generation of additional polymeric material by these cells. When fouling occurs, even mechanical cleaning does not remove all traces of the biofilm. Previously fouled and cleaned surfaces are more rapidly colonized than new surfaces. Residual biofilm materials promote colonization and reduce the lag time before significant fouling reappears. Biofilms on heat exchange surfaces act as insulating barriers. Heat exchanger performance begins to deteriorate as soon as biofilm thickness exceeds that of the laminar flow region. A small

FIG. 22. Microbiological growth on tube surfaces.

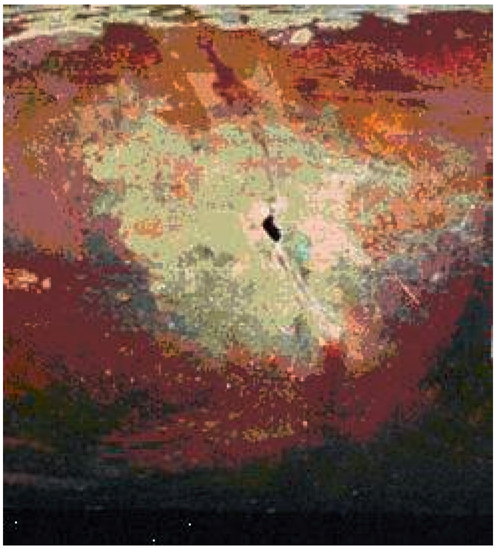

FIG. 23. Failure caused by microbial accelerated corrosion.

increase in the apparent thickness of the laminar region due to biofilm growth has a significant impact on heat transfer. A thin biofilm reduces heat transfer by an amount equal to a large increase in exchanger tube wall thickness. For example, the resistance to heat transfer of a 1 mm thick accumulation of biofilm on a low carbon steel exchanger wall is equivalent to an 80 mm increase in tube wall thickness.

Biofilms can influence corrosion of fouled metal surfaces in a variety of ways (Fig. 24). Depending on the materials involved, the microbial reactions can accelerate ongoing corrosion processes, and even the byproducts of microbial reactions can also be aggressive to the metal. Additionally, biofilms can prevent corrosion inhibitors from reaching the metal surface for passivation. All these process are referred to as microbial influenced corrosion (MIC).

A slime control programme involves frequent monitoring of cooling systems. Regular monitoring of system data can identify trends, and periodic system inspections can reveal whether or not fouling is occurring. Test coupons and test heat exchangers can also be used in operating systems to facilitate monitoring without interrupting system operation. Deposits collected from cooling systems can be analysed in the laboratory to determine their chemical composition and biological content. If a deposit has a significant microbiological content, its contents should be identified for treatment. The laboratory can identify the agents as predominantly algal, bacterial or fungal, either microscopically or by routine cultural isolation and identification. Microbial counts can also be performed to determine whether populations within the system are stable, increasing or decreasing. Sole reliance on bulk water counts will not provide sufficient information on the extent of surface fouling. Results must be

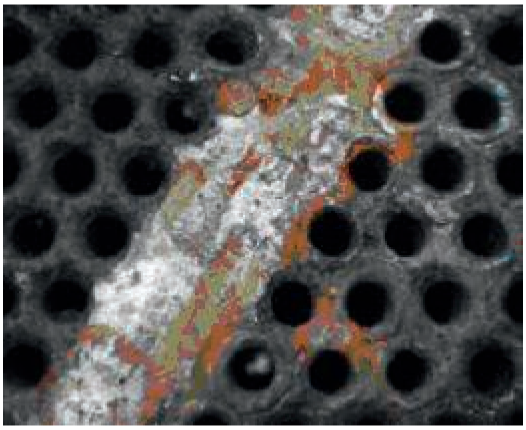

FIG. 24. Microbial influenced corrosion with consequent blocking of heat exchanger tubes.

interpreted in light of operating conditions at the time of sample collection. For example, in an untreated system, a healthy, stable biofilm population may be present while bulk water counts are low, because few sessile organisms are being released from the fouled surface. If an antimicrobial is applied, bulk water counts may actually increase dramatically. This is due to disruption of the biofilm and sloughing of sessile organisms into the bulk water [65].

For a better diagnosis, it is necessary to use microbial monitoring techniques that allow more direct assessment of surface conditions. It is possible to clean a known surface area and suspend removed organisms in a known volume of sterile water. After this water is plated, back-calculation provides an approximation of the number of organisms on the original surface. Another technique involves monitoring biochemical activity on a surface of a known area. A biofouled specimen is incubated with a suitable substrate. The concentration of reaction product found after a specific contact time relates to the numbers and health of organisms on the surface, and consequently can be used as a measure of biofouling.

Regardless of which target population or monitoring technique is used, a single, isolated data point has little meaning. Various data must be compiled to generate a profile of microbiological trends in the system. This record should also include observations on equipment performance and operating conditions at the time of sample collection, thereby providing a meaningful context for interpretation of new data. After it is determined that treatment is necessary to solve a fouling problem, an effective product must be chosen. Preliminary choices may be made only if the causative microbial agent is known, because the spectrum of activity of all antimicrobials is not the same: some effectively control algae but not bacteria; for others, the reverse is true.

Knowledge of how different antimicrobials affect microorganisms is also useful in choosing the appropriate treatment. Some kill the organisms they contact. Others inhibit growth of organisms but do not necessarily kill them. These biostats can be effective if a suitable concentration is maintained in the system for a sufficient time (a continuous concentration is ideal). A laboratory evaluation of the relative effectiveness of antimicrobials should be performed. This helps to identify those likely to work against the fouling organisms in the system and to eliminate those with little chance of success. Because the goal of antimicrobial treatment is control or elimination of biofilm organisms, it is helpful to conduct the evaluation with sessile organisms found in deposits, as well as planktonic organisms in the flowing water.

Generally, cleanup of a fouled system requires higher concentrations of intermittently fed treatment, while maintenance of a clean system can be achieved with low level continuous or semi-continuous feed. Given a certain level of fouling, the shorter the exposure time allowed by system operating conditions, the higher is the required antimicrobial concentration. Conversely, if exposure times are long, control of the same level of fouling may be achieved with lower antimicrobial dosages.

Circulating systems can be treated continuously or intermittently, although intermittent treatment programmes are more common. The purpose of intermittent treatment in these systems is to generate a high concentration of antimicrobial, which will penetrate and disrupt the biofilm and eventually dissipate. When the treatment level drops below the toxic threshold, microbial growth begins again. After a period of multiplication, new growth is removed with another shock dose. As stated earlier, previously fouled surfaces can be re-colonized at an accelerated rate. Therefore, the period for growth and removal may vary within a system and will certainly vary among systems, even those using the same water source.

In the planning of a slime control programme, any chemical demand of process waters for the antimicrobial being used must also be considered. Failure to allow for the chemical demand may prevent attainment of the necessary threshold concentration and may lead to the failure of the treatment programme. The compatibility of the antimicrobial with other treatments added to the water should also be considered. Many system variables influence the behaviour of microbes in the system, and the effects of antimicrobials can also be influenced by these variables. Therefore, careful consideration must be given to the determination of whether, when and where to treat a cooling water system.

Antimicrobials used for microbiological control can be broadly divided into two groups: oxidizing and non-oxidizing. Examples of oxidizers are chlorine and bromine. Only a relative distinction can be made between oxidizing and non-oxidizing antimicrobials, because certain non-oxidizers have weak to mild oxidizing properties. The more significant difference between the two groups relates to mode of action. Non-oxidizing antimicrobials exert their effects on microorganisms by reaction with specific cell components or reaction pathways in the cell. Oxidizing antimicrobials are believed to kill by a more indiscriminate oxidation of chemical species on the surface or within the cell. An understanding of the chemistries and modes of action of antimicrobials is needed to ensure their proper use and an appreciation of their limitations. Two characteristic mechanisms typify many of the non-oxidizing chemicals applied to cooling systems for biofouling control: in one mechanism, microbes are inhibited or killed as a result of damage to the cell membrane; in the other, microbial death results from damage to the biochemical machinery involved in energy production or energy utilization.

Quaternary ammonium compounds are cationic surface-active molecules. They damage the cell membranes of bacteria, fungi and algae. At low concentrations, these compounds are biostatic because many organisms can survive in a damaged state for some time. However, at medium to high concentrations, quaternary ammonium compounds can control the organisms.

Many antimicrobials interfere with energy metabolism. Because all microbial activity ultimately depends on the orderly transfer of energy, it can be anticipated that interference with the many energy-yielding or energy trapping reactions will have serious consequences for the cell. Antimicrobials known to inhibit energy metabolism include organotins, bis (trichloromethyl) sulfone, methylenebis (thiocyanate) (MBT), Beta-bromo-Beta-nitrostyrene (BNS), dodecylguanidine salts, dibromonitrilopropionamide (DBNPA) and bromonitropropanediol (BNPD). All of these compounds are effective when applied in sufficient concentrations. Dodecylguanidine salts also have surfactant properties, which probably contribute to their effectiveness. Some antimicrobials used in cooling systems are compounds that spontaneously break down in water, thereby alleviating some potential environmental hazards. This chemical breakdown is often accompanied by a reduction in the toxicity of the compound. The compound can be added to the cooling water system, accomplish its task of killing the microbes in the system, and then break down into less noxious chemicals. Among the antimicrobials that have this attribute are BNS, MBT, DBNPA and BNPD [65].

4.4.9. Chemical treatment programmes for secondary circuit systems

In a conventional chemical treatment programme, an oxidizing biocide is added in combination with scale and corrosion inhibitors to the secondary system.

The amount of specific chemicals to be added as corrosion inhibitors, or as a dispersant or as a biocide depend on aspects related to the system and the nature of the chemical product. These aspects include: the extent of use of the secondary circuit (continuous or intermittent); the size of the system; the materials of construction of the heat exchanger and the cooling towers; the contaminants in the water (which are often site specific); the extent to which the environment is polluting in the vicinity of the research reactor installation; whether the region is tropical or temperate; the ratio of water volume to metal surface area; the specific chemicals in the corrosion inhibitor; the dispersant or anti-deposit agent and the biocide (which varies with the supplier and dictates other water parameters such as pH, requiring the addition of other chemicals). Recommendations for water chemistry limits for the secondary system are provided in Section 6.3.

Hence, a set of procedures to treat secondary circuit water is site-specific; but there are some common aspects. The chemicals supplied by the local supplier would often require dilution and the diluted solutions are dosed into the system with the help of dosing pumps. Separate dosing pumps are often recommended for the different products. The amount to be dosed is dictated by the nature of the product and other parameters. Several aspects need to be considered. Some of the product is lost in the blow downs. System water losses also include those due to drift and evaporation. Drift involves loss of chemical products, while evaporation does not. Hence, if the cycles of concentration are specified (which depends on the type of cooling tower and the nature of the corrosion inhibitor), the amount of blow down is calculated. Drift and evaporation losses are system dependent and often specified by the cooling tower manufacturer. Knowing these three parameters, the amount of make-up water and chemicals lost are calculated, and the latter accordingly added to the system with dosing pumps.

The programme is complemented with a corrosion surveillance programme, as recommended in Section 7.3.

5. MEASURING DEVICES AND METHODOLOGY

5.1. INTRODUCTION

An essential part of a water quality management system is a sampling programme in which sampling frequency, collection positions and sampling procedures are well defined. Many documents specify the parameters and recommended levels for water quality management, yet very few discuss the methods, procedures, collecting points, on-line methods vs. grab samples, equipment and frequency of measurement. This Section provides a comprehensive overview of practical information on water sampling and analysis for good water quality management. Water parameters and constituent species discussed in this Section are based on those from the list of the main parameters discussed in Section 2. Recommendations of limits for specific water parameters and constituent species for research reactor systems are discussed in Section 6.

5.2. ON-LINE VERSUS OFF-LINE MEASUREMENTS

A distinction can be made between ‘on-line’ and ‘off-line’ measurements. On-line measurements provide near immediate information on the most important water quality parameters such as pH, conductivity and temperature. On-line measurements are typically performed with a high frequency (from several times per 24 hours up to continuously) at a fixed position in the reactor water system, e.g. in the outlet pipe of the primary cooling water. The measurement can be made directly on the mainstream, with the measuring device in contact with the fluid, or a small fraction of the cooling water is (automatically) tapped and transferred to a measuring device. The results are logged and processed in the control room. In this way, deviations from normal operating conditions are readily revealed, leaving enough time for investigation actions, such as an inspection of the performance of the resin beds and mitigation actions, as needed. On-line methods are available for pH, conductivity, temperature, redox potential, various ionic species (Cl^-, F^-, Na^+ , K^+) using ion selective electrodes, dissolved organic compounds (DOC) and gamma spectrometry.

In order to keep the amount of radioactive waste to a minimum, it is recommended to have the devices designed such that the tapped volume of cooling water is returned into the system after analysis.

Off-line measurements are typically performed with a lower frequency, up to several times a year. They are made with the aim of confirming the calibration of devices used for on-line measurements, to allow measurements from other points of the system (where on-line measurements are not feasible), or to allow a more detailed analysis of the composition of the water. In this case, water samples are manually taken at fixed positions and analysed in a laboratory to determine the concentrations of the different species. The analytical procedures are usually more time consuming and complex. The results allow a more detailed analysis of the composition of the cooling water and provide insight into the evolution of water composition on a long term basis, which may act as a basis for future actions with regard to, for instance, the maintenance of resin beds.

Off-line measurements may also be considered in case the results from on-line measurements fall outside preset limits established in the water quality management programme and other known conditions, such as the need for the regeneration of the resin beds, do not give a satisfactory explanation. Off-line measurements may then provide additional information to determine the cause of such abnormalities.

5.3. RECOMMENDED EQUIPMENT AND TECHNIQUES

At present, a wide range of analytical equipment is commercially available. Table 8 presents a list of equipment and well-established analytical techniques available for determination and analysis of the various parameters and constituents of water. These techniques are summarized in this section.

Several techniques must be applied to obtain a complete analysis of the water sample. There is no such thing as ‘the’ single technique that provides a complete set of water quality information. The final choice of the equipment to be used is largely dictated by the availability of the chemical-analytical infrastructure. Yet, some remarks and recommendations with regard to the selection of the techniques can be made.

5.3.1. pH

The pH is probably one of the most frequently measured parameters in water chemistry. Most popular pH sensors are similar to the one shown in Fig. 25, which uses a glass membrane as the pH sensitive medium. The

TABLE 8. ANALYTICAL TECHNIQUES AND EQUIPMENT FOR DETERMINATION AND ANALYSIS OF WATER PARAMETER AND CONSTITUENTS

Parameter/constituent	Equipment/technique
pH	pH metre
Conductivity	Conductometer
Temperature	Thermocouple or RTD
Fe^{2+}	ICP-MS, ICP-AES, AAS
Cu^{+}	ICP-MS, ICP-AES, AAS
Al^{3+}	ICP-MS, ICP-AES, AAS
Ag^{+}	ICP-MS, ICP-AES, AAS
Cl^{-}	IC, ISE, UV-VIS
NO_2^-	IC, colourimetry
TSS	Analytical balance
^{137}Cs	Gamma spectrometry
Na^{+}	ICP-MS, ICP-AES, AAS
K^{+}	ICP-MS, ICP-AES, AAS
Ca^{2+}	ICP-MS, ICP-AES, AAS
Mg^{2+}	ICP-MS, ICP-AES, AAS
Hg+	ICP-MS, AAS
NO_3^-	IC, colourimetry
NH_4^+	IC, colourimetry
CO_3^{2-}	IC
H_2O_2	Fluorimetry
O_2 (dissolved)	Membrane electrode
^{3}H	LSC
^{60}Co	Gamma spectrometry
$^{131}I/^{133}I$	Gamma spectrometry

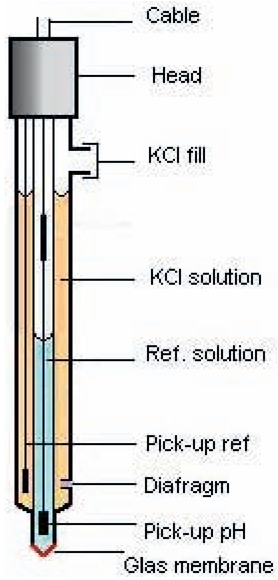

FIG. 25. Combined glass electrode.

potential of the glass membrane is picked up at the inner side of the membrane, and a reference electrode is separated from the water sample by means of a diaphragm or a conductive gel.

Despite numerous technical advances, pH determination is still not straightforward. The measurement is strongly influenced by the composition of the water, its temperature and its conductivity [67, 68]. Care must be taken when using conventional equipment. The ion-poor or low conductivity character of cooling water, in combination with the high electrical resistance of the sensing glass membrane of conventional glass electrodes, significantly hampers accurate determination of the pH resulting incorrect results. The use of pressurized electrodes allows measurements under pressure.

5.3.2. Conductivity

A wide range of conductometers are available; a meter with an analysis domain between 0 and 1000 µS/cm is recommended. It is common for the various instruments available that measurements of a sample with a very high — or in contrast — a very low conductivity may be problematic.

The conductivity equipment is more robust than a pH meter and is less sensitive to upsets in the system, making the conductivity a more reliably measured parameter for assessment of the water quality.

For laboratory measurements, Pt black surface type electrodes, as shown in Fig. 26, or goldplated stainless steel electrodes are recommended. It is also recommended that the measurement of conductivity should be performed using alternating current (AC) in order to prevent polarization of the electrodes.

5.3.3. Temperature

There are a series of devices that can be used for temperature measurements. The most common are thermocouples resistance temperature detectors (RTDs). Thermocouples use the principle discovered by Thomas Seebeck in 1821, that an electromotive force (emf) is created whenever the two extremes of a metal wire are subject to different temperatures. Joining one extremity of two dissimilar metals, the emf measured on the other extremity is proportional to the temperature difference between the two extremities. Because they have been widely used, a series of standards have been established for thermocouples, including specific pair of wires, connectors, geometry and types of junctions. Standard tables have been also developed correlating the emf, as a function of the measured temperature, for each type of thermocouple. The most common types of thermocouples are type J, type K, type E and type T. Table 9 shows the main characteristics of each of them [9].

FIG. 26. Conductivity electrode.

TABLE 9. MAIN CHARACTERISTICS OF MOST COMMON THERMOCOUPLES

Type of thermocouple	Wires	Temperature range (°C)
J	Fe versus (Cu + 43% Ni)	–210 to +1200
K	(Ni + 10% Cr) vs (Ni + 2% Al + 2% Mn + 1% Si)	–270 to +1372
E	(Ni + 10% Cr) vs (Cu + 43% Ni)	–270 to +1000
T	Cu vs (Cu + 43% Ni)	–270 to +400

RTDs use the principle that for some materials the electrical resistance is highly dependent of the temperature. Because of its high precision, Platinum is the most common type of RTD, and is sometimes referred to as platinum resistance thermometer (PRTs). Other elements used for RTDs are nickel and copper.

Once the specific thermocouple or RTD is properly calibrated, any one of them can be routinely used for measuring the temperature of the water in the cooling system. However the user must consider that Platinum RTDs present better precision and lower drift, i.e. better stability. Therefore, for high precision measurements of temperature, requiring deviations smaller than 0.5°C, Platinum RTDs are recommended. If higher deviations are accepted, then thermocouples can be used.

However, the signal from RTDs may be affected by neutrons and gamma radiation, therefore, for measurements close to the reactor core, thermocouples are recommended.

5.3.4. Analysis of metals

Inductively coupled plasma-mass spectrometry (ICP-MS) and inductively coupled plasma-atomic emission spectrometry (ICP–AES) are fully accepted techniques for metal analysis. ICP-MS is recommended by leading institutes such as the American Public Health Association and Water Environment Federation [69]. Both techniques have low detection limits for metals and offer the advantage of simultaneous (within one run) analysis of all metals in a sample. Up to the 1980s, atomic absorption spectrometry (AAS) was the leading technique for metal analysis. In particular, when equipped with a graphite furnace, this technique still is capable of producing high quality data. The main disadvantage of this technique is that it is time-consuming. In contrast to the ICP techniques, AAS is only capable of measuring one element at a time. In addition, for the analysis of Hg, the AAS must be equipped with a cold-vapour assembly.

5.3.5. Analysis of anions

Over the last decade, ion chromatography (IC) has become the leading technique for the analysis of anions, and in some special cases for metals as well. For most IC instruments, several chromatography columns for various sets of anions and cations are available. During an IC measurement run, all anions in a sample are sequentially measured depending on the selected column. Other relevant, well established techniques are ion selective electrode (ISE), ultraviolet spectrophotometry (UV-VIS) and colourimetry. ISE is still widely applied but more laborious than IC. Like AAS, only one element at a time is measured with ISE.

5.3.6. Other constituents

Dissolved oxygen: the use of an O_2 sensitive membrane electrode is recommended. This technique overcomes many of the limitations and restrictions of the classic iodometric method.

Tritium: Liquid scintillation (LSC) is a well-established technique for the determination of tritium activity (concentration) in aqueous solutions. Most radiological laboratories have access to LSC equipment.

Other radioactive nuclides (^{137}Cs, ^{60}Co, ^{131}I, etc.): Gamma spectrometry is the preferred technique to determine radioactive isotopes and their activity levels in aqueous samples, assuming that the activity is high enough. For lower level samples, larger volumes must be collected, which then must be dried/evaporated to increase the concentration of the radio isotopes before it is gamma counted. In some cases, such as ^{137}Cs, a carrier can be added before evaporation and the precipitate is then gamma counted.

5.4. SAMPLING

5.4.1. Selection of sampling points

Careful selection of the sampling sites is a very important consideration in a water quality management programme. In general, sampling should be performed at the locations where the water is expected to approximate the average composition for the entire water bulk of interest. If this is not the case, for example, a sampling location close to the resin beds, a non-representative composition of the water quality, is obtained, which in turn may lead to unnecessary or counterproductive measures. Therefore, the primary cooling or pool water should preferably be sampled straight from the main flow. Figure 27 shows recommended sampling points for pH measurements in a system with an on-line purification system. For the reactor pool, additional sampling points of the basin may be considered. However, it should be noted that basins are commonly equipped with ‘jet systems’ in order to keep the incoming water for a prolonged period at sufficient depth in order to minimize exposure to ^{16}N. This creates turbulence and circulation in the basin, leaving surface water as the most suitable candidate for analysis.

It is also important to point out that in some designs of reactor and/or fuel storage basin, regions with very low circulation flow, or even stagnated water are present. Due to the high probability that these regions can concentrate impurities, they need special attention. In order to be conservative, it is recommended that the worst position (with lowest circulation flow) be selected as the sampling location, and specific sampling procedures be established for these points.

5.4.2. Collecting samples

ISO 5667–3:2003 [70] gives general guidance on the precautions to be taken to preserve and transport all water samples including those for biological analyses but not those intended for microbiological analysis. These guidelines are particularly appropriate when spot or composite samples cannot be analysed on-site and have to be transported to a laboratory for analysis.

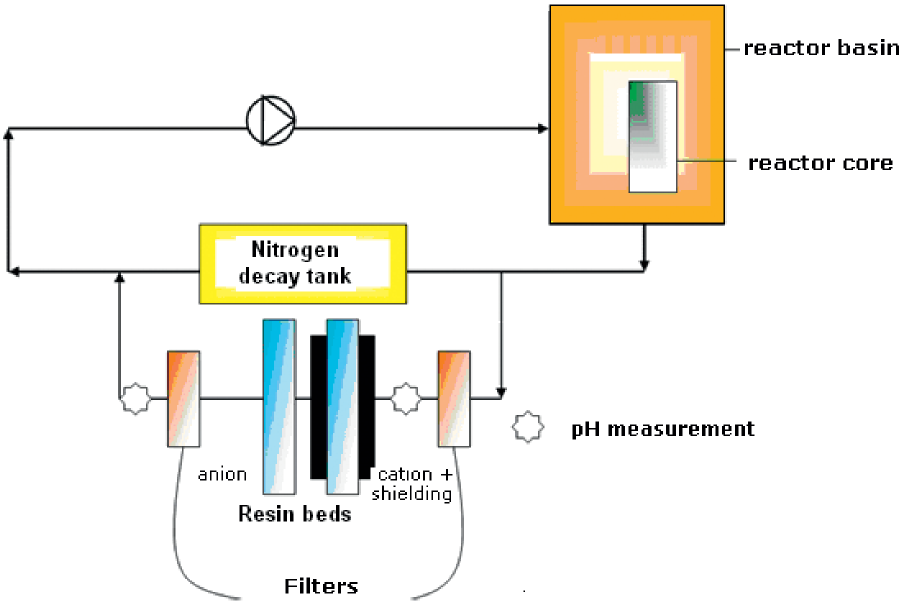

FIG. 27. *Example of sampling point locations.*

5.4.2.1. *Precautions to avoid contamination of the water sample*

The success-failure ratio of the analyses of aqueous samples highly depends on the precautions taken before and during the measuring procedure, including water sampling. An important complicating factor in the analyses of a medium such as cooling water is the (very) low concentration one is dealing with. As a result, even slight contamination of the samples may significantly influence the results which may have severe consequences for the water management programme. Contamination sources may be external as well as internal. A well known source of external contamination is 'fingertip' — contact between relatively pure water and any piece of equipment that has been held in the hand may easily be contaminated with NaCl. Another notorious external source is dust. Sample bottles should never be left open exposed to open air. Internal contamination sources are remnants or traces of other samples which have polluted other samples. Thorough cleaning of all devices and equipment minimizes the risk of external contamination.

5.4.2.2. *Sample bottles*

Off-line measurement programmes may involve repeated analysis of one sample by several techniques. Therefore, sufficient large sample volumes are necessary. Samples for measurement of the individual anions and cations require sample volumes of 50 to 100 ml. Care must be taken of the containers in which the samples are collected and stored. HDPE screw-lock bottles, as shown in Figure 28, are recommended. Given the low concentrations of the individual cations and anions in cooling water, it is of utmost importance that the containers are thoroughly cleaned. Care should be taken that cleaning is performed in a clean, ventilated environment. After cleaning, preferably with a dishwasher, the containers should be thoroughly rinsed with ultra pure water and alcohol and dried in upside down position on a tissue before the lock is put on its place. The cleaned bottles should be stored in a closed cabinet.

Use of disposable gloves is strongly recommended to prevent contamination of the containers and lock. Direct contact with the fingers may result in erroneous results especially for Na and Cl.

5.4.2.3. *Sampling from a basin*

When a sample is needed from the top of the basin, the sample bottle can just be submerged and filled. First, rinse the bottle by filling it with the water to be sampled and discarding the contents three times, then fill the bottle

FIG. 28. Typical HDPE bottle.

and close it as soon as possible. If particles are present at the surface of the basin water, they will tend to skim from the region where the sample will be taken.

5.4.2.4. Sampling from a sample point in a tube

If the circuit contains a sampling point, relief valve or water tap, the sample can be collected there. As in the previous case, by filling the bottle with the water to be sampled and discarding the contents three times before sampling, the contamination risk is minimized. To avoid contamination from air, or if wanting to measure dissolved gases in the sample, the bottle should be placed in a clean bucket, allowing the water to flow in the bottle (30 minutes is a typical value). The bottle is then closed under the water level in the bucket.

5.4.2.5. Water (reagent)

Water is a frequently used reagent during chemical analyses of samples; it is used to dilute acids or samples. In addition, water is used to clean and rinse laboratoryequipment and devices. In order to avoid (external) contamination of cooling water samples, it is necessary to use ultra pure water.

Several types of water cleaning devices to clean the sampling apparatus or to dilute reagents or samples as part of the sample procedure are commercially available. These devices generate ultra pure water from ordinary tap water. Most devices allow for the production of water with different grades of purity. The use of reagent water with a resistance of 18.2 MΩcm is recommended. Storage of the ultra pure water in teflon bottles is preferred.

5.4.2.6. Pipette tips

Pipettes are used during the various stages of sample preparation and analyses. Pipette tips should be disposed of after use. Fresh tips are commonly supplied in cardboard boxes, making them vulnerable to contamination of dust and filth before use. It is therefore recommended to store the tips in a screw-top bottle with ultra pure water. After shaking to rinse the tips, the tips are stored in another bottle with fresh ultra pure water. Use of a pair of plastic tweezers is recommended when handling the tips. Prior to use, the tips are taken out with a set of plastic tweezers and dried in an oven at 40–50°C.

5.4.2.7. Sample preparation and storage

Care should be taken that the bottle is completely filled in order to minimize the effect of atmospheric CO_2 on the composition (pH) of the sample. After taking the water samples, the samples must be filtrated to get rid of particles that may disturb further processing and analysis of dissolved species. Filtration devices in vacuum with filters with a porosity of 0.45 μm are commonly used for this purpose. The filtered particles should be analysed separately.

After each use, the sample bottle or device is washed with demineralized water with a maximum conductivity of 0.3 µS/cm. It is then dried in the oven and kept for a new analysis. Before and at storage times during the processing of the sample, the sample bottles should preferably be stored in a refrigerator.

Acidification of the water samples for ICP/metal NH_4^+ analysis is a common practice to prevent the formation of precipitates during storage and processing of the samples. The addition of a small amount of commercially available ultrapure concentrated HNO_3 is recommended.

For IC, pH, conductivity and dissolved organic compounds (DOC) analysis, no sample preparation is needed, but the period after opening the bottle and analysis should be as short as possible. For occasional analysis of individual organic compounds, the common extraction pre-concentration procedures are sufficient.

5.5. PROCEDURES FOR WATER ANALYSIS

In general, the procedure for water analysis is facility and system dependent. Therefore, rather than prescribing a standard format for a procedure analysis of water samples, some generic aspects of the procedures, including consideration in their preparation, are highlighted. Well written procedures determine, to a high degree, the success of the analyses, independent of the type of reactor, cooling system and equipment used.

In order to improve procedures for ‘off-line’ measurements, it is recommended that they be revised or reassessed at least once every two years. Procedures for ‘on-line’ measurements are system dependent, and must be revised every time the system is modified, or whenever some deficiency is detected. It is also necessary to establish how to ensure the calibration of ‘on-line’ measurements. In general, this is done by ‘off-line’ measurements, but standard samples, such as those used for ‘off-line’ equipment can also be used. In general, it is always possible to check the method performance using solutions with known concentrations of components in comparable matrices and range, and use of control charts, e.g. a Shewhart chart, for the observation of long term performance. Also, information on repeatability and bias can be obtained analysing blind samples and participation in suitable round robins.

5.5.1. Analytical procedures or protocols

Most laboratories have well-established analytical protocols for the analyses of water samples by state of the art techniques. Therefore, reference is made to recommended analytical protocols jointly drafted by the American Public Health Association, the American Water Works Association and the Water Environment Federation in the Standard Methods for the Examination of Water and Wastewater [69].

Table 10 lists some suggested protocols for laboratorial analysis of water, including an estimate of the accuracy and precision. The recommended monitoring programme, with specific parameters for the water quality management of each system of a research reactor, is presented in Section 6.

6. RECOMMENDED PRACTICES FOR MANAGEMENT OF WATER QUALITY

Previous sections in this report described degradation of reactor fuel and structural materials in contact with water, methods to improve the quality of the water, and techniques to measure the water quality parameters. This Section provides recommendations for management of the water quality including:

- Limits to water quality parameters to avoid excessive degradation of the fuel and structural materials;
- Sampling of water to evaluate water quality parameters;
- Practices to maintain good water quality.

TABLE 10. LIST OF SUGGESTED PROTOCOLS

Parameter/ constituent	Device	Method	Accuracy (A), Precision (P)*
pH	pH meter	ISO 10523:1994 and ISO/DIS 26149 Water quality — Determination of pH Water quality — Determination of pH ASTM D 1293–78; Standard methods for the examination of the water and waste water, 21 edition 2005, section 4500-H^+	A ±0.1 unity
Conductivity	Conductometer	ISO7888:1985 Water quality — Determination of electrical conductivity ASTM D1125-77 Conductivity of water; Standard methods for the examination of the water and waste water, 21 edition 2005, section 2510	P 0.1–1.0%
TSS	Filters, filtration device, analytical balance, photometer	ISO 11923:1997 Water quality — Determination of suspended solids by filtration through glass-fibre filters ISO 7027:1999 Water quality — Determination of turbidity	
Cl^-	UV-VIS	Chloride in water, ASTM D 512-74	A 10–15%
Cl^-, SO_4^{2-}, NO_3^-	IC	ISO 10304-1:2007 Water quality — Determination of dissolved anions by liquid chromatography of ions — Part 1: Determination of bromide, chloride, fluoride, nitrate, nitrite, phosphate and sulphate ASTM Standard methods for the examination of the water and waste water, 21 edition 2005, section 4110	A ± 5%
Metals (cations)	ICP	ISO 11885:2007 Water quality — Determination of selected elements by inductively coupled plasma optical emission spectrometry (ICP-OES) ASTM Standard methods for the examination of the water and wastewater, 21 edition 2005, section 3125	P ±5%
Dissolved oxygen	Membrane electrode	ISO 5814:1990 Water quality — Determination of dissolved oxygen — Electrochemical probe method Standard methods for the examination of the water and waste water, 21 edition 2005, section 4500-O	A ± 0.1 mg/l P ± 0.05 mg/l
Beta, Tritium, I-131	Spectrometry	ISO 9697:1992 Water quality — Measurement of gross beta activity in non-saline water ISO 9698:1989 Water quality — Determination of tritium activity concentration — Liquid scintillation counting method *ASTM D4785–00a	

* ‘Accuracy’ is defined as the deviation of measured value from the true value, caused by systematic errors in the procedure, as determined on (international) standards, and ‘precision’ is defined as degree of agreement among replicate analyses on a sample.

Sections 6.1 to 6.4 list the recommended limits for water quality parameters, water sampling, and maintenance practices for: the primary circuit; the fuel cooling and storage basin; the secondary cooling circuit; and the water make-up system and reservoir, respectively. The limits are aimed at avoiding degradation to the most susceptible materials and components in the system. The limits are drawn from fundamental knowledge of effects of water on materials, from operational experience from reactor systems and other industrial water systems, and from expert knowledge of IAEA consultants.

Specific operational constraints at reactor sites may preclude meeting these recommended limits or there may be physical conditions in the system, for example, excessive sludge in a fuel storage pool, that impede meeting these limits immediately. In cases like this, a water quality management programme includes planning for actions to eliminate and/or mitigate the sources of impurities. Other conditions, such as an excursion in the water quality, may occur temporarily during operation.

In addition, a corrosion surveillance programme (CSP) is an important part of water quality management to support verification that the actual water quality conditions during operation in a reactor system are not causing significant corrosion to limit continued operation of the system, or if corrosion is observed, a timely response to the condition can be implemented. This topic is briefly discussed in this Section, and extensively in Section 7.

6.1. PRIMARY COOLING SYSTEM

6.1.1. Introduction

Typically, the primary cooling system includes the reactor tank or pool, the decay tank, the circulation pumps, the heat exchangers, and circulation piping as shown in Figures 15, 16 and 17 of Section 4.2, for low, intermediate and high power reactors, respectively. Some reactors may have more than one circuit to remove the total heat produced in the reactor; others may include a redundant circuit and, where installed, an anti-siphon system. In many cases, the primary cooling system is an open system in which an extension of the reactor pool is used as spent fuel decay and storage pool.

Water volume in the primary system can range from a few cubic metres, for very small power facilities, in which case water is mainly used as radiological shielding, to hundreds of cubic metres. To illustrate with figures, in the RA1 Research Reactor of Argentina, the water volume is 1.2 m^3, whereas the water volume in the primary system of the 14 MW TRIGA reactor, located in the Institute for Nuclear Research, in Pitesti, Romania, is approximately 700 m^3.

During operation of the reactor, the various components of the cooling system are constantly exposed to water. This constant exposure makes the cooling system potentially vulnerable to degradation processes including corrosion, EC and flow-induced fatigue or wear. Corrosion modes of attack are the primary forms of degradation and are strongly dependent on the quality of the cooling water.

As explained in Section 3.2, in research reactor systems, aluminium and aluminium alloys are very susceptible materials to localized corrosion attack (pitting, crevice and galvanic-couple). In case of fuel cladding, localized corrosion attack may lead to through clad breaches and result in the release of fission products into the system. Also, excessive corrosion reactions between the cooling water and the aluminium cladding of the fuel elements may potentially lead to general deterioration of the cladding and loss of good heat transfer conditions between the fuel and the cooling water. As noted in Section 1, for aluminium clad fuels, it is important to consider the conditions of reactor operation in order to avoid excessive oxide layer buildup that leads to a high metal/oxide interface temperature, especially when the reactor operates under high heat flux conditions. If this occurs, the corrosion process can be accelerated, endangering the integrity of the fuel elements and eventually promoting the release of fissile material and fission products into the primary cooling system. This effect is strongly dependent on the pH and temperature of the water, and relatively independent of all other water parameters [4]. Therefore, controlling the pH and temperature of the water is a pre-requisite for maintenance of good quality water in the primary cooling system.

The main objective of the recommendations that follow is to establish parameters and procedures in order to reduce the likelihood of corrosion attack on the aluminium clad fuel elements, and aluminium structures of the primary cooling system. These recommendations include those for stainless steel- and Zircaloy-clad fuels, and thus the limits are also appropriate to avoid corrosion of these cladding materials.

6.1.2. Recommended limits for water quality parameters in the primary cooling system

Pure water is of prime importance to keep high fuel performance, low overall circuit corrosion and low environmental radiation levels in a research reactor. Therefore, the primary cooling system has the most stringent requirements among all the reactor water systems.

In order to maintain good quality water in the primary system, it is recommended that its physical parameters be maintained within the values shown in Table 11. To accomplish this, a purification system (water purification and treatment system or filter deionizer system) (see Section 4.1), is needed to provide and maintain high quality water.

Note that for the water of the primary cooling system of a research reactor, continuous filtration, using the water purification system, is the only recommendation to eliminate impurities from the water, especially the Cl^-

TABLE 11. RECOMMENDED PHYSICAL-CHEMICAL PARAMETERS, LIMITS AND MONITORING FREQUENCIES FOR THE WATER IN THE PRIMARY SYSTEM OF A RESEARCH REACTOR

Parameter	Value (limit)	Monitoring frequency
Conductivity (*)	< 1.0 µS/cm	On-line; and confirmation of laboratory sample twice a week
pH (*)	Between 5 and 6.5	On-line; and confirmation of laboratory sample twice a week
Chloride (Cl^-)	< 0.05 mg/L	Twice per week laboratory sample
Carbon (from graphite)	< 0.05 mg/L	Once per year laboratory sample
Silver (total)	< 0.05 mg/L	Monthly laboratory sample
Copper (total)	< 0.05 mg/L	Monthly laboratory sample
Nitrate (NO_3^-), mg/L	< 0.05 mg/L	Twice per week laboratory sample
Dissolved substances	< 0.1 mg/L	Monthly laboratory sample
Fe (total)	< 0.1 mg/L	Monthly laboratory sample
Sulphate (SO_4^{2-}), mg/L	< 0.1 mg/L	Twice per week laboratory sample
Solids, mg/L	< 5 mg/L	Monthly laboratory sample
Ca, Na, Mg	< 50 ppb (each)	Once per month laboratory sample
Turbidity (***)	(See note below)	
Al, Zn, Sr, Ba, Pb, Cr, Co	< 50 ppb	Monthly laboratory sample
Radiation level (**)	(See note below)	Whenever a water sample is drawn

(*) For conductivity and pH, it is recommended to have on-line measurements on the inlet and outlet of the purification system, and to make periodic laboratory measurements from representative samples.

(**) In addition to the established in Section 6.1.3.1, a gamma scan of a water sample is recommended to identify the presence of radioisotopes that would have come from failed fuel (e.g. Cs-137) and that may have come from activated corrosion products (e.g. Fe-54). No specific limits are set. The minimum recommended frequency for the gamma scanning is once a month, and the presence of radioisotope species, and their limits, shall be evaluated on case by case basis. Additional monitoring for radioactivity is discussed in Section 6.1.3.

(***) Turbidity should be reduced, as necessary, to provide visual clarity in the water system.

ions, and maintain conductivity low. No chemical product will ever be used to adjust the parameters of the water on the primary cooling system.

A special note must be made with respect to graphite, given the deleterious effect it produces considering that it is cathodic with respect to aluminium. All the possible measures should be taken to avoid contact of graphite with water, especially if it used as a lubricant in fabrication of components inserted into the basin. Graphite is not easy to detect through chemical analysis; however, an estimation of the amount of loose graphite particles in the water can be performed by means of filtering and calcination. This method will give an approximation in excess, because it will also include some organic compounds.

The radioactivity level of the water is a useful indicator of water purity since it will increase by activation of products carried by the fluid through the reactor core. In addition, monitoring of water and/or ambient radioactivity is typically required for reactor safety reasons. The monitoring system is dependent on the reactor power, size and other characteristics. Ambient radioactivity detectors should be set in the reactor room, and also in other sections of the primary circuit: in pumps room, purification systems, and other rooms where personnel may be near. Activity limits must be set in accordance with requirements of the corresponding regulatory body for an operation licence, which is specific for each reactor.

Despite the stated conductivity limit value of the table (1 µS/cm), it is recommended that the purification system be designed so that with fresh or regenerated resins, the conductivity of the water leaving the purification system is below 0.3 µS/cm. This means that the resins should be regenerated when the water leaving the purification system reaches the defined target value of 0.3 µS/cm. Section 4.1 provides additional discussion of purification systems.

Considering that the water in the reactor pool can be contaminated with debris from inorganic and organic materials and microorganisms, which tend to accumulate on all exposed surfaces, the use of “skimmers” that constantly collect water from the pool surface is recommended in order to remove surface debris. It is also recommended to periodically aspire the surfaces of all structures and the bottom of the pool. For this operation, the aspired water shall be directed to an independent water system. It is recommended that this cleaning operation be done at least once every six months. Because collected products will cause an increase in exposed radiation dose, this operation must be performed under the supervision of the radiation protection supervisor of the facility and the gathered material must be disposed accordingly. Depending on the reactor application, the reactor pool can be totally or partially covered. In this case, the time interval between cleaning operations may be extended.

When the reactor is operated only a few days (e.g. two to five days) per month, or it is on ‘temporary shutdown’, on-line monitoring is not necessary during the shutdown period. However, the off-line monitoring frequency, or periodic sampling, established in Table 11, still applies to both cases.

6.1.3. Reactor primary system water sampling and measuring protocols

A distinction must be made between the sampling procedures for measurement of pH and conductivity, and other parameters. The values of pH and conductivity provide the operator with vital basic information to estimate the quality of the water and the performance of the purification system. Their remote on-line monitoring at the inlet and outlet of the purification system is important because access to the primary cooling system during reactor operation is limited. Also, on-line measurement avoids exposure of the water to CO_2 from the atmosphere, which may have a significant influence on the sampling results.

It is also recommended that sampling and determination of the chemical composition of the primary cooling water be performed off-line in order to confirm on-line measurements. Access to the sampling points in various locations of the water system for off-line monitoring is typically available. A sample volume of 50 ml is enough for most determinations; however, a minimum recommended volume of 100 ml will reduce the possibility of handling contamination, allow for a full list analysis, and allow repetition of analysis in case of necessity. Details on water sampling and analysis methodology are presented in Section 5.

In selecting the sampling point, it is necessary to select always points that will produce conservative results. For some of the indicated parameters, sampling and measurements may be necessary in more than one point of the primary system.

Water sampling at a single point is accurate only if the water composition and other characteristics are homogeneous. This may not be true when stagnant conditions are present that may create a gradient in concentration of impurity species**.** In these cases, proper water monitoring would require to collect samples at different points, and at various depths in the reactor pool, for example. Alternatively, periodic water circulation should be carried out in order to make it uniform. Circulation rates of at least twice the total water volumes per week are recommended.

6.1.3.1. Conductivity and radioactivity

The actions to measure water quality are reactor dependent. As mentioned above, standard procedures for reactor operation typically include some type of measurements for water quality, water radioactivity and room radiation level. Water quality is typically monitored through conductivity measurements, performed both on-line (automatically) and off-line (manually, through sampling). In the first case, a console instrument provides a continuous reading; in the second, periodic sampling from an extraction point in the primary circuit is carried out. If the reactor is operating, access to the tank extraction point may be restricted. At a minimum, the species and monitoring should be performed as specified in Table 11, and provision should be made to enable access to the water sample extraction point. As mentioned above, when selecting the sampling point, it is necessary to consider points that will produce conservative results. In some cases, sampling and measurements may be necessary in more than one point of the system.

On-line radiation levels should be monitored in several points along the primary circuit, such as in the pump room, the water purification room and the reactor pool room.

The radioactive particles and dissolved species in the water should be retained in purification filters and resins; hence, the filters and deionizers may have to be regenerated or changed from time to time, even if they are still in working condition. An unexpected high radiation level on the filter or resin media is an indication of an abnormal condition such as excessive corrosion or leak of nuclear material from the fuel. The radiation level on the filtering system is reactor dependent, and the maximum allowable value (set point) must be established during the commissioning of the facility. A radiation monitor must continuously monitor the radiation level, and if the set point is reached, the reactor should be shut down for maintenance or to identify the source of problem. To increase the availability of the reactor, it is recommended to set a lower value as ‘alarm-level’, so that when the ‘alarm level’ is reached, the operator can plan a maintenance programme before the set-point is reached. In case failed fuel is kept in the reactor pool, it should be stored in vented containers and isolated from the pool in order to avoid further water contamination.

Records of the water quality results and the maintenance activities should be maintained for the life of the system.

6.2. DECAY AND SPENT FUEL STORAGE BASINS

6.2.1. Introduction

Fuel discharged from the reactor core immediately following operation in the reactor requires cooling. To provide residual heat removal and radiation shielding, the fuel is typically stored in water decay basins before it is taken to interim storage, prior to ultimate disposition. The period for interim storage can be for many decades. In this Section, the fuel decay basin and fuel storage basin are assumed to have the same characteristics, and the discussion applies to both. As explained above, in many cases, the fuel decay and storage pool may be part of the reactor pool. In this case, they have to be treated as established in Section 6.1.

Impurities in the water of the basins used for fuel decay or interim storage can have several consequences. Aggressive ionic species, un-dissolved particulates (if settled on the fuel cladding), and several microorganisms can accelerate the fuel corrosion rate. Excessive corrosion can cloud the water, and if through-clad penetration occurs, the concentration of radioisotopes (fission products) on the water can reach unacceptable values. Therefore, in order to maintain the integrity of the fuel for many years, it is necessary to use a purification system, to ensure and maintain good water quality, and minimize corrosion attack of the fuel cladding.

As established for the primary cooling system, for storage basins, the utilization of purification systems is based on a filter and resin bed system to keep the water quality within specified limits. Flocculants may be added to remove turbidity in the water. However, the use of flocculants with subsequent filter of the debris would be a special case of water quality management; considerations including impact to criticality and other potential impacts to the safety basis of the facility must be addressed before using any type of flocculants. Water treatment and purification systems to enable clean up of the water for the fuel storage basins are discussed in Section 4.3.

Similar to considerations for the primary cooling system, aluminium and magnesium alloys are the most susceptible materials to corrosion attack in reactor systems, and the recommendations in this Section are aimed at avoiding excessive corrosion of these materials as the materials for fuel cladding, storage racks, or basin liners. Magnesium must be kept in high pH water to avoid corrosion. Water quality limits for storage of magnesium clad (e.g. Magnox) fuel are not provided in this document.

Once again, the recommendations for water quality encompass those for stainless steel and Zircaloy clad fuels, and thus the limits for aluminium clad fuels recommended in this section are appropriate to avoid corrosion for these cladding materials.

6.2.2. Recommended limits and monitoring frequency for water quality parameters in decay and spent fuel storage basins

Table 12 shows recommended operational limits for water in decay and fuel storage basin. Aluminium and iron species in the basins are indicators of corrosion of aluminium and iron. The operational limits and monitoring

TABLE 12. RECOMMENDED PHYSICAL-CHEMICAL PARAMETERS, LIMITS AND MONITORING FREQUENCIES FOR WATER IN FUEL DECAY AND STORAGE BASINS

Parameter	Value (limit)	Monitoring frequency
pH	4.5 to 7	Weekly
Conductivity	< 10 µS/cm	Weekly
Solids	< 5 mg/L	Every six months
Cu concentration	< 0.1 mg/L	Every six months
Cl concentration	< 0.1 mg/L	Every six months
Nitrate (NO_3^-), mg/L	< 10 mg/L	Every six months
Sulphate (SO_4^{2-}), mg/L	< 10 mg/L	Every six months
Fe concentration	< 1.0 mg/L	Every six months
Al concentration	< 1.0 mg/L	Every six months
Temperature	< 45°C	Monthly
Radioactivity level (*)	(See note below)	Weekly
Turbidity (**)	(See note below)	

(*) Water radioactivity level and the presence of radioisotope species should be measured whenever a water sample is drawn or once a week. A gamma scan is recommended to measure the presence of radioisotopes that would have come from failed fuel (e.g. Cs-137). No specific limits are set. The presence of radioisotope species should be evaluated on a case by case basis. Measurement of the activity from filters and resin columns should be performed to detect the presence of leaking fuel.

(**) Turbidity should be reduced, as necessary, to provide visual clarity in the water system.

frequency that are applied in a specific spent fuel storage basin should be at or below the recommended limits. These limits are recommended to assure corrosion minimization, and if strictly met continuously throughout the storage period, corrosion attack should be minimal through decades of storage.

The sampling should be performed at several locations in the basin to obtain sufficient confidence of the chemistry conditions throughout the basin, as discussed in Section 5 as well as the analytical methods to measure the water quality parameters. As in the primary system, water sampling at a single point is accurate only if the water composition and other characteristics are homogeneous. This may not be true when stagnant conditions are present that may create a gradient in concentration of impurity species**.** In these cases, proper water monitoring would require to collect samples, for example, at different points and at various depths in the reactor pool,. Alternatively, periodic water circulation should be carried out in order to make it uniform. Circulation rates of at least two times the total water volumes per week are recommended

Other important control procedures for fuel decay and storage basins are to eliminate any possibility of galvanic couples such as aluminium/stainless steel. Also, the storage basin should be designed to avoid crevice and promote circulation, as practical, in the system. Sludge that may have accumulated on the floor of the basin should be periodically removed as it is a source for new dissolved impurity species, or undissolved solids if they become re-suspended and settle on the fuel and storage materials.

Records of the water quality results and the maintenance activities should be maintained for the life of the system as historical records as part of a basin chemistry monitoring programme.

6.2.3. Corrosion monitoring to evaluate water quality impact on fuel decay and storage basins

A corrosion monitoring or surveillance programme to monitor corrosion is recommended for planned storage of research reactor spent nuclear fuel in decay and basin storage systems. The programme would involve emplacement and periodic withdrawal of corrosion coupons. Weight changes, oxide analysis and pitting evaluation should be performed to evaluate the mode and extent of corrosion attack. The results of the corrosion evaluation would be compared to the water chemistry during the immersion period of the corrosion coupons and against the water quality limits. The collective results could be used to upgrade the water quality controls if corrosion attack was observed, or relax the monitoring if the corrosion attack was minimal.

Periodic inspection of the fuel is an excellent method to evaluate the impact of the water on the corrosion of the fuel. Visual examination using underwater video is a typical technique used for the inspection. The direct examination of the fuel in a periodic inspection programme is recommended to be part of the water quality management practices for fuel in spent fuel storage basins.

Additional guidance for a CSP is described in Section 7.

6.3. SECONDARY CIRCUIT

6.3.1. Introduction

The secondary cooling system or secondary circuit is an integral part of a research reactor installation. This circuit comprises of the heat exchanger, piping, pumps and the cooling tower. Heat is transferred from the primary coolant to the secondary coolant in the heat exchanger. The secondary circuit coolant is typically water, and its quality control is essential to prevent the formation of deposit scales or foulants on metallic surfaces, corrosion of metallic components and build up of microbiological growth. Both, deposits and biological growth reduce heat transfer efficiency. Corrosion could lead to leakages and/or breakdown of the cooling system structural materials that are typically carbon steel.

This Section describes secondary coolant systems and practices for its quality management. Information is presented on:

- Secondary cooling systems layout;
- Water quality requirements, for startup water, make-up water and the circulating water;
- Treatment of water for use in the secondary circuit;
- Treatment of circulating water;
- Monitoring of water quality;
- Corrosion surveillance; and
- Treatment of discharge.

6.3.2. Secondary cooling systems

Secondary circuits at research reactor installations are similar to industrial cooling systems. In general, three types of cooling water systems are used:

- Once through system
- Open system
- Closed system.

In the once through system, the cooling water, having gone through the heat exchanger, does not return to it. The water returns to the source, or is discarded. This system is used if large quantities of water of adequate quality are available. This system does not have a cooling tower and its maintenance costs are low. The only treatment given to the water in this system is intermittent chlorination. Other types of water treatments are not used in once through systems, because they are not cost effective.

In the open system or open circulating cooling system, the same water is used repeatedly to cool process equipment. Heat absorbed from the process is dissipated to allow reuse of the water. Cooling towers, spray ponds or evaporative condensers are used to dissipate the heat. Open systems use a large amount of water and discharge smaller amounts compared to once-thru systems. A schematic diagram of this system is shown in Fig. 29. The open system is used when the water source is limited. This system is widely used in many industries and also for secondary circuit of research reactors.

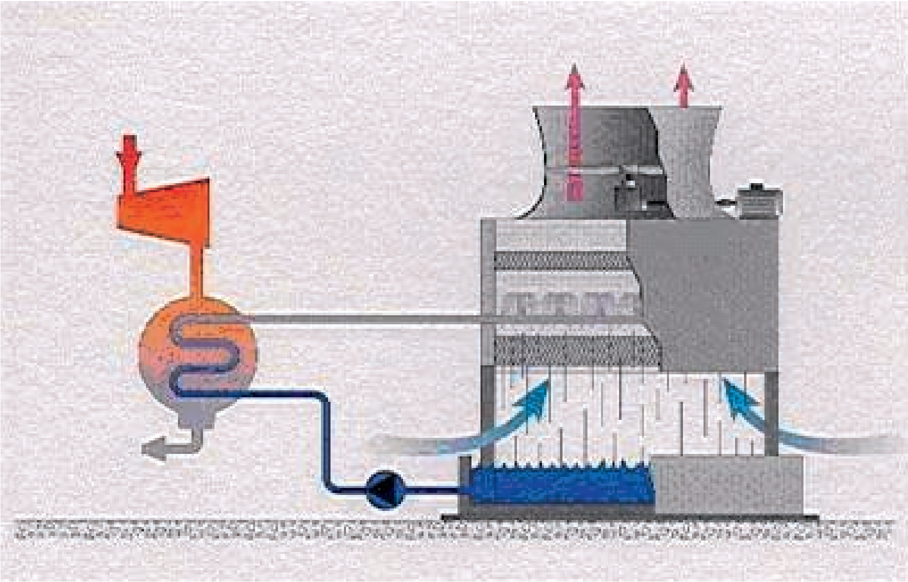

FIG. 29. A secondary cooling circuit, consisting of heat exchanger, piping and cooling tower.

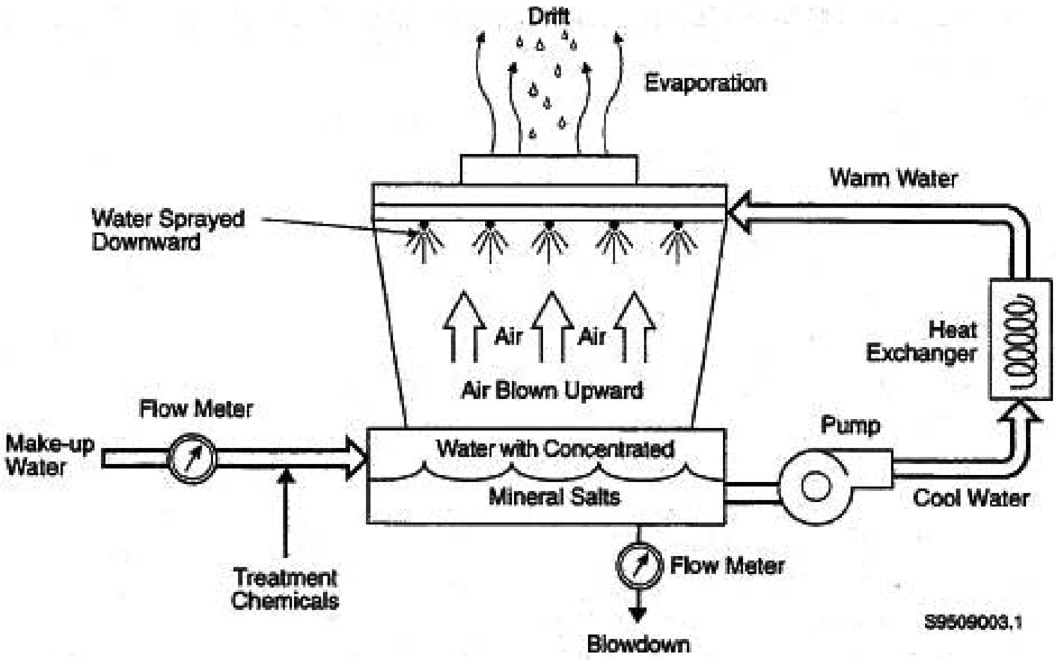

FIG. 30. Schematic diagram of a typical cooling tower. Note water loss due to drift, evaporation and blow down.

The main advantage of the open system is that the coolant can be chemically treated to protect the system. The main disadvantage of this system is the increase in concentration of chemicals and contaminants in the circulating water due to evaporation losses requiring periodic blow downs and replacement with make-up to maintain the level of dissolved solids within acceptable limits (see Fig. 30).

Cooling towers are the most common method used to dissipate heat in open circulating cooling systems. They are designed to provide intimate air/water contact. Heat rejection is primarily by evaporation of part of the cooling water. Some sensible heat loss (direct cooling of the water by the air) also occurs, but it is only a minor portion of the total heat rejection. Cooling towers are classified by the type of draft (natural or mechanical) and the direction of airflow (crossflow or counterflow). Mechanical draft towers are further subdivided into forced or induced draft towers [65, 66].

6.3.3. Water used in the secondary circuit

The source of water used in the secondary circuit is often from municipal supplies or from any major source of water, such as a reservoir, lake or river in the vicinity of the research reactor facility. Water quality requirements for the secondary circuit are similar to that used in any other industry, where heat from operating systems is removed in cooling towers. Table 13 lists the recommended levels of certain parameters in the secondary circuit water.

TABLE 13. RECOMMENDED PHYSICAL-CHEMICAL PARAMETERS TO BE MONITORED IN THE WATER OF SECONDARY CIRCUIT, WITH LIMITS, AND MONITORING FREQUENCIES

Parameter/constituent	Value (limit)	Monitoring frequency
Turbidity	5 NTU (max)	Monthly
Colour	0	Monthly
Odour	None	Monthly
Total alkalinity ($CaCO_3$)	300 ppm (max)	Monthly
Total hardness ($CaCO_3$)	300 ppm (max)	Monthly
pH	Between 6 and 8	Monthly
Conductivity $\mu S.cm^{-1}$	2000 (max)	Monthly
Chlorides	200 (max)	Monthly
Langlier Index	Between –0.5 and + 0.5	Monthly
Total dissolved solids (NaCl)(*)	1350 mg/L (max)	Monthly
Total bacteria (Col/100 mL)	100 000 (max)	Monthly
Phenols	N*0.001 mg/L (**)	Every three months
Arsenic, cadmium, cyanide and selenium	N*0.01 mg/L (**)	Every three months
Chromium, manganese, lead and silver	N*0.05 mg/L (**)	Every three months
Carbon extracted from coliforms	N*0.2 mg/L (**)	Every three months
Iron	N*0.3 mg/L (**)	Every three months
Alkyl sulphonated benzene	N*0.5 mg/L (**)	Every three months
Copper and barium	N*1.0 mg/L (**)	Every three months
Fluoride	N*1.5 mg/L (**)	Every three months
Zinc	N*5.0 mg/L (**)	Every three months
Nitrate	N*45.0 mg/L (**)	Every three months
Sulphate	N*250.0 mg/L (**)	Every three months

(*) In addition to NaCl, other solids can also be dissolved in solution. However, since NaCl is the main constituent, this parameter is traditionally expressed in this form.

(**) These are reference values, where N is the number of ‘cycles of concentration’, as described in Section 4.4.7.9. As explained in this section, a limit of 3 is recommended for open cooling circuits of research reactors. However, when appropriate inhibitors to control scale or deposits are used, cooling systems can be operated at higher cycles of concentration.

As discussed in Section 4, waters from municipal supplies typically do not require further treatment prior to use in the secondary circuit. However, situations may exist in which water supplied by some municipalities, or from natural bodies may require treatment. Details on the treatment of water for the secondary circuit can be found in Section 4.4.

6.3.4. Treatment of secondary circuit water

The water circulating in the secondary circuit usually flows through carbon steel pipelines, or through pipelines and valves made of synthetic polymer based material to the heat exchanger, (usually made of carbon steel shell with copper tubes) and the cooling towers. In a tube-shell type of heat exchanger, the choice of whether the secondary water passes through the tubes or on the shell side depends largely on the materials of construction of the tube, the shell and other design features. However, to facilitate the cleaning process of the heat exchanger and to maintain its efficiency to the heat transfer process, it is recommended that the secondary water flows through the tubes, with primary water on the shell side. As mentioned, the secondary circuit has scales, foulants and microbiological concentrations that can deposit on metallic surfaces, and need to be removed from time to time. Because of the geometry of the tubes bundle in a heat exchanger, the removal of these impurities from the tubes on the shell side is a very difficult task, with no guarantee that all impurities can be removed. Spray jet systems are commercially available to mechanically dislodge and flush debris from the tube interiors.

The two objectives of secondary water treatment are to: prevent corrosion that could lead to leakages and contamination of water from one circuit with that of the other; and prevent deterioration of the heat exchanger efficiency. The basic treatment consists of preventive actions and additions to inhibit deposit formation and microbiological growth, and to maintain the water parameters and the constituents below the limits listed in Table 13. Details on the chemical treatment to reduce deposit formation and microbiological growth can be found in Section 4.4. However, since the prescription for treating the water with inhibitors depends on the quality of the water, an expert in this area should be consulted. To maintain the water parameters and the constituents below the limiting values listed in Table 13, the only recommendation, in addition to cleaning the cooling tower as described in Section 6.3.5, is to perform blow down and add makeup water to retain the specified ‘cycles of concentration’ described in Section 4.4.7.9.

Contamination of the primary water with the less pure secondary water can be easily detected by the marked increase in conductivity of the primary water. On the other hand, contamination of the secondary water with the purer, but radioactive primary water can be also easily detected by increase of radiation level of the secondary water. Therefore, ‘on-line’ monitoring of the secondary water for radioactivity is recommended. Regarding the deterioration of the heat exchanger efficiency, it will be easily detected by an increase in the temperature of the water in the primary cooling system.

Finally, it is important to note that in the highly oxygenated secondary cooling tower, carbon steel corrodes. As a result, the concentration of dissolved iron ions and the amount of detached corrosion products in the circulating water increases with continued circulation. The ratio of secondary circuit water volume to total area of metallic surfaces is another important factor to be considered. The lesser the volume of secondary coolant, the higher the number of times the same water circulates in a given time. Consequently, the water very quickly becomes saturated with contaminants, i.e. the lower the volume of water in the secondary circuit, the less time is necessary to reach the established ‘cycles of concentration’ for the system.

6.3.5. Sludge removal from the secondary circuit

The solids that accumulate in the secondary cooling circuit consist of both dislodged corrosion products and deposits. The deposits on all secondary circuit surfaces often result from precipitation of constituents in the water that have exceeded their solubility limit. Periodic blow downs helps maintain the concentration of dissolved constituents at desirable levels, which would not precipitate to form the solids and eventually form sludge. The dislodged and precipitated solids typically accumulate in regions of the system where water flow rates are low such as in the cooling tower basin. This is the only part of the whole secondary circuit where the water is nearly stagnant and hence the region for accumulation of any solids carried by the circulating water.

One of the recommended procedures for secondary circuit maintenance is periodic cleaning of the cooling tower basin in order to avoid sludge material from returning to the system. This is performed during reactor down time by jetting with water all parts of the cooling tower in contact with the secondary circuit water and by shovelling the loose sludge from the cooling tower basin. This is also performed when the ‘cycles of concentration’ go beyond specified values in spite of the ongoing treatment.

To avoid debris from entering the piping system, it is recommended to include a stainless steel net (mesh) or perforated plate at the inlet to the system. The mesh size would be optimal to preclude debris entrance, but it should not cause a significant loss of pressure or water flow rate.

6.3.6. Secondary circuit water sampling and measurement

The procedure for taking water samples to measure specific constituents in the secondary circuit is often site-specific and depends on aspects such as distance of cooling towers from heat exchangers, existence of near-stationary zones, and differences in water levels between cooling towers and heat exchangers. Nevertheless, certain general guidelines are provided, both for withdrawing water samples and procedures to measure certain constituents on-site, or in a laboratory that is part of the research reactor facility. Many of the constituents that need to be monitored at infrequent intervals should be determined in certified laboratories using appropriate equipment and/or techniques, depending on the accuracy of measurement, as discussed in Section 5.

The water samples should be drawn from the pipeline carrying the water to the cooling tower, during operation. The quantity of sample should be sufficient to conduct all the measurements, usually 3–5 litres and in a glass or synthetic bottle that has previously been rinsed with the same cooling water that is being collected for analysis. Care should be exercised in not selecting a bottle made of a material that could leach any undesirable constituent and thereby mask the measured results. If the water sample is to be sent to an external laboratory for analysis, it should be sent as soon as possible.

The frequency of sample collection varies to some extent. Systems where water treatment has just been initiated require more frequent control, say three times higher (the monitoring frequency being one third of that listed in Table 13) than those systems with ongoing treatments. This frequency is recommended provided that on-line monitoring of parameters such as temperature, pH and conductivity are carried out.

It is recommended that the parameters turbidity, colour and odour be measured at-site. In this context third-party suppliers often provide water treatment in addition to supplying the chemicals to treat the water. Most of the suppliers provide services related to water analysis, which includes the monitoring of constituents in the treated water. These companies withdraw water samples at specified intervals and provide detailed analysis of the water, including the level of chemicals needed to treat the water.

It is also recommended that the monitoring programme for the water in the secondary circuit be maintained even when the reactor is shut down for extended periods. In this case, the water samples should be taken from outlets as close as possible to the heat exchanger.

It is recommended that the amounts of the different constituents of the secondary circuit water be recorded in a log book to enable water quality charts to be drawn. The records should be maintained for the life of the system.

In the case of research reactors in countries where winter temperatures could freeze the water in secondary circuit during shutdown, it is recommended that the water be drained if other options specific to the research reactor facility are not in place.

6.3.7. The secondary circuit corrosion surveillance programme

It is of utmost importance to establish a secondary circuit corrosion surveillance programme. This consists of exposing a set of standard coupons, made with the main material used for construction of the pipelines in the secondary circuit, in a bypass circuit of the water returning to the cooling tower, for a specified period (usually three months) followed by their withdrawal and evaluation. The withdrawn coupons are cleaned thoroughly to remove all the corrosion products and weighed. The weight loss due to corrosion and the corrosion rate of the coupons are determined. The objective of this exercise is to ascertain the state of the inner surfaces of the cooling circuit that is in contact with the flowing water. Data in the form of the extent of corrosion of the coupons, expressed in milligrams per square decimetre per day (mdd), reflects the rate of corrosion of the inner walls of the pipelines. This also helps monitor the effectiveness of the water treatments. Further details of a secondary circuit CSP are given in Section 7.

Other recommended practices include visual inspection of specific critical parts of the system in contact with the cooling water, for example, the heat exchanger, major curves in the pipelines, filters for solids and cooling towers. This practice not only enables verification of the effectiveness of the treatments given to the secondary water, but also to ensure and evaluate the extent of deposits, clogging if any, formation of slime, and corrosion of specific areas. Additional details about corrosion of carbon steels and copper alloys are provided in Section 3.

Inspection of the piping using non-destructive examination techniques such as ultrasonic testing (UT) provide information on the condition of metal piping and help ensure its structural integrity. It is recommended that the piping be inspected as part of an in-service inspection programme. At a minimum, an inspection of the piping for thinning and pitting using UT, as an example technique, should be performed when the piping reaches 50% of its expected lifetime as defined by consumption of its corrosion allowance.

It is recommended that the secondary circuit CSP be maintained even during shutdown periods of the reactor.

6.3.8. Treatment of blow down

It is understood that the maximum amount of chemicals and compounds that can be discharged into drains or other major water bodies, such as streams, rivers and lakes, are dictated by the specific national legislation of each Member State. In general, the maximum allowable concentration depends on whether the discharge is into a drain or a major water body. Table 14 shows some typical values. These values are country dependent and may be modified from time to time due to environmental legislation.

For the example presented, the maximum permissible amount for zinc is 5 ppm in water discharged from an installation. Since the recommended concentration of zinc in the corrosion inhibitor to effectively treat metallic surfaces is 5 ppm, the limiting permissible amount for zinc in the water to be discharged does not pose a problem since the secondary circuit discharge mixes with other discharges without zinc, from the same installation, lowering the final concentration.

Other compounds normally found in secondary circuit waters are phosphonates (also used as a corrosion inhibitor), chelates and amines (used as anti-scaling agents), phenols, quaternary ammonium compounds, organosulphur compounds and carbamates. Most standards do not specify the maximum limiting values for these items in the discharge. However, since many of these compounds increase the biological oxygen demand (BOD) of the water (i.e. they reduce the amount of dissolved oxygen in water), most standards specify the maximum BOD of the major water body at the point of discharge. Secondary circuit waters may therefore require treatment or dilution to maintain these species below acceptable values.

6.4. MAKE-UP SYSTEMS AND RESERVOIRS

The purpose of the make-up system is to replenish the reactor tank with primary circuit grade water in order to compensate for losses due to evaporation or other effects. This water is intermittently incorporated to the primary coolant; therefore, it must comply with all the requirements established for the primary coolant water for both quality and maintenance procedures, as described in Section 6.1.

If the facility has an emergency core cooling system (ECCS), the water in this system, in contrast, is intended to be used to provide refrigeration and shielding to the reactor core in case of lack of primary coolant water. This could occur in a loss of coolant accident (LOCA). In these kinds of situations, the water quality is not a big concern, the main objective is to provide the necessary amount of water to the reactor in the shortest possible time, assuring that it will not add positive reactivity to the reactor.

In some planned or unplanned events that are not emergency situations, the ingress of the ECCS water volume may affect the corrosion behaviour. In these cases, the reactor may continue with its normal routine after the ingress problem has been solved. However, the use of poor quality water in the ECCS system may produce undesirable corrosion damage that will impede normal operation. For this reason, it is strongly recommended that the water in ECCS tanks be treated and maintained at a good quality standard. This has been recognized in nuclear power reactors, where the ECCS manuals establish water attributes in levels similar to that of primary circuits [71].

Water in ECCS tanks would not need a very frequent preservation routine, because it remains essentially stagnant, in contact only with the reservoir material. If this is a corrosion resistant metal, as stainless steel, or lined with a layer of a stable substance, as a good epoxy resin, water purity should remain at a good level and last for a

TABLE 14. TYPICAL LIMITING VALUES OF SPECIFIC ITEMS IN WATER DISCHARGED INTO DRAINS AND MAJOR WATER BODIES (*)

Item	Discharge into drains (mg/L*)	Discharge into major water bodies (mg/L **)
Mercury	1.5	0.01
Silver or selenium	1.5	0.02
Arsenic or cadmium	1.5	0.2
Cyanide	0.2	0.2
Lead	1.5	0.5
Copper	1.5	1.0
Barium or boron	—	5.0
Dissolved manganese	—	1.0
BOD	—	60
Sulphide	1.0	—
Nickel	2.0	2.0
Tin	4.0	4.0
Phenol	5.0	0.5
Zinc	5.0	5.0
Fluoride	10.0	10.0
Dissolved iron	15.0	15.0
Sulphates	1000	—
Oil and grease	150 mL/L	100 mL/L
pH	6.0–10.0	5.0–9.0
Sedimented solids	20 mL/L	1.0 mL/L
Temperature	>40°C	>40°C

* These values are country dependent and may be modified from time to time due to environmental legislation.
** Unless specified in the respective line, all values are in mg/l.

some time without maintenance. In these conditions, ECCS water quality should be checked for the parameters listed on Table 15 on a quarterly basis. Ambient dust, powder, loose particles and other elements in the air, and insects are an important source of water pollution. Hence, it is strongly recommended that the ECCS tanks be closed; otherwise, a cover of a material similar to that of the tank should be provided to bring the necessary protection, or the maintenance routine will have to include procedures to remove floating elements with a skimmer and more frequent purification in order to maintain the water parameter below the limits established in Table 15. Any poison used in the system for reactor shutdown (e.g. $GdNO_3$) should be evaluated by a corrosion expert for compatibility with the system materials.

TABLE 15. RECOMMENDED PHYSICAL-CHEMICAL PARAMETERS AND MONITORING FREQUENCIES FOR THE WATER IN THE ECC SYSTEM

Parameter	Value (limit)	Monitoring frequency
Conductivity	< 3.0 µS/cm	Every three months
pH	Between 4.5 and 7.0	Every three months
Dissolved substances	< 1 mg/L	Every three months
Chloride (Cl^-)	< 0.1 mg/L	Every three months
Fe (total)	< 0.02 mg/L	Every three months
Copper (total)	<0.01 mg/L	Every three months
Nitrate (NO_3^-), mg/L	< 1 mg/L	Every three months
Sulphate (SO_4^{2-}), mg/L	< 1 mg/L	Every three months
Solids, mg/L	< 5 mg/L	Every three months

7. CORROSION SURVEILLANCE PROGRAMMES

7.1. INTRODUCTION

A CSP is an important part of the water quality management programme. It is performed in addition to the recommended practices for water quality management described in Section 6, and not as a substitute. It is made to support confirmation that the actual water quality conditions, during operation of the reactor, are not causing corrosion significant to limit continued operation of the system.

This Section provides guidelines for the planning, set-up, execution, and evaluation activities for corrosion surveillance programmes. The guidelines are for primary circuit and fuel storage basins that focus on aluminium fuel cladding as the material of concern (Section 7.2), and structural materials of secondary systems (Section 7.3). The set-up of a CSP using aluminium coupons is detailed in Section 7.2. The use of corrosion rate meters is discussed in Section 7.3.

Much of the information in Section 7.2 is based on the knowledge gained through the coordinated research project (CRP) on ‘Corrosion of Research Reactor Aluminium Clad Spent Fuel in Water’ supported by the IAEA between 1996 and 2001. The uniform application of corrosion surveillance coupons was the focus of this CRP [7].

Periodic inspection of the fuel is an excellent method to evaluate the impact of the water on the corrosion of the fuel under extended storage. Visual examination using underwater video is a typical technique used for the inspection [72]. The direct examination of the fuel in a periodic inspection programme is recommended to be part of the water quality management practices for fuel in spent fuel storage basins. No additional guidelines for corrosion surveillance using periodic inspection are provided in this publication.

In general, the guidelines for corrosion surveillance are applicable to any reactor water system. However, it is important to emphasize its importance for the primary cooling system and for fuel storage basin. For these systems, the CSP is an essential part of the water quality management programme.

7.2. PRIMARY CIRCUIT AND FUEL STORAGE BASIN CORROSION SURVEILLANCE PROGRAMME

7.2.1. Introduction

The purpose of a CSP in a research reactor facility is to provide early detection of corrosion of components, structures and/or the nuclear fuel in contact with the water. The need for a CSP depends on the expected life of the facility, the duration of residence of fuel in the reactor pool, or storage basin, and the reactivity of the fuel materials in water. A CSP is done by evaluating the effects of prevailing water parameters at either facility on the extent of corrosion. In research reactor facilities that were built in recent years, a CSP is established during the design stage. However, for most operating research reactor facilities, which are over 30 years old, a specific CSP needs to be established.

It is well known that good quality water is essential to prevent corrosion in the research reactor or in the spent fuel basin. However, certain water parameters such as conductivity, chloride ion content and some other ions, in quantities well below levels of concern, have a synergistic effect on the pitting corrosion behaviour of aluminium alloys [73]. Therefore, maintenance of water parameters within specified limits is not reason enough for complacency about corrosion of fuel cladding. A well planned and executed CSP would give the research reactor or spent fuel basin manager an insight into the state of fuel cladding and/or metallic structural materials in terms of corrosion.

Typically, a CSP involves the exposure of a set of test coupons to the research reactor or basin water for a pre-determined period followed by its evaluation to detect for corrosion. Techniques such as electrochemical noise have also been used to conduct corrosion surveillance, but to a much less extent. The CSP also involves the determination of water parameters at periodic intervals. The combined results from the evaluation of corrosion coupons and the water quality parameter measurements provide the basis for evaluation of corrosion on the fuel cladding and other structural materials due to exposure to the water during the time of immersion of the materials. The results also include effects of any transients in water parameters, something that often goes unperceived in the absence of a CSP.

A CSP involves planning and execution steps as described in the following paragraphs.

7.2.2. Planning a CSP

Planning involves the establishment of actions as follows:

(a) **Listing of metallic materials exposed to the research reactor or spent fuel basin water**: A variety of metallic materials are often used in research reactor or in spent fuel basins. For the CSP, only alloys that are of major concern need be selected. The most important material is that used as the fuel cladding (usually aluminium alloys), followed by any other thin walled aluminium alloy component that if corroded or perforated lead to concerns. Materials that are prone to corrosion and form voluminous corrosion products, which in turn could result in further corrosion of the fuel cladding, should be included. Other metals that could form a bimetallic couple with the fuel cladding should be also included in the list of materials.

(b) **Specification of alloy composition, microstructure, heat treatment and surface condition, and selection of materials for the programme**: In addition to knowing the designation of the alloy and its nominal composition from standard tables, it is essential to know, if possible, the exact composition. Small deviations in composition result in formation of alloy phases or intermetallics. It is important to know the metallurgical state of the alloys of construction. The microstructure, grain orientation, inclusions, intermetallic precipitates and other second phases influence corrosion and are often the points for initiation of corrosion, especially in aluminium alloys. The type of heat treatment given to an alloy alters its composition and its stress state. These also influence the corrosion behaviour of the alloy. One of the last stages in the manufacturing processes of research reactor fuel plates is surface treatment. Many surface defects are removed and a thicker surface oxide is grown. These in turn reduce the number of defects at which pits can initiate, and the latter protects the aluminium surface. Hence, knowledge of the surface state is essential to produce a test coupon with alloy and surface characteristics similar to that of the fuel cladding. There are cases in which reactor components and fuel storage racks are made of stainless steel. If such is the case, it is essential to select a stainless steel with composition as close to that of the storage rack for coupling to the aluminium surveillance coupon. If the reactor component or storage rack is made of an aluminium alloy, it is also important that this alloy be selected**.** Having selected the materials, specimens (samples) of the same in the form of circular disk type coupons are used in the test.

(c) **Specifying dimensions of coupons, the insulating separator and the rack**: Most CSPs use circular coupons, although of different diameters. The standard coupons used in a CSP have a circular design with a diameter of 70 mm, but they can be modified as necessary to be used in the programme. The diameter of coupons used in the IAEA’s CRP Corrosion of Spent Aluminium Clad Research Reactor Fuel in Water was less than that specified in standards for conducting similar tests. This was due to the restricted space in basins and for ease of transport of coupons and racks.

(d) **Specifying configuration of the coupons with respect to nature of corrosion — crevice and bimetallic**: Since the objective of a CSP is to determine the corrosion susceptibility of metal coupons in situations similar, if not identical, to fuel cladding and/or other reactor/basin structural components, it is important that coupons be configured to simulate geometric conditions similar to that of fuel and components in the research reactor pool or storage basin. In this context, any crevices between components in the research reactor or bimetallic contacts should be reproduced. Crevice coupled coupons or bimetallic coupled coupons should simulate existing crevices or bimetallic contacts and added to the test racks.

(e) **Specifying the duration of the programme**: An ideal CSP is one that is carried out throughout the life time of the research reactor or the spent fuel storage basin. In such a CSP, test coupons are always awaiting withdrawal after specified durations. If a specific facility is unable to conduct a continuous CSP, it is recommended that a three year programme be initiated.

(f) **Specifying the frequency of corrosion monitoring**: The frequency of corrosion monitoring is the periodicity at which racks of test coupons are withdrawn from the research reactor pool or spent fuel storage basin. For pools or basins with very good water quality management, it is recommended to establish programmes starting with yearly withdrawal of the racks, and after the first three years, the withdrawal period can be extended to two, three and five years, followed by five year intervals until decommissioning of the facility. For pools or basins with poor quality water or with a significant amount of settled solids, the racks should be withdrawn at a six month or even a three month interval. The period for withdrawal may be extended when the water quality improves and the incidence of corrosion gives subsides to the extension. It is important to emphasize that at the end of a test period, the entire rack of coupons needs to be removed. It is not recommended that one or more coupons be removed from a rack, and the rack with the remaining coupons return to the pool or basin. Experience has shown that only with utmost care can coupons be prevented from drying before a withdrawn rack is partially disassembled for removal of some coupons, prior to its return to the pool. A partially dried coupon, if returned to the pool or basin, does not represent or reproduce conditions similar to that of a fuel cladding or reactor component exposed to the same environment. More details on immersion/withdrawal frequency is given in Section 7.2.3.3.

(g) **Specifying the frequency for monitoring water parameters**: For the CSP, it is recommended to monitor (measure) the water parameters according to the same frequency established in Section 6.

(h) **Specifying the location for the rack(s) within the research reactor or spent fuel basin**: The location for immersing a rack with test coupons should be a region of the research reactor pool where water turbulence is the least and/or renewal of water is the least. Metals in general are more prone to corrosion in such regions. In a spent fuel basin, the location for immersing coupons should be as close as possible to the spent fuels, but not in contact with the fuels. Other aspects to be borne in mind while selecting the location, especially in spent fuel pools, are:
- The test coupon rack should not hinder regular fuel handling.
- The rack should not be knocked about during regular reactor or basin operations,
- The rack should not be exposed to excessive amounts of settled solids, unless of course it does reproduce conditions similar to that of stored fuels.

(i) **Specifying protocol and collector for settled solids evaluation in terms of quantity and composition**: Most research reactor pool or storage basin water surfaces have dust, which if unskimmed, become wetted and settle on surfaces inside the pool or basin. It is therefore recommended, as part of a CSP, to determine the amount of settled solids as well as their composition. Details on the sources of settled solids, their effects on corrosion of coupons and components, and procedures to collect and analyse the solids are given in Section 3.2.3.7 and in Refs [8, 35].

(j) **Selection of coupons/racks manufacturer/supplier**: Having decided on the materials, the duration of the programme and the frequency of withdrawal of racks, it is essential to ensure that adequate material is available before embarking on the CSP. Ideally, the Al alloys to be used for making coupons should have the requisites mentioned earlier. It is important that a manufacturer of the coupons and racks be made aware of the requirements, especially in terms of final surface conditions of the coupons. It is also important to ensure if facilities are available to adequately identify racks and suspend them in the basin. It is recommend that coupons used to monitor fuel corrosion be supplied by the fuel manufacturer, as ‘dummy’ samples without nuclear material.

(k) **Laboratory facilities for water analysis, sediment analysis, and coupon evaluation**: Conducting periodic water analysis and final coupon evaluation are the two main parts of any CSP, hence, facilities to conduct them are essential. Sediment analysis, although important is a recommended complement to a CSP. Most research reactor facilities are equipped to determine certain water parameters. However, analyses for specific constituents in the water samples or in the settled solids are carried out at other in-house or near-by laboratories. A well equipped metallurgical laboratory is often sufficient to evaluate test coupons.

7.2.3. Execution guidelines

Execution involves actions related to preparing the test coupons and racks, immersion/withdrawal of the coupons, and corrosion evaluation of the coupons, as described in the paragraphs below.

7.2.3.1. Preparation of coupons and racks

CSPs are designed to help evaluate the effect of water parameters on the corrosion of fuel assemblies and other reactor pool or spent fuel basin structures. In this context, it should be emphasized that both MTR type fuel assemblies and Russian origin reactor fuels are always stored vertically, with the fuel plates or tubes also vertical. Most CSP use racks in which coupons are assembled horizontally and not vertically as fuel plates are within fuel assemblies. Experience gained in the IAEA supported CRP Corrosion of Spent Aluminium Clad Fuel in Water revealed that horizontal coupons are more susceptible to corrosion than vertical coupons. It is therefore recommended that CSP use horizontal coupons as it is a much more severe condition and therefore provide an early and conservative indication of the fuel corrosion.

Different types of stainless steel racks were used in the two phases of the IAEA coordinated CRP and in a regional CSP for Latin America (RLA) [7, 8]. The models used in the CRP and the RLA evolved from other designs, and are recommended. The insulating separator should be non-porous and resistant to radiation, like dense alpha-alumina. A typical rack is composed of coupons, in the form of disks, assembled using insulating washers as separators. Figure 31 shows a typical rack with the coupons. The coupons are made of materials that effectively represent the materials used in the research reactor and exposed to the reactor water environment or the spent fuel storage basin that also contains primary circuit quality water. Experience gained from the use of racks and coupons similar to those shown in Fig. 31 revealed that one of the parameters that affect coupon corrosion is settled solids from the reactor or spent fuel basin water; i.e. the top surfaces of coupons higher up in the rack are more prone to corrosion compared to similar coupon surfaces further down in the rack. Hence, it is recommended that for conducting CSP in waters where settled solids have a marked influence, the thickness of the separators be about

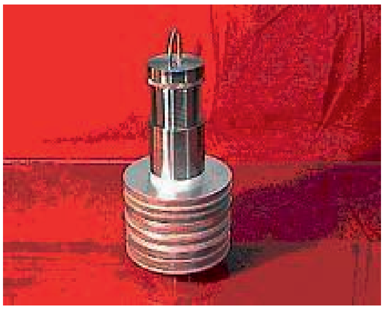

FIG. 31. A typical corrosion test rack with coupons.

2.5 cm. Such thick separators would reduce the shadowing effects of coupons on those immediately below it. If thick separators are not available, it is recommended that more than one separator be used to increase the space between successive coupons in a rack.

The coupon assembly should also reproduce bimetallic contacts and crevices. Figures 32 and 33 show typical coupon configurations to simulate bimetallic contacts and crevices. Figure 34 shows a sketch of a crevice washer (separator), and Fig. 35, a typical coupon assembly, or test rack, containing 70 coupons.

The following is a list of suggested coupons that should be considered in a CSP for research reactors or spent fuel storage basins using aluminium and/or aluminium alloys for fuel cladding and as structural materials:

(a) **Individual coupons:**
Coupons made of 32 mm φ aluminium alloy discs (include fuel clad and storage rack materials including discs with weld beads).

(b) **Bimetallic coupled coupons:**

- Coupons made of 32 mm φ aluminium alloys (include fuel clad and storage rack materials) disks in contact with larger 70 φ mm disk coupons that would be the cathode in a galvanic couple (e.g. AISI 304 SS coupons);

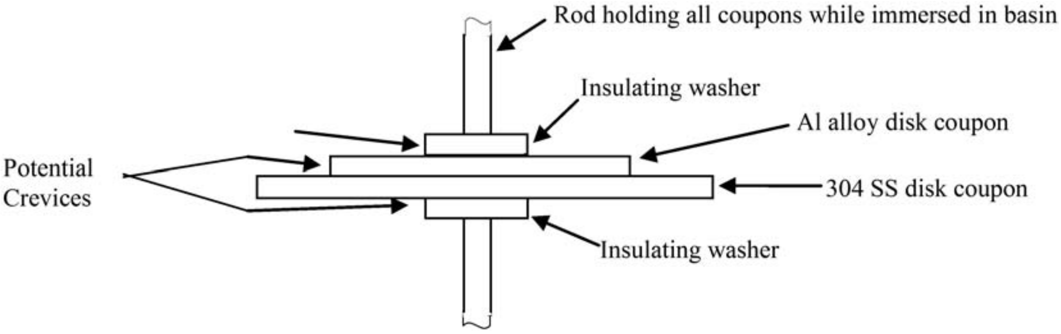

FIG. 32. Schematic diagram of a galvanic coupon subassembly showing the crevice between the coupons and between the coupons and washers.

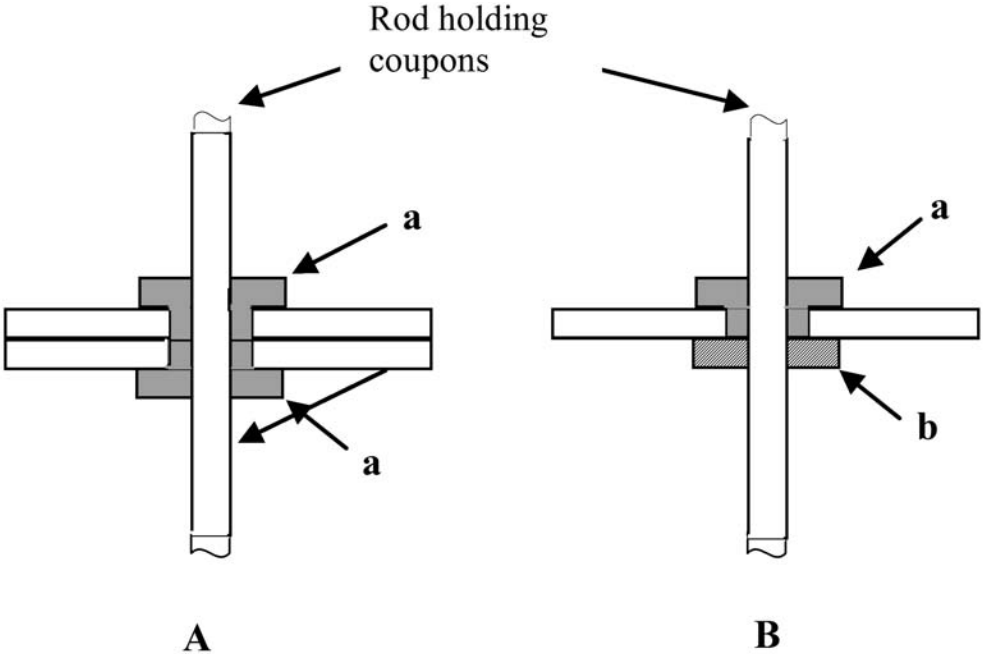

FIG. 33. Schematic diagram of (A) bimetallic coupled coupons and (B) an individual coupon, with insulating separators. Separator ‘a’ prevents bimetallic contact between the coupled coupons and the metal rod as well as with other coupons above or below it. Separator ‘b’ can be either flat or serrated as shown in Fig. 34.

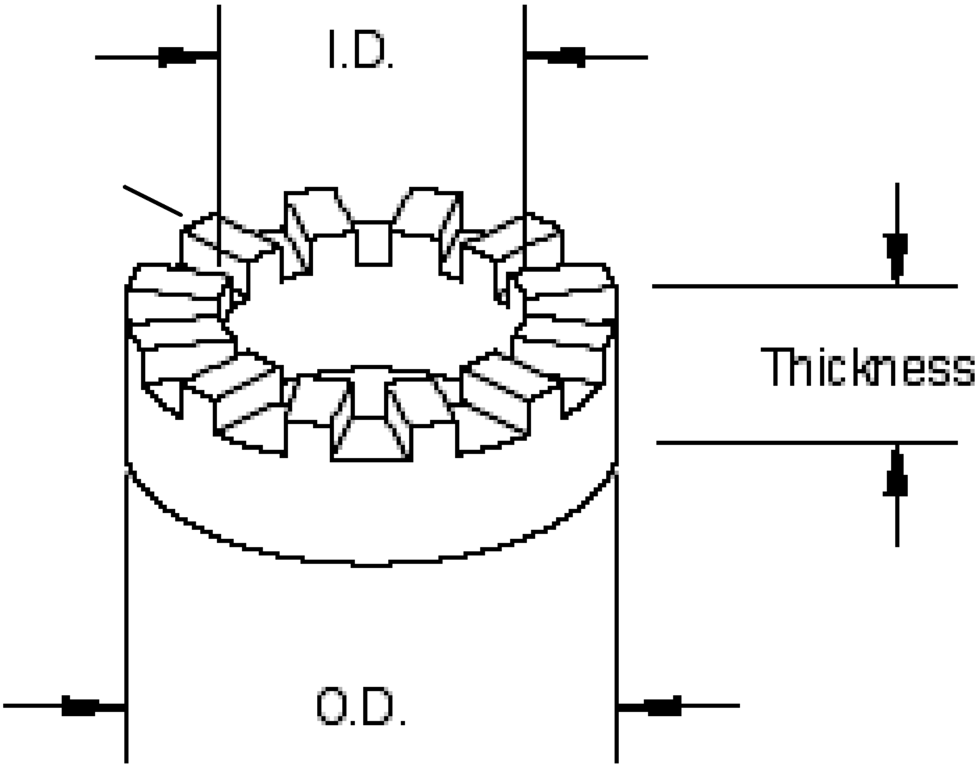

FIG. 34. Schematic diagram of a serrated separator to create crevices on coupons.

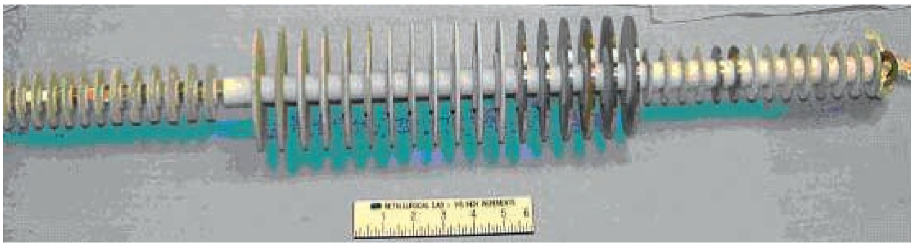

FIG. 35. A coupon assembly used in a research reactor CSP with 32 and 70 mm φ coupons. The white area between the coupons is a PTFE separator, used to isolate the central stainless steel rod from the coupon and the coupons from one another.

- — Coupons made of 32 mm φ aluminium alloys (include fuel clad and storage rack materials) disks in contact with larger 70 mm φ coupons of a different aluminium alloy (include fuel clad and storage rack materials) (for example, 70 mm φ AA 1100 in contact with a 32 mm φ AA 6061 and/or another 70 mm φ AA 1100 in contact with a 32 mm φ AA 6063).

(c) **Crevice coupled coupons:**

- — Coupons made of 32 mm φ aluminium alloys (include fuel clad and storage rack materials including disks with weld beads) disks next to a coupon of the same alloy and of the same size;
- — Coupons made of 32 φ mm aluminium alloy (include fuel clad and storage rack materials) disks next to a coupon of the same size and alloy, but with a serrated TFE washer on one side of the coupon, as shown in Fig. 34.

(d) **Other coupons:**

Inclusion of coupons of other alloys is recommended, as long they are representative of materials used in the research reactor or storage basin facility.

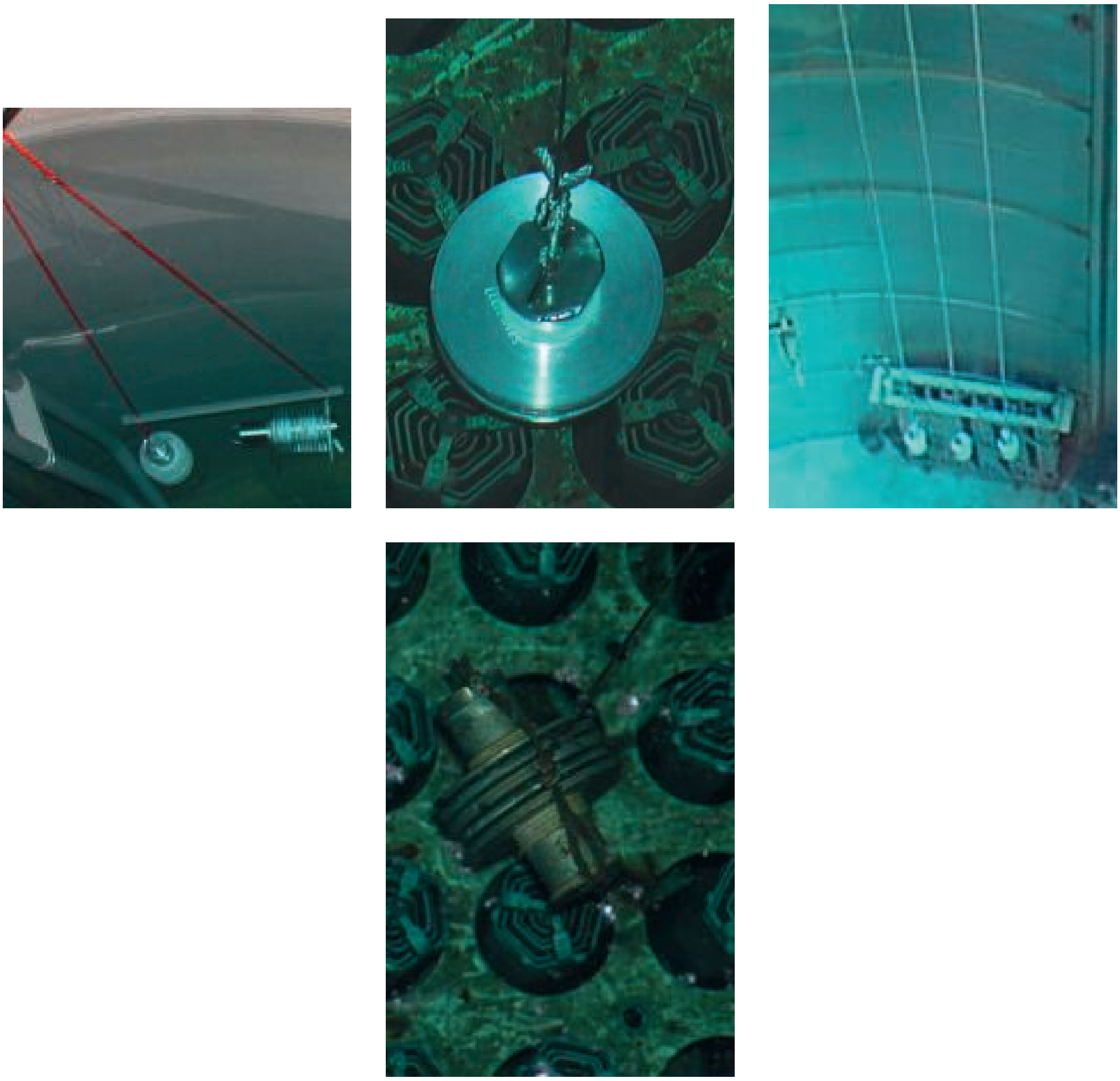

FIG. 36. *Coupon assemblies in fuel storage pools.*

7.2.3.2. Immersion location

The test coupon rack should be positioned or placed at a region where the water flow conditions are minimal. (i.e. with the most unfavourable environment conditions, especially in terms of corrosion). In the case of storage basins, the test coupon racks should be located at or near the fuel in the pool. One or more locations should be selected if some locations have stagnant water conditions or are otherwise distinct. The test coupon racks should be positioned several meters below the surface of the pool, and those that are part of a CSP campaign should be positioned together in order to enable evaluation of corrosion data as a function of exposure duration. Figure 36 shows some typical coupon assemblies in storage pools.

7.2.3.3. Immersion/withdrawal frequency

The number of test coupon assemblies or racks to be used in a CSP must be consistent with the expected life of the facility, and with the duration of interim storage of spent fuel. The programme should enable surveillance throughout the desired service life of the reactor water system or spent fuel basin. In the case of an initial three years programme, scheduled annual withdrawals are recommended for reactor, decay and storage pools. After the first three years, the withdrawal period can be extended to two, three and five years, followed by five years intervals until decommissioning of the facility.

Test coupons in a separate rack can also be immersed after the programme has been initiated. For example, if measures have been taken to improve water quality based on prior results from the CSP, it is recommended that a new test coupon rack be included in the CSP to re-evaluate the effect of the new water parameters on coupon corrosion.

7.2.3.4. Coupon evaluation

Coupons may be radioactively contaminated in the pool and should be handled in contamination facilities. Withdrawn test coupon racks are typically placed inside a chamber fitted with adequate facilities to handle contaminated coupons and racks. The following are recommended steps for a full evaluation of aluminium coupons withdrawn from reactor or spent fuel storage pools.

Coupons are identified (alloy and coupon ID number), dried, weighed and their weights recorded. The two sides of the coupons are photographed. If necessary, all these activities are done inside the chamber. Based on a visual inspection, selected coupons are cleaned using 16M nitric acid for a minimum of 30 minutes, rinsed with deionized or distilled water, inspected for residual surface oxide and in the case of retained surface oxide, cleaned again with nitric acid, taking care to avoid acid attack of the coupon. After drying, the coupons are again weighed, photographed and the information recorded.

Pit locations are identified and examined visually. Pit measurements are carried out with an optical microscope as per ASTM G-46 [74] (determining the average and maximum pit depths and pit density over a 0.58 mm^2 area) or with automated imaging equipment, if available. The number of pits in areas of 0.762 × 0.762 mm is counted, and the pit density determined over the 0.58 mm^2 area. The average pit depth is determined considering the ten deepest pits. If the average pit depth is determined with less than ten pits, this should indicated in the records. The coupon weights and pit data are compiled and reported in the form of graphs.

7.2.4. Reporting CSP results

At the time of coupon evaluation, a report should be prepared about the state of the coupons as a function of water parameters and duration of exposure.

For the coupons, the report may include the following:

- Photographs of the coupons before and after cleaning with captions; high magnification photographs of pits if essential; photographs to enable comparisons with previously ones;
- Corrosion results as percentage weight change (individual coupons) and normalized weight change (galvanic coupons) in the form of a bar chart to enable comparison with previous results;
- Pitting density and pit depths (average and maximum) of individual and creviced coupons, and comparisons with past pit depths data.
- Evaluation of the CSP results showing the correlation of the results of coupon corrosion evaluation and water parameters; and a correlation of the results of coupon corrosion with surface state of spent fuel cladding and/or other structural components.
- An evaluation of possible effects on reactor structures and fuel cladding for the duration that they are expected to remain in the pool.
- Proposed actions, if necessary, to alter water parameters and to verify fuel cladding integrity.

A reference ‘test protocol’, prepared for use in the IAEA CRP Corrosion of Research Reactor Aluminium Clad Spent Fuel in Water and the Regional Project for Latin America (RLA) Management of Spent Research Reactor Fuel in Latin America [75], is described in Annex I.

FIG. 37. *Difference concepts of sediment collector [8].*

FIG. 38. *Collector made of aluminium, with diameter equal to 20 cm [8].*

7.2.5. Evaluation of settled solids

To evaluate the amount and composition of settled solids, collectors have to be placed in the vicinity of the corrosion coupon racks for a predetermined time, followed by its withdrawal and determination of the amount of solids and its composition. In principle, the programme can start with two collectors, to be withdrawn after intervals that can vary from six months to one year, for the first collector, and one to two years for the second collector, respectively. The necessity to continue with the evaluation will depend on the results obtained.

7.2.5.1. The settled solids collector

A variety of collectors can be used. Figures 37 and 38 show some collectors used in a special programme to evaluate the effect of settled solids in aluminium [8]. The main criterion in the design of the collector is to prevent the collection of solids floating on the pool/basin surface at the time of withdrawal of the collector, therefore the lids of the collector need to be placed prior to its removal. This criterion takes into consideration that not all material floating on the pool surface is wetted and settles on surfaces.

Unless it can originate galvanic corrosion, the recommended material for construction of the collector is stainless steel in order to avoid eventual mixing of settled solids with aluminium induced corrosion products.

7.2.5.2. Settled solids analysis

The following is a reference procedure for analysis of the settled solids: after removal of the collectors, stir the water and pass it through a filter. The sediments are then collected on a filter paper, dried in an oven at 100ºC for

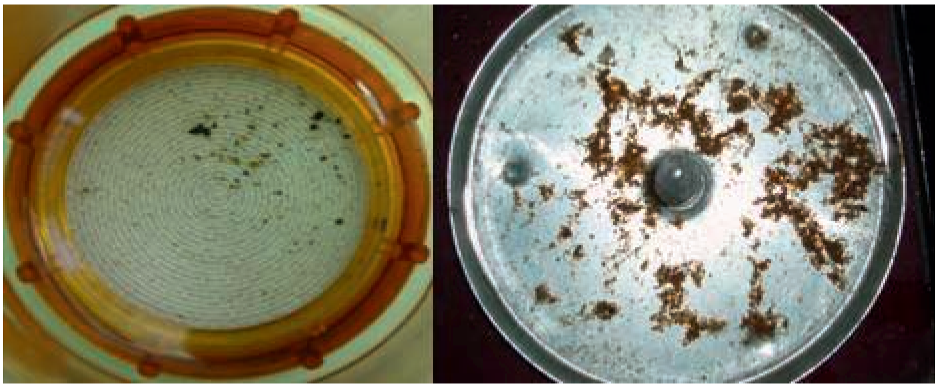

FIG. 39. Typical settled solids on a Millipore filter (left) and on the collector (right) [8].

24 hours, weighed, photographed and mixed, and representative specimens are extracted for analysis. The technique used for analysis will depend on the equipment available. It can be scanning electron microscope (SEM), energy dispersive spectroscopy (EDS), X ray diffraction (XRD), X ray fluorescence (XRF), or mass spectrometry. Figure 39 shows the typical appearance of the sediments.

7.2.5.3. Reporting results of settled solids analysis

A report should be prepared showing the main results of the settled solids analysis, including: (a) photographs of the dried sediments, with immersion and withdrawal dates; (b) water parameters as monitored during the time in which the collectors were immersed; (c) mass collected and average deposition rate, in $\mu g/(cm^2 \cdot month)$; (d) composition, based on the analysis; (e) additional results and information based on the technique selected for analysis; (f) eventual correlation between the results of settled solids and tested coupons; and (g) proposed actions, if necessary, to minimize settled solids in the reactor pool or spent fuel storage basin.

7.3. THE SECONDARY CIRCUIT

7.3.1. Introduction

The secondary circuit in research reactor installations is more prone to corrosion, scale deposits formation and biofouling than the primary circuit for reasons discussed in detail in Sections 4 and 6. Hence it is of importance to put in place a programme to monitor the effects of process parameters on corrosion, deposit formation and biofouling as these affect the heat transfer efficiency of the secondary circuit.

Corrosion monitoring for a secondary circuit typically involves the practice of measuring the corrosivity of process conditions by the use of ‘probes’, which are inserted into the process stream and are continuously exposed to the process stream condition. The corrosion monitoring ‘probes’ can be mechanical, electrical or electrochemical devices. These probes are an essential element of all corrosion monitoring systems. The nature of the sensors depends on the various individual techniques used for monitoring, but often a corrosion sensor can be viewed as an instrumented coupon. In older systems, electronic sensor leads were usually employed for these purposes and to relay the sensor signals to a signal processing unit. Advances in microelectronics are facilitating sensor signal conditioning and processing by microchips, which can essentially be considered integral to the sensor units.

Some corrosion measurement techniques can be used on-line, constantly exposed to the process stream, while others provide off-line measurement, such as that determined in a laboratory analysis. Some techniques give a direct measure of metal loss or corrosion rate, while others are used to infer that there may be a corrosive environment.

Real time corrosion measurements refer to highly sensitive measurements, with a signal response taking place essentially instantaneously as the corrosion rate changes. Numerous real time corrosion monitoring programmes in diverse branches of industry have revealed that the severity of corrosion damage is rarely uniform with time.

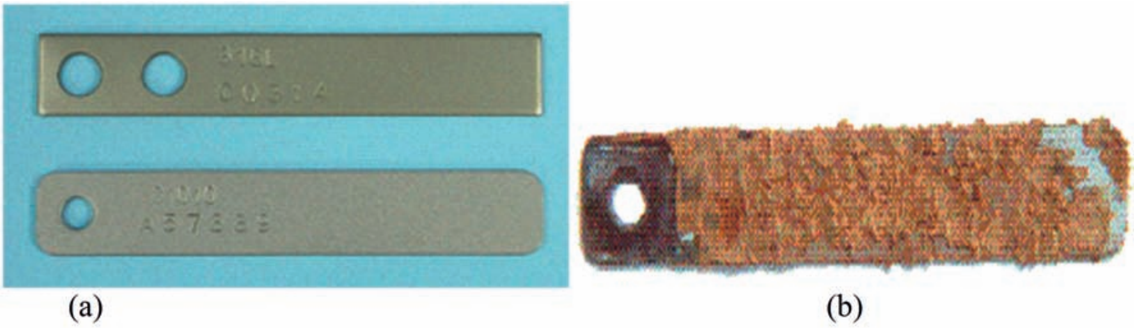

FIG. 40. Typical corrosion coupons. (a) Unused coupons; (b) corroded steel coupon [76].

Complementary data from other relevant sources such as process parameter logging and inspection reports can be acquired together with the data from corrosion sensors for use as input to the management information system.

Tools commonly used in corrosion monitoring include metal corrosion coupons, instantaneous corrosion rate meters, and heated surfaces such as test heat exchangers and other specific apparatus. Data obtained from these devices can be used to optimize an inhibitor treatment programme and to maintain the plant equipment in the best possible condition.

For the secondary circuit, it is recommended to implement a CSP using corrosion coupons. If resources are available, then the programme should be complemented with the installation of real time meters, as described in the next sections.

7.3.2. Corrosion monitoring using corrosion coupons

Weight loss analysis of metal coupons is the simplest and most reliable method used for monitoring corrosion in cooling systems. A weighed sample (coupon) of the metal or alloy under consideration is introduced into a rack installed in a bypass section of the circuit before the heat exchanger, with continuous but controlled water flow past the coupons. The coupons are removed after a reasonable time interval, cleaned of all corrosion products and reweighed. The weight loss is converted to a quantitative measure of thickness loss, or average corrosion rate using proper conversion equations, and the visual appearance of the coupon provides an assessment of the type of corrosion and the amount of deposition in the system. In addition, measurement of pit depths on the coupon can indicate the severity of the pitting. These coupons can be manufactured or acquired in standard sizes, but to be representative, the composition and metallurgical state of the coupons should be similar to that of the materials used in the manufacture of the system components. Figure 40 [76] shows a typical corrosion coupon, both unused and after the test. One disadvantage of coupons is their lack to simulate the temperature condition of the real component, usually resulting in a lower temperature than that of the actual heat exchanger tubes. In addition, only a time-weighted average corrosion rate is obtained.

The main advantages of using coupons to monitor corrosion are: (a) low costs; (b) simplicty of implementation; (c) obtain information about most forms of corrosion mechanisms.

The disadvantages include: (a) a relative short measurement period of usually one to three months; (b) no real time measurement and it is usually an on-line exposure followed by off-line analysis; and (c) the need for historical data to establish trends.

In most cooling circuit corrosion monitoring systems, copper and mild steel coupons are used: the copper coupons are exposed for periods between three and six months; the mild steel coupons are exposed for one to three months. When initiating a CSP for the secondary circuit based on coupon corrosion monitoring, it is recommended to remove the coupons and evaluate the extent of corrosion following 1 month of exposure for steel coupons, and three months for copper coupons. An adjustment may be made to the withdrawal period based on acquired experience. For example, if no corrosion is observed for the steel coupons, the period for withdrawal period may be extended to three months; similarly, the withdrawal period may be extended to six months for the copper coupons if no corrosion attack to the copper is observed. Removed coupons should be replaced by new, similar coupons to sustain the surveillance programme.

For best results, both the uniform corrosion rate and maximum pit rate must be measured. The uniform corrosion rate is based on the weight loss of the coupon during the exposure period. The maximum pit rate involves measuring pits in various regions of the coupon. Mild steels in certain situations tend to pit rather than corrode uniformly. Hence, the reporting of uniform corrosion rates tends to underestimate the extent of corrosion of the system.

7.3.3. Corrosion rate meters

Additional corrosion monitoring tools have been developed by various instrument manufacturers and water treatment companies. Instantaneous corrosion rate meters can measure the corrosion rate at any given point in time. Instrument methods fall into two general categories: electrical resistance and linear polarization. With either technique, corrosion measurements are made quickly without removal of the sensing device. The electrical resistance method is based on measuring the increase in the electrical resistance of a test electrode as it becomes thinner due to corrosion. This method has its disadvantages: conductive deposits forming on the probe can cause misleading results, temperature fluctuations must be compensated for, and pitting characteristics cannot be determined accurately. The method based on linear polarization at low applied potentials provides instantaneous corrosion rate data that can be read directly from the instrument face in actual corrosion rate units (mm per year). Systems using two or three electrodes are available. This method offers the maximum in performance, simplicity and reliability. Corrosion rate meters can be used to assess changes in the corrosion rate as a function of time. They respond to sudden changes in system conditions, such as chlorine levels and inhibitor treatment levels. Combined with recording devices, they can be powerful tools in diagnosing the causes of corrosion or optimizing inhibitor treatment programmes [65].

Other monitoring apparatus have been used in cooling circuits with heat exchangers and cooling towers. These apparatuses can be used in the secondary circuits of research reactor installations to monitor not only corrosion, but also scale formation and fouling. Examples of these apparatus include:

- Test heat exchangers: Small heat exchangers that can be set up to simulate operating conditions in the plant. They provide a convenient way to evaluate corrosion and fouling tendencies on heat transfer surfaces and to measure changes in heat transfer efficiency. A typical design uses cooling water on the tube side and condensing steam as a heat source on the shell side. If the test heat exchanger is insulated, a meaningful “U” (overall heat transfer coefficient) can be calculated.
- BETZ MonitAll Apparatus: This is designed to measure corrosion and deposition under heat transfer conditions. Cooling water flows over a heated specimen tube section within a glass shell. The specimen tube section is slid onto an electrical heater probe. Thermocouples measure bulk water temperature and tube-side skin temperature. The heat flux and flow velocity can be controlled to simulate plant conditions. The tubes are available in various metallurgical conditions and are pre-weighed for corrosion rate determination. The tube is visible through the glass enclosure, allowing direct observation of corrosion and scaling tendencies. Scaling/fouling can be quantified through temperature and flow measurements [65].
- The BETZ Cosmos (Cooling System Monitoring Station), a portable data acquisition station that monitors key parameters of a cooling system. The piping and instrumentation cabinet includes flow, pH and conductivity sensors as well as a corrosion coupon rack, a corrosion rate probe and a MonitAll unit. Data from all of these devices are fed into the data acquisition system. The accumulated data can be printed directly by the built-in printer or can be downloaded to a personal computer for spreadsheet analysis [65].

7.3.4. Secondary circuit corrosion report

A periodic report of results should be prepared for the secondary circuit including the following:

- Water parameters, as listed in Table 13.
- Photographs of the coupons before and after cleaning with captions, with high magnification photographs of pits. An attempt must be made to obtain photographs that enable comparison with previous ones.
- Corrosion results as percentage weight change (individual coupons) and normalized weight change in the form of a bar chart to enable comparison with previous results.
- Evaluation of results showing the correlation of the results of coupon corrosion with surface state of pipe thickness and/or other structural components.

— An evaluation of possible effects on secondary circuit components and structures for the duration that they are expected lifetime.
— Proposed actions, if any, to alter water parameters, reduce extent of settled solids and verify circuit integrity.

The periodicity of the report should be according to the replacement of the corrosion coupons.

8. QUALITY ASSURANCE

8.1. INTRODUCTION

Good water quality management is not only a matter of applying the best available techniques and procedures, but also of providing convincing evidence on what has been done. Quality assurance, or QA, is the activity of providing evidence needed to establish quality in work and to demonstrate that activities that require good quality are being performed effectively. QA activities are actions necessary to provide enough confidence that a product or service will comply with the given requirements for quality.

All research reactors need a QA programme for all phases of their lifetime in order to demonstrate the fulfilment of the basic requirements given in the IAEA Code on Quality Assurance for Safety in Nuclear Power Plants and other Nuclear Installations [77, 78].

The research reactor QA programme should be developed, implemented and maintained by the responsible organization and it should include detailed procedures of how work is to be managed, performed and assessed. It also includes the organizational structure, functional responsibilities, levels of authority and interfaces for those managing, performing and assessing the adequacy of work. The quality assurance programme should address planning, scheduling and resource considerations. Procedures should include training and qualification, non-conformance control and corrective actions, document control and records.

The responsible organization should also be responsible for the establishment and implementation of the overall QA programme. If the responsible organization delegates the work of establishing and implementing all or a part of the overall programme to other organizations, it should retain responsibility for the effectiveness of the programme in all circumstances. A recommendation on how to establish and implement the QA programme is given in Safety Guide Q1 in Ref. [77].

For a research reactor, the water QA programme is a specific part of the overall QA programme for the facility. It establishes the requirements for the water quality management programme in all parts of the facility, and provides the objectives, principles and guidance for the programme.

It is important to note that the adopted water QA programme is also applicable to external suppliers of services related to the water management programme.

8.2. RELEVANT QUALITY SYSTEMS

The organization responsible for the research reactor should make a deliberate determination about which quality standard is more suitable for its water quality management programme, considering that it must be compatible with the overall QA programme for the facility. Successful quality systems that can be used to establish a good water quality management programme are: Good Laboratory Practices (GLP), ISO 9001 and ISO 17025.

8.2.1. Good Laboratory Practice (GLP)

Principles of GLP is a management system outlined by the Organisation for Economic Co-operation and Development (OECD) to ensure the consistency and ***reliability*** of results The purpose of the Principles of Good Laboratory Practice is to promote the development of quality test data. Comparable quality of test data forms the basis for the mutual acceptance of data among countries. If individual countries can confidently rely on test data developed in other countries, duplicative testing can be avoided, thereby saving time and resources. The application of the Principles should help to avoid the creation of technical barriers to trade, and further improve the protection of human health and the environment.

Although its primary objective is to ensure the generation of high quality and reliable test data related to the safety of industrial chemical substances, the Principles system is applicable to all ***laboratories*** and research organizations in the development of their laboratorial activities, including water quality management [79]. GLP is not a real standard, but rather, more like an informal agreement. The items that are usually mentioned are useful, but there are no fixed rules and obligations. Therefore, results obtained from a laboratory that claims to be working compliant to GLP cannot be used when legal aspects are involved.

8.2.2. ISO 9001

ISO 9001:2000 [80] is the standard that provides a set of standardized requirements for a quality management system, regardless of what the user organization does, its size, or whether it is in the private or public sector. It is the only standard in the family against which organizations can be certified — although certification is not a compulsory requirement of the standard. ISO 9001 concerns how things are organized at a site/institute. There are clear rules in ISO 9001, and if accredited for ISO 9001, the site/institute will be audited regularly on your ISO 9001 performance.

The ISO 9001:2000 standard provides a tried and tested framework for taking a systematic approach to managing the organization's processes in order to continuously improve the quality of its products and services.

It is important to observe that ISO 9001:2000 lays down what requirements the institute’s quality system must meet, but does not dictate how they should be met in any particular organization. This leaves great scope and flexibility for implementation in different business sectors and business cultures, as well as in different national cultures.

The standard requires the organization itself to audit its ISO 9001:2000 based quality system to verify that it is systematically and effectively managing its processes, or, that it is fully in control of its activities. In addition, the organization may invite its clients to audit the quality system in order to give them confidence that the organization is capable of delivering products or services as specified.

Finally, the organization may engage the services of an independent quality system certification body to obtain an ISO 9001:2000 certificate of conformity. This last option has proved to be extremely popular in the market-place due to the perceived credibility of an independent assessment.

The organization may thus avoid multiple audits by its clients, or reduce the frequency or duration of client audits. The certificate can also serve as a business reference between the organization and potential clients, especially when supplier and client are new to each other, or far removed geographically, as in an export context.

Typical ISO 9001:2000 items emphasize human resources (training, definition of responsibilities); management structure; development of procedures for product/service realization; and traceability, measurements, analysis and improvement. It also specifies some compulsory documents for control of documents, records, internal audits, non-conforming product/service, and corrective and preventive actions.

ISO 9001 is a quality system that has been successfully used for quality management (including water quality management), in some research reactors [81, 82].

8.2.3. ISO 17025

ISO/IEC 17025:2005 [83] specifies the general requirements for the controls to carry out tests and/or calibrations, including sampling. It covers testing and calibration performed using standard methods, non-standard methods, and laboratory developed methods. It is applicable to all organizations performing tests and/or calibrations. These include, for example, first, second and third party laboratories, and laboratories where testing and/or calibration forms part of inspection and product certification

ISO/IEC 17025:2005 is applicable to all laboratories regardless of the number of personnel or the extent of the scope of testing and/or calibration activities. When a laboratory does not undertake one or more of the activities covered by the standard, such as sampling and the design/development of new methods, the requirements of those clauses do not apply.

ISO/IEC 17025:2005 is used by laboratories in developing their management system for quality, administrative and technical operations. Laboratory customers, regulatory authorities and accreditation bodies may also use it in confirming or recognizing the competence of laboratories. The standard is not intended to be used as the basis for certification of laboratories, and it does not cover compliance with regulatory and safety requirements on the operation of laboratories.

ISO/IEC 17025 items include:

- Organization of the laboratory (overlap with ISO 9001 item);
- Training of staff and employees;
- Instruments, maintenance, calibration;
- Chemicals, quality, traceability;
- Procedures, methods of measurements, calibration;
- Reporting;
- How to deal with complaints (overlap with ISO 9001 item).

When reliability of data is essential, an ISO 17025-compliant programme is strongly recommended. The accredited results from a ISO 17025 certificated laboratory are traceable to generally accepted International Standards, and information about the property of the data (bias and precision) is available as well. Generally these results/data are as reliable as can be obtained. In case of accidents or arguments between producers and users, results/data obtained using ISO 17025 will have the highest legal value.

8.3. DOCUMENTS AND RECORDS

Documentation of the water QA programme should be structured so that it is appropriate to the organization and the work it performs, and is available in language appropriate to the users. Its structure and format should also be flexible enough to accommodate changes in policy, strategic aims, quality standards, regulatory requirements and other statutes, as well as feedback from implementation and lessons learned from other plants and facilities. Documents such as procedures, instructions, specifications and drawings, or other media, which describe processes, specify requirements or establish design, should be prepared, reviewed, approved, issued, distributed, authorized, revised, and as required, validated. All personnel preparing, revising, reviewing or approving documents shall be specifically assigned to this work and be given access to appropriate information up which to base their input. The primary consideration should be to ensure that the documents are suitable for use by the appropriate personnel and that the contents are clear, concise and unambiguous, whatever the format. Personnel using documents should be aware of and use appropriate and correct documents.

Records that describe the status, results, characteristics of items and services, performance of processes and represent objective evidence of quality shall be specified, prepared, reviewed, approved and maintained. All records shall be legible, complete and identifiable. A records system shall be established to provide for the identification, collection, indexing, filing, storing, maintenance, retrieval and disposal of records. Retention times of records and associated test materials and specimens shall be established to be consistent with the type of records, material and specimens involved.

Inspection and testing of specified items, services and processes shall be conducted using established acceptance and performance criteria. The level of inspection and testing and the degree of independence of personnel shall be established.

Whenever applicable, produced documents need to specify clear responsibilities for revision, approval and audits, as well the necessary periodicity for revision.

In general, the documents related to the water QA programme, must consider/address the following topics, related to water quality management in a research reactor:

- Planning;
- Procedures;
- Calibration standards;
- Methods of measurements;

- Methods for laboratory analysis;
- Sampling techniques; and frequency;
- Instruments maintenance and calibration;
- Training;
- Traceability;
- Technical audits;
- Reports and results;
- Acceptance criteria;
- Performance evaluation;
- Alternatives for dealing with non-conformities.

As a first approach, it is suggested to consider a ‘top–down’ structure for the documents to be produced. Using this structure, a single Operational Procedure (OP) can be issued for each major system, for example:

- OP#1 Maintenance and Control of Water in Primary System;
- OP#2 Maintenance and Control of Water in Secondary Circuit;
- OP#3 Maintenance and Control of Water in Spent Fuel Storage Basin;
- OP#4 Maintenance and Control of Water in Emergency Core Cooling System;
- OP#5 Maintenance and Control or Water in Make-Up System;
- OP#6 Operation of Primary Water Purification System;
- OP#7 Calibration Programme for Equipments Used in the Water Management Programme.

In this example, OP#N is a representative format for the procedure identification, which must be established in accordance with the facility overall QA programme. On each procedure it is necessary to specify periodicity, specific work and technical instructions, applicable forms, records, acceptance criteria, non-conformity actions and responsibilities. Work and technical instructions are typically a one page procedure establishing the step by step activities related to components and systems operation; maintenance and tests; modifications and calibrations. For the water components and systems, it must also consider radiation protection and chemistry activities. The type and format of working documents can vary considerably depending on the application involved. Annex V of Safety Guide Q1 in Ref. [77] contains an example of the format of a working instruction, and Annex II illustrates the structure and contents of a typical procedure.

8.4. ADDITIONAL CONSIDERATIONS FOR A WATER MANAGEMENT QA PROGRAMME

Records of the water quality management programme and the related maintenance activities should be maintained for the life of the facility and allow easy identification for traceability.

The results of the on-line water quality parameter measurements should be judged daily. Every week, the on-line instruments should be inspected visually for leakage, similar failures, error messages from instruments, and flow and pressure settings. Relevant information should be mentioned in the facility log book.

The calibration programme and procedures must also consider the importance of ‘traceability’ in the process. Calibration must be performed using traceable primary standards or certified reference materials. A **Primary Standard** “is designated or widely acknowledged as having the highest metrological qualities and whose value is accepted without reference to other standards of the same quality”, and a **Certified Reference Material (CRM)** “is a reference material one or more of whose property values are certified by a technically valid procedure, accompanied by a certificate or other documentation that is issued by a certifying body.” Ref. [84] gives a specific example of selection and use of accurate, traceable conductivity standards.

During scheduled shutdowns of the reactor, maintenance verification and, if necessary, recalibrations should be done on water quality instrumentation. All relevant values should be noted, including the measured values before and after the verification/calibration.

When measurements, data, or observed results are outside of the limits or expected conditions, and if an action plan is not in place for this case, a five step systematic approach will be helpful, considering the following:

(1) Why did it happen?
(2) What was the impact of the incident?
(3) Find a solution to be sure it will not happen again.
(4) Check if the solution is sufficient (operational).
(5) Discuss the incident with operation staff at group meetings.

9. CASE STUDIES

9.1. OPERATIONAL EXPERIENCE IN THE IEA-R1 RESEARCH REACTOR: EFFECT OF A TEMPERATURE EXCURSION[4]

9.1.1. Introduction

IEA-R1 is a pool type, light water moderated, beryllium and graphite reflected research reactor, at the Instituto de Pesquisas Energéticas e Nucleares (IPEN), which is part of the Brazilian Nuclear Energy Commission. Although designed to operate at 5 MW, IEA-R1 has operated at 2 MW during most of its life. This reactor is being used to perform research in nuclear and solid state physics, radiochemistry and radiobiology, production of radioisotopes and to give irradiation services.

The spent fuel storage section (SFSS) is located at one end of the IEA-R1 reactor pool and contains racks for long term storage of spent fuel elements (FE), and short term storage of FE while loading and unloading the reactor core. The racks were originally made of aluminium sections bolted together and suspended from the walls of the pool at a depth of 6 m. In 1977, when the reactor pool liner was changed from ceramic tiles to stainless steel, the aluminium racks were replaced with stainless steel racks. In 2003, the stainless steel racks were lined with an aluminium alloy to minimize bimetallic contact between the aluminium alloy of the FE and the stainless steel of the racks and thus prevent galvanic corrosion of the FE.

Typical values of water parameters of the SFSS, which are the same as that of the reactor pool, are shown in Table 16. These parameters are maintained with the help of two water purification systems.

9.1.2. The Problem: Staining of aluminium surfaces

The IEA-R1 reactor has operated for over 45 years at 2 MW. In February of 2004, the reactor’s power was increased to its rated capacity of 5 MW. The three main water parameters: pH, conductivity and temperature of the primary circuit of this reactor are monitored periodically. In May 2004, the IEA-R1 reactor manager expressed concerns that all aluminium alloy surfaces inside the reactor pool that are normally bright and light grey were turning dark grey. This was first observed on structural components and later on fuel cladding surfaces. A variety of reasons were initially put forth to explain the staining of the Al surfaces and included possible breach of fuel cladding followed by release of fission products and subsequent deposition of one or more components of the fission products on all surfaces.

9.1.3. The corrosion monitoring projects

At the time the Al surfaces were observed to stain, Brazil and in particular IPEN, was actively involved in the IAEA supported the CRP Corrosion of Al-clad Spent Research Reactor Fuel in Water as well as the Regional Project for Latin America (RLA),Management of Spent Research Reactor Fuel. The activities within these projects consisted of exposing coupons of various aluminium alloys in stainless steel test racks in the spent fuel wet storage section of this reactor for predetermined periods followed by evaluation of the coupons to determine the extent of

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[4] A similar paper was produced for Ref. [8]. The reason to include this paper here is to have all pertinent material compiled in a single publication.

TABLE 16. TYPICAL VALUES OF WATER PARAMETERS AT THE IEA-R1 SFSS

Parameters	Units	Typical Values
pH	—	5.5 to 6.5
Conductivity	µS/cm	<2.0
Chloride ions	ppm	<0.02
Iron ions	ppm	<0.001
Sodium ion	ppm	<0.4
Temperature	°C	25 to 40
Total solids dissolved	ppm	<2
^{99}Mo	Bq/L	<310
^{131}I	Bq/L	<90
^{133}I	Bq/L	<430
^{132}Te	Bq/L	<95
^{239}Np	Bq/L	<750

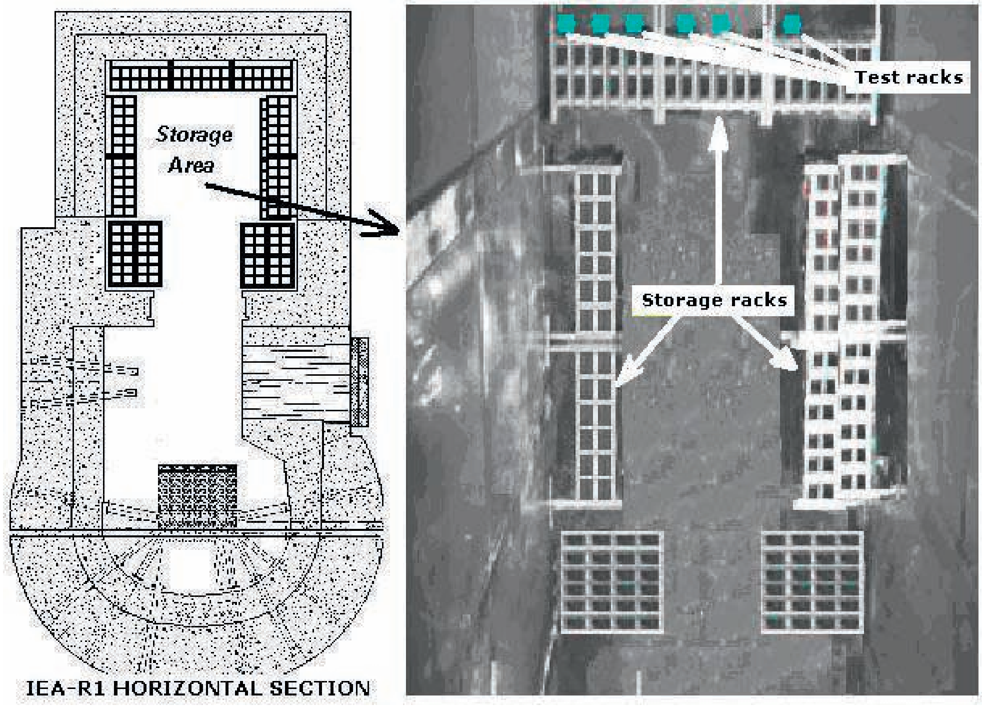

FIG. 41. Position of coupon racks in the IEA-R1 reactor spent fuel storage section.

their corrosion as a function of water parameters. Figure 41 shows the position of the test racks in relation to the reactor core and the fuel storage racks in the SFSS.

Test racks with a number of coupons in different orientations were immersed in July 2002 with programmed withdrawals of one test rack a year in each of the projects. One set of test racks had been withdrawn in July 2003 and the second set of test racks of the RLA project was scheduled for withdrawal in July 2004. These test racks contained mainly aluminium alloys AA 1100 and AA 6061 coupons with composition as shown in Table 17. To throw more light on the unforeseen staining of the aluminium surfaces in the IEA-R1 reactor pool, the Chief

TABLE 17. CHEMICAL COMPOSITION OF ALUMINIUM ALLOYS [WT %]

Alloy	Cu	Mg	Mn	Si	Fe	Ti	Zn	Cr	Al
AA 1100	0.16	<0.1	0.05	0.16	0.48	0.005	0.03	0.005	Balance
AA 6061	0.25	0.94	0.12	0.65	0.24	0.04	0.03	0.04	Balance

Scientific Investigator of the CRP and RLA projects in IPEN decided to withdraw one test rack (R2) of the RLA project, two months prior to its programmed withdrawal, i.e. test rack R2 was withdrawn in May 2004, after 22 months of exposure instead of the scheduled 24 months. This test rack was then disassembled and the coupons were prepared for examination as per procedures outlined in Section 7 and Annex I.

The three main parameters, temperature, conductivity and pH, of the reactor pool were monitored at regular intervals. Other pool water quality parameters were monitored at less frequent intervals. A graphical presentation of the three water parameters during the period 2002–2004 is shown in Fig. 42.

9.1.4. Coupon evaluation

The coupons of test rack R2 were placed next to corresponding coupons from test rack R1 (withdrawn in July 2003 after 12 months of exposure) for comparison, as shown in Fig. 43. It was evident that the surfaces of coupons of test rack R2 were darker and stained. The extent of staining was similar to that observed on the other Al surfaces within the reactor pool.

9.1.4.1. Coupon surface analysis

To determine the cause of staining of Al coupon surfaces in the reactor water, specimens of the two alloys, AA 1100 and AA 6061, exposed for 12 and 22 months (nominal two years) were taken for examination in a scanning electron microscope (SEM) and for X ray diffraction (XRD) analysis. The SEM micrographs of the surfaces of AA 1100 and AA 6061 exposed for 12 and 22 months are shown in Figs 44 and 45. Energy dispersive spectroscopic analysis of these surfaces are shown in Figs 46 and 47, revealing significantly higher oxygen peaks on surfaces of the two alloys exposed for two years compared with those exposed for one year.

The X ray diffractograms of the surfaces of AA 1100 and AA 6061 exposed for 12 and 22 months are shown in Fig. 48. The surfaces exposed for 22 months (two years nominal) revealed peaks of the aluminium oxide bayerite whereas that exposed for 12 months did not. The SEM micrographs in Figs 44 and 45 also revealed marked differences in the morphology of the oxide formed on the coupon exposed for two years, compared with that formed on the coupon exposed for one year. Bayerite is a type of Al oxide that forms at temperatures below 70ºC (see Section 3.2). The type of oxide formed on the AA 1100 surfaces exposed for 12 months was ‘boehmite’; the oxide formed on the surface of the same alloy exposed for 22 months was ‘bayerite’.

9.1.5. Reactor pool water temperature excursion

The three water parameters shown in Fig. 42 during the period when the two test racks were exposed to the reactor coolant was scrutinized. These parameters were well within their prescribed limits. However, the only parameter that showed some deviation was temperature. Test rack R1 remained exposed to water in the temperature range 25–38ºC, whereas test rack R2 remained exposed to water in the temperature range 25–50ºC. Coincidentally, during the period from January to May 2004, the reactor power had been raised from 2 MW to 5 MW. The main concern was that this reactor was designed to operate at 5 MW and the pool temperature was within the specified limits, as also shown in Fig. 42. The increased average water temperature during this above-mentioned period was attributed to insufficient cooling of the circulating primary water in the heat exchanger. Although the pump was adequately dimensioned for the increased flow rate necessary for reactor operation at 5 MW, the flow valves were partially closed to prevent excessive vibration of the heat exchanger tubes. This in turn resulted in inadequate water flow through the reactor core and consequent gradual increase in pool water temperature. Although the reasons for the pool water temperature increase had been deciphered, there were still concerns about the staining of aluminium surfaces exposed to the pool water that had increased by just 10ºC.

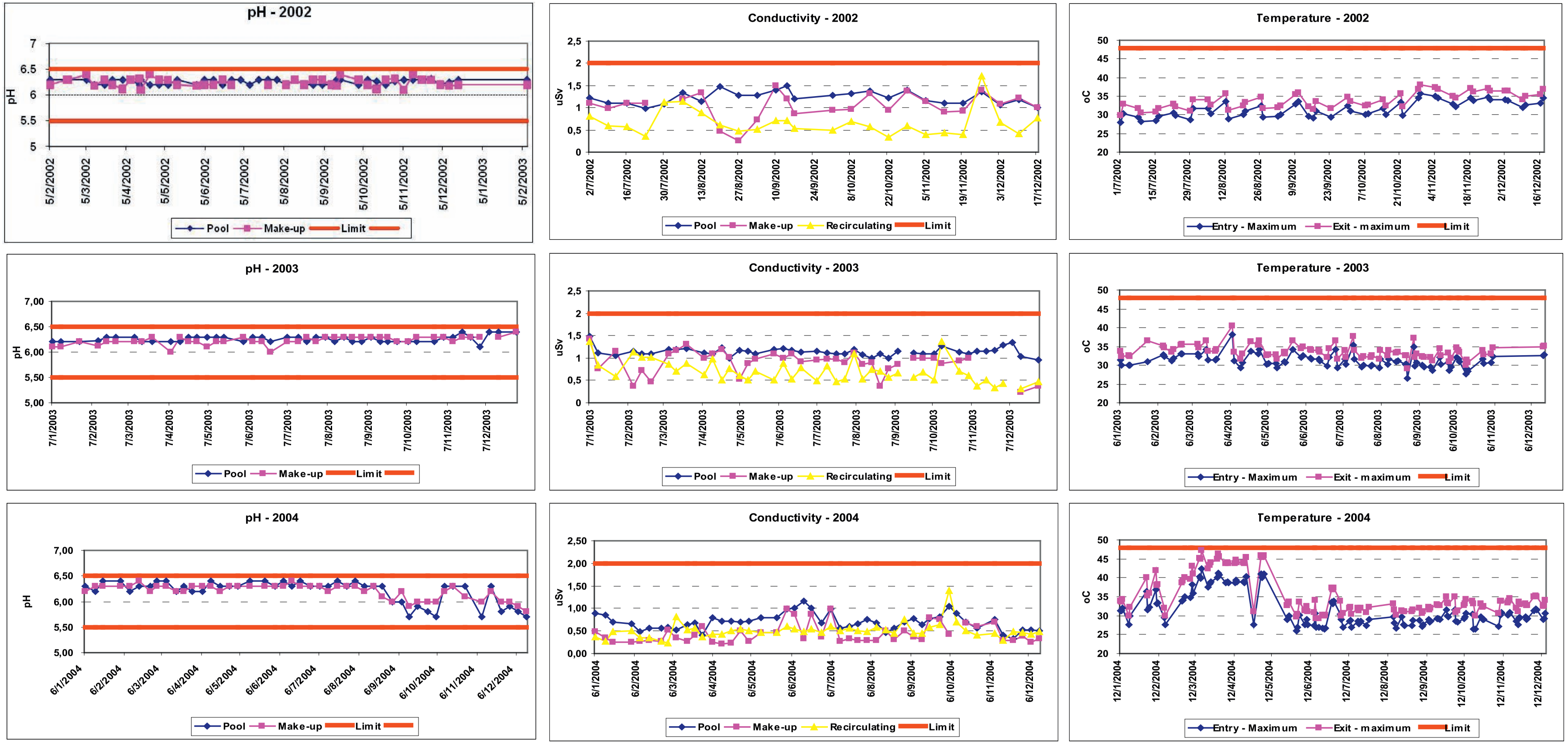

FIG. 42. pH, conductivity and temperature of water in the IEA-R1 SFSS during the period 2002-2004.

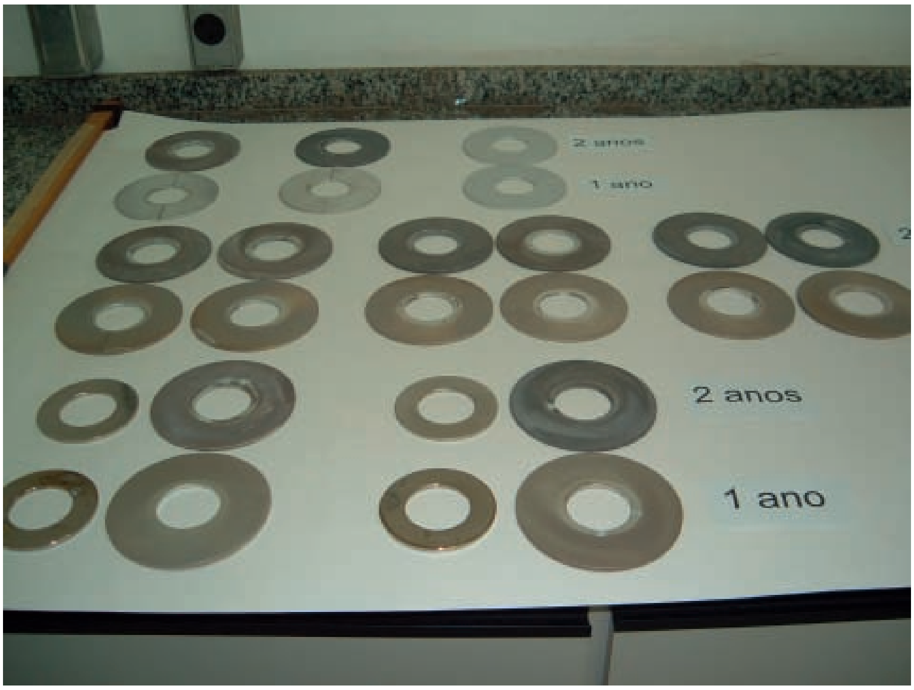

FIG. 43. Photograph of coupons of test rack R1 exposed for 12 months (one year) and of test rack R2 exposed for 22 months (two years) to IEA-R1 SFSS.

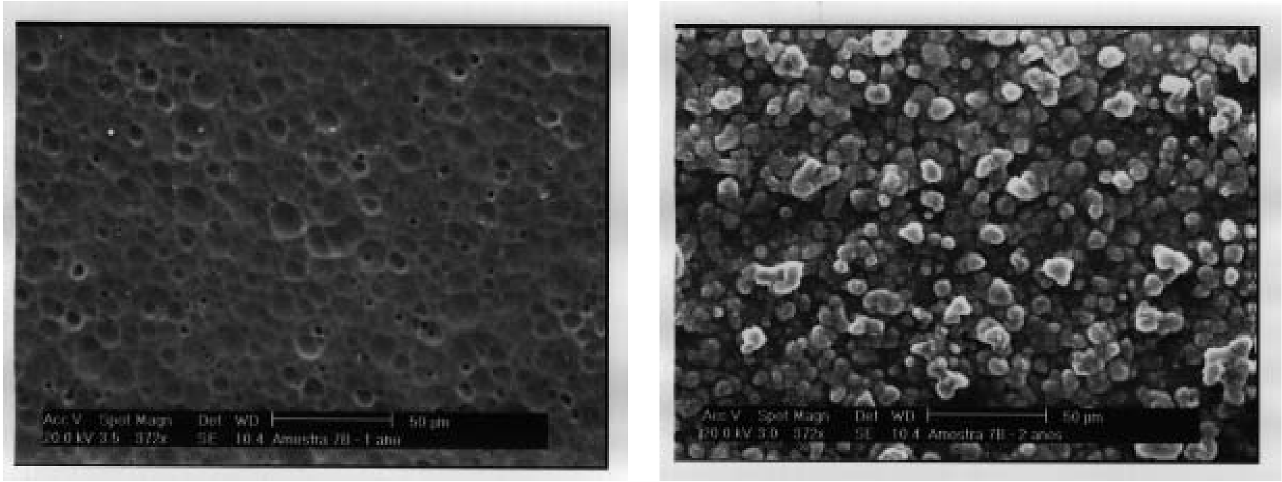

FIG. 44. Scanning electron microscope micrographs of AA 1100 coupon exposed for 12 months (left) and 22 months (right) to IEA-R1 SFSS.

9.1.6. Prognostics

The stained regions on the Al alloy surfaces within the reactor pool were due to the Al oxide ‘bayerite’ that formed at the higher temperature. Although the temperature difference was just 10ºC, this was sufficient for the nature of the oxide formed on Al alloy surfaces to change and display a different colour. Although the reactor personnel were aware of the higher pool water temperature, they were not concerned as it was still within acceptable limits. However, when the surfaces of various aluminium alloy components started darkening, it caused concerns. The corrosion monitoring programme put to rest these concerns.

This case study highlights one of the advantages of an ongoing corrosion monitoring programme. A programme of this nature monitors the corrosion behaviour of in-reactor type materials as a function of various operational parameters.

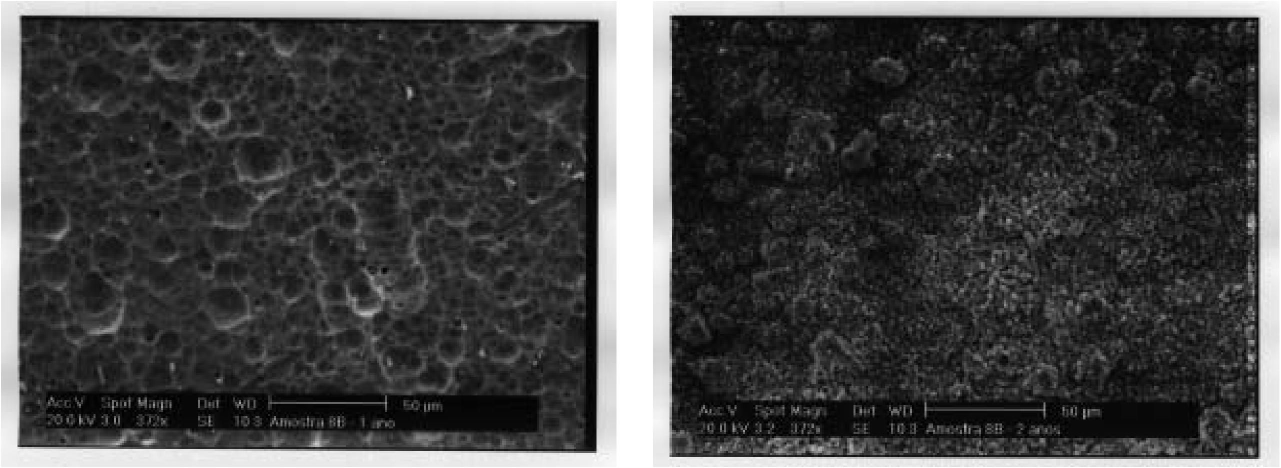

FIG. 45. Scanning electron microscope micrographs of AA 6061 coupons exposed for 12 months (left) and 22 months (right) to IEA-R1 SFSS.

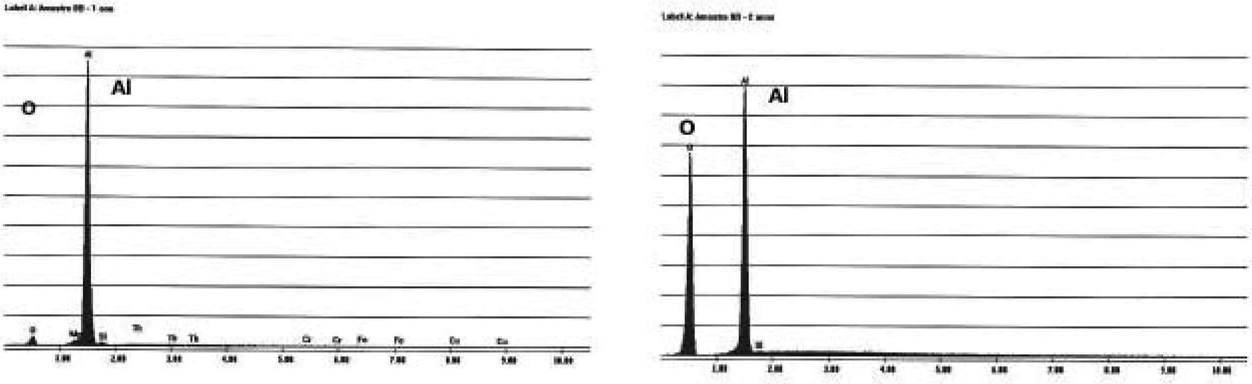

FIG. 46. EDS results of the surfaces of AA 6061 coupons exposed for 12 (left) and 22 months (right).

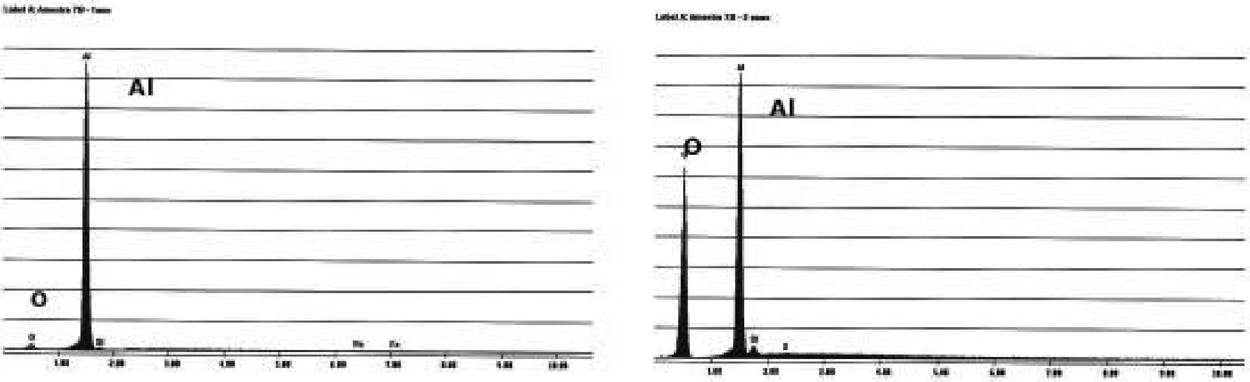

FIG. 47. EDS results of the surfaces of AA 1100 coupons exposed for 12 (left) and 22 months (right).

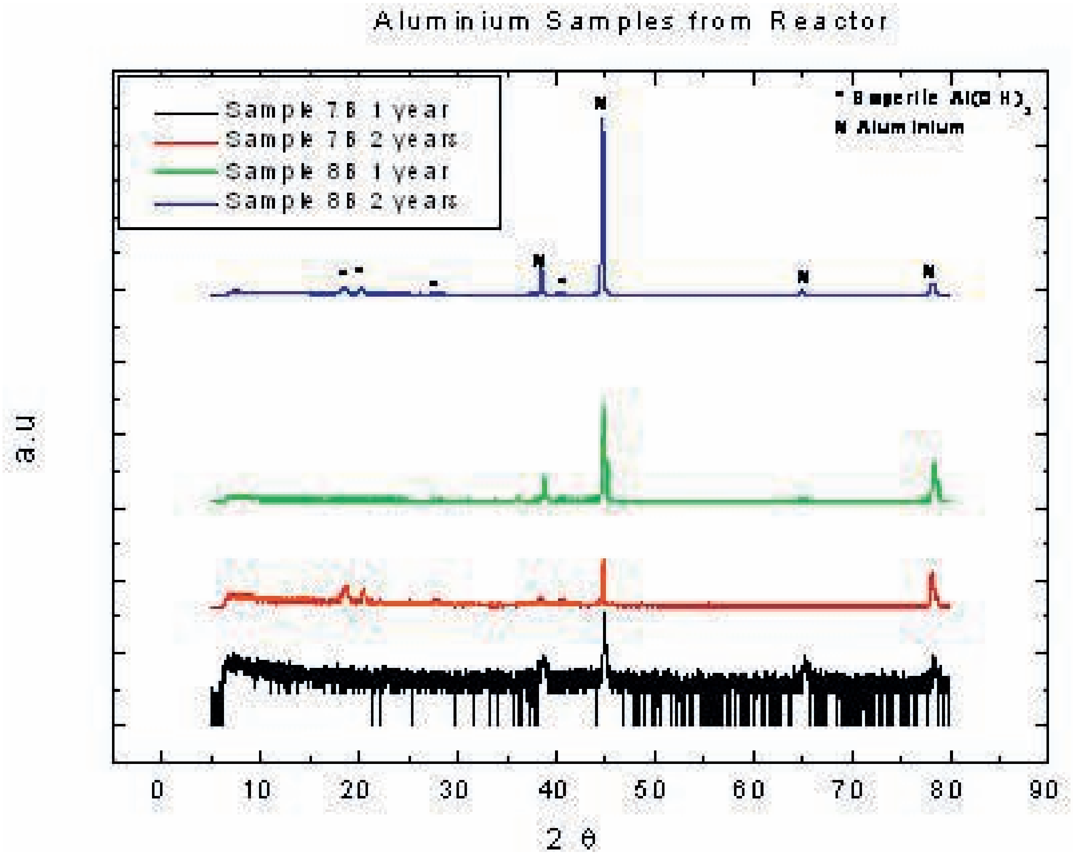

FIG. 48. X ray diffractograms of the surfaces of coupons exposed for one and two years to the reactor pool.

9.2. OPERATIONAL EXPERIENCE IN WATER QUALITY MANAGEMENT IN TRANSITION OF SPENT FUEL DECAY BASINS TO A SPENT FUEL STORAGE BASIN AT THE SAVANNAH RIVER SITE

9.2.1. Overview of Fuel Storage History at the Savannah River Site

Heavy water-cooled and moderated reactors to produce nuclear materials for the defence mission of the United States were operated at the Savannah River Site (SRS) in Aiken, South Carolina, starting in the mid- to late-1950s. The production fuel was removed from the reactor and cooled in large basins with light water (approximately 3–4 million gallons) typically for only several months up to 18 months to achieve a measure of radioactive decay prior to transfer for processing and chemical separations.

The U.S. Department of Energy (DOE) decided to cease general processing of nuclear materials in 1989. Subsequently, the reactor basins that had been used for temporary storage for spent fuel to remove decay heat were to be used for extended storage of spent nuclear fuel beginning at that time. This included production reactor fuels stored in the K, L and P-Reactor basins.

An inventory of research and test reactor fuels at the site had been in extended storage in the Receiving Basin for Offsite Fuel (RBOF) facility. The RBOF was a smaller size basin (approximately 600 000 gallons) in which fuel was in extended storage with good water quality maintained at 1–3 μS/cm using mixed bed, continuously operated deionizers. The production reactors were permanently shut down, and most of the production reactor fuel was processed. All remaining fuel at the site that had not been processed was transferred to the L-Basin by 2003, including the fuel from the RBOF.

The water in the reactor basins had been periodically deionized using portable deionizers procured in the 1960s. The deionizers were rotated between the basins to control radioactivity levels since the fuel did not remain in the basins for extended storage times. The conductivity of the basin water from the 1960s through the 1980s was maintained in the range of 60–70 μS/cm. With the suspension in fuel processing in 1989, the production reactor fuel remained in the basins. The deionizer availability was limited, and the water quality conditions that were never optimized for corrosion control, deteriorated. The aluminium fuel and components suffered pitting and galvanic corrosion attack that became apparent in 1992–1993 [85, 86].

From 1994 to 1996, a Disassembly Basin Upgrade Project was conducted, comprising the following improvements and corrosion mitigation actions:

— Continuous deionization with cation and anion resins;
— Deionized make-up water;
— Sludge removal;
— Improved basin level indication;
— New aluminium racks for fuel storage;
— New monitoring wells.

These improvements are listed in the DOE Plan of Action to Resolve Spent Fuel Vulnerabilities [87], and started with immediate actions including a new sand filter in 1994, beginning of deionization using the portable deionizers 1994, and with a large mixed-bed portable system in 1995. An upgrade to chemistry specifications and controls was implemented in 1995, and galvanic couples in storage systems were removed from 1995 to 1998.

Prior to the aggressive deionization campaign, the K-Basin had reached a maximum conductivity of 180 µS/cm, the L-Basin a maximum conductivity of 160 µS/cm, and the P-Basin a maximum conductivity of 165 µS/cm in 1994.

Deionization using the existing SRS portable deionizers began in L-Basin in 1994. The water was improved from the 160 to 96 µ S/cm, and the chloride concentration from 18 to 11 ppm. In July 1995, a vendor was contracted to accelerate the deionization of the SRS basins. The vendor installed portable mixed bed deionization equipment in L-Basin. The conductivity was reduced from approximately 110 µS/cm to about 8 µS/cm in 2.5 months. The SRS portable deionizers were again used in L-Basin when the vendor transferred his equipment to K-Basin. The SRS portable deionizers further lowered the conductivity in L-Basin to 1.8 µS/cm by March 1996.

In October 1995, the vendor equipment was installed in the K-Basin. By March 1996, the K-Basin conductivity was 2.5 µS/cm. The anion (chloride, nitrate, sulphate) concentrations were reduced to about 0.5 ppm in the L and K-Basins. The site purchased the deionization equipment from the vendor at the completion of the contract in early 1996. The present configuration of the L-Basin Water Chemistry Control System is described below.

9.2.2. Corrosion monitoring to demonstrate non-aggressive water quality

A corrosion monitoring or surveillance programme was first instituted in 1992 [26]. The programme involved emplacement and periodic withdrawal of corrosion coupons to evaluate the aggressiveness of the water conditions to aluminium corrosion. The results of the programme showed the effects of poor water quality and also demonstrated that the water quality improvements were effective at reducing the corrosion attack to aluminium.

A summary treatise of the factors important to corrosion of aluminium fuel materials is provided in Refs [7, 47]. Basin storage and water quality conditions at present are good, and only localized attack in crevice conditions has been observed in the surveillance specimens [88]. The Spent Fuel Project Basin Water Chemistry Control Programme [89] is the site operations programme to monitor and set water quality parameters.

At present, spent nuclear fuels from research reactor around the world with materials of US origin are being received at the site and stored in the L-Basin. This includes research reactor fuel from domestic (US reactors) and foreign (non-US) research reactors. The predominant fuel types are research reactor fuel with aluminium alloy cladding and aluminium based fuel. Approximately 10 000 Materials Test Reactor Equivalent assemblies are being stored in L-Basin at present. Other fuel materials that are in the L-Basin storage inventory include stainless steel and Zircaloy cladding with uranium oxide fuel.

The following sections briefly describe the corrosion attack of production reactor fuel while under poor water quality in the SRS basins in the early 1990s, as described above, and the water chemistry control system that has provided good water quality for aluminium fuel storage in the L-Basin at SRS since 1996.

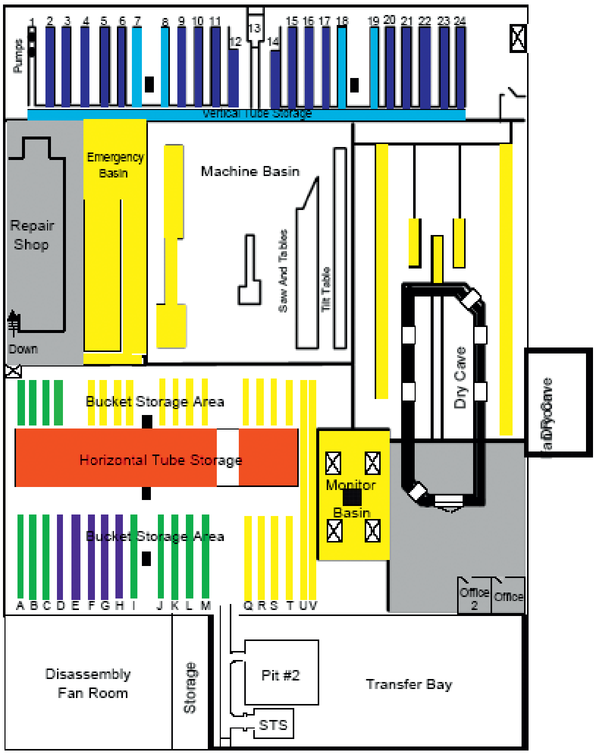

FIG. 49. Map of the L-Basin configuration for spent nuclear fuel storage.

9.2.3. L-Basin configuration

The L-Basin is a 3 375 000 million gallon volume structure constructed of reinforced concrete and coated with vinyl paint. The basin is divided into seven interconnected sections from 17 to 50 feet deep. Figure 49 shows the configuration of the L-Basin for spent fuel storage. The L-Basin fuel storage configuration consists of vertical and horizontal tube storage, and bucket storage. The current L-Basin inventory includes approximately 10 000 Materials Test Reactor Equivalent Fuel assemblies with aluminium cladding, and 700 assemblies with stainless steel or Zircaloy cladding.

Oversize cans are used to store severely damaged and failed fuel and fuel pieces. Damaged or degraded cladding or structural deformation of a fuel assembly, if significant, can result in radiological, criticality safety, waste and accountability issues. The management of damaged spent nuclear fuel in the USA. including a description of the vented, oversize cans used at SRS for continued underwater storage of damaged fuel, is provided in Ref. [90]. Aluminium-based fuel with minor breaches of the cladding can be safely stored directly in the L-Basin.

9.2.4. Corrosion incidence in SRS fuel storage basins

The storage experience at SRS, and experience from basin storage at many sites worldwide, show that storage of aluminium-based fuel materials in water basins is the most challenging issue of research reactor materials due to the need to avoid conditions aggressive to corrosion of the aluminium. Corrosion control and surveillance activities were developed at SRS to minimize aluminium cladding corrosion through water chemistry operational limits and storage configurations to avoid galvanic couple incompatibilities. These activities were driven by the incidence of corrosion in the production reactor cooling basins summarized through photographs in the figures that follow.

Figures 50–52 [92] show the corrosion attack suffered by production fuels and target materials, and basin storage components. The extended storage of the aluminium clad fuel and target materials under the poor water quality of the basins in the early 1990s caused an incidence of pitting corrosion and galvanic corrosion in the materials. As discussed, the corrosion incidence occurred when the water chemistry was aggressive to aluminium with the primary causes of high conductivity (up to 180 µS/cm), high chloride (up to 18 ppm) and galvanic couples.

FIG. 50. Mark-22 assembly in (aluminium) vertical tube storage with Type 304L stainless steel hangers. Aluminium corrosion products are at scratches on the outer surface of the Mark 22 and at the aluminium–stainless steel interface at the hanger.

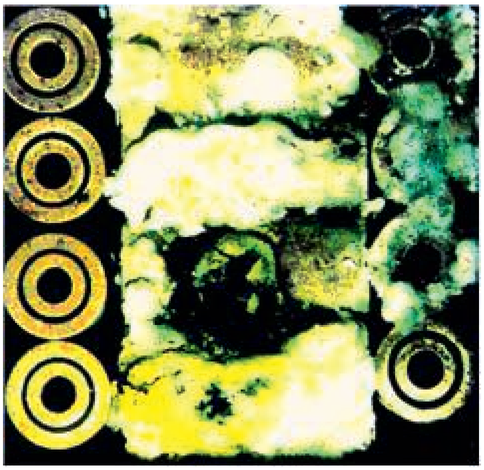

FIG. 51. Mark 31A targets in stainless steel bucket storage. Reference [92] provides post-storage metallographic analysis of these aluminium clad, uranium metal materials.

Figure 53 shows results from the CSP that the rapid, aggressive corrosion attack of aluminium in the SRS basins had been eliminated by 2001.

The results of the ongoing CSP show that localized corrosion at crevices and at galvanic couple interface regions can still occur [88] in the present good water quality of the L-Basin (see basin operating limits in

Table 18 in the next section) after several years of exposure. However, the corrosion coupon specimen design was optimized to cause corrosion attack, and no evidence of actual fuel attack under the good water quality conditions has been observed.

It is also import to highlight that no incidence of microbiological influenced corrosion has been detected in the SRS basins [91]. An ongoing microbial monitoring programme provides data and information to the extended basin storage.

FIG. 52. SRS basin storage rack. Corrosion nodules from pitting corrosion of the aluminium storage racks after 35 years of basin service in water not optimized in chemistry control for aluminium corrosion.

K-Basin 1992 **K-Basin 2001**

FIG. 53. Aluminum component immersion test (CIT) corrosion specimens in K-Basin stored during aggressive water chemistry (~180 µS/cm, ~10 ppm Cl) for 12 months (left photograph) and during improved water chemistry (~10 µS/cm, ~1 ppm Cl) for 45 months (right photograph).

9.2.5. L-Basin water chemistry control system

L-Basin uses zeolite and ion exchange resins for basin chemistry control for control of corrosion of the fuel. The system consists of two sand filter vessels, one zeolite train and two deionizer resin trains. The sand filter system contains sand and anthracite (coal) to remove insoluble particles. The recirculation flow through the sand filter is 1,600 gpm.

A portion of the flow (200 gal/min) from the sand filter enters the zeolite and ion exchange resin systems, as indicated in Fig. 54. The zeolite train is a single pass, molecular sieve and ion exchange system that effectively remove caesium and strontium ions from the water after is passes through the sand filters and before it enters the anion and cation resin train. The zeolite train has two vessels, which consist of 100 ft^3 total of zeolite.

The anion and cation train is specifically designed to minimize corrosion by removing and replacing any deleterious ions that have not been removed by the zeolite. The ion exchange resins used in the L-Basin system are porous polystyrene/divinylbenzene copolymers. The resin is mostly polystyrene with some divinylbenzene cross-linking for strength.

The resins are similar except for the amount of divinylbenzene and the attached functional groups. The cation resin contains 8% divinylbenzene, and the functional group is $SO_3^-H^+$. The anion resin contains 4% divinylbenzene, and the functional group is CH_2–$N^+(CH_3)3OH^-$.

The two anion vessels contain a total of approximately 70 ft^3 of resin. The two cation vessels contain a total of approximately 50 ft^3 of resin. The dual anion and cation train configuration provides redundancy in ion exchange capability and the resin ratio ensures that both resin vessels will be spent at approximately the same time.

Activity limits for the resin train are established to meet the safety basis for the facility. These limits translate into basin water operational activity limits for caesium and alpha activity, as shown in Table 18, which shows also the present operational limits for pH, conductivity and ionic species in L-Basin.

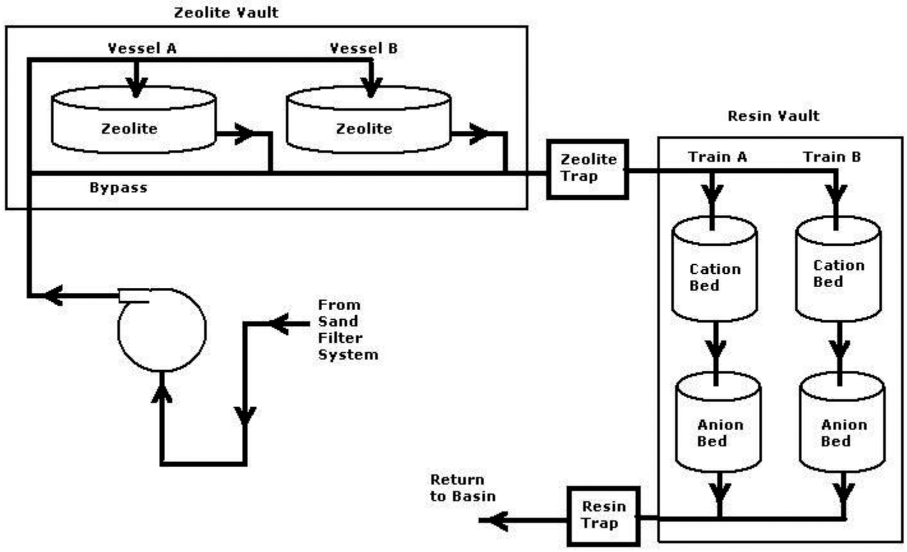

FIG. 54. Water chemistry control system layout for L-Basin.

TABLE 18. L-BASIN WATER OPERATIONAL LIMITS

Water quality parameters	Operatinglimit	Monitoringfrequency
pH	5.5–8.5	Weekly
Conductivity	10 µS/cm	Weekly
Activity	Cs-137:500 dis/min/mL Alpha: 3 dis/min/mL Tritium: 0.4 µCi/ml (8.88×10^5 dis/min/mL)	Weekly Monthly Every six months
Cu Concentration	0.1 ppm	Each six months
Hg Concentration	0.014 ppm	Each six months
Cl Concentration	0.1 ppm	Each six months
Fe	1.0 ppm	Each six months
Al	1.0 ppm	Each six months
Temperature	45°C	Monthly

9.3. OPERATIONAL EXPERIENCE IN RA6 RESEARCH REACTOR (ARGENTINA): CORROSION INDUCED BY SETTLED SOLIDS IN GOOD QUALITY WATER[5]

9.3.1. Introduction

The RA6 reactor was built by INVAP Company for the National Atomic Energy Commission of Argentina (CNEA). The reactor started operation in October 1982. This open pool, Multi-Purpose Reactor (MPR), is located in the Bariloche Atomic Centre, some 1650 km SW from the city of Buenos Aires. It was intended mainly for training and research, but it also serves for the production of radioisotopes at a small laboratory scale, neutron activation analysis, BNCT and as a test bench. Table 19 contains a list of relevant specifications.

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[5] A full report of this case study is found in Ref. [8].

TABLE 19. TECHNICAL DETAILS OF RESEARCH REACTOR RA6 UP TO 2007

REACTOR	
Type:	Open pool
Power:	500 kW thermal power
Average thermal flux at irradiation position:	5×10^{12} n/(cm^2 s)
CORE	
Fuel:	Enriched uranium (in process of conversion to LEU[a])
Fuel element:	Plate type clad in aluminium
Coolant:	Light water (forced downward flow: 100 m^3/h)
Moderator:	Light water
Reflector:	Graphite–light water
Control:	Four absorbing rods in Ag–In–Cd
Core configuration:	Variable
CORE COOLING	
Type:	Centrifugal pump
Heat exchanger:	Plate type
SECONDARY SYSTEM	
Type:	Cooling tower — centrifugal pump: 150 m^3/h
WATER CLEANUP SYSTEM	
Type:	Mixed bed ion exchange column
Quantity:	1 column, 1 filter
Conductivity at outlet:	Less than 2 µS/cm
REACTOR POOL (TANK)	
Diameter:	2.4 m
Height:	9.5 m
Material:	Stainless steel
SPENT FUEL POOL (AUXILIARY POOL)	
Section:	1 × 1.5 m
Height:	4 m
Material:	Stainless steel
SHIELDING FOR REACTOR POOL AND SPENT FUEL POOL	
Axial:	Light water
Radial:	Light water — reinforced heavy concrete

[a] Reactor fully converted in January 2009.

During the various corrosion surveillance programmes carried out in the framework of different IAEA’s projects, RA6 always stood among the reactors that showed the best water quality records. although its specifications establish a conductivity limit of 2 µS/cm at the outlet of the water purification system, the many independent chemical analysis performed showed that the value measured near the core rarely goes over 1 µS/cm, which makes this reactor a valid example of proper water maintenance.

Given that both the design and construction of the cleaning system do not have any special characteristic with respect to other reactors of the same kind, the reason of the high quality performance must be found on the strict keeping of operational schedules.

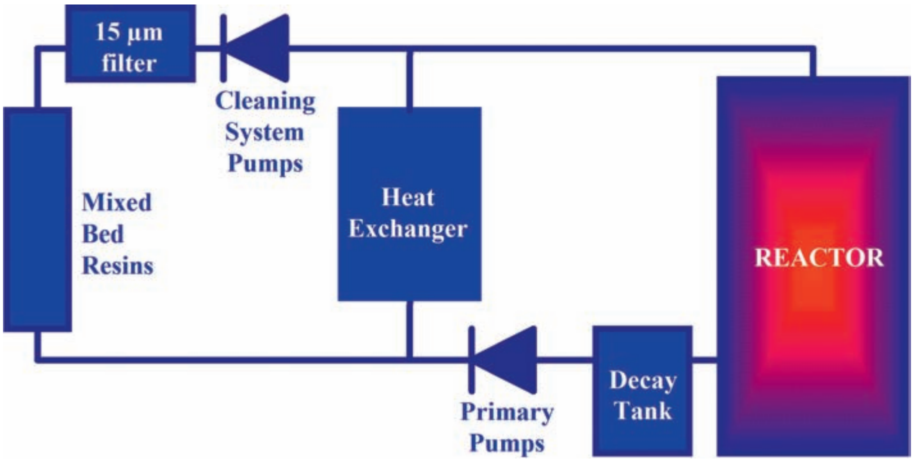

FIG. 55. Schematic layout of the water purification system.

9.3.2. Water cleanup system

There are two different water purification arrangements in the primary circuit: one dedicated to the coolant water and other for maintenance of the reactor water reservoir tank. In the secondary circuit, the water is not treated.

9.3.3. Coolant purification array

The main purposes of this installation are: first, to keep the primary coolant in a high purity degree (resistivity between 0.7 and 4 µS/cm, pH between 5.5 and 7), in order to reduce the corrosion of materials in contact; and second, to eliminate fission or corrosion products and active impurities in order to lower the primary activity and reduce the personnel exposition to radiation. The system takes part of the primary coolant water after the heat exchanger outlet and carries it through one or two parallel pumps to the mixed bed resins, prior to being re-injected just before the main primary pump. During this procedure, the fluid also passes through a filter, which holds particles larger than 15 µm and another device designed to retain resin particles, should these inadvertently get released from the resin column. This set-up is depicted in Fig. 55.

Table 20 contains specific technical data related to the different components of the purification system. The system operates continuously when the reactor is in use and water parameters (conductivity and pH) are continuously monitored through a proper instrumentation in the main reactor console.

Despite the required 2 µS/cm limit, the RA6 standard adopted practice is to keep the conductivity in the range 0.5 to 1 µS/cm. Whenever the conductivity reaches 0.8 µS/cm, the mixed bed resins columns are changed and a regeneration procedure is started in the old ones. This is carried out until the conductivity value at the outlet is 0.4 µS/cm.

9.3.4. Reservoir water purification

The purpose of this equipment is to maintain the good water quality of the demineralized water needed to feed the reactor water reservoir tank and the spent fuel pool. It is similar to the one described in previous section, but operates discontinuously; it is only used to replenish those facilities with water of the required purity. Table 21 contains the data related to this circuit.

It takes water from the reservoir tank and injects it into the primary circuit, between the decay tank and the primary pump, or through the mouth of the reactor pool. With respect to the spent fuel pool, this operation takes place whenever a low level is detected.

TABLE 20. TECHNICAL DETAILS OF THE PURIFICATION SYSTEM

MIXED BED DEMINERALIZER	
Flowing rate	5 m^3/h
Pressure loss	0.45 kg/cm^2
CIRCULATION PUMPS (TWO)	
Type	One-step centrifugal
Shell	Vertical
Impeller	Closed
Action	Electrical motor
Power	4 CV at 2900 rev./min
Differential height	35 m
Flowing rate	5 m^3/h
Working temperature	45 ºC
Circuit material	SS 316
FILTERS	
Type	‘Y’ for resin retention

TABLE 21. TECHNICAL DATA FOR THE PURIFICATION SYSTEM OF THE WATER RESERVOIR TANK

MIXED BED DEMINERALIZER	
Flowing rate	2 m^3/h
Pressure loss	0.25 kg/cm^2
CIRCULATION PUMPS (TWO)	
Type	One-step centrifugal
Shell	Vertical
Impeller	Closed
Action	Electrical motor
Power	2 CV at 2900 rev./min
Differential height	25 m
Flowing rate	2 m^3/h
Working temperature	10–42 ºC
Circuit material	CS and bronze (rotor)
FILTERS	
Type	‘Y’ for resin retention

9.3.5. Secondary circuit water maintenance

As stated before, line water without further treatment is used in the secondary circuit. Only a coarse filter is used to separate large elements, like leaves or other similar objects. Tap water in the RA6 environment is relatively pure, because it mainly originates from ice melts. Some normal parameters are: conductivity 30 µS/cm and pH 7.

The secondary circuit is mainly composed of a circulation pump, a heat exchanger and a cooling tower. Materials in contact with the fluid are: fibreglass reinforced plastic (FRP), stainless steel 316, carbon steel and iron casting. Information on secondary system components can be found in Table 22.

TABLE 22. TECHNICAL DETAILS OF SECONDARY CIRCUIT COMPONENTS

CIRCULATION PUMP	
Type	Centrifugal
Shell	Vertical
Impeller	Closed and radial with double curvature paddles
Action	Electrical motor
Power	35 CV at 2900 rev./min
Differential height	50 m
Flowing rate	100 m^3/h
Working temperature	10–35 ºC
Circuit material	Iron casting shell and bronze rotor
HEAT EXCHANGER	
Type	Plate
Exchanged heat	450 000 kcal/h
Circuit material	SS 316
COOLING TOWER	
Type	Single cell, countercurrent flow, forced draw
Flow rate	130 m^3/h
Inlet-Outlet temperature	20ºC and 16ºC
Circuit Material	FRP (fibreglass-reinforced plastic)

TABLE 23. HEAT EXCHANGER TECHNICAL DETAILS

Fluid	Primary side	Secondary side
	Demineralized water	Line water
Flow rate (m^3/h)	150	100
Inlet temperature (ºC)	~26	~16
Outlet temperature (ºC)	~23.5	~20
Maximum pressure (kg/cm^2)	4.5	5.4
Fouling factor (h m^2) ºC/kcal	0	0.0002

Table 23 contains specific data of the secondary system heat exchanger.

9.3.6. Corrosion performance

Historic records show negligible unexpected impact of fission or activation products in the RA6 primary water activity during 25 operation years. The observed fission product background activity was more related with contamination of the fuel during previous burnup at the RA3 reactor. This reactor used to be loaded with HEU, which was normally burnt up to 45–50%. The RA6 was fuelled with some of these elements, which also sustained immersion in the RA3 basin for around ten years. There has not been a corrosion case since the start, either in fuels or in any other component. This is not only corroborated by the activity levels, but it is also supported by visual observations performed on external fuel plates of elements deposited in the spent fuel pool.

A good example of the water quality level was obtained during the development of various IAEA projects, devoted to study the corrosion of aluminium clad MTR fuel in spent fuel water basins and in long term immersion

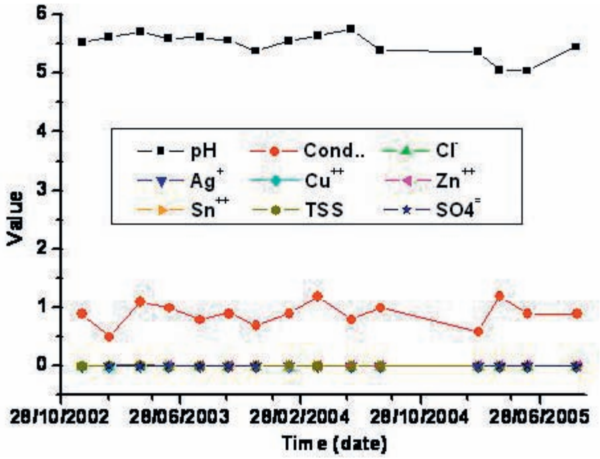

FIG. 56. Water chemistry evolution in the RA6 reactor pool. Conductivity is given in µS/cm, pH in pH units. Total soluble solids (TSS) and dissolved ions in ppm.

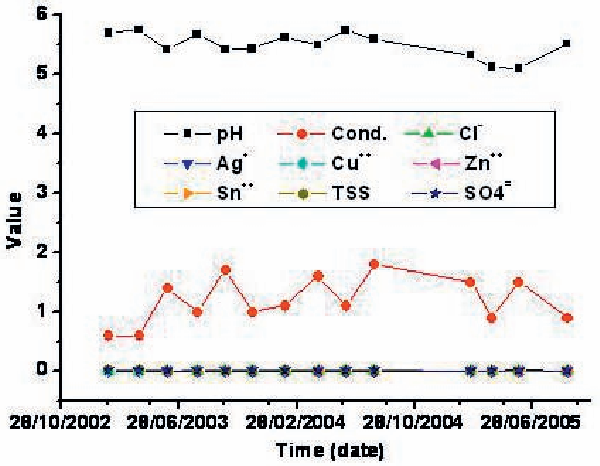

FIG. 57. Water chemistry evolution in the RA6 spent fuel pool. Conductivity is displayed in µS/cm, pH in pH units. Total soluble solids (TSSs) and dissolved ions in ppm.

of fuels in reactor pools [7, 35]. As a part of the standard monitoring procedures used in those programmes, a systematic control of water quality in both the reactor pool and the spent fuel pool was carried out during several years. Figure 56 shows the results obtained for the reactor pool, which clearly demonstrate a good level of water upkeep. Conductivity is always below the 1 µS/cm level, pH around 5.5 and all dissolved species below the detection limit.

In the spent fuel pool, the situation is similar, as seen Fig. 57. Only the conductivity tends to increase to higher values (always below the 2 µS/cm limit) before going back to 1 µS/cm or less, which is a result of the discontinuous purification method.

9.3.7. Water management programme

The water management programme in the RA6 research reactor is performed following the instructions of the RA6 Preventive Maintenance Manual [93]. This document establishes the maintenance programme and methodology for components, equipments and systems, with the purpose of obtaining an adequate RA6 level of security and availability.

As for the QA system, it is described in the corresponding quality manual [94], elaborated following the recommendations of the IAEA [77], as well as of local mandatory standards [95, 96]. Also, two procedures of the CNEA had to be considered [97, 98]. The quality manual mentioned above was put into effect starting 30 January 2006.

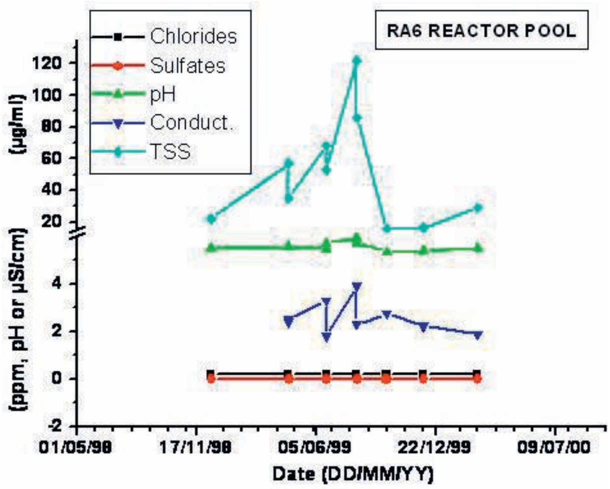

FIG. 58. Evolution of chemical variables in the RA6 reactor pool.

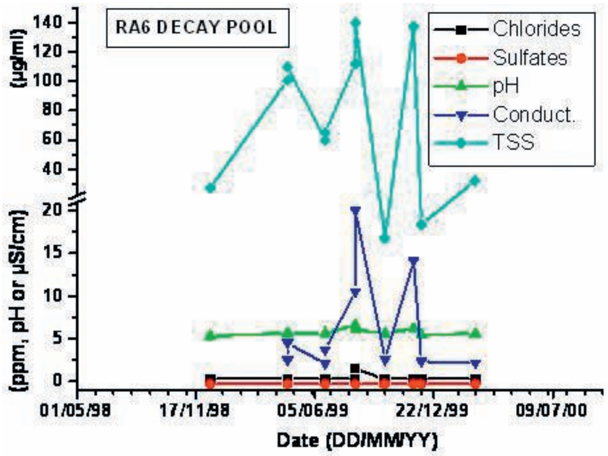

FIG. 59. Evolution of chemical variables in the RA6 spent fuel pool.

A particular situation took place during installation of BNCT facilities in 1999. During the building period, not enough care was taken to avoid the debris originated in the construction work to be spread over the reactor and adjacent rooms. The waters both in the reactor pool and in the spent fuel pool become contaminated with some of these materials. As a result, several water parameters, mainly conductivity and total suspended solids (TSSs), showed excursions from the normal working range. Since the reactor was not in operation during that lapse, this situation was not evident for reactor operators. However, the problem did show up in the regular monitoring procedure performed in the framework of the active IAEA CRP [7]. One important factor that highlighted these events was that the water sampling for the surveillance programme was conducted from the mouth of both pools, whereas the on-line continuous monitoring is performed at the exit of the mixed bed ion exchangers. Figures 58 and 59 depict the variation of the main parameters during the perturbation period.

Consistent with the observed phenomenon, indications of incipient corrosion were found on coupons that had been immersed in the spent fuel pool during that period of time. Figure 60 shows a case in which an island of pits was produced in a location were particles had settled on the aluminium surface. At higher magnifications, spots of deep attack can be identified.

Similar effects could not be verified on other coupons, immersed in the reactor pool. The higher degree of water movement in this case may have prevented the falling dust particles from becoming sediments on the corrosion coupons. Specific information on the mechanisms of sediment induced corrosion on aluminium alloys is included in Section 3.2.3.7 and in Ref. [8].

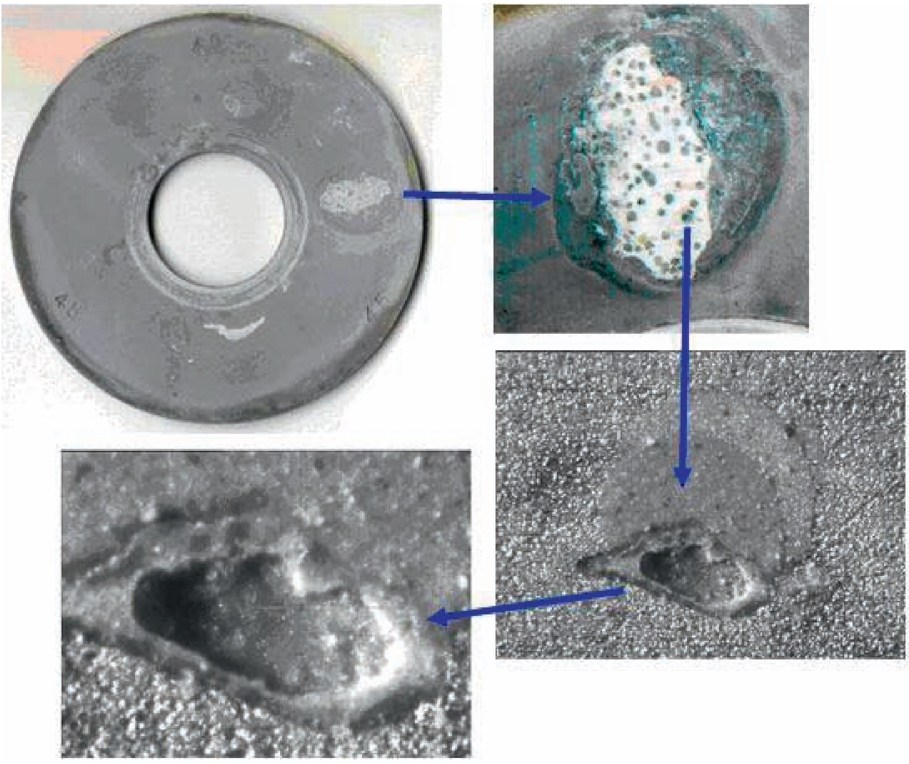

FIG. 60. Pitting induced by dust on an aluminium corrosion coupon immersed in the RA6 spent fuel pool. Disc diameter: 100 mm.

9.3.8. Conclusions

Analysis of corrosion of aluminium coupons immersed in the good quality water of RA6 installations demonstrated that the pitting like process originated from iron oxide particles produced by corrosion of the spent fuel pool's painted carbon steel cover and other type of particles released during the construction of irradiation facilities. This demonstrates that a good water management quality programme not only involves a good control of the water chemical composition, but also protection against dust and other solid particles falling on the reactor and pool components. Particles ability to settle on metal surfaces to form sediments increases the possibility of producing corrosion on aluminium alloys. In the specific case of the RA6, water movement, which is usually significant, has impeded the mentioned phenomenon to take place in the reactor pool.

9.4. MEASUREMENT OF PH AND CONDUCTIVITY IN THE HFR RESEARCH REACTOR, PETTEN (NETHERLANDS)

9.4.1. Introduction

In the summer of 2007, a new analytical system for the measurement of the pH and conductivity water was installed to monitor the quality of primary cooling and basin waters of the HFR research reactor, Petten. A description of the new hardware is presented in this report.

9.4.2. The High Flux Reactor

The High Flux Reactor (HFR) is a 45 MW research reactor, located in Petten, Netherlands. The reactor, shown in Figs 61 and 62, is owned by the European Commission, and the licence holder is Nuclear Research & Consultancy Group (NRG).

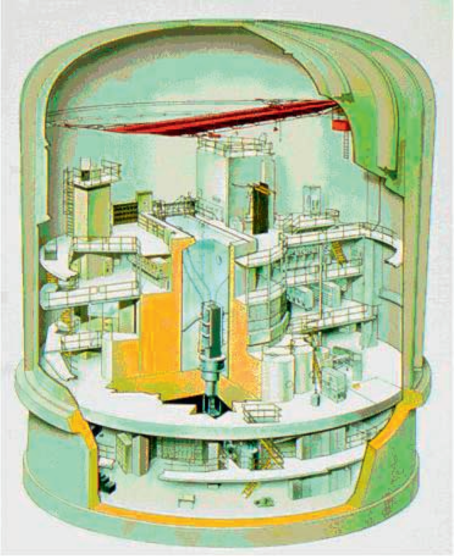

FIG. 61. The HFR research reactor building.

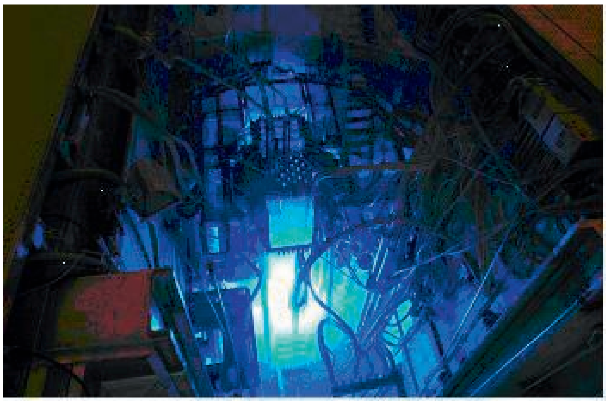

FIG. 62. View of HFR core.

TABLE 24. OPERATIONAL LIMITS FOR THE PRIMARY COOLING CIRCUIT AND BASIN SYSTEM OF THE HFR

	pH	Conductivity (µS/cm)
Primary cooling system	5.5–7.5	0.1–0.2
Basin water	5.5–7.5	1–2

In 1961, the reactor became critical for the first time, and in 1962, it started regular operation at 20 MW. In 1966, the reactor power was increased to 30 MW, and in 1970, to 45 MW. In 1984, the reactor vessel was replaced. Typically, an annual reactor programme comprises 290 full power days distributed over 11 cycles of four weeks, including a three day stop, and two maintenance periods.

Two main water bearing systems can be distinguished: the primary cooling system for cooling the reactor core and transfer the heat to the secondary cooling circuit, and the basin system. The primary cooling circuit has a volume of 151m^3. The basin system comprises two storage basins, one for storage of in-core components, experiments and isotope capsules (106m^3), and one for storage of spent fuel elements and experiments waiting for dismantling in hot cells (84m^3). Table 24 shows the operational limits for the two systems, and Figs 63 and 64 show the respective diagrams. Demineralized feed water is produced on-site using a facility that produces water with conductivity at around 0.055 µS/cm. Water quality is monitored by measurement of pH and conductivity. Measurements are performed every 8 hours for both systems.

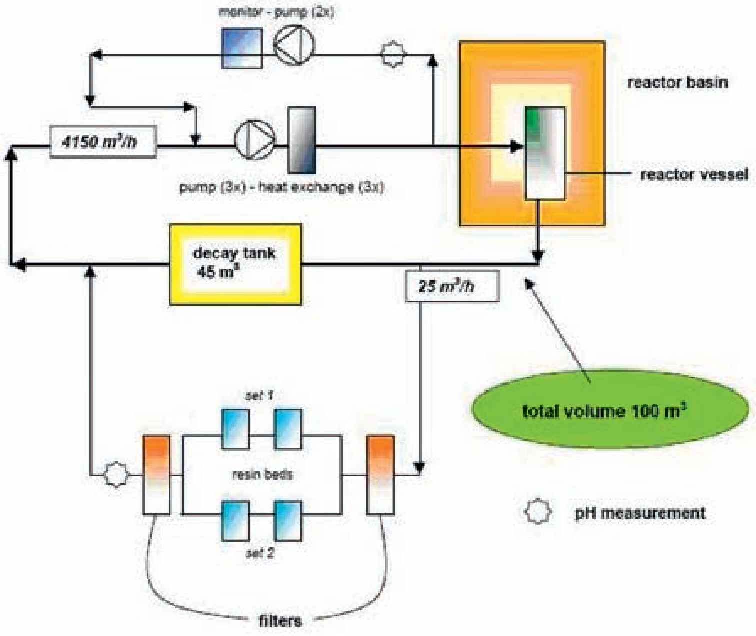

FIG. 63. Primary cooling system.

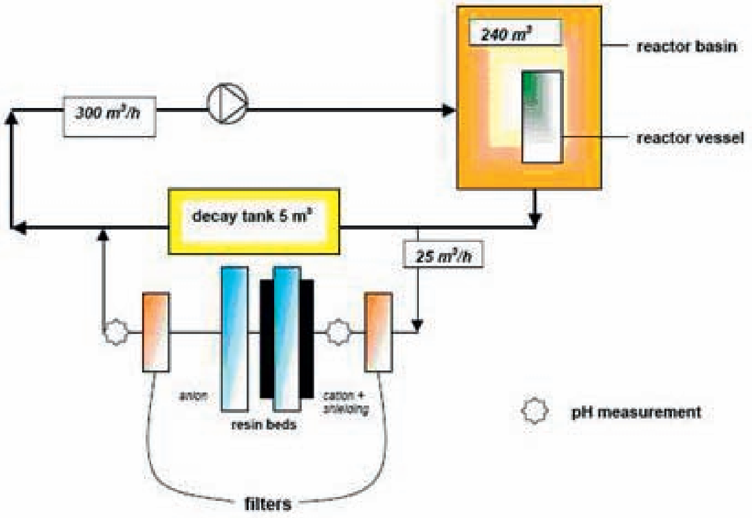

FIG. 64. HFR basin configuration.

The old pH/conductivity measuring system was first installed to check the performance of the demineralization system. Later on, it was decided to also use it to monitor the quality of the water in the basin and primary cooling system. It was an ‘off-line’ system, with samples being discharged to the drain system. When the equipment became too old (more than ten years), it was decided to replace it using a more modern system.

9.4.3. The new pH and conductivity measuring station

The new measuring station, shown in Fig. 65, consists of a combined pH–conductivity meter installed in an industrial housing. The pH electrode is equipped with a flat glass membrane and a reference electrode, which is suited for measurements under high pressures. The pH electrode is suitable for pH measurements in demineralized water. It is provided with an extra platinum grounding electrode, which enables measurement of the pH and reference electrode by means of separated, high impedance amplifiers. This is important because pure demineralized water has a relatively high electrical resistance (and thus low conductivity), complicating

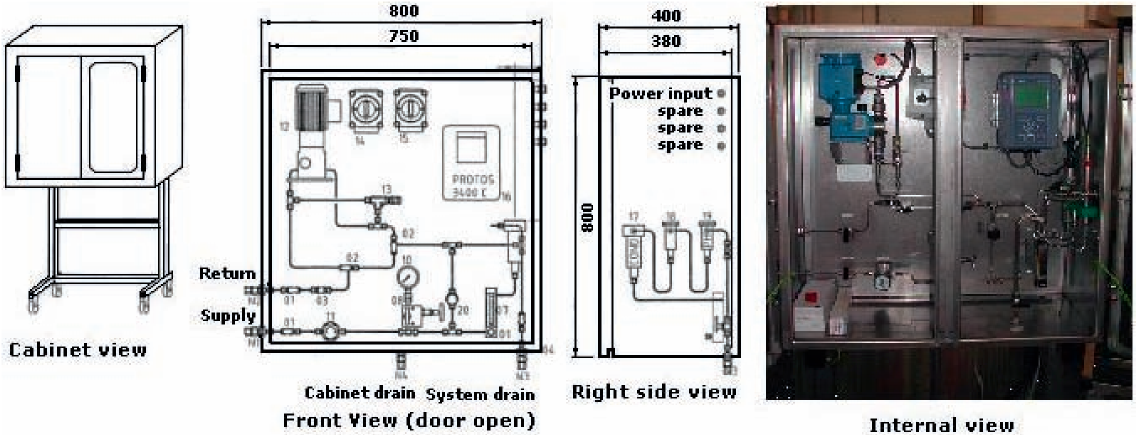

FIG. 65. The new pH and conductivity measuring station.

performance of measurement with a pH meter using a high impedance glass membrane as a sensor. Some features of the measuring station are:

- — It has a user-friendly operation with limited maintenance, because it can operate in a stand-alone mode;
- — All relevant data is displayed in a clear format, with capability to show results in the reactor control room;
- — There is disturbance of the sample during sampling, viz. interaction with the atmosphere;
- — Tubing and connections are made of stainless steel, so that contact with open air is avoided;
- — There is a large capacity for storing and retrieving historic data, through the use of a memory card for storage of measurements and log data;
- — The pH/conductivity system is designed for operation in low conductivity water under pressure;
- — The pH electrode is a gel type reference electrode, max 8 bar, equipped with a glass membrane with a relative low resistance. pH amplifier with a sufficient high input impedance;
- — The conductivity sensor is especially suitable for measurements at 4 bar (max 10 bar);
- — Temperature compensation: pH and conductivity measurements;
- — Electrodes and electronics are designed to allow performing self tests of the system;
- — Simulation sensors allow to verify the working conditions of the electronics and the data acquisition module;
- — In order to check functioning of the pH electrode, a set of pH buffers (pH4, pH7) are included. These standards are based on NIST standards;
- — The equipment has an independent pump to allow significant measurements when the reactor is not in operation;
- — Water flow is about 5 L/min, considered more than sufficient to guarantee an appropriate response speed, and representative measurements;
- — During operation, the pressure of the incoming water is 2 bar; dropping to 1 bar when leaving the system, always well below the maximum pressures to which the pH and conductivity electrodes may be exposed, i.e. 8 bar and 10 bar, respectively;
- — The conductivity meter is frequently checked by measuring a calibrated solution, prepared by an accredited laboratory (in this case, ECN, the Department of Engineering and Services);
- — The pH meter is frequently checked by having the buffer solutions used analyzed and controlled by an accredited laboratory (in this case, ECN, the Department of Engineering and Services).

9.5. OPERATIONAL EXPERIENCE AT CSF, ARGENTINA: INFLUENCE OF WATER QUALITY IN ALUMINIUM CORROSION[6]

Several experimental nuclear reactors have been put into service in Argentina since the early 1960s. All of them use aluminium clad fuel, mostly of the MTR type. The RA3 reactor, located at the Ezeiza Atomic Centre (some 40 km from Buenos Aires) is the bigger one, now running at power levels of up to 10MW; this open pool reactor started by burning 90% enriched uranium, and the fuel plates were made of pure (99.7%) aluminium. It was converted to use 20% enriched uranium at the end of the 1980s, when the fuel plates begun to be manufactured with AA6061 alloy. RA3 spent fuel elements were normally maintained in a decay pool situated in the same reactor area for a period of time ranging from one to several years, before they were deposited in the nearby Central Storage Facility (CSF) where they have been stored for more than 30 years. Figure 66 shows a view of the CSF. It is composed of an array of vertical buried steel tubes, distributed in lines that share the same water. These channels are surrounded by a compacted special soil enclosed in an underground brick wall precinct in order to prevent water leakage. There are two sectors, each with six lines of 17 tubes, for a total of 204 channels.

Two spent fuel elements can be accommodated in each position, one on top of the other, as shown in Fig. 67, but one tube is left empty at the end of every line (as channel numbers 97, 164, 181 and 198, marked in Fig. 66), for service purposes. Although provisions were made for water circulation and purification, the maintenance procedure was halted in the past, and the water remained stagnant. As time passed, activity in the water gave indication of increasing fuel degradation. At the end of the 1970s, a visual inspection during an occasional fuel shipment to the RA6 reactor in the Bariloche Atomic Centre, which was being fed with fuel already burnt in RA3, revealed that many of these elements were covered by a brownish layer. After analysis, it was shown to be composed mainly by hematite particles (iron oxide). This substance was determined to have originated in the corrosion of the channels caps, manufactured with painted carbon steel. Also, when steps were taken to proceed with fuel repatriation to the country of origin, other visual examination operations revealed the occurrence of corrosion processes on the stored fuel elements, examples of which are depicted in Section 3.2 [99].

The deleterious effect of hematite particles (iron oxide) on aluminium alloys has been studied and verified in laboratory tests (see Section 3.2). It may have been the starting point of the deterioration cycle. Once the water quality became degraded, corrosion went on easier in water with higher conductivity and dissolved substances, which were supplied by the fuel material dissolution.

After the experience obtained from a first IAEA CRP that took place between 1996 and 2000, a gradual improvement of the water quality conditions was implemented. The first step was to establish a periodic water

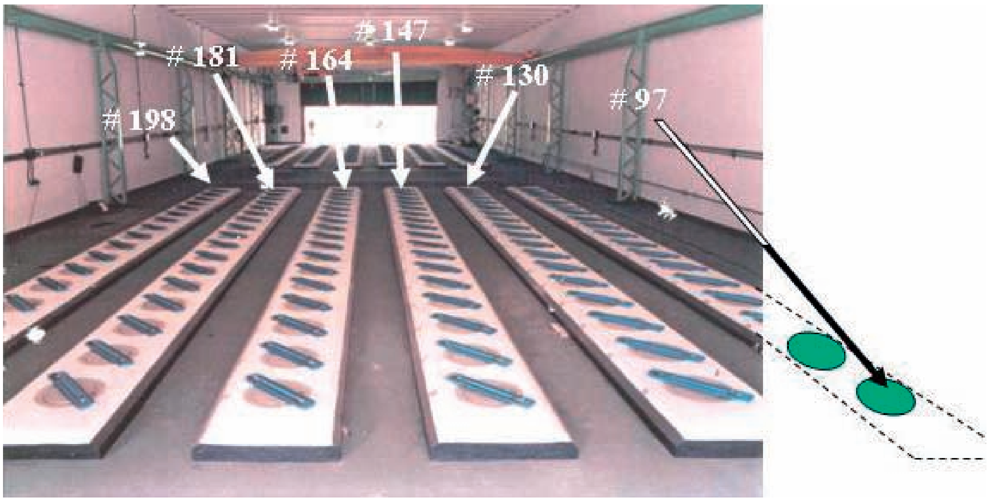

FIG. 66. Central Storage Facility (CSF) located in Ezeiza, Argentina. Several empty channels are indicated.

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[6] A full report of this case study is found in Ref. [8].

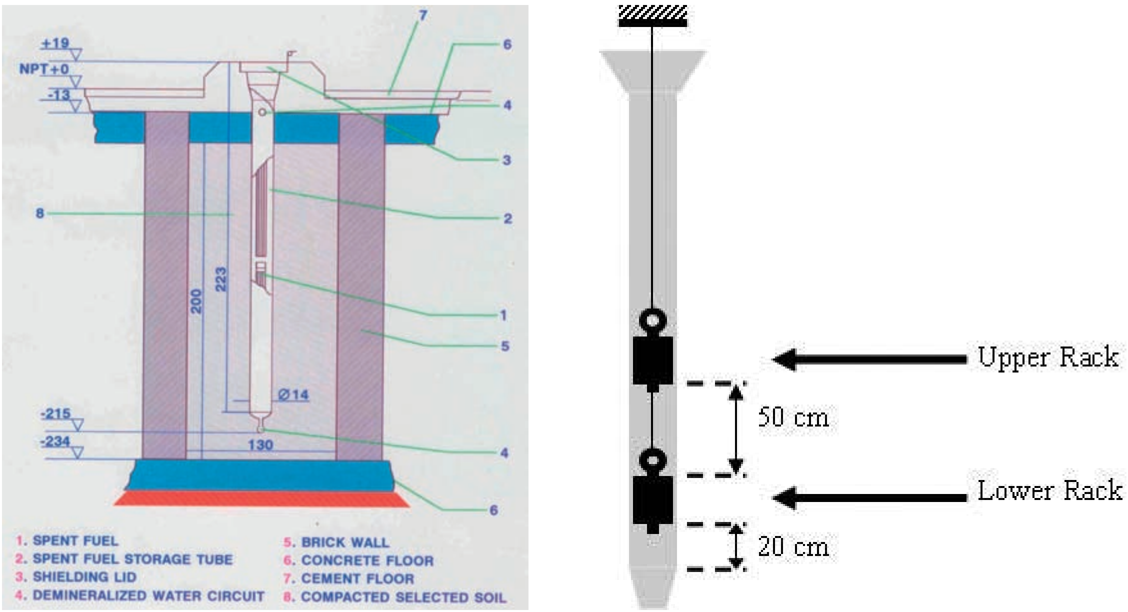

FIG. 67. Schematic drawing of a spent fuel storage tub, showing the vertical position of test racks in the channels (on the right).

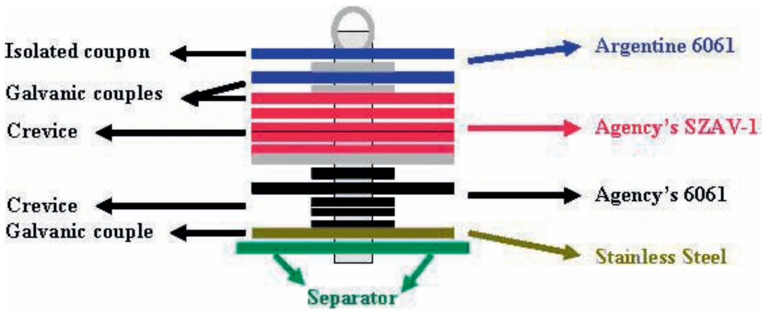

FIG. 68. Composition of test racks and coupon order.

cleaning procedure for the line that includes position No. 97. Hence, it was decided to perform corrosion tests in all the mentioned channels. By doing this, it was expected to make evident the importance of water maintenance to minimize corrosion of aluminium spent fuel elements.

Two test racks especially designed for an IAEA CRP on corrosion of research reactor aluminium clad spent fuel [8] were immersed in the selected channels. They were set 20 cm above the bottom to avoid contact with sludge and separated some 50 cm between them, as shown in Fig. 67. A variety of coupons in form of discs were hooked in each test rack, including, inter alia, different aluminium alloys, some forming galvanic couples with stainless steel, some having crevices and various geometric configurations, as depicted in Fig. 68. More information on this exercise can be found in the final report of this CRP [8].

The full experimental programme included testing of racks in vertical position (horizontal coupons) in channels 97 and 198, and racks horizontally positioned (vertical coupons) in channels 164 and 181. Also, periodic water chemical analysis was performed in all locations. Finally, a stainless steel container was dipped into one channel in order to collect dust and other particles that could eventually fall into the water. This sediment collector was withdrawn at the end of a specific period of time and its contents analysed. For the sake of clarification on the effect of water purity on corrosion, only the results obtained in the vertical racks will be described. The full analysis of the overall work can be found in the final report [8].

Clear differences were verified in the aspects of racks extracted from channels #97 and #198 from the first withdrawal operation. As shown in Figs 69 and 70, the first one had a cleaner appearance, with no obvious signs of corrosion, whereas the second one had clear evidence of significant corrosion, with massive production of aluminium hydroxide in some places, apparently related to a galvanically coupled coupon.

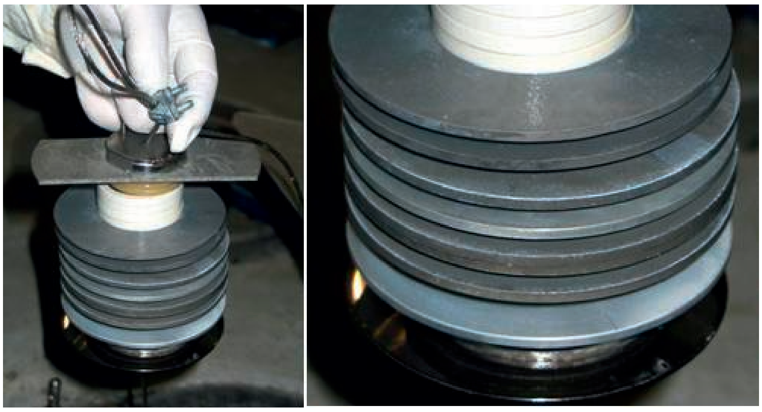

FIG. 69. Rack 1 upon withdrawal from channel No. 97. No visible signs of corrosion.

FIG. 70. Aspect of rack 1 on withdrawal from channel No. 198. Detail showing strong galvanic attack.

FIG. 71. Comparison of racks appearance right after extraction from channels 97 and 198.

The top coupons of both racks were covered by a deposit of white particles, which according to their appearance, seem to be formed by aluminium hydroxide nodules, although in the rack extracted from channel #198, this layer seems to be much denser, as shown in Figs 71 and 72.

Sediment induced pitting had been previously verified in similar aluminium coupons immersed in the same site during the first CRP [7]. In that occasion, pits of up to 500 μm in depth had been produced in a 60 day period. The pits were found underneath sites where white aluminium hydroxide nodules had been formed. This hydroxide was generated as a result of the pitting process. Although the amount of particles settled on aluminium coupons surfaces may be similar in the two channels, the larger size of aluminium hydroxide nodules formed in channel #198 indicate that the pitting corrosion took place more readily in this location.

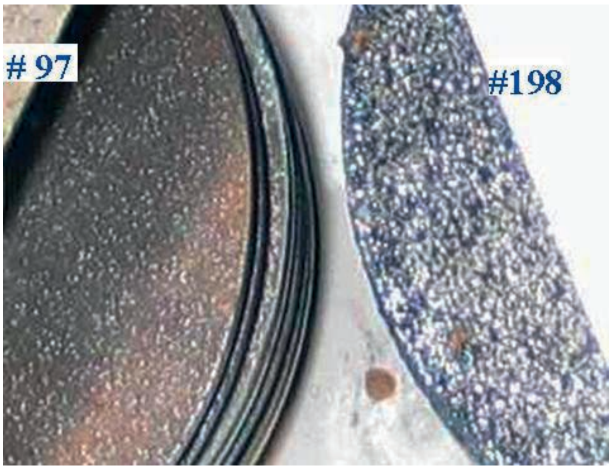

FIG. 72. Detail of Fig. 71.

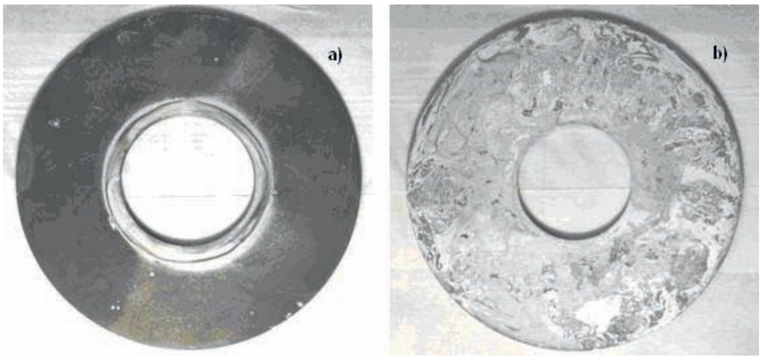

FIG. 73. Different type of surface appearance: (a) free surface; (b) surface inside crevice.

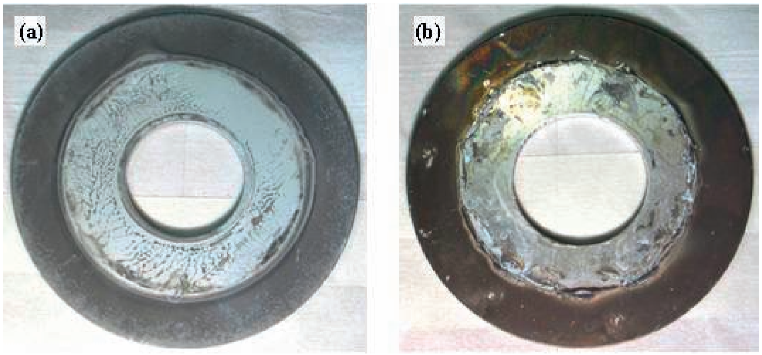

FIG. 74. Comparison of galvanic corrosion in channels 97 (a) and 198 (b).

There were other typical features belonging to the specific type of tested samples, which were observed in all racks upon disassembling. A uniform oxide layer grew on free surfaces, whereas an uneven layer was formed inside crevices and galvanic couples (Figs 73(a) and 73(b)). In the second case, there were regions where the bare metal could be seen, probably because the two surfaces of the sandwiches were in contact at those points, impeding water ingress. Other zones had oxides of different thicknesses, thus giving the irregular depicted aspect.

The inner parts of the galvanic couples showed aspects similar to those of crevices; however, in some cases, as coupons extracted from channel #198, corrosion attack could be seen at the edge of the steel disc, as shown in Fig. 74. Although galvanic effects had been encountered in most cases, there was a notable corrosion increment in waters of higher conductivity, as shown in Figure 74. A more detailed view of the attacked region can be seen in Figure 75.

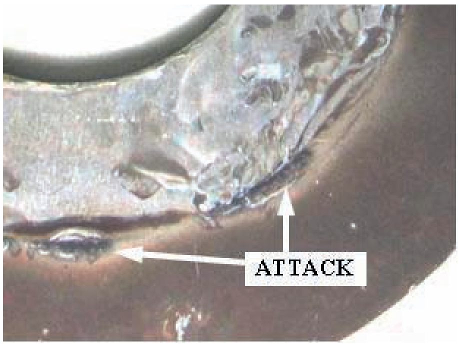

FIG. 75. Detail of attack on galvanic couple (enlargement of Fig. 74(b)).

TABLE 25. WATER CHEMICAL ANALYSIS FOR CHANNEL #198

DD/MM/YY	pH (units)	Conduct. (µS/cm)	Cl^- (mg/L)	SO_4^- (mg/mL)	NO_2^- (µg/mL)	NO_3^- (µg/mL)	TSS (mg/L)
03/03/2003	6.60	53	1.6	0.6	2.5	0.7	0.080
23/07/2003	7.60	57	1.5	—	4.2	0.7	0.050
03/12/2003	6.15	63	1.6	0.3	4.2	0.6	0.112
24/03/2004	7.42	59	1.6	0.2	0.4	0.7	0.040
20/05/2004	7.28	55	1.7	0.3	1.4	0.7	0.024
18/11/2004	6.18	55	3.1	0.1	—	2.3	0.087
23/05/2005	6.18	66	4.9	0.7	—	3.5	0.071
01/10/2005	—	—	3.1	0.9	—	4.0	—

TABLE 26. WATER CHEMICAL ANALYSIS FOR CHANNEL 97

DD/MM/YY	pH (units)	Conduct. (µS/cm)	Cl^- (mg/L)	SO_4^- (mg/mL)	NO_2^- (µg/mL)	NO_3^- (µg/mL)	TSS (mg/L)
03/03/2003	—	—	—	—	—	—	—
23/07/2003	—	—	—	—	—	—	—
03/12/2003	7.19	3	0.1	0.0	0.0	0.1	0.008
24/03/2004	7.63	4	0.3	0.3	0.3	0.3	0.011
20/05/2004	7.52	3	0.2	0.6	0.0	0.9	0.004
18/11/2004	5.36	4	5.1	9.8	—	1.9	0.003
23/05/2005	5.36	4	0.8	<0.1	—	<0.1	0.057
01/10/2005	—	—	0.2	<0.1	—	0.5	—

Table 25 and 26 show the results of the periodic analysis of water from tubes #198 and #97, respectively. As can clearly be seen, water quality in channel #97 was one order of magnitude better than that of channel #198, as indicated by key parameters conductivity, chloride content and total suspended solids (TSS).

There is a clear correlation between the water quality and the observed corrosion effects. Oxidation, galvanic and pitting corrosion are much more noticeable in the coupons extracted from channel 198. Also, particles settled on aluminium surfaces, known to promote particle induced pitting, seem to have been able to develop aluminium hydroxide blisters only in this case.

This finding is consistent with the knowledge related with aluminium corrosion in water, as detailed in Section 3.2. All the degradation mechanisms depend directly of water quality, as measured by its conductivity, pH and ion content, especially that of chlorides. The influence of conductivity is related to the electrochemical nature of the corrosion processes; it directly affects the capability to produce the electric charge exchange needed for all these mechanisms; pH is fundamental in determining the stability of the protective oxide layer; finally, the ion content determines the probability of starting a pitting process.

As mentioned above, water quality in channel 97 was one order of magnitude better than that of channel 198. However, it is necessary to emphasize that it was still not ideal. The optimum situation would be to have conductivity below 1 µS/cm, no detectable amounts of dissolved ions and continuous circulation. Nevertheless, it is important to mention that even the limited cleaning operation performed resulted in a significant improvement in the corrosion conditions of the system, which was evident from the different behaviour observed.

Appendix I

REFERENCE TEST PROTOCOL FOR A CORROSION SURVEILLANCE PROGRAMME

I.1. INTRODUCTION

This appendix presents relevant parts of the original Test Protocol, prepared for use in the IAEA Coordinated Research Project (CRP) Corrosion of Research Reactor Aluminium Clad Spent Fuel in Water and the Regional Project for Latin America (RLA) Management of Spent Research Reactor Fuel in Latin America” [7, 8]. It is intended to be used as a reference when preparing the CSP of reactor pool or spent fuel storage basin for the specific facility.

Many details can be gleaned from this reference protocol for structuring and conducting a CSP. As a reference, the rack and coupons shown in Figure 31 of Section 7.2 were used in these projects.

This annex does not contemplate actions for evaluation of settled solids. When preparing the specific test programme and procedure for settled solids evaluation, it is recommended to use information given in Section 7.2.5 and in Ref. [8].

I.2. DEFINITIONS

Corrosion coupon or coupon is the circular disk of aluminium alloy or stainless steel.

The **rack** consists of the central support tube on which a set of coupons and ceramic spacers are assembled and held in place with a nut. The rack typically has a hook to enable it to be hung in the basin.

Basin is the contained volume of water used for storing spent fuels.

I.3. PRE-ASSEMBLY OF RACKS

An example of coupon preparation is given:

- The coupons should be 100 mm in diameter and 3 mm thick, and the diameter of the central hole should be 30 mm. Remove the burr and grind/polish the two surfaces to almost mirror finish.
- Identify the coupons with numbers. The numbering system chosen should be logical and carefully recorded at the beginning of the test, and adhered to throughout the programme. Identify the coupons either by laser scribing or by punching the identification number close to the inner edge.
- Photograph the front and back of each coupon.
- Weigh individual coupons (optional).
- Apply chemical treatment of aluminium alloy coupons:
  1. ‘Pickle’ the coupon by immersion in 10 wt% NaOH at 70–80ºC for 30 s (in Tank-I).
  2. Remove the coupon and brush the two sides while rinsing it in flowing deionized water for 1 minute (in Tank-II).
  3. Rinse coupon with flowing deionized water at room temperature for 1 minute (in Tank-III).
  4. Neutralize coupon by immersion in a 5% solution of HNO_3 (by volume) at room temperature for 1 min (in Tank-IV).
  5. Rinse coupon with flowing deionized water for 1 min (in Tank-III).
  6. Again pickle coupon by immersion in Tank-I for 30 s.
  7. Repeat steps 2, 3, 4 and 5.
  8. Immerse coupon in Tank-III for 5 min.
  9. Rinse coupon in flowing deionized water for 1 min.
  10. Dry coupon in hot air (180º C) for 1 min.

I.4. ASSEMBLY OF RACK

- Assemble coupons in a specified order. If scratched coupons are to be included (to simulate damaged Al surfaces), they should be assembled in the rack with the scratch side facing upwards. The stainless steel coupons should be below all aluminium alloy coupons.
- Tighten the top hanger-nut by hand until tight and then give a further 10° turn.
- Photograph the assembled rack.
- Attach a stainless steel rope to the hanger of the rack. (Do not use a rope made of any synthetic material, as they degrade under radiation)

I.5. IMMERSION OF RACKS IN REACTOR POOL OR SPENT FUEL BASIN

- Select the location for immersing the rack, bearing in mind the precautions outlined in the planning stage.
- Suspend the racks as soon as possible after assembly.
- Suspend the racks using a stainless steel wire or rope. Use stainless steel clips instead of tying a knot as these seldom hold, especially if the rope is ≥2 mm thick. Previous experience has shown that nylon ropes disintegrate in the presence of radiation.
- In the case of a spent fuel storage basin, position the rack in the vicinity of spent fuel if possible.
- Position the rack(s) above the pool/basin floor. Do not allow the rack or any of the coupons to touch the walls or floor of the pool/basin, sludge or other metallic components.
- Identify the test rack with a label containing adequate information about the rack and those responsible for carrying out the test (to prevent tampering or inadvertent removal or repositioning of the rack).
- Record the date of immersion.
- Record the location of the rack (depth, distance from walls etc.). Make a sketch of the reactor pool or spent fuel basin and the position of the test rack: (a) as a reminder of the position of the rack and (b) for use in the final report.

I.6. ACTIONS DURING THE TEST

- Measure the radiation field intensity near the rack at periodic intervals (in R/h, or Sievert/h).
- Monitor the water chemistry at periodical intervals.
- Determine all the impurities in the basin water, such as chlorides, sulphates, nitrates, nitrites, carbonates, bicarbonates, iron, copper, silver, mercury, aluminium and other cations or anions. This should be done once a month during the first six months with water samples taken preferably from the vicinity of the immersed rack. After six months, the impurities whose levels have remained constant need not be measured again. However, monthly determinations of certain impurities that influence aluminium alloy corrosion should continue, such as chlorides, sulphates, iron, copper and other heavy metal ions.
- Report the actual values of the impurities in the pool/basin waters together with the dates of measurement. Averaged values of several measurements should not be reported.
- Indicate flow conditions near the rack (flowing or static), rate of or frequency of renewal of water in the basin etc.
- Observe and record the presence of loose particles on the pool/basin surface and/or coupon surface, and if they appear to be causing any corrosion problems.
- Prepare and immerse a sediment collector in the vicinity of the test rack for a period of 4–6 months to determine the quantity and composition of solids that settle on the surfaces of the coupons. Sediment collectors have been used in the CRP and the RLA programme. The sediment collector should have a lid, which should be in place primarily when the collector is being withdrawn from the pool/basin to prevent collection of solids floating on the surface of the basin.
- Express the quantity of solids that settle in the basin in micrograms per square centimetre per month.

I.7. REMOVAL AND EXAMINATION OF COUPONS

Note: Remember to have all the necessary accessories for examination of the rack and the coupons ready, prior to removing the rack from the pool/basin.

- Withdraw the rack from the pool/basin.
- Measure pH of water on the external surface of coupons.
- Compare the measured pH with that of the bulk water.
- Photograph the rack prior to disassembly. Photograph all points of interest including any corrosion of the edges.
- Remove the coupons from the rack.
- Photograph the front and back of each coupon. A small card with a note about the material, immersion time and coupon identity should be photographed in true colour together with the coupon.
- Make observations of specific corrosion phenomena for each coupon, including ease of removal (ease of separation of crevice/bimetallic coupons), amount and type of loose deposits, staining, discolouration, pitting, tenacious or loose oxides, and raised or embedded particles (can be felt with a gloved finger), etc.
- Measure pH (with pH paper) on the contact surfaces of crevice and bimetallic coupons, and compare with bulk water pH and with that on the outer surface of the coupon.
- Decontaminate the coupon while still wet by washing in running tap water (or in a bucket of basin/reactor water). The surface of the coupon should be scrubbed with a gloved hand to remove the gel like aluminium oxide. If carried out at this stage, this procedure will reduce the extent of contamination of the coupon to a large extent. Should the surface oxide dry, it will harden, and it would be much more difficult to remove and the coupon would continue contaminated.

I.8. DETAILED EXAMINATION IN THE LABORATORY

- Decontaminate coupons, if required, with a *chloride free* detergent and rinse with deionized water.
- Air dry/wipe.
- To evaluate pitted aluminium coupons, using an image analysis system, remove the surface oxide with an inhibited acid solution.
- To determine pit depths using the calibrated focusing technique, ensure that there are no oxides in the pits.
- Pit depths can also be determined using the standard metallographic technique (repeated polishing followed by optical microscopy).

I.8.1. Pitting corrosion

- Photograph pits.
- Determine pit depths.
- Ensure that the final evaluation focuses on the deepest pits and is carried out by sectioning and polishing, as in the preparation of all metallographic coupons.
- Section through the deepest part of the pit.

I.8.2. Crevice corrosion

- Perform visual and photographic inspection, together with determination of pH using pH paper, preferably in the range of 4–9 with measurement intervals of 0.1.
- Carry out metallographic analysis only if pits are observed on the contact area.
- Ensure that evaluation of pitting in the crevice follows the above instructions for pitting.

I.8.3. Galvanic (bimetallic) corrosion

Galvanic couples should be treated in precisely the same way as crevice couples.

Appendix II

EXAMPLE OF OPERATIONAL PROCEDURE FOR WATER QUALITY CONTROL

Procedure number **OP-ROD-1001-01**

WATER QUALITY CONTROL FOR THE PRIMARY COOLING SYSTEM

Note: This is a fictitious procedure, and its purpose is only to serve as a reference for the user. The real procedure must be developed according to the overall quality assurance programme chosen for the facility.

1 — Purpose

To monitor water quality in the primary cooling system and maintain it within limits specified in the Safety Analysis Report, chapter 18, section 18.3.

2 — Application

Water in the primary cooling system.[7]

3 — Definitions and Acronyms

OP — Operational procedure[8]
PG — Management procedure
ROD — Reactor operation division[8]
LWA — Laboratory for water analysis
Logbook

4 — Reference Documents

PG-REACTOR-0501 — Document Structure and Definitions
PG-REACTOR-0302 — Reactor Organizational Chart
OP-REACTOR-1007 — Operational Procedure for the Reactor Primary Cooling System
WI-ROD-0706-04 — Work Instruction for Operation of the Pool Water Purification System
WI-ROD-0706-05 — Work Instruction for Operation of the Make-up System
WI-ROD-1001-01 — Work Instruction for Water Sampling in the Reactor Pool
WI-ROD-1001-02 — Work Instruction for Water Sampling in the Water Purification System
WI-ROD-1001-08 — Work Instruction for Measuring Water pH Using …..
WI-ROD-1001-09 — Work Instruction for Measuring Conductivity Using ….
WI-ROD-1001-10 — Work Instruction for Measuring Chlorides Using….
WI-ROD-1001-11 — Work Instruction for Regeneration of Resins in the Pool Water Purification System
FM-ROD-1001-01 — Annual Schedule for Primary System Water Sampling
FM-ROD-1001-02 — Tag for Identification of Sampled Water
FM-ROD-1001-03 — Receipt for Delivery of Sampled Water

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[7] In this procedure, an assumption is made that the reactor pool is part of the primary cooling system.

[8] In some cases this definition is made on the overall quality assurance manual for the facility.

5 — Procedure

In order to keep the water parameters within limits specified in the Safety Analysis Report, chapter 18, Section 18.3, the following actions need to be taken:

5.1 — Obtain authorization from the Responsible Reactor Senior Operator

The Responsible Reactor Senior Operator, who is responsible for authorizing activities impacting reactor operations and requesting support from the Radiation Protection team, must be informed prior to any water sampling operation.

5.2 — Pool water sampling

The place to collect the pool water sample is the corner closest to the fuel storage racks, on the right side of the pool when looking from the control room, about 1 m from the pool side, and about 30 cm from the water surface. Sampling shall be in accordance to WI-ROD-1001-01. The number of samples will depend on the analysis to be made, according to the table in OP-REACTOR-1007, and as scheduled in FM-ROD-1001-01. All samples shall be identified according to WI-ROD-1001-01 and using FM-ROD-1001-02.

5.3 — Sampling from the Water Purification System

The places to collect the water in the water purification system are the tap located about 2 m before entrance of the purification system and the tap right after the flowmeter FE-05. Sampling must be performed according to WI-ROD-1001-02, and samples must be identified as described in WI-ROD-1001-02, using tags FM-ROD-1001-02. The number of samples depends on the analysis to be performed, according to table in OP-REACTOR-1007, and as scheduled on FM-ROD-1001-01.

5.4 — Measurements

After sampling, collected water sample must be taken to LWA for immediate analysis of pH, conductivity and chlorides, according to WI-ROD-1001-08, WI-ROD-1001-09, and WI-ROD-1001-10, respectively.

For chemical composition and determination of radioactive components, when applicable, samples need to be transferred to the Radiochemistry Division, as soon as practicable and delivered using FM-ROD-1001-03.

5.5 —Analysis

All measurements shall be compared with limits established in the Safety Analysis Report, chapter 18, Section 18.3, and the results reported to the Responsible Reactor Senior Operator for registration in the Reactor Log Book. Follow-up actions, if necessary, shall be described and recorded in the Reactor Log Book.

6 — Responsibilities

Water quality team (as defined on PG-REACTOR-0302) is responsible for establishing the Annual Schedule for Primary System Water Sampling (using FM-ROD-1001-01) , and for sampling the water, according to the sampling programme established.

Radiological protection team (as defined in PG-REACTOR-0302) is responsible to give the necessary support for sampling water in the reactor pool and in the water purification system, monitoring radiation levels to ensure radiological safety in execution of the sampling procedure.

Responsible Reactor Senior Operator (as defined in PG-REACTOR-0302) is responsible for the authorization of the sampling activity; request for support from the Radiation Protection team; registration of the results of measurement analysis in reactor Log Book; and follow-up actions, if necessary, to maintain the water quality within limits specified in the Safety Analysis Report, chapter 18, Section 18.3.

Reactor Chief (as defined on PG-REACTOR-0302) is responsible for approval of the Annual Schedule for Primary System Water Sampling, and to inform it to the Reactor Senior Operators .

REVISION	WRITTEN BY[9]	APPROVED BY[9]	DATE

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[9] Name and signature.

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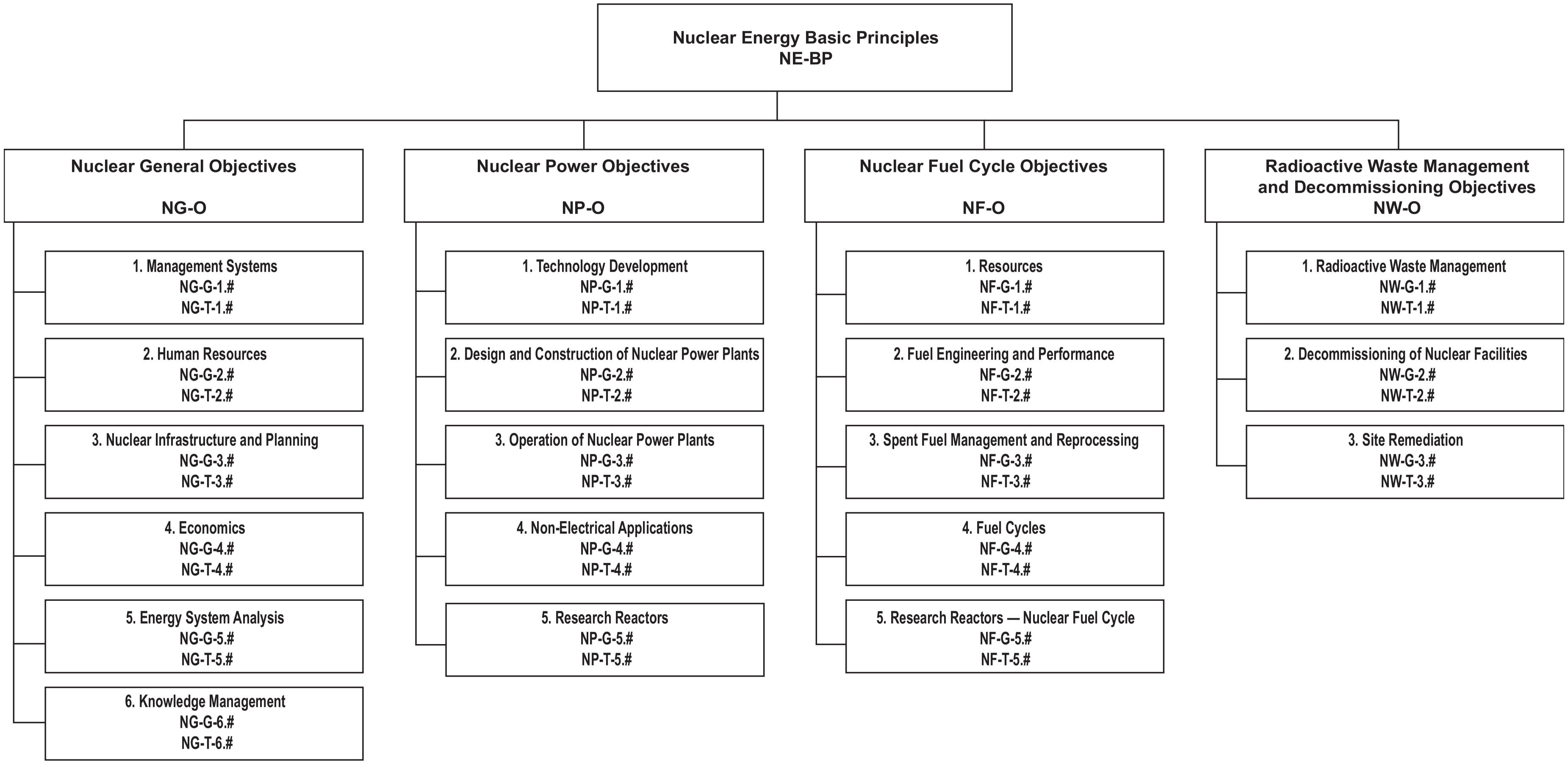

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