

Review

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Corrosion control of nuclear steam generators under normal operation and plant-outage conditions: a review

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Abstract: Nuclear steam generators (NSGs) are key components of nuclear power plants (NPPs) since their reliability affects the overall plant performance. Corrosion control of steam generators under operation and during plant outages is attained by proper design, adequate material selection and control of water chemistry in the entire secondary cooling circuit. This article reviews the types of steam generators, the materials used for their construction (with a special focus on tubing alloys), the corrosion processes that may occur under operation and the strategies to preserve steam generators and other components of the secondary cooling system from corrosion during plant outages.

Keywords: corrosion; heat transfer crevice; hydrazine lay-up; pressurized water reactor; steam generator; stress corrosion cracking.

1 Introduction

1.1 Nuclear power plants

Nuclear power plants (NPPs) use the heat released by a nuclear fission reaction to produce steam which in turn drives a turbine. Then an electric generator converts the kinetic energy of the turbine into electricity. Various designs of NPPs have been developed throughout the years

(Meiswinkel et al. 2013). The most common NPP designs can be classified into two groups depending on whether the steam is generated in a primary or in a secondary cooling circuit. Boiling water reactors (BRWs) produce steam within the reactor pressure vessel that is directly sent to the turbines. On the other hand, NPPs which produce steam in a secondary circuit include pressurized water reactors (PWRs), water-moderated water-cooled energy reactors (WWERs), and pressurized heavy water reactors (PHWRs). NPPs of this group have a primary cooling circuit at a high pressure which transfers heat to a secondary cooling circuit at a lower pressure that produces the steam. Overall, this latter group amounts to 350 (77%) of the 454 operational NPPs deployed worldwide which represent a total net electrical capacity of 400 GW as of December 2018 (IAEA 2018a,c). PWRs are western light water reactor designs while WWERs are their Russian analogous. Distinguishing between them is useful given the significant differences on steam generator design and selected materials for tubing (Asmolov et al. 2017; IAEA 2011a). PWRs and WWERs are light water reactors. PHWRs use heavy water as coolant and moderator since their nuclear fuel contains natural or slightly-enriched uranium. Most of PHWRs are Canada deuterium-uranium (CANDU) reactors, though there are other designs (Garland 2014).

1.2 Primary and secondary cooling systems

The primary cooling system of PWRs/WWERs/PHWRs carries radioactive water through a loop within a containment building that encloses the nuclear reactor. The primary circuit includes the reactor pressure vessel, pressurizer, recirculating pumps, steam generators and connecting piping. CANDU reactor designs use horizontal pressure tubes instead of a large pressure vessel.

The secondary cooling system is a loop that carries non-radioactive water through a Rankine water-steam cycle. Pressurized steam from the steam generators flows out the containment building and feeds the high-pressure

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steam turbine where it expands. At a lower pressure, the steam passes through the moisture separator reheater, it is sent to the low-pressure turbine(s) and then to the condensers where full condensation occurs. Condensers are heat exchangers cooled by a tertiary cooling system, such as a river, lake or cooling tower. The coolant is pumped back as feedwater to the steam generators entering the containment building. Steam turbines, reheater, condensers, pumps and connecting piping comprise the balance of plant (BOP), which is outside the containment building.

NPPs distinguish among various operational status modes that vary according to the type of plant and the manufacturer. It is useful to distinguish four status modes from the viewpoint of the secondary cooling system.

- Start-up: period of increasing temperature and pressure before power operation.
- Power operation: period of regular operation of the plant with the reactor in a critical condition.
- Shutdown: period of power decrease and heat removal only by steam generators.
- Outage (lay-up/maintenance): period from shutdown, when the residual heat removal system becomes operational, to start-up, when pressure and temperature in steam generators start to increase. The coolant temperature is typically below 100 °C (Kawamura et al. 2019).

In case that the radioactivity level of the outgoing steam is above regulatory limits the NPP must be shut down immediately, with all the safety and economic issues that this involves. The maximum allowable leak rate from the primary to the secondary coolant systems is 23.65 L/h for PWRs in USA, 10–15 kg/h for CANDU PHWRs in Canada, and 4 L/h per steam generator of WWERs in Russia (IAEA 2011a). Consequently, the main concern in the design, construction, operation, lay-up and maintenance of the steam generators is to preserve the complete separation between the radioactive water of the primary circuit and the non-radioactive water of the secondary circuit (Green and Hetsroni 1995; IAEA 2011a).

1.3 Integrity of the secondary cooling system

Field experience indicates steam generators are the key components of the secondary cooling system since their reliability affects the overall plant performance. Nuclear steam generators (NSGs) are shell-and-tube heat exchangers where the primary coolant flows inside the tubes

and the secondary coolant is converted into steam in the shell side. Degradation of NSGs forces unscheduled or extended outages, preventive or corrective maintenance work, and it adds costs in terms of repair work, loss of power and personnel radiation exposure. Various forms of degradation may affect the NSGs. Those of the tubing are the primary concern due to safety reasons. Tubing degradation is affected by NSG design, materials selection and primary and secondary water chemistries (IAEA 2011a). The root cause of most NSG tube failures is the formation of a locally aggressive chemistry due to the accumulation of deposits and corrosive agents on the tube external surface (Drexler 2017). NSG tubes are made of selected corrosion-resistant alloys. However, other parts of the NSGs and the BOP are made of materials which may be less resistant to various forms of corrosion (IAEA 2011a). Minimizing the corrosion rate of these components helps to preserve the integrity of the NSG tubing since corrosion products are transported to and accumulated into the NSGs, especially during start-up (Drexler 2017). NPPs have periodical outages for refuelling and/or maintenance where the integrity of the primary and secondary cooling systems must be preserved. In the case of the secondary circuit, the main concerns are the preservation of the NSGs during the outage and the safe and efficient performance of the system in the subsequent start-up and power operation. Consequently, appropriate lay-up conditions are set not only for NSGs but also for BOP equipment to minimize the transport of corrosion products to the NSGs after the outage (EPRI 2005; IAEA 2011a).

The purpose of this article is to review the corrosion control measures in NSGs and, in a lesser extent balance of plant equipment, under normal operation and in plant-outage conditions. As explained above, the focus is on steam generators for being the key components. This review covers the types of NSGs, selected tubing materials, tubing degradation processes, corrosion of NSG shells, secondary water chemistry and corrosion control measures at plant outages. The state of the art of the different options presently used for the lay-up of NSG and BOP equipment at plant outages is specially emphasised.

2 Nuclear steam generators

Presently, there are approximately 1300 NSGs in service worldwide (Riznic 2017). NPPs have generally 2 or 4 steam generators whose expected lifetime is of 40 years or more (Staeble and Gorman 2003). In a NSG, the primary coolant flows through the inside of a bundle of tubes, at high pressure, while the secondary coolant flows around the

outside of the tubes, at a lower pressure. Typical pressures at the primary and secondary sides of NSGs are listed in Table 1 for various types of NPPs. Due to the significant pressure gradient, in case of a tube leak, the radioactive primary coolant is quickly released into the secondary coolant. More than 50% of the reactor coolant pressure boundary is associated with the NSG tubing. NPPs have typically more than 10,000 NSG tubes making up a total length of 200–600 km, depending on the particular design. The wall thickness of the tubes is of 1.0–1.5 mm (Diercks et al. 1999; IAEA 2007, 2011a; Paine and Gustafsson 1994). Degradation and eventual failure of NSG tubing occur mostly during operation of the NPP. However, tubing degradation is greatly affected by the preservation of the entire secondary circuit during outages. Several types of tubing degradation appear after some ageing of the plants (IAEA 2011a). This is important since 65 % of the NPPs worldwide have more than 30 years in operation (IAEA 2018a). In fact, some NSGs of these plants have already been replaced (Naraine and Riznic 2017; Paine and Gustafsson 1994; Wilson and Buford 2001).

2.1 Types of steam generators

There are three different designs of NSGs presently used in NPPs, namely:

- Recirculating vertical U-tube boiling steam generators,
- Once-through superheated steam generators, and
- Recirculating horizontal/collector boiling steam generators.

PWRs use either recirculating vertical or once-through NSGs while CANDU PHWRs use the recirculating vertical type. WWERs use horizontal/collector NSGs, which are also of the recirculating type, but with horizontal instead of vertical tubes (IAEA 2007; Paine and Gustafsson 1994; Tapping et al. 2000).

Most of NSGs are of the recirculating vertical type (Figure 1). They carry the primary system coolant through U tubes with a tubesheet at the bottom of the steam generator

Table 1: Typical pressures in NSGs primary and secondary sides (IAEA 2007, 2011a; Tapping 2012).

NPP	Pressure in the primary side of NSGs (MPa)	Pressure in the secondary side of NSGs (MPa)
PWR	15.5–17.2	7.7–8.3
WWER	15.7–16.2	6.3–6.9
CANDU PHWR	~10	4.7–5.1

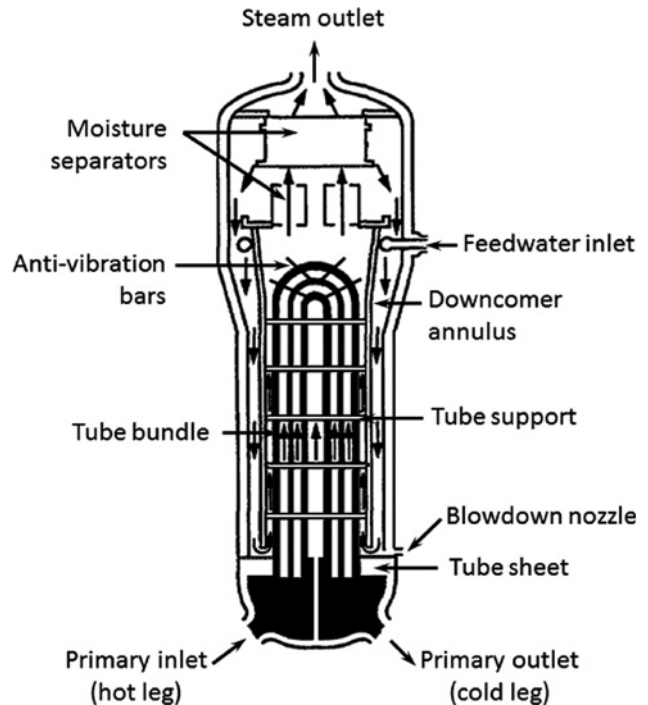


Figure 1: Scheme of a recirculating vertical U-tube boiling steam generator. Adapted from (IAEA 2011a).

and inverted U bends at the top of the tube bundle. The secondary system coolant is fed through a feedwater nozzle into the downcomer, where it mixes with recirculating water draining from the moisture separators. Secondary water partially converts into steam as it passes through the tube bundle upwards while the remaining water (~75%) is recirculated into the downcomer. Some designs include an economiser (preheater) that uses the remaining heat of the cold leg to preheat the feedwater. For PWRs, typical NSG hot and cold leg temperatures are 315–330 and 280–295 °C, respectively. NSGs of CANDU reactors are smaller than those of PWRs and they use lower hot and cold leg temperatures of 290–310 and 250–265 °C, respectively (Green and Hetsroni 1995; Paine and Gustafsson 1994; Tapping et al. 2000).

Once-through superheated steam generators have straight tubes which carry the primary water from top to bottom (Figure 2). Typically, the primary coolant enters the steam generator at 316–327 °C and leaves at 291–293 °C. Feedwater enters the shell side; it flows down through an annulus where it becomes saturated by mixing with steam. Then it is almost completely converted into steam and superheated in a single pass from bottom to top (Green and Hetsroni 1995; Paine and Gustafsson 1994).

Horizontal/collector boiling steam generators are a particular type of recirculating NSGs used by WWERs (Figure 3). They are shell-and-tube heat exchangers where

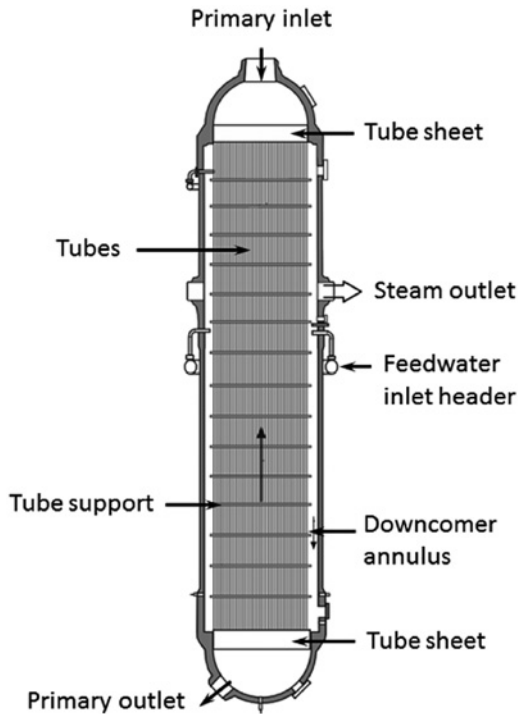


Figure 2: Scheme of a once-through superheated steam generator. Adapted from (Staehele and Gorman 2003).

the primary coolant enters through a vertical tubesheet (called collector), it flows horizontally through a U-shaped tube bundle and exits through a second vertical collector. The inlet/outlet temperatures of the primary coolant are 297/270 °C or 320/289 °C depending on the design (WWER 440 and WWER 1000, respectively). The secondary water is fed to the middle of the tube bundle in WWER 440 NSGs, and to the top of the hot side of the tube bundle in WWER 1000 NSGs. The produced steam is

collected at the top of the vessel. The main difference between the vertical and horizontal designs of recirculating steam generators is the circulation of the two-phase mixture in the secondary side. In the horizontal design the height of the water/steam interface changes along the path from the hot collector to the cold collector due to the temperature gradient (IAEA 2007, 2011a; Papp and Vacek 2017; ROSATOM 2016). The main advantage of the horizontal design is avoiding the accumulation of sludge at the top of the tubesheet (TTS). However, vertical designs require less space within reactor building (Staehele and Gorman 2003).

Recirculating vertical and horizontal NSGs remove a small percentage of the coolant (1% or less) on an intermittent or continuous basis. This flow, called blowdown, limits the amount of impurities in the coolant. Recirculating vertical NSGs collect the blowdown at the tubesheet (Figure 1). The blowdown strategy for recirculating horizontal NSGs is more complicated. There is a narrow pocket between the shell and the hot/cold collector where the flow is practically zero and sludge concentrates. Blowdown is performed at these sites and also at cold and hot sides of the shell (Figure 3). Once-through NSGs do not use blowdown in normal operation (Laroche 2017; Papp and Vacek 2017).

3 Corrosion control of steam generators under normal operation

3.1 Materials used in the secondary circuit

Carbon/low-alloy steels, stainless steels and nickel alloys are used in secondary cooling circuits of all NPPs while some plants may also specify copper or titanium alloys, mainly as condenser tubing materials.

Carbon and low-alloy steels are used for steam, condensate and feedwater piping, feedwater heater shells, moisture separators and condenser shells. Stainless steels are used in low-pressure feedwater heater tubing, condenser tubing, tube support plates (TSP) and steam generator tubing of WWERs. Copper alloys were widely applied in the past as tubing materials of reheaters, feedwater heaters and condensers. Their use have decreased due to corrosion problems of the alloys themselves and also to problems caused by copper ions (Cu^{2+}) released into the circuit. NPPs with mixed metallurgy (copper and iron alloys) face restrictions in the secondary water chemistry. These issues are discussed later in the text. Titanium alloys

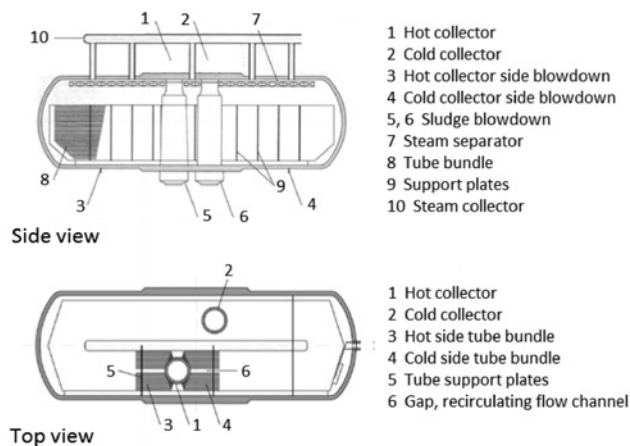


Figure 3: Scheme of a horizontal/collector boiling steam generator. Adapted from (Papp and Vacek 2017).

are used in cast pumps and valves, condenser tubes and the final stage buckets in low-pressure turbines. Nickel alloys are used in steam generator tubing. This topic is fully expanded in the following section since NSG tubing alloys are a part of the pressure boundary (EPRI 1992, 2005). Table 2 shows the materials used in the construction of steam generators.

3.2 NSG tubing alloys: metallurgy and corrosion susceptibility

Materials for the construction of PWR/PHWR NSG tubes include Ni-Cr-Fe alloys 600 (UNS N06600) and 690 (UNS N06690), Fe-Ni-Cr alloy 800 (UNS N08800) and Ni-Cu alloy 400 (UNS N04400). Tubing of WWER NSGs is made of 08Ch18N10T austenitic stainless steel which is a titanium-stabilised steel equivalent to the type 321 (UNS S32100) (Dutta 2009; IAEA 2007, 2011a). Table 3 shows the chemical composition of the alloy tubing materials.

In western countries, austenitic stainless steels such as 304 (UNS S30400) and 316 (UNS S31600), were initially considered as NSG tubing materials. However, it was soon evidenced that they suffer chloride-induced stress corrosion cracking (SCC) with transgranular cracks in high-temperature water (Dutta 2009). Then, nuclear industry turned to alloy 600 which appeared as a material immune to SCC since SCC submodes other than the chloride-induced were less known or unknown for this material (Staehele 2016). After some years in service, it was realized that alloy 600 was prone to SCC in pure water at high temperature, especially in the mill annealed condition (alloy 600MA). Since this SCC submode occurred in the

inside of the tubes it was called primary water SCC (PWSCC). Alloy 600MA is also susceptible to alkaline SCC. The susceptibility to PWSCC/alkaline SCC is mitigated when the grain boundaries of alloy 600 are covered with carbides. In the 1970s, vendors started to produce this carbide precipitation by a thermal treatment at about 705 °C for 15 h leading to alloy 600TT. However, carbide precipitation may sensitize the material due to chromium depletion at grain boundaries. Chromium has to be replenished at the grain boundaries or else the tubes are susceptible to outer diameter SCC (ODSCC), on the secondary side, in oxidizing acidic conditions. Thermal treatments are also used for stress relief of tubes (Staehele and Gorman 2003, 2004a,b). Once-through NSGs are subjected to full furnace stress relief which, in the case of alloy 600, has led to a sensitised microstructure called alloy 600SR (Pocock and Levstek 1974).

Alloy 690, which doubles the chromium content of alloy 600, was first introduced in 1989 to the nuclear industry as a NSG tubing material. This alloy is used in the thermally-aged condition (alloy 690TT) with a heat treatment of at least 10 h at 716 °C. No cracking on alloy 690TT NSG tubes has been reported until present day under service conditions though laboratory tests indicate that alloy 690TT is not immune to SCC, especially in cold work conditions. Alloy 690TT superseded alloy 600MA, 600TT and 600SR tubing for NSG though there are still many NSGs with alloy 600 tubing in operation (Staehele and Gorman 2003, 2004a,b).

Nuclear grade alloy 800 (alloy 800NG) has been used as NSG tubing since the early 1970s. Improvements of alloy 800NG with respect to standard alloy 800 include a reduced carbon content, an increased stabilisation ratio of titanium content over carbon and carbon plus nitrogen contents (to minimize sensitisation), and slightly increased chromium and nickel contents to improve resistance to pitting and chloride-induced SCC. Alloy 800NG is highly-resistant to alkaline SCC and almost immune to PWSCC. Based on the good results obtained in long-term operation this material is still used today (Tapping 2012).

Some of the first CANDU NPPs used Ni-Cu alloy 400 as NSG tubing material. The corrosion properties of alloy 400 are good though it is very sensitive to the presence of oxygen in secondary water, even at very low concentrations (Tapping et al. 2000).

Austenitic stainless steel used for tubing in Russian WWER NSGs is prone to chloride-induced SCC which occurs in the presence of oxygen, chloride ions, and high temperature. Both intergranular and transgranular cracks have been observed which, in many cases, propagates from corroding pits (IAEA 2007).

Table 2: Alloys used in the construction of nuclear steam generators (IAEA 2011a; Staehele and Gorman 2003).

Alloys	Applications
Ni-Cr-Fe alloys 600 and 690 Fe-Ni-Cr alloy 800 Ni-Cu alloy 400 ^{a,b} Austenitic stainless steel 08Ch18N10T	Tubing and tubesheet/ collector cladding
Ferritic stainless steels 405, 409, 410 Carbon steel ASTM A285 Grade C ^c	Tube support plates
Ferritic low alloy steels SA-302 Grade B, SA-508 Grade 1, SA-533 Grade B, SA-533 type A Class 1, SA-106 Grade B, Bainitic low alloy steel 10GN2MFA ^c Carbon steel 22 K ^c	Shell, feedwater nozzle, thermal sleeve inside the feedwater nozzle

^aUsed in some CANDU plants.

^bNot in use nowadays.

^cUsed in WWERs.

Table 3: Chemical composition (wt. %) alloys used for NSG tubing.

Alloys	Ni	Cr	Fe	Cu	Mn	C	Si	S	Others
08Ch18N10T	9–12	17–19	Bal.	–	<2	<0.08	<1	<0.03	0.3–0.7 Ti
UNS N08800	30–35	19–23	>39.5	<0.75	<1.5	<0.1	<1	<0.015	0.15–0.6 Al 0.15–0.6 Ti
UNS N06600	>72	14–17	6–10	<0.5	<1	<0.15	<0.5	<0.015	
UNS N06690	>58	27–31	7–11	<0.5	<1	<0.15	<0.5	<0.015	
UNS N04400	>63	–	<2.5	28–34	<2	<0.3	<0.5	<0.024	

3.3 Tube failure

From a plant management perspective, tube failure occurs when the indication obtained by non-destructive examination requires that the tube must be repaired or removed from service. Only a small proportion of failed tubes actually leaked primary coolant to the secondary coolant system. Failed tubes are plugged or repaired by sleeving. The type and frequency of tubing degradation have been affected by changes in design, materials and water chemistry (IAEA 2011a).

3.4 Heat-transfer crevices

As mentioned above, most of tube failures results from the formation of a locally aggressive chemistry on the tube external surface. Heat-transfer crevices (HTCs) are involved in the development of such local chemistries. HTCs are crevices affected by a temperature gradient which leads to local water boiling within them. Corrosion products (mainly iron species) transported into the NSG may form deposits in particular flow-restricted areas. When these deposits are in contact with the heat-transfer surfaces of tubes a dry-to-wet interface is formed. The inner part of the deposit, in contact with the tube, is dry while its outer surface remains wet. Permanent boiling occurs at the interface leading to a nucleate boiling site. Consequently, the less volatile impurities, such as chloride and sulphate, concentrate to produce high local concentrations of aggressive chemicals from nominally pure water. This “hideout” mechanism is driven by the boiling process. Concentration of chemical species within the HTC may result in a crevice solution either acidic or alkaline. Strong cations (Na^+ and K^+) alkalinize the crevice while strong anions (Cl^- and SO_4^{2-}) produce an acidic crevice solution. Enrichment factors for the non-volatile impurities within HTCs are in the range of 10^4 – 10^6 times the bulk concentration (Drexler 2017; Staehle and Gorman 2003). On the contrary, in a conventional or non-heat transfer crevice

local acidic conditions result from preferential anodic dissolution of the metal and subsequent hydrolysis of the metal cation within the crevice. Supporting cathodic reactions occur preferentially on the boldly exposed metal. This can lead to a differential-aeration corrosion cell in carbon steel or to crevice corrosion in passive metals (Szkłarska-Smiałowska 2005).

Figure 4 shows the three types of HTCs that form in tubing of recirculating vertical NSGs: a) at the TTS, b) at the sludge that eventually develops on the TTS, and c) at the TSP. Figure 5 shows various types of TSPs which form crevices with the tubes in recirculating vertical NSGs: a) drilled hole, b) egg crate/lattice bars, and c) broached hole (Green and Hetsroni 1995; Staehle and Gorman 2003). Line contact arrangements (egg crate and broached hole TSPs) have replaced the drilled hole TSP which has a larger surface-to-surface contact. Blockage of TSPs holes by accumulation of corrosion products in the gaps may cause steam generator clogging (Drexler 2017). Tubes are installed to the tube sheet by mechanical rolling, hydraulic expansion, or explosive expansion, followed by seal welding. Crevices of different length form between the tube and the tube sheet depending on the particular design (Figure 6). Early designs included a part-depth roll that was replaced by a full-depth roll or expansion, which significantly shortened the length of the crevice. Standard full-depth expansion used nowadays leaves a 3-to-6-mm-long crevice near the TTS to avoid “overexpansion” which may damage the tube. In some cases, the full-depth expansion is followed by a mechanical hard roll called “kiss roll” (IAEA 2011a; Staehle and Gorman 2003).

Concentration of chemicals on the secondary side preferentially occurs in HTCs and, in a lesser extent, on other surfaces through which heat is transferred, such as the upper bundle of once-through steam generators where boiling readily occurs. When NPPs shut down a process called hideout return occurs which is the diffusion to the bulk water of impurities accumulated in HTCs during operation.

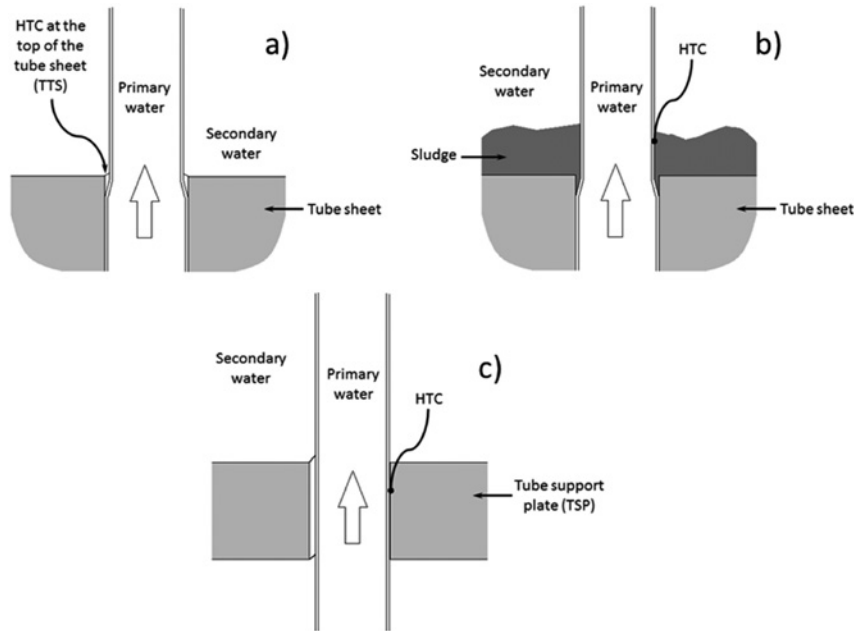


Figure 4: Heat-transfer crevices formed in tubes of recirculating vertical and once-through NSGs (a) at the top of the tubesheet (TTS), (b) at the sludge on the TTS, and (c) at the tube support plates (TSP). Adapted from (Staehele and Gorman 2003).

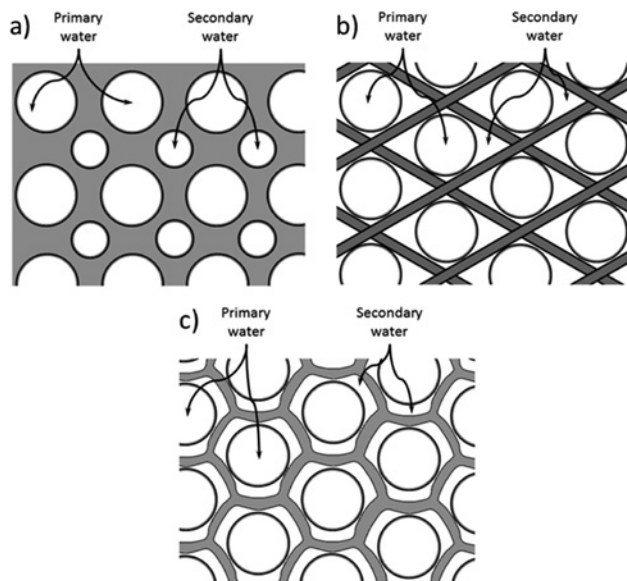


Figure 5: Types of TSPs which form crevices with the tubes in recirculating vertical and once-through NSGs: (a) drilled hole, (b) egg crate, and (c) broached hole. Adapted from (Green and Hetsroni 1995; Staehele and Gorman 2003).

3.5 Tube degradation processes

Various degradation processes have affected NSG tubes to date, namely: wastage, denting, pitting corrosion, intergranular corrosion, SCC, and mechanically-aided processes (fretting, sliding and impact wear and fatigue). They are briefly reviewed below.

3.5.1 Wastage

Wastage is the colloquial name of a type of general corrosion that appeared under deposits in NSGs with phosphate chemistry. Wastage occurred at tubesheet crevices, sludge piles, TSPs and anti-vibration bars (AVBs). This type of degradation resulted from lowering the Na^+ to PO_4^{3-} molar ratio to avoid alkaline SCC and intergranular corrosion. Phosphate wastage has been ascribed to a local acidic chemistry resulting from the precipitation of phosphate phases. Alternative explanations point out the existence of a chemical complex which increases the solubility of nickel. Wastage is not observed nowadays since the phosphate chemistry has been abandoned (IAEA 2011a; Staehele and Gorman 2003).

3.5.2 Denting

Denting is the constriction of the tube at the intersection of a carbon steel TSP or, in a lesser extent, at the TTS. It is produced by the build-up of deposits and the growth of corrosion products with an increased volume within the gaps. Dents induce tensile stresses which eventually may lead to some types of SCC, decrease the fatigue resistance of tubes and produce flow blockage. Historically, denting started to happen when NPPs switched from phosphate chemistry to all-volatile treatment (AVT) in NSGs with carbon steel TSPs. AVT chemistry does not provide any buffering to solution pH at HTC and it is more sensitive to secondary water contamination than phosphate

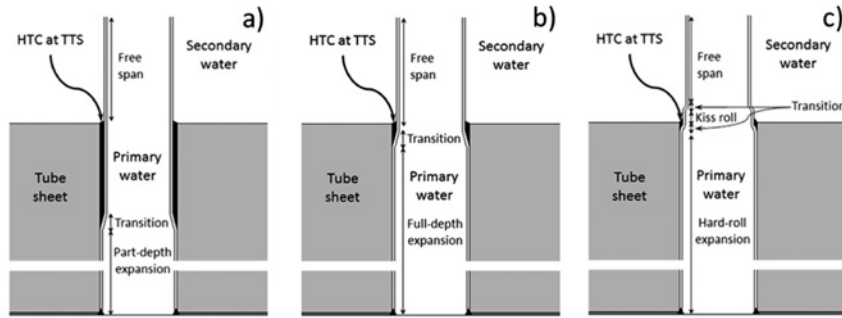


Figure 6: Tube sheet geometries: (a) partially expanded, (b) fully expanded, and (c) fully expanded with top “kiss” roll. Adapted from (Staehele and Gorman 2003).

chemistry. NPPs that use seawater or brackish water in the tertiary cooling system suffered the first cases of denting. The drilled hole TSP (Figure 5a) is more likely to cause denting of tubes since the contact area between the tube and the TSP is large. Denting occurred mainly on the hot leg side of NSGs. High concentrations of chlorides and sulphates in the bulk water and oxidising species, such as dissolved oxygen and copper ions, promote carbon steel corrosion and thus denting. The use of stainless steel TSPs with line contact tube support geometries (Figure 5b and c) eliminated the problem. In present designs of NSGs denting is only likely at the TTS due to the presence of carbon steel beads left after shot peening. The crevice depth at the TTS can be minimised but not eliminated (Figure 6). Therefore, the risk of denting can only be further reduced by avoiding the precipitation and build-up of ferrous deposits at these location (IAEA 2011a; Staehele and Gorman 2003).

3.5.3 Pitting corrosion

Pitting corrosion is a form of localised corrosion that occurs in metallic materials covered by a passive film in the presence of specific anions, especially under oxidizing conditions. Corrosion-resistant materials used for NSG tubing are prone to pitting corrosion. Chloride, and in a lesser extent sulphate, are detrimental anions present in secondary water as impurities which typically induce pitting corrosion of passive alloys. Oxidising conditions promoted by dissolved oxygen and soluble copper ions increase pitting corrosion susceptibility since it occurs above a critical potential. Alike denting, switching from phosphate chemistry to AVT led to an increasing incidence of pitting corrosion due to the lack of pH buffer capacity of AVT chemistry in HTCs along with high impurity levels. Locations of typical occurrence of pitting corrosion in recirculating vertical NSGs include the tube sheet sludge pile region and tube-to-TSP crevices (Figure 4). There are reported cases of pitting corrosion in

tubes of alloy 600MA and stainless steel 304 in PWRs, and tubes of alloys 400 and 800NG in CANDU plants. In some cases, pits appeared below deposits so it is referred to as underdeposit corrosion. Pitting corrosion is a frequent type of tube degradation in WWERs due to the high pitting susceptibility of stainless steel 08Ch18N10T and the high concentrations of chlorides in the secondary water. It is common that corrosion pits lead to SCC cracks in WWER NSG tubes (IAEA 2007, 2011a; Szklarska-Smialowska 2005).

3.5.4 Intergranular corrosion

Intergranular corrosion or intergranular attack is a localised form of corrosion that occurs preferentially along the grain boundaries. Grain boundaries are particularly disordered zones of the alloy where transport processes occur more quickly and impurities tend to concentrate. Tubing materials include chromium-containing alloys that form carbides in a temperature range which depends on the particular alloy, but it is roughly from 350 to 900 °C (Sedriks 1996; Was 1990). As explained in a previous section, grain boundary precipitation of carbides provides a more resistant microstructure to some types of SCC. Therefore, fabrication processes of modern NSG tubing alloys (alloys 600TT, 600SR and 690TT) involve a heat treatment of carbide precipitation. Carbide precipitation starts at grain boundaries and produces the chromium depletion of adjacent locations. For longer ageing times, chromium is replenished at these sites. However, alloy 600SR was used for tubing of once-through NSG in the sensitised condition. Some of these tubes have suffered intergranular attack in HTCs that is generally attributed to partially reduced sulphur species, such as thiosulfates. In a lesser extent, intergranular corrosion is also reported for alloy 800NG tubing. Alloy 400 tubing is susceptible to intergranular corrosion in acidic solutions which may occur in crevices. This phenomenon is attributed to the segregation of sulphur and phosphorus to the grain

boundaries (De and Bose 1993). Intergranular corrosion has been shown in association with or giving rise to intergranular SCC cracks in NSG tubes. This type of degradation have affected mainly alloys 600MA, 600SR, 08Ch18N10T, and in a lesser extent, alloys 600TT and 800NG (Dutta 2009; Gorman 2017; IAEA 2011a).

3.5.5 Stress corrosion cracking

SCC is a type of cracking that a material with a susceptible microstructure and under tensile stress may suffer when exposed to a corrosive environment. SSC produces intergranular or transgranular cracks depending on the material/environment system. Generally, SCC cracks are branched and start at pits, dents, frets, fatigue cracks or other micro or macro surface defect. As stated above, microstructure of the alloy tubing play a significant role in the SCC susceptibility. SCC may appear after very long incubation times. Therefore, their incidence is expected to increase as NPPs age (IAEA 2011b; Raja and Shoji 2011).

Staehele and Gorman (2003, 2004a,b) distinguish nine different SCC submodes affecting NSG tubes according to their unique dependence on a set of primary variables, namely: pH, potential, chemical species, alloy composition, alloy structure, temperature, and stress. The four main submodes are low-potential SCC (LPSCC), alkaline SCC (AkSCC), acidic SCC (AcSCC) and high-potential SCC (HPSCC). Other less frequent SCC submodes include lead SCC (PbSCC), reduced-sulphur SCC (Sy-SCC), doped-steam SCC (DSSCC), organic SCC (OgSCC) and low-temperature SCC (LTSCC). LPSCC is the appropriate name of PWSCC since it occurs at low electrochemical potentials. The so-called ODSCC includes all the variety of SCC submodes that produces tube cracking from the secondary side (IAEA 2011a; Staehele and Gorman 2003, 2004a,b).

LP/PWSCC is the only cracking mode that may occur both in the primary and secondary sides of NSG tubes. It has been a major cause of tube failure in recirculating vertical NSGs with alloy 600MA tubing and once-through NSGs with 600SR tubing. The effect of alloy microstructure on the occurrence of PW/LPSCC has been discussed in a previous section. The highest incidence of this phenomenon has been reported from the primary side. Cracks occur at locations on the inside surfaces of tubes with high residual stresses, such as the roll transition regions in the tube sheets, the U-bend regions of tubes with a small bend radius, dents at the tube support plate, tubesheet, or sludge pile. PW/LPSCC cracks are intergranular. They may grow either axially or circumferentially depending on the particular location (cracks grow perpendicularly to the maximum principal stress). Alike all others SCC submodes,

PW/LPSCC is thermally activated and thus more frequent on the hot leg side of the NSGs. NSGs of CANDU plants operate at lower temperatures and they have not suffered PW/LPSCC even though alloy 600MA has been used as tubing material. Alloy 600TT has experienced PW/LPSCC in locations with significant cold work due to fabrication processes, such as kiss-roll transitions (Figure 6). Alloys 690TT, 800NG and 400 do not suffer PW/LPSCC (Gorman 2017; IAEA 2011a; Staehele 2016; Staehele and Gorman 2003, 2004a,b).

In the nuclear industry, it is common to describe all the SCC processes starting from the outer surface of NSG tubes as ODSCC, even though they result from completely different SCC submodes. The nine SCC submodes described by Staehele and Gorman (2003, 2004a,b) are mostly associated with the HTCs described in Figure 4, and in a much lesser extent with the free span of the tubes. Cracks may be either intergranular or transgranular depending on the particular submode though most reported cracks are intergranular. They may grow axially or circumferentially depending on the direction of the stress. ODSCC has affected mainly tubes of alloys 600MA and 600SR, and with less frequency, tubes of alloys 600TT and 800NG. Staehele and Gorman (2003, 2004a,b) provide a comprehensive treatment of the SCC phenomenology in PWR NSGs.

Chloride-induced SCC, frequently associated with previous chloride pitting corrosion, is the main degradation mechanism affecting NSG tubing of WWERs. This type of SCC is included within the submode of acidic SCC. The high incidence of SCC results from the high susceptibility of the tubing alloy (austenitic stainless steel 08Ch18N10T) and poor secondary side water chemistry. Reported water chemistry issues include high concentrations of dissolved oxygen and chloride, low pH values (below 7.8), presence of organic compounds (such as acetic acid) and formation of porous crud deposits where chlorides concentrate. SCC occurs more frequently near the hot collectors (Gorman 2017; IAEA 2011a).

3.5.6 Mechanically-aided degradation processes

Flow-induced vibrations at particular locations of the secondary side of NSGs are associated with all the mechanically-aided degradation processes which affect the tubes. Recirculating vertical NSGs with high recirculation flow factors produce flow-induced vibration in the U-bend region where steam and water flow at high rates. This is aggravated by poorly designed or misplaced AVBs. These vibrations may lead to various types of mechanically-aided degradation processes, namely fretting, sliding and impact

wear, and fatigue. Fretting wear is a type of mechanical damage produced by small amplitude oscillations between continuously rubbing surfaces. Fretting wear of NSG tubes may occur due to the oscillatory motion at the contact between tubes, or between a tube and a TSP. Beside the U-bend regions of the tube bundle, NSGs zones where fretting wear has been reported include the economiser and broached hole TSPs clogged with corrosion products. Sliding wear is produced by vibration of relatively large amplitude which results in intermittent sliding contact between tubes and TSPs. Impact wear of tubes results from loose parts and debris transported by the flow. Reported failures of NSG tubes due to mechanically-aided damage (excluding fatigue) in order of relevance are as follows: fretting wear at AVBs, impact wear damage by loose parts and fretting wear in the economiser region. Fretted tubes are more susceptible to fatigue or SCC crack initiation (Hassan 2017; IAEA 2011a)

Fatigue is a progressive and localised type of damage that occurs on materials subjected to cycling loading. If the applied stress amplitude is lower than the material yield strength but higher than its fatigue limit high-cycle fatigue takes place. Conversely, low-cycle fatigue occurs if the applied stress amplitude exceeds the elastic limit of the material. Simultaneous presence of a corrosive environment generally results in a more rapid material failure when compared to a non-corrosive or reference environment (dry air). This type of degradation is called corrosion fatigue. If crack growth rates in the corrosive and reference environments are the same, failure is ascribed essentially to fatigue. Conversely, if the corrosive environment accelerates the damage failure is ascribed to corrosion fatigue. Fatigue and corrosion fatigue produce transgranular cracks. Fracture surfaces display typical striations (Milella 2013). Fatigue damage of NSGs tubes occurs due to combination of high vibration amplitude and low fatigue strength of materials. Dents, fret marks and SCC cracks in tubes may be initiation sites for fatigue cracking. Transgranular SCC and fatigue cracks may be hard to distinguish. Flow-induced vibration that occurs in the U-bend region of recirculating vertical NSGs make the portion of the tube located at the top TSP susceptible to high-cycle fatigue failure. In once-through NSGs failure of tubes by fatigue is reported in an upper region, near a missing row of tubes, known as inspection lane. Instead of superheated steam, water droplets form at this particular location. Vibration is produced by the flow of steam bending towards the periphery of the bundle. High-cycle fatigue in once-through NSGs is environmentally assisted (*i. e.* corrosion fatigue) since impurities concentrated at deposits play a

significant role in the cracking. Overall limited cases of damage by (corrosion) fatigue in NSG tubes have been reported. However, these types of failure produce rapidly growing circumferential cracks resulting in large leaks which are difficult to detect and prevent. Alloy 600MA has been particularly affected by this phenomenon while alloys 600TT, 690TT and 800NG have been free from this type of damage. Fatigue degradation does not occur in recirculating horizontal NSGs of WWERs (Gorman 2017; IAEA 2011a).

3.6 Degradation of NSG shell, feedwater nozzle, piping (secondary) and inlet nozzle (primary)

Corrosion fatigue, high-cycle thermal fatigue, SCC and flow-assisted corrosion (FAC) are the main degradation modes that have affected the shell, feedwater nozzle, piping (from the secondary side) and inlet nozzle (from the primary side) in recirculating NSGs. CANDU plants have not suffered these types of degradation. Failure of the feedwater nozzle is critical since it would cause a much larger leak than a crack on the shell, and it would be difficult to isolate from the steam generator. A significant leak in the secondary side of the steam generator leads to its rapid blowdown, which in turn produces a temperature increase of the tubes. Therefore, the integrity of already degraded tubes would be particularly compromised (IAEA 2011a,b; MacDonald et al. 1996).

3.6.1 Corrosion fatigue and high-cycle fatigue

Some shells of recirculating vertical NSGs of PWRs in the USA have suffered damage in the upper girth weld. Figure 7 shows the location of girth welds. This type of damage is attributed to corrosion fatigue under the combined effects of cyclic stresses of high-amplitude and low-frequency, and a coolant containing oxygen and copper oxides. Circumferential cracks have been observed mainly in the heat-affected zone of the upper girth weld which has lower fracture toughness than that of the base metal. It is speculated that the presence of oxygen and copper oxides (due to copper alloys in the secondary circuit) resulted in the formation of pits where fatigue cracks initiated. Thermal fatigue cycles on the shell result from fluctuations in the water level of the steam generator. Feedwater impingement on the girth weld may occur during transients of low water level. It produces high stresses thus assisting the weld degradation process (IAEA 2011a; MacDonald et al. 1996).

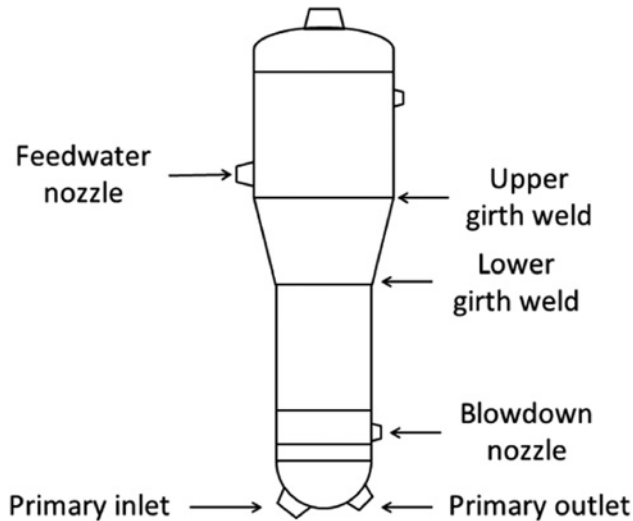


Figure 7: Recirculating vertical steam generator of PWRs showing girth welds. Adapted from (IAEA 2011a).

Horizontal feedwater pipes and feedwater nozzles have shown cracks on the lower piping halves. Figure 8 shows the feedwater nozzle of a recirculating vertical NSG joint to the feedwater pipe by a weld, and the thermal sleeve. Cracking has been attributed to thermal fatigue resulting from cycling stressing due to thermal stratification. The intensity and propagation rate of cracking depend on the stress amplitude and on the frequency of the cycling stress. Thermal stratification may occur when the auxiliary feedwater system operates under low flow conditions during hot stand-by. In horizontal sections of the pipes, cool water flows along the bottom while hot water flows along the top of the piping. In such conditions, two different stressors have been identified which combined lead to fatigue damage: cyclic local stratification and thermal stripping. Cyclic local stratification is caused by small fluctuations in the auxiliary feedwater flow which produce changes in the height of the interface between cold and hot layers. Such changes in the elevation of the interface lead to significant stress changes in the pipe cross section. Thermal stripping occurs due to the turbulent mixing of the water layers which results in high-cycle fatigue crack initiation. It is thought that cracks produced by thermal stripping are propagated by cyclic local stratification. Cracking has been also observed in the transition region between the feedwater nozzle and the pipe weld due to high concentration of stress. High-cycle fatigue has been reported in the feedwater nozzle due to leakage of feedwater through the joint between the nozzle and the thermal sleeve. Thermal stresses may produce fatigue cracks in the nozzle bore, nozzle blend radius, and the inside surface of the shell, as observed in Figure 8. Piping material (carbon

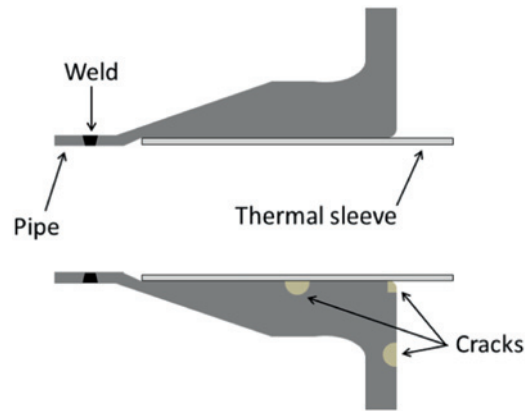


Figure 8: Feedwater nozzle sites susceptible to high cycle thermal fatigue damage. Adapted from (MacDonald et al. 1996).

steel) and shell material (low alloy steel) are susceptible to corrosion fatigue when they contain MnS inclusions.

3.6.2 Stress corrosion cracking

The low alloy steel used for the construction of NSGs shells is susceptible to SCC in oxygenated secondary water containing copper oxides. Residual stresses from welds along with operating stresses provide tensile stresses sufficiently high for SCC to happen. Damage occurs in the inside surface of the girth welds where circumferential cracks of the transgranular type have been reported (Figure 7). Corrosion fatigue cracks are also transgranular though applied stresses are cyclic. Transgranular SCC cracks and corrosion fatigue cracks are not always easy to distinguish, even though the former cracks tend to be branched. From a practical viewpoint, load history is analysed: if the ratio of the minimum to the maximum stress intensity factors is lower than 0.95 the damage is ascribed to corrosion fatigue; otherwise, stress is considered constant and the damage is attributed to SCC. Theoretical analysis and field experience indicate that SCC cracks produce a measurable leak before leading to the vessel rupture (IAEA 2011a,b; MacDonald et al. 1996).

SCC has been reported in the inlet nozzle (hot leg) of the primary side of eleven NSGs at five Japanese PWRs. Axial cracks were reported on the inner diameter of the nozzle, at the inner alloy 600 weld. Failure is ascribed to LP/PWSCC due to strong residual stresses from machining of the surface (IAEA 2011a,b).

Collectors of WWERs have suffered SCC. Hot and cold collectors are fabricated from low alloy steel and clad with austenitic stainless steel on the inside. Cracks have been found only in the cold collectors though indications have also been reported for hot collectors. Cracks usually

start at pits formed in the crevice between the collector hole and a non-expanded tube. These crevices may be as 20-mm deep. They tend to accumulate deposits, which in the case of the hot collector are dense and hinder the water ingress. On the contrary, porous deposits which accumulate impurities form in the cold collector. MnS inclusions are preferential sites of pit/crack initiation. Penetration of the wall occurs only after cracking of several ligaments. Penetration of cracks into the collector results in wall ductile cladding failure. Tensile stresses in the material occur due to the expansion of the tubes into the collectors. Residual stresses near yields stress are reported in the collector ligaments. SCC is aggravated by acidic pH, chloride concentrations above the specified limit of 150 µg/kg and oxidising conditions promoted by dissolved oxygen and copper ions (IAEA 2007, 2011a).

3.6.3 Flow-assisted corrosion

FAC affects carbon steel piping carrying feedwater and wet steam. Under normal operation a thin layer of iron oxide, mostly magnetite (Fe_3O_4), forms on the inside surface of carbon steel piping. This layer provides protection to the underlying metal slowing down its corrosion. Water flow at high rates disrupts this protective layer resulting in the exposure of bare metal to the corrosive environment. Thus

carbon steel corrodes at a much higher rate. Pipe thinning may lead to a catastrophic failure, especially if a large pressure pulse occurs in the system. FAC may take place in wet steam lines only if an annular flow of liquid water develops in contact with the pipe. Replacement of carbon steels by low alloy steels of higher chromium content reduces significantly the incidence of FAC. FAC is particularly severe in the temperature range from 100 to 200 °C, being 180 °C the temperature of highest susceptibility. The rate of pipe thinning by FAC drastically decreases for $\text{pH}_{25^\circ\text{C}} > 9.5$ obtained by ammonia additions. Small oxygen additions help to develop a less soluble/more protective oxide, as it will be discussed later. Locations associated to high linear velocity of water, such as low-radius elbows, are particularly prone to FAC. Feedwater distribution systems of WWERs have suffered severe cases of FAC. In western type PWRs, FAC has led to fatal accidents in the USA and Japan (IAEA 2011a; MacDonald et al. 1996; Remy and Bouchacourt 1992).

3.7 State-of-the-art of corrosion control of nuclear steam generators under operation

Table 4 shows corrosion problems that have been reported in NSGs throughout their lifetime along with the current

Table 4: Corrosion problems reported in NSGs under operation.

Corrosion mode	Affected parts	Current corrosion control strategies
Wastage	Tubes (TSPs, TTSs, AVBs)	Solved by switching from phosphate chemistry to AVT
Denting	Tubes (TSPs, TTSs)	Solved by changing (drilled-hole) carbon steel TSPs by contact-line stainless steel TSPs. Still possible at TTSs due to carbon steel beads from shot peening.
Pitting corrosion	Tubes (HTCs)	Minimised/solved by water chemistry control
Intergranular corrosion	Tubes (HTCs)	Minimised/solved by proper heat treatment of alloy 600, and switching to higher chromium alloys (690TT and 800NG). Susceptible alloy 400 no longer used.
Stress corrosion cracking	Tubes (TSPs, TTSs, free span)	LP/PWSCC mitigated by proper heat treatment of alloy 600. Solved by using alloys 690TT and 800NG. Nine possible submodes of ODSCC mitigated by a variety of measures: water chemistry control, appropriate design, alloy composition and heat treatment. Probability of SCC damage increases as NPP ages.
	Shell (girth weld, inlet nozzle, hot collectors)	Minimised by water chemistry control, minimisation of residual/operational stresses and improved alloy metallurgy (control of MnS inclusions)
Fretting, sliding and impact wear	Tubes (ABVs, clogged TSPs, economiser)	Solved by improved design of AVBs, water chemistry control, elimination of loose parts and debris
Corrosion fatigue / fatigue	Tubes (top TSP, inspection line)	Minimised by improved design based on inputs from thermalhydraulics codes
	Shell (upper girth weld)	Minimised/solved by control of MnS inclusions of alloys, water chemistry control, and avoidance of fluctuations in water level
Flow-assisted corrosion	Feedwater nozzle and horizontal pipes	Minimised by control of MnS inclusions of alloys, appropriate design of feedwater nozzle, distribution system, and balance of plant, and changes in operation modality to soften thermal cycling effects.
	Piping	Minimised/solved by water chemistry control, use of more alloyed steels, and improved design of piping system

corrosion control strategies. Some of the corrosion modes have been mitigated to a large extent or even eliminated while others remain as pervasive degradation processes that might occur as plants age. It is worth to mention that the high incidence of degradation processes such as wastage, denting, pitting corrosion and SCC during 1970s and 1980s is mainly due to poor water chemistry control and deficient design/materials selection of tubes and TSPs. Nowadays, NSGs are a more mature technology. Their design, material selection and water chemistry have evolved to rule out or delay most of the corrosion processes that frequently appeared in the past. In this context, SCC of tubes is the most complex and pervasive corrosion mode due to the many submodes it displays and the lack of precise understanding of the underlying mechanisms involved.

Table 5 shows a summary of degradation modes that have suffered the various tubing alloys along with their current status. Considered degradation modes are those associated with the alloy composition and microstructure. Mechanically-aided degradation modes are not included since they largely depend on the steam generator design.

Alloy 600, in its various metallurgical conditions (600MA, 600SR and 600TT), and alloy 400 have been abandoned as tubing materials. Alloy 600 is inherently less resistant to LP/PWSCC and alkaline SCC than alloys 690TT and 800NG due to its chemical composition. Alloy 400 tubes are difficult to inspect with standard eddy current coils due to its ferromagnetism. Moreover, its corrosion resistance significantly decreases when small amounts of oxygen are present in secondary water.

Alloys 690TT and 800NG are the current materials of choice for NSG tubing in PWR/PHWR mainly based on an outstanding performance and abundant in-service experience, respectively. Alloy 690TT has no corrosion issues reported to date while alloy 800NG has a larger in-service experience. SCC submodes may appear after long incubation periods and accelerated laboratory tests have shown alloy 690TT may suffer SCC, especially in the cold-work condition (Moss et al. 2018; Zhai et al. 2017). Therefore, immunity of alloy 690TT to the various SCC submodes cannot be claimed. Presently, alloy 690TT is the preferred material for NSG tubing in France, Japan and USA while alloy 800NG is used in Argentina, Belgium, Brazil, Canada, Germany, Netherlands, Republic of Korea, Spain and Switzerland. WWER NSGs use austenitic stainless steel 08Ch18N10T tubing (Gorman 2017; IAEA 2011a).

4 Secondary water chemistry

The objective of the water chemistry control in the secondary cooling system is to ensure the integrity of materials of the system components and to maintain the heat transfer performance. To this purpose, the transport of corrosion products and impurities to the NSGs is kept as low as possible and sufficiently reducing conditions are established. Although the secondary water chemistry control is focused on the integrity of the NSG tubes, minimizing the overall corrosion of NSGs and of BOP equipment is also important since all corrosion products accumulate in the NSGs. The steam generators are sinks of non-volatile species in the entire secondary circuit. Minimization of corrosion

Table 5: Summary of degradation modes and current status of tubing alloys.

Tubing alloy	NPP and NSG types	Degradation modes ^a	Current status
600MA	PWR/PHWR recirculating vertical NSGs	LP/PWSCC, ODSCC, intergranular corrosion, wastage (phosphate chemistry), denting, pitting corrosion	Not specified but still present in old units
600SR	PWR once-through NSGs and PHWR recirculating vertical NSGs	LP/PWSCC, ODSCC, intergranular corrosion,	Not specified but still present in old units
600TT	PWR/PHWR recirculating vertical NSGs	LP/PWSCC, ODSCC, intergranular corrosion.	Not specified but still present in old units
400	CANDU PHWR recirculating vertical NSGs	Pitting corrosion, intergranular corrosion	Not specified but still present in old units
690TT	PWR recirculating vertical and once-through NSGs	No confirmed corrosion to date	Specified for PWR recirculating vertical and once-through NSGs
800NG	PWR/PHWR recirculating vertical NSGs	Pitting corrosion and wastage (phosphate chemistry), ODSCC, intergranular corrosion	Specified for PWR/PHWR recirculating vertical NSGs
08Ch18N10T	WWER recirculating horizontal NSGs	Chloride-induced pitting corrosion and SCC	Specified for WWER recirculating horizontal NSGs

^aMechanically-aided degradation modes are not considered since they depend on the NSG design in a large extent (Gorman 2017; IAEA 2011a).

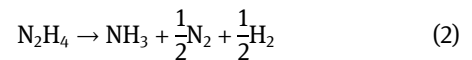
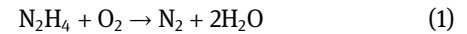
products and impurities entering NSGs also improves their thermal efficiency and avoids thermo-hydraulic issues. Fouling of the tube bundle decreases the overall heat-transfer coefficient leading to a decrease of both the thermal power and the outlet pressure of the steam generators (Drexler 2017; IAEA 2011a; Kawamura et al. 2019).

NPPs use water chemistry guidelines that specify values of a set of control and diagnostic parameters for an efficient and reliable operation. Control parameters determine the overall chemistry conditions and diagnostic parameters give complementary information. Control parameters have limit values for start-up, power operation, shutdown and lay-up that trigger different action levels when deviations occur. Typical control parameters include $\text{pH}_{25^\circ\text{C}}$, oxygen concentration, cation conductivity, etc., which are measured in different parts of the secondary circuit. Japanese PWR water chemistry guidelines define a third type of parameter, called conditioning parameter, which is given by the scavenger concentration and pH of the feedwater. Chemistry guidelines are customised according to the particular design and materials of the secondary circuit components (IAEA 2011a; Kawamura et al. 2019).

Low oxygen and low impurity concentrations along with a moderately alkaline pH in secondary water minimise corrosion of steam generators. Historically, there have been two approaches to secondary water chemistry aiming at minimizing corrosion in HTCs: phosphate chemistry treatment and all-volatile treatment. Phosphate chemistry provides buffering of local solutions and the formation of an easy-to-remove sludge. However, it was soon realised that HTCs may become alkaline, leading to SCC or intergranular corrosion of tubes; or acidic, leading to wastage. Attempts to find a solution by modifying the $\text{Na}^+/\text{PO}_4^{3-}$ molar ratio in the bulk water were unsuccessful and phosphate chemistry was abandoned. Most of NPPs moved from phosphate chemistry to AVT from mid-1970s to 1980s. The last plant to switch chemistries was the Argentinean PHWR Atucha I, in 2009 (IAEA 2011a). AVT uses ammonia (NH_3) and/or amines to set an alkaline pH and an oxygen scavenger to remove any dissolved oxygen. AVT chemistry is free from any precipitation of solids. However, it does not provide any buffer capacity and require high-purity feedwater to minimize the concentration of impurities in HTCs. Once-through steam generators have applied AVT chemistry from the beginning since they are not compatible with phosphate chemistry. Recirculating vertical and horizontal NSGs switched from phosphate to AVT chemistry (IAEA 2011a; Pocock and Levstek 1974).

Mechanical deaeration along with the addition of a chemical oxygen scavenger are applied to meet the requirement of a reducing environment in the secondary

circuit. A mechanical deaerator removes dissolved oxygen and any other non-condensable gas from the coolant as it enters the feedwater storage tank. Oxygen concentration in feedwater may be reduced down to $7 \mu\text{g}/\text{kg}$ by mechanical deaeration. Further oxygen removal is accomplished by adding a scavenger, which is generally hydrazine (N_2H_4). Hydrazine reacts with oxygen according to Eq. (1) and it also thermally decomposes into ammonia according to Eq. (2). Typical concentration of hydrazine in the secondary water is about $100 \mu\text{g}/\text{kg}$.



The resistance to FAC of carbon steel piping and steam generator internals decreases at very low electrochemical potentials (Millet et al. 2002). Consequently, the concentration of scavenger in the secondary circuit is selected by weighting the effects of a reducing potential on tubing alloys and on FAC of carbon steel components. Some NPPs add a small amount of oxygen in particular places of the secondary circuit affected by FAC, such as the feedwater train. Oxygen shifts the potential to higher values promoting the formation of haematite (Fe_2O_3) films which are less soluble than the magnetite films formed at low potentials. Depending on whether an oxidizing or a reducing environment is selected the water chemistry programme is called AVT(O) and AVT(R), respectively (Drexler 2017; IAEA 2011a).

Secondary water with a relatively high pH helps to protect the steam generators from corrosion and minimises the ingress of corrosion products (particularly iron species). pH is measured in feedwater at room temperature ($\text{pH}_{25^\circ\text{C}}$). However, the pH of interest is that at the real operating temperature (pH_T). pH_T is estimated by considering the properties of water and the various dissolved species at the operating temperature and pressure. Figure 9 indicates that corrosion rate of carbon steel at 250°C minimises at $\text{pH}_{25^\circ\text{C}} \approx 10$. This is the target pH of the secondary water in NPPs with all-ferrous metallurgy. In steady state conditions, hydrazine additions of $100 \mu\text{g}/\text{kg}$ produce $5\text{--}10 \text{ mg}/\text{kg}$ of ammonia in feedwater by thermal decomposition which results in a $\text{pH}_{25^\circ\text{C}}$ from 9.8 to 10. Note that hydrazine is consumed at a higher rate than ammonia. Thus, the dosing of a single chemical satisfies the need of reducing conditions and a high pH. This type of water chemistry, which uses only ammonia to control the pH in the secondary water, is called high AVT. High AVT has been effective in avoiding FAC and minimizing corrosion products transport. Hydrazine concentration for high AVT ranges from 80 to $200 \mu\text{g}/\text{kg}$ (Drexler 2017; IAEA 2011a).

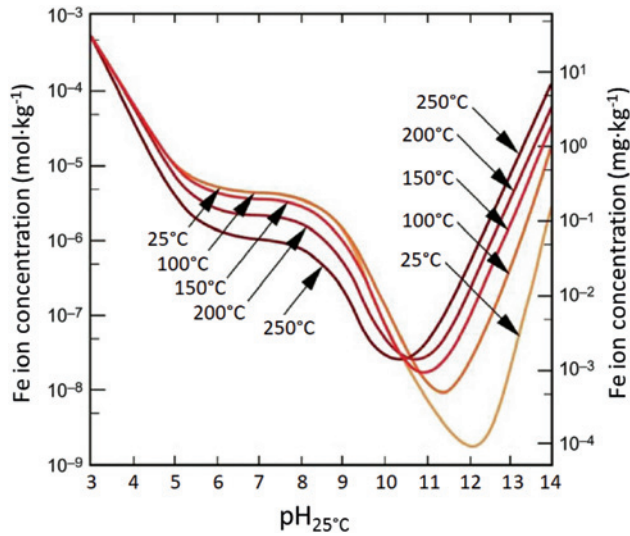


Figure 9: Concentration of Fe ion released into water as a function of $\text{pH}_{25^\circ\text{C}}$ at different temperatures. Adapted from (Drexler 2017).

Some NPPs have copper alloy components, such as condenser tubes, in the secondary circuit. Corrosion rate of copper alloys is minimal at $\text{pH}_{25^\circ\text{C}} = 8.8$. The compromise solution for these plants is to limit the $\text{pH}_{25^\circ\text{C}}$ to a maximum of 9.2 to protect the copper alloy components from alkaline corrosion. Ammonia concentration is also limited since it is deleterious to copper-bearing materials. Soluble copper (Cu^{2+}) released from copper alloys corrosion is oxidizing and enhances degradation processes like denting, pitting, intergranular corrosion and SCC. This type of water chemistry, which is compatible with copper alloy components, is called low AVT and it uses alkaline agents other than ammonia (mostly morpholine) to maintain the target pH value. Low AVT chemistry uses organic amines as alkalizing agents besides the ammonia obtained from thermally-decomposed hydrazine. The most common species among the so-called alternative amines are morpholine, ethanol-amine (ETA), dimethyl-amine (DMA) and methyl-propanol-amine (MPA). The solution alkalinity is determined by the dissociation constant of the selected amine and its concentration. The distribution ratio coefficient (K_D) is defined as the relative concentration of the amine in the water and steam phases. $K_D < 1$ indicates the amine is more concentrated in the liquid phase than in the steam while $K_D > 1$ indicates the amine is more volatile and adequate to protect the condensate pipelines downstream (Drexler 2017). Amine selection and dosage are based on their dissociation constants and distribution ratio coefficients (Millet et al. 2002; Turner and Khumsa-Ang 2017). Some NPPs use a mix of amines, each one with a different purpose of protecting some specific part of the secondary

circuit. The disadvantage of organic amines with regard to ammonia is their thermal decomposition into organic acids. Amines lead to an alkaline pH while organic acids production results in an unintended lower pH (Drexler 2017; IAEA 2011a; Staehle and Gorman 2003).

The need of controlling the chemistry within HTCs resulted in the development of different strategies such as molar ratio control (MRC), boric acid treatment (BAT) and TiO_2 addition. Crack-growth rates of tubing alloys in HTCs are at a minimum for intermediate pH values which corresponds to the minimum solubility of NiO. This led nuclear industry to develop MRC, for recirculating vertical NSGs, which is a method aiming to keep a near-neutral pH in HTCs. MRC is based on the assumption that the pH_T in the HTCs solution depends on the ratio of strong cations to strong anions. The concentrations of these species in crevices cannot be measured though they may be estimated by analysing the hideout return. Thus the molar ratio can be conveniently adjusted for the next operating cycle. MRC often involves the addition of NH_4Cl in the $\mu\text{g}/\text{kg}$ range. There is no general agreement on the effectiveness of MRC. The addition of a polluting agent as deleterious as chloride to secondary water is at odds with current corrosion guidelines (IAEA 2011a; Staehle and Gorman 2003). Another practice implemented in some NPPs is the on-line addition of boric acid to neutralize the alkalinity in HTCs. The boric acid treatment was used in plants with alloy 600MA tubing, highly sensitive to alkaline SCC. BAT successfully stopped denting, but on-going SCC still continued. Addition of TiO_2 has also been used with the same purpose. This method has proven effective when applied to clean crevices (not packed with sludge). WWER plants add LiOH periodically to secondary water for neutralizing the detrimental effect of strong acid anions, such as chloride, on the localized corrosion of NSG tubing (IAEA 2011a; Staehle and Gorman 2003).

Corrosion products in the secondary circuit may be removed from NSGs during outages by mechanical and/or chemical cleaning. Mechanical cleaning methods are tailored for the various designs of NSGs. Water jet lancing of TTS (called sludge lancing) is a common cleaning process used to remove deposits accumulated at the bottom of recirculating vertical NSGs. Sludge lancing may be also applied to other parts of the tube bundle. Steam generator flush or soaks are applied to remove impurities from crevices after sludge lancing. Steam generator flush promotes flushing of crevices by cycles of heating followed by depressurizing of the NSG secondary side. These cycles produce the boiling of solution in crevices so that steam bubbles help to expel the impurities away from crevices. Steam generator soaks at temperatures from 90 to 150 °C

are other effective way to promote the release of impurities from crevices. Once-through steam generators suffer from clogging of broached hole TSPs. Water slap and pressure pulse cleaning methods were developed to dislodge these deposits. Both methods use bursts of pressurized nitrogen that push water upward at a high velocity against the TSPs (IAEA 2011a; Varrin 2017).

Chemical cleaning methods involve the injection of one or more chemical solutions into the NSG. On-line cleaning methods may be performed during plant shut-down or start-up with the advantage of using the decay heat of the plant. They need high temperature and require a short application time due to fast reaction kinetics. Off-line cleaning methods are applied during scheduled outages after full shutdown. They need lower temperatures but longer application times than on-line methods. Chemical cleaning methods are also classified as “hard” or “soft” depending on their use of high or low concentrations of chemicals, respectively. Chemical cleaning has two main disadvantages: 1) produces some slight corrosion of pressure boundary and internal structural materials, particularly of those made of carbon and low alloy steel; and 2) produces significant amounts of waste that must be stored, treated and disposed. Details of the various chemical cleaning methods that are presently available can be found elsewhere (IAEA 2011a; Varrin 2017).

Injection of surface-active agents is a complementary approach to cleaning processes which help to remove corrosion products via the blowdown system. The two available technologies to this purpose are dispersants and film-forming amines (FFAs). Dispersants adsorb on the corrosion product particles and impedes their accumulation on sludge piles by electrical repulsion. FFAs act as a barrier between the metal or metal oxide and water. They lower the corrosion rate of the metal and help to release deposits and impurities adsorbed on metallic surfaces. These technologies may be applied during power operation, shutdown, lay-up and/or start-up (Drexler 2017).

5 Corrosion control of steam generators and balance of plant equipment in plant-outage conditions

NPPs experience planned outages of different lengths due to refuelling, scheduled maintenance, refurbishments, etc., or forced outages due to the unanticipated breakdown of a component. Preservation of the secondary circuit

during outages is of major importance to avoid corrosion of NSGs and BOP equipment and minimise the transport of deposits and impurities in the subsequent start-up and power operation. The selected lay-up strategy during the outage depends on the outage length, type of materials to be protected from corrosion, maintenance activities during the outage, radiation protection, authorised methods and available systems and devices. The secondary circuit may be separated in suitable subsystems that can be preserved in different conditions (EPRI 1992, 2005; IAEA 2011a).

Metallic corrosion requires anodic and cathodic reactions plus electrolytic and electronic conduction to take place. Consequently, it may be avoided/mitigated by suppressing/hindering any of these processes. Lay-up programmes either exclude moisture (dry lay-up), which provides the electrolyte, or oxygen (wet lay-up), which provides the main cathodic reaction (EPRI 2005; IAEA 2011a).

5.1 Dry lay-up

Dry lay-up requires the complete draining of water from the component to be preserved. Then, clean and dry air is blown through the system. Metallic corrosion is avoided if the thin water film formed on metal surfaces is dried out, due to the lack of an electrolyte. Atmospheric corrosion studies on carbon steel, which is the least corrosion-resistant material in the secondary circuit, provide the requirements for the dry air. Corrosion rate of carbon steel is negligible when the relative humidity of air is below 60% in an atmosphere free of pollutants. However, when metallic surfaces are contaminated with deliquescent salts they remain wetted at a significantly lower relative humidity. Capillary condensation may also occur at low relative humidity on porous corrosion products (Roberge 2011). There is no information to date about any deliquescence effect of corrosion products and impurities in NSGs and BOP components in dry lay-up environments.

Conditions for an efficient dry lay-up in unpolluted atmospheres are as follows:

- Air renewal rate of 1 system volume per hour.
- Dew point below 10 °C or relative humidity at 20 °C below 50%.
- Absolute humidity below 7.2 g H₂O/kg air.

Incomplete draining of the system to be protected may result in accelerated and/or localised corrosion when oxygen is present. Figure 10a shows an area particularly susceptible to pitting corrosion at the intersection between metal, air and liquid due to concentration of impurities.

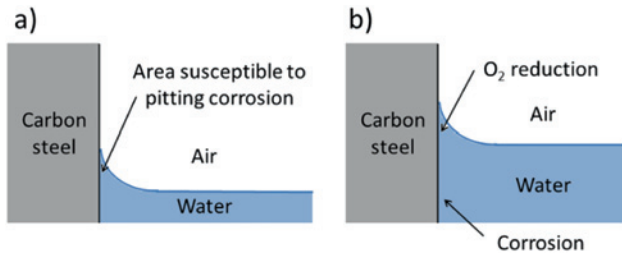


Figure 10: (a) Area of susceptibility to pitting corrosion at a not completely drained location and (b) areas of preferential oxygen reduction and corrosion in a differential-aeration cell.

This situation may occur at partially drained locations (IAEA 2011a). As corrosion progresses local conductivity of solution increases due to metal dissolution which may result in the development of a differential-aeration cell. This situation only occurs when the water level is significant (not a moisture layer). In differential-aeration cells oxygen reduction preferentially occurs at locations with high oxygen availability (near interfaces) while metallic corrosion shifts to areas well below the water level (Figure 10b).

Design of wet lay-up systems requires the calculation of internal surface areas of equipment and the moisture load to be removed. Initially, lay up is performed in open systems. Once the desired conditions are attained components may be isolated and maintained in the dry state in closed systems which results in significant power consumption savings (EPRI 1992).

For the dry lay-up of NSGs, nitrogen is recommended instead of air to prevent the contact of oxygen with the steam generator, particularly for units with carbon steel TSPs, due to the risk of denting. Oxidising and wet conditions may promote denting during long outages. In such conditions, denting is more likely than in operation. However, some countries have banned the use of nitrogen for this purpose due to safety concerns (risk of anoxia for personnel). In these cases, hot air should be used to dry the steam generator as quickly as possible. The risk of denting is eliminated once the liquid phase evaporates. Dry lay-up of NSGs is generally considered for outages longer than 2 weeks or when maintenance activities, such as mechanical cleaning, are performed. For very long outages, more stringent requirements apply and relative humidity at 20 °C should be kept below 30%. Dry lay-up is generally used for BOP systems such as steam and extraction systems, high and low pressure turbines, condensate and feedwater systems, and condensers. Dry lay-up does not release any waste into the environment. If the climate at the plant location is arid or semi-arid and ambient air has sufficiently low humidity during the entire outage, air may be directly

circulated to the system. This option is cost-effective since the use of dehumidification devices is avoided. A disadvantage of dry lay-up is the need of controlling the quality of dry air to keep a low relative humidity. Hot conditions are initially needed since hot dry air dissolves more humidity than cold air. Dry lay-up is hard or even impossible to implement after wet lay-up when the system is cold. An additional disadvantage of dry lay-up is the hardening of the sludge which makes it more difficult to remove (EPRI 1992; IAEA 2011a; Rabeau et al. 2002).

5.2 Wet lay-up

Wet lay-up applies to systems filled with water plus some conditioning agents. The fundamentals of this lay-up strategy are similar to those of the water chemistry used in operation:

- Removal of oxygen by a scavenger to slow down corrosion of materials due to the absence of a powerful oxidant in solution (oxygen).
- Adequate pH control at a value that minimizes the dissolution rate of the spontaneously-developed oxide film.

In accord with AVT chemistry, hydrazine is generally used as an oxygen scavenger and ammonia or amines are added to keep a sufficiently alkaline pH. The secondary water used in operation may be easily conditioned for wet lay-up during the shutdown of the plant. Steam generators eventually cease to operate as the reactor shuts down and the residual heat removal system is used for further reactor cooling. Then those subsystems of the secondary loop that do not need maintenance activities in the outage may be isolated with the operating medium. The concentration of hydrazine in the secondary system must be increased several orders of magnitude as the plant cools down due to the significant slowdown of the scavenging reaction (Eq. (1)) and the increase of oxygen solubility as temperature decreases. The typical hydrazine concentration of 0.1 mg/kg in operating conditions is increased to 10–20 mg/kg during shutdown. $\text{pH}_{25^\circ\text{C}} \approx 12$ minimises carbon steel corrosion at room temperature (Figure 9). However, such a high pH value cannot be attained by ammonia or amines additions. Moreover, the excess alkalinity with respect to the optimal $\text{pH}_{25^\circ\text{C}}$ at 250 °C should be neutralized by acid additions before plant start-up. The practical solution is keeping the highest pH attained by moderate ammonia or amines additions.

Figure 11 shows recirculating systems used to ensure the proper mixing and distribution of chemicals in the wet lay-up of once-through and recirculating vertical NSGs

(EPRI 1992; Pocock and Levstek 1974). Conditions generally used for an efficient wet lay-up in the presence of an air phase are as follows:

- Oxygen concentration below 0.1 mg/kg for temperatures below 100 °C.
- Hydrazine concentration above 75 mg/kg.
- Ammonia/amine(s) additions to keep $\text{pH}_{25^\circ\text{C}}$ above 9.8.
- Sodium, chloride and sulphate concentrations below 1000 $\mu\text{g}/\text{kg}$.

Reaction between hydrazine and oxygen (Eq. (1)) occurs in a one-to-one ratio by weight. The oxygen concentration in air-saturated water is approximately 8 mg/kg (Baboian 2002). Thus, the target hydrazine concentration of 75 mg/kg at the end of the lay-up period represents approximately 9.4 times that of oxygen at saturation. To meet this requirement, French utilities consider the length in days (d) of the wet lay-up period and a constant consumption rate of hydrazine of 7 mg/(kg day) to calculate the minimal hydrazine concentration required at the beginning, $[\text{N}_2\text{H}_4]_0$ (Eq. (3)). This approach requires the beforehand knowledge of the outage duration. Hydrazine is stable at room temperature (reaction of Eq. (2) does not occur) and it only reacts to an appreciable extent with oxygen dissolved in water; thus, all hydrazine consumption is assumed to be due to Eq. (1). The consumption rate of 7 mg/(kg day) applies for water in contact with air. Although it is not explicitly mentioned, it is assumed oxygen in the gas phase is replenished continuously (open system) and its concentration is that of air.

Some NPPs use nitrogen sparging and/or a positive nitrogen overpressure (nitrogen blanket). Nitrogen sparging helps to homogenise hydrazine concentration more quickly and also removes oxygen by displacement. Nitrogen blanket provides a lower oxygen partial pressure in the gas phase which in turn produces oxygen saturation

in water at a lower concentration. Hydrazine concentrations as low as 20 mg/kg are reported when nitrogen sparging/blanket is used for NSG lay-up. Some plants reported problems with nitrogen leaks via isolation valves which resulted in increasing volumes of spent nitrogen. As in the case of dry lay-up, the use of nitrogen may be banned by local regulations (EPRI 1992, 2005; IAEA 2011a; Rabeau et al. 2002).

$$[\text{N}_2\text{H}_4]_0 = 75 + (7 \cdot d)\text{mg}/\text{kg} \quad (3)$$

Wet lay-up is used either for short or long outages in steam generators, condensate and feedwater systems, auxiliary boilers and intermediate cooling systems (IAEA 2011a). In equipment under wet lay-up, water acts as a shield to radiation allowing less dosimetry. Drawbacks of wet lay-up include the difficult homogenisation of additives in stagnant solutions and the need of disposing of the excess of hydrazine before the start-up. Hydrazine may cause several adverse health effects on humans, it is genotoxic, potentially carcinogenic, and has noxious effects to aquatic environments (Choudhary and Hansen 1998). Consequently, it cannot be discharged into the environment without proper treatment (EPRI 2005; Pacey et al. 2011; Rabeau et al. 2002). The use of hydrazine has been or will be restricted in some countries and alternatives are being sought (Kawamura et al. 2019; Tsubakizaki et al. 2009).

5.3 Lay-up guidelines

Fossil-fuel boiler experience and laboratory studies show that proper lay-up chemistry can provide corrosion protection for six months or longer. However, outage lengths of NPPs tend to be shorter. Refuelling of PWRs, which was typically performed in 45–60 days in the 1990s, nowadays takes 25 days. EPRI (Electric Power Research Institute, USA) establishes threshold values of control parameters in full wet lay-up conditions (temperature below 93 °C, or 200 °F) for PWR NSGs of the recirculating vertical and once-through types. They are indicated in Table 6. An action is required if any of the control parameters are above/below its corresponding threshold values. Oxygen scavengers other than hydrazine may be used if qualified by the utility. Their appropriate limits should be established. Control parameters should be monitored three times per week for recirculating vertical NSGs, and every other day for once-through NSGs, until stable values are attained. Then, they can be measured on a weekly basis. Some plants with recirculating NSGs control the oxygen concentration in the fill source prior or during water fill. If oxygen control of the

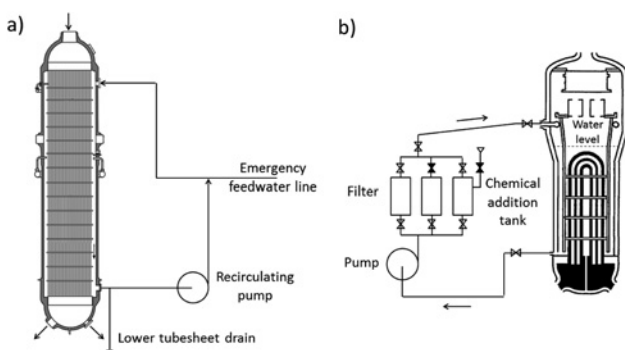


Figure 11: Scheme of (a) Once-through and (b) recirculating vertical NSGs wet lay-up systems. Adapted from (EPRI 1992; Pocock and Levstek 1974).

fill source is not performed compensatory actions should be taken, such as nitrogen sparging or the addition of a reducing agent. In plants with once-through NSGs routine monitoring of the oxygen concentration is not required if hydrazine concentration is within normal range. Water used to fill the steam generators should contain $[O_2] < 100 \mu\text{g}/\text{kg}$. In all cases, the concentrations of sodium (Na^+), chloride (Cl^-) and sulphate (SO_4^{2-}) should be below $100 \mu\text{g}/\text{kg}$ prior to heat-up above 93°C (200°F) (EPRI 1992, 2005).

Japanese guidelines establish two types of wet lay-up conditions. Both of them specify lower hydrazine concentrations with regard to EPRI and French lay-up guidelines.

- (1) Only hydrazine additions to maintain reducing conditions (note that hydrazine shows an alkaline hydrolysis).
- (2) A mixture of hydrazine and ammonia to maintain both reducing and alkaline conditions.

Table 6: Control parameters and thresholds for full wet lay-up of PWR NSGs according to EPRI (EPRI 2005).

Control parameter	Recirculating NSGs Initiate action	Once-through NSGs Initiate action
$\text{pH}_{25^\circ\text{C}}$	< 9.5	< 9.5
$[\text{N}_2\text{H}_4]$, mg/kg	< 75	< 75 or > 500
$[\text{Na}^+]$, $\mu\text{g}/\text{kg}$	> 1000	> 1000
$[\text{Cl}^-]$, $\mu\text{g}/\text{kg}$	> 1000	> 1000
$[\text{SO}_4^{2-}]$, $\mu\text{g}/\text{kg}$	> 1000	> 1000
$[\text{O}_2]$, $\mu\text{g}/\text{kg}^a$	> 100	–

^aMeasured at the steam generator fill source.

Table 7: Diagnostic parameters and recommended values for PWR NSGs blowdown water during wet lay-up (Kawamura et al. 2019).

Diagnostic parameter		Recommended values	Frequency
$\text{pH}_{25^\circ\text{C}}$		≥ 10	Appropriate ^a
$[\text{N}_2\text{H}_4]$, mg/kg	with NH_3	$20\text{--}500^b$	Appropriate ^a
	only N_2H_4	$50\text{--}500^b$	Appropriate ^a
	(no NH_3)		
$[\text{Na}^+]$, $\mu\text{g}/\text{kg}^c$		–	Appropriate
$[\text{Cl}^-]$, $\mu\text{g}/\text{kg}^c$		–	Appropriate
$[\text{SO}_4^{2-}]$, $\mu\text{g}/\text{kg}^c$		–	Appropriate

^aCheck the decreasing trend within 1–2 weeks during the outage. If the decreasing trend is small, an appropriate check should be performed during the outage.

^bBased on the field data, the initial decline in the concentration should be set, and the value should be within the recommended range for using/not using ammonia.

^cWhen feed water is supplied from the make-up water storage tank, the purity of the make-up water should be checked.

Table 7 indicates diagnostic parameters and recommended values for blowdown water of steam generators during wet lay-up. For wet lay-up with ammonia, the recommended threshold of $\text{pH}_{25^\circ\text{C}} \geq 10$ is meant to ensure the long-term integrity of materials in the secondary cooling circuit. The applied criterion assumes that adding $10 \text{ mg}/\text{kg}$ of hydrazine counteracts the effect of $8 \text{ mg}/\text{kg}$ of dissolved oxygen, which is the oxygen concentration in air-saturated water (Baboian 2002). The lower limit of $[\text{N}_2\text{H}_4] = 20 \text{ mg}/\text{kg}$ counteracts twice the concentration of dissolved oxygen at saturation. In the absence of ammonia, the lower limit of $[\text{N}_2\text{H}_4]$ increases to $50 \text{ mg}/\text{kg}$. This accounts for $20 \text{ mg}/\text{kg}$ as hydrazine for the lay-up (pH control) plus 3 times ($30 \text{ mg}/\text{kg}$) the concentration used to counteract dissolved oxygen at saturation. The decreasing trends of $\text{pH}_{25^\circ\text{C}}$ and $[\text{N}_2\text{H}_4]$ should be checked within the first 1–2 weeks and then appropriate monitoring frequency should be decided. Neither recommended values nor monitoring frequencies are stated for the concentrations of sodium, sulphate and chloride since no adverse effects are expected on the integrity of components at lay-up temperatures (Kawamura et al. 2019).

Table 8 indicates diagnostic parameters and recommended values for the feed water or deaerator tank water during wet lay-up by Japanese PWRs. Steam generators are isolated from the secondary circuit during wet lay-up; therefore, impurities are not expected to enter them. Impurity contamination of the secondary coolant is checked by measuring cation conductivity, turbidity, and the concentrations of iron, sodium, chloride and lead. Recommended values for turbidity and $[\text{Fe}^{2+}]$ are based on field experience in Japanese PWRs. The recommended value for $[\text{O}_2]$ is 10 times the concentration of oxygen at the start of heat-up. Concentrations of sodium and chloride are used to check the purification of the feedwater. Recommended values are below $0.5 \mu\text{g}/\text{kg}$, which are also the control values at the start of heat-up. Lead is included among diagnostic parameters since it may be present in minute amounts as a contaminant in the NH_3 chemical additive. The monitoring frequency of diagnostic parameters is one time during wet lay-up. Recommended values should be checked prior to filling in the NSG with feedwater (Kawamura et al. 2019).

For outages of up to 7 days, steam generators are neither opened nor drained before start-up. In such cases, EPRI indicates steam generators do not need to be placed in full wet lay-up though conditions indicated in Table 6 should be met to the practicable extent (EPRI 2005). For such short outages, French utilities prescribe a hydrazine concentration of $100 \text{ mg}/\text{kg}$ and ammonia addition to obtain $\text{pH}_{25^\circ\text{C}} = 9.4\text{--}9.8$ for plants with high-AVT chemistry.

Table 8: Diagnostic parameters and recommended values for feedwater or deaerator tank water during the wet lay-up (Kawamura et al. 2019).

Diagnostic parameter	Recommended values	Frequency
Cation conductivity, mS/m ($\mu\text{S}/\text{cm}$)	≤ 0.03 (≤ 0.3)	One time ^a
Turbidity, mg/kg	≤ 1	One time ^a
[Fe ²⁺], $\mu\text{g}/\text{kg}$	≤ 100	One time ^a
[O ₂], $\mu\text{g}/\text{kg}$	≤ 50	One time ^a
[Na ⁺], $\mu\text{g}/\text{kg}$	≤ 0.5	One time ^a
[Cl ⁻], $\mu\text{g}/\text{kg}$	≤ 0.5	One time ^a
[Pb ²⁺], $\mu\text{g}/\text{kg}$	≤ 1	One time ^a

^aMonitoring frequency is one time during wet lay-up. Recommended values are checked prior to filling in the NSG with feed water.

For NPPs with low-AVT chemistry, hydrazine concentration of 30 mg/kg and $\text{pH}_{25^\circ\text{C}} = 9.2\text{--}9.5$ are indicated which may be attained with morpholine present from operation (Rabeau et al. 2002).

For outage durations between 7 and 30 days, French plants apply full wet lay-up. High-AVT plants use 200 mg/kg of hydrazine and set a $\text{pH}_{25^\circ\text{C}} = 10.4\text{--}10.6$ by ammonia additions. Low-AVT plants use 400 mg/kg of hydrazine and $\text{pH}_{25^\circ\text{C}} = 9.8\text{--}10.2$ with no further additions of any alkalizing agent. For outages longer than two weeks, dry lay-up may be considered. Outages longer than one month (*e. g.* refuelling) may need a dry lay-up before sludge lancing. However, this practice is considered to produce sludge hardening as stated above. After the lancing, wet lay-up is applied with 200 mg/kg of hydrazine and $\text{pH}_{25^\circ\text{C}} = 10.4\text{--}10.6$ (Rabeau et al. 2002).

Table 9 summarises the current lay-up strategy of EDF (Électricité de France, a French electric utility company) for NSGs and components of the secondary circuit (Alos Ramos et al. 2014).

5.4 Alternative lay-up technology: surface-active agents

Surface-active agents are additives meant to control the corrosion products in the secondary circuit. Their application is involved with power operation, shutdown, lay-up and start-up. Besides preserving NSGs and BOP equipment during outages they also help to remove deposits during lay-up and subsequent start-up. Surface-active agents may be a complement of dry/wet lay-up strategies. These technologies have originated in the fossil-fired power industry and have been slowly adopted by the nuclear industry after proper qualification. Surface-active agents include polymeric dispersants, mainly polyacrylic acid (PAA), and FFAs (Drexler 2017).

Polymeric dispersants may be injected during the power operation, wet lay-up or start-up. Nuclear industry has qualified high-molecular-weight PAA of high purity for its use as a dispersant. Dispersants prevent corrosion products from depositing on NSG surfaces so they are removed with the blowdown. PAA is thought to adsorb on the corrosion particle avoiding its coalescence into a larger deposit due to electrical repulsion. PAA is particularly effective in preventing magnetite deposition. Injection of PAA during wet lay-up of NSGs increases the removal of impurities such as calcium (Ca^{2+}), magnesium (Mg^{2+}), aluminium (Al^{3+}) and silica (SiO_2), the so-called “hardness species” (Betova et al. 2014; Fruzzetti 2009; Turner and Khumsa-Ang 2017).

FFAs are commonly injected in operation or before the shutdown of the plant to preserve the secondary circuit. They are organic substances with specific functional groups. Their strong affinity to metal surfaces is due to the free electron pair of the amine nitrogen. The inhibitor effect of FFAs is attributed to the formation and maintenance of a very thin film on the metal surface that acts as a barrier against

Table 9: Specifications of EDF for the lay-up of the secondary system (Alos Ramos et al. 2014).

System	Lay-up method	Parameter	Frequency	Expected value	Limit value
Feed train, steam reheating system (tube and shell side, condenser (secondary side))	Drain and dry with dry air	Relative humidity (%)	Once per day until stable, then three times per week	30	40
Steam Generator	Drain and dry with dry air	Relative humidity (%)	Once per day until stable, then three times per week	30	40
	Wet	[N ₂ H ₄] (uncatalysed)	Once per week	Equation (3)	75
		$\text{pH}_{25^\circ\text{C}}$ obtained with an alkalizing agent ^a	Once per week	9.8–10.1	9.7–10.3

^aAmmonia, ethanolamine or morpholine.

corrosive substances. Injection of FFAs before or during the shutdown leads to protection of internal surfaces during shutdown periods irrespective of whether dry or wet lay-up is selected. This alternative lay-up technology has resulted in reduced corrosion product transport on start-up in fossil fuel and nuclear plants and it is currently under research by EPRI. FFAs are particularly suitable for long-term shutdowns which involve dry lay-up, such as refurbishment outages (Betova et al. 2014; EPRI 2014; Hater et al. 2014; Odar 2017; The International Association for the Properties of Water and Steam 2016). Presently, a new lay-up concept using FFAs is available which has many advantages:

- The whole steam-water cycle may be put in lay-up in one step
- The protective film is stable for a long time in aggressive environments
- Dryers are not required for systems open to the atmosphere which saves significant costs
- Hydrazine is not required for filled systems, such as steam generators (Drexler et al. 2015).

5.5 Lay-up experience reported in NPPs worldwide

NPPs follow the industry lay-up guidelines detailed in the previous section during outages. This section focuses in particular experiences reported in literature which are not fully covered by the lay-up guidelines (3.3).

Crystal River-3 was an 860 MWe PWR with two once-through NSGs with alloy 600TT tubing. Their secondary circuit metallurgy was all ferrous with the exception of the titanium alloy condenser tubes. When the plant was shut down for upgrading in September 1996 a phased approach was taken to lay-up the BOP since the length of the outage was unknown. Based on favourable experience of extended outage the specified lay-up method for most BOP systems and components was wet lay-up with 1–2 mg/kg of catalysed hydrazine and pH of 9.5–9.8 attained through morpholine addition. The two once-through NSGs with alloy 600TT tubing were placed in wet lay-up during the 17-month outage. Wet lay-up chemistry consisted on maintaining 100 mg/kg morpholine and 75 mg/kg catalysed hydrazine via a recirculation loop plus a nitrogen blanket over non-wetted surfaces (Thompson and Kassen 1999).

Comanche Peak NPP comprises two 1150 MWe PWR units. In 2007, all the NSGs of Unit 1 were replaced by Westinghouse Model Delta 76 steam generators with alloy 690TT tubing. Steam generators of Unit 2 have alloy 600TT tubing and stainless steel TSPs. Reported secondary water chemistry for both units consists of 30 mg/kg morpholine, 200 µg/kg DMA plus minimal hydrazine concentration to

control FAC. For the wet lay-up of NSGs, Comanche Peak units follow the industry guidelines (Table 6) with the addition of DMA soaks of up to 20 mg/kg. This high concentration of DMA is reported to be beneficial in loosening deposits so that they are easy to remove during drain/fill and start-up clean up. The BOP system is drained and left as-is during the scheduled outage. Since the secondary circuit operates with low hydrazine, minimum threshold oxygen, and high-pH mixed oxides with high oxidation state (haematite-magnetite blends) are formed during operation. Such oxides are highly stable at shutdown conditions and do not require shutdown protection. This strategy does not apply for magnetite-rich oxides in high-hydrazine, low-oxygen, and low-pH chemistries which would require a more reducing environment during the outage (Fellers et al. 2002).

CANDU reactors change fuel bundles one at a time in regular operation, while PWRs have scheduled refuelling outages. CANDU reactors need a very long retubing outage after 25–30 years of service in order to change the fuel channels. Every fuel channel includes a calandria tube, which isolates the primary coolant from the moderator (heavy water in both cases) and a pressure tube, which contains the fuel bundles and the secondary coolant (light water). The length of this retubing outage is of 18 months or longer. During the outage the main components of the primary and secondary systems circuits must be put in lay-up. Stuart et al. (2008) states four strategies for the lay-up of systems and components during the retubing outage:

- Systems filled and circulating under normal operating and chemistry conditions. This strategy may be economically non-viable as a general option due to the high pumping costs involved.
- Wet lay-up under stagnant conditions or with minimal circulation.
- Dry lay-up with a blanket (oxygen-free).
- Dry lay-up with air.

The recommended lay-up for each system depends on the materials and the impact of the retubing activities. The most critical lay-up is that of the primary circuit which involves complete reactor defueling. In the present case, the recommendations for preserving the secondary circuit made up of alloy 800, carbon steel, stainless steel and titanium alloys are reported. It is advised to move the steam cycle from normal full operation to lay-up conditions as quickly as possible. NSGs should be isolated under wet lay-up with appropriate hydrazine dosing along with nitrogen blanket. The system should be pressurized slightly over the ambient pressure and the oxygen content of the blanket should be monitored periodically. Canadian CANDU-6 reactors have isolated the NSGs from the rest of the circuit

by retrofitting a boiler wet lay-up loop. Water is removed from the blowdown lines and returned at feedwater or reheater lines. Dry lay-up of NSGs with air may be allowed for a short period of time for their maintenance and inspection. Long-term dry lay-up of NSGs is discouraged due to the difficulty of completely draining the water.

Dry-air flow is recommended for the lay-up of main steam, condensate and feedwater systems. These systems will be initially exposed to the turbine building atmosphere before draining is complete. Wet lay-up is not advisable for these systems in long outages since it is not possible to exclude oxygen. Dryers are used to maintain the carbon steel components under an atmosphere of dry air by removing any residual water.

Impurities are expected to accumulate in the steam cycle during long-term lay-up. Consequently, it is recommended to drain and fill the components before start-up. In the restart of the reactor, oxygen concentration will be at saturation in the secondary circuit and an excess of hydrazine will be needed. Once vacuum in the condenser is enough for the deaerator to be operational hydrazine concentration may be lowered. Hold periods of high blowdown flow are included in the start-up. They are needed to remove the impurities from crevices and deposits (hideout return) (Stuart et al. 2008).

Commercial products based on FFAs offer an alternative strategy for long-term lay-up of the entire steam cycle components. Reported experience from fossil-fuel steam cycles shows that application of FFAs allows long-term dry or wet lay-up with minimal further measures. The dosage of hydrazine is reduced in wet lay-up and the use of dryers is avoided in dry lay-up (Hater et al. 2014; Wagner and Czempik 2016). The earliest report on lay-up with FFAs in the nuclear industry is from two Armenian NPPs of the type WWER that were shut down after an earthquake, in December 1988. The secondary circuit was preserved by the injection of 2% octadecylamine (ODA) water emulsion to the suction of feed pumps at almost full power. When unit 2 was recommissioned in 1995, after 69 months of preservation, satisfactory water chemistry was reached in shorter times than before the outage (Betova et al. 2014). More recently, FFAs-based products have been applied in Almaraz units 1 and 2 (PWR, Spain) since 2011, Embalse (CANDU PHWR, Argentina) since 2015, and Borssele (PWR, Netherlands) since 2017 (Odar 2017). The CANDU reactor Embalse was shutdown in 2015 for modernization work which included reactor retubing, the replacement of its four steam generators and a power increase of 6%. FFA treatment, based in ODA, was applied before plant shutdown to preserve the steam cycle components. Hydrophobicity of selected condenser tubes was determined before Embalse NPP was reconnected to the power grid, in June 2019,

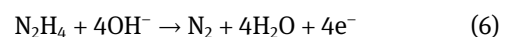
proving that a film of the applied FFA was still present (Chocron 2019).

5.6 Review of research relevant to lay-up conditions

There are several issues that motivate research on optimizing the currently used lay-up conditions. The varying length of NPPs outages is one of the main drivers of research. Shorter plant outages may be managed with less stringent chemistry requirements (EPRI 2005). Regulations in many countries prioritize the connection of renewable energy plants to the power grid (IAEA 2018b). In such scenario, NPPs may be subjected to frequent short- and long-term stand-by periods. Very long outages are expected as NPPs age due to needed refurbishments. Dry lay-up with FFAs is particularly suitable for such applications. Regulator policies on the discharge of toxic chemicals, such as hydrazine, to the environment foster research on lowering the dose of hydrazine or replacing it by another environmentally friendly scavenger (Kawamura et al. 2019; Long et al. 2002; Rabeau et al. 2002; Tsubakizaki et al. 2009).

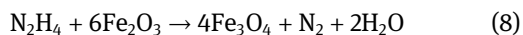
5.6.1 Mechanism of corrosion inhibition by hydrazine

The inhibition of corrosion by hydrazine is generally attributed to the oxygen scavenging reaction according to Eq. (1). In its simplest form, this mechanism is homogeneous. Alternatively, oxygen reduction (Eq. (4)), which drives iron corrosion (Eq. (5)) in the absence of hydrazine, may be balanced by oxidation of hydrazine according to Eq. (6). The overall reaction for this latter mechanism (Eq. (4) plus Eq. (6)) is equivalent to Eq. (1). However, anodic and cathodic reactions may occur preferentially at particular locations on the metal surface (Gouda and Sayed 1973). This mechanism is heterogeneous, and it is affected by the metallic surface area to water volume ratio, presence of protective/non-protective layers, species in solution, etc. (Shams el din and Arain 1989)



Hydrazine has a relatively low distribution ratio coefficient and displays an alkaline reaction in water according to Eq. (7), with $\text{pK}_a = 8.1$. As a comparison, pK_a for ammonia is 9.21 ($\text{NH}_3 + \text{H}^+ \rightarrow \text{NH}_4^+$) (Hall 1957). Besides oxygen

removal hydrazine also reduces haematite into protective magnetite according to Eq. (8).



Hydrazine may promote open circuit potential ennoblement of steel, which is odd for scavengers since they are cathodic inhibitors. Gouda and Sayed (1973) propose that hydrazine is preferentially adsorbed at the local anodes, such as pores in the oxide film, inducing anodic polarization. When some of the anodic areas are covered by hydrazine the overall corrosion rate decreases but the attack is distributed over smaller anodic areas resulting in intensified localized attack. However, after a certain critical concentration of hydrazine is reached, potential ennoblement occurs with a simultaneous drop in corrosion rate. This critical concentration would be associated with the complete blocking of the pores by hydrazine (Gouda and Sayed 1973).

Commercial formulations of hydrazine used by some utilities for oxygen scavenging are catalysed by additions of inorganic and/or organic compounds which make them more reactive and less volatile than reagent-grade hydrazine. Catalysed hydrazine is generally marketed as a 35% aqueous solution of hydrazine. Its performance as an oxygen scavenger is significantly better than that of pure hydrazine (Andries and Couturier 2000; Huang et al. 2004; Noack 1977a,b, 1982). Noack (1982) reports the effect of a proprietary organic catalyst added to hydrazine on the rate of oxygen removal from water. Testing solution was a pH 10 carbonate-bicarbonate buffer and initial reactant concentrations were 0.5 mg/L O_2 and 2.0 mg/L N_2H_4 (molar ratio of 1:4). The device used for testing was a 2.5-L glass reactor with no apparent metallic surfaces. Consequently, we can infer that any occurring reaction was homogeneous. The concentration of the catalyst in the commercial product was 0.0057 parts (weight) of catalyst per part of hydrazine. Noack (1982) reports an initiation period indicating the existence of several reaction steps for the oxygen/hydrazine reaction. He tested the existence of two simultaneous reactions: one first order in each of the reactants and another one of zero order. However, the derived kinetics equation failed to account for runs above 45 °C and it was discarded. Addition of the catalyst results in a significant improvement in the rates of oxygen removal, at least up to 65 °C (Noack 1982).

Shams el din and Arain (1989) studied the kinetics of oxygen scavenging by catalysed hydrazine in water, between 30 and 80 °C. They used a commercial product marketed under the trade name of Scav-Ox® II, which

contains 0.2% by weight of a partially volatile non-specified organic catalyst. The rate of hydrazine removal from solution, due to its reaction with oxygen, increases with increasing temperatures and solution pH. The reaction kinetics is of first order with respect to hydrazine and also to oxygen. For non-catalysed hydrazine, kinetics of one-half order with respect to hydrazine and first order with respect to oxygen is reported (Dalgaard and Sanford 1982). Shams el din and Arain (1989) indicate that, during the initiation, consumption of reactants occurs at much higher rates than later on. This has been ascribed to a parallel reaction mechanism which involves hydrazine hydrate. In acidic solutions of $\text{pH} \leq 2.5$, even at 80 °C, catalysed hydrazine is stable and does not appreciably react with oxygen. The reaction rate constant increases linearly between pH 4 and 9 and it remains constant for $\text{pH} \geq 10$. According to Shams el din and Arain (1989), the observed reaction-rate-vs.-pH behaviour results from the acid/base equilibrium of Eq. (7). Hydrazine oxidation rate increases as it loses a proton being pH-independent for $\text{pH} \geq 10.15$, when it is fully deprotonated. The reaction rate of Eq. (1) is not affected by the ionic strength of solution. However, addition of particular species may either retard or catalyse hydrazine oxidation. For instance, ammonia enhances the reaction while morpholine is a retardant.

5.6.2 Application of hydrazine in wet lay-up

Hydrazine is an efficient oxygen scavenger at the operating temperature of steam generators. However, wet lay-up occurs near room temperature where hydrazine reaction with oxygen is sluggish, thus significantly higher concentrations are needed. The concentration of hydrazine may be lowered if a nitrogen blanket is used. EPRI recommends nitrogen sparging to homogenise the hydrazine concentration and remove oxygen. However, EDF prohibits the use of a nitrogen blanket due to safety hazards (EPRI 2005; Long et al. 2002).

Figure 12 shows a potential vs. pH diagram for various half cells potentially involved in the wet lay-up of steam generators and BOP, at 25 °C. The pH range of interest for this application is roughly between 9 and 11. The half-cell potential for $\text{N}_2/\text{N}_2\text{H}_4$ is plotted for two hydrazine concentrations (100 and 400 mg/kg or ppm) which differ in only 9 mV between them. Hydrazine is able to reduce all the oxides formed on steels and nickel alloys in lay-up conditions, with the only exception of Cr_2O_3 , from a thermodynamics viewpoint. Half-cell potential comparison indicates N_2H_4 is powerful enough to reduce O_2 , and even H_2O . Consequently, a very low open circuit potential would be expected for any metal/alloy, in hydrazine-containing

solutions. However, reduction of N_2H_4 is quite slow at room temperature and open circuit potentials of metals are well above the N_2/N_2H_4 half-cell potential. Figure 12 shows open circuit potentials of carbon steel A106C and alloys 600, 690 and 800 in simulating lay-up solutions. Passive alloys show significant potential ennoblement with regard to the actively corroding carbon steel (Rodríguez and Kappes n.d.)

EDF carried out a study on the appropriate conditions for wet lay-up of carbon steel components by varying the gas phase and the hydrazine concentration. Rabeau et al. (2002) performed 500-h tests in pH-10 solutions, at room temperature. Ammonia and, in some cases, hydrazine were used as alkalinizing agents. The metal surface to water volume ratio was $44 \text{ cm}^2/\text{L}$, which is similar to that of a steam generator. They tested hydrazine concentrations of 0, 75, 200 and 400 mg/kg, with nitrogen and air as gas phases. Uncatalysed hydrazine was used. Under an air gas phase, there was a linear decrease of the hydrazine content with time at approximately 7.9 mg/kg/day irrespective of the initial hydrazine concentration. It is not clear whether the experimental setup was a closed system and thus the oxygen concentration in the gas phase decreased with time, or it was an open system with constant oxygen concentration in the gas phase. The consumption rate obtained for hydrazine supports the use of Eq. (3), whose slope is 7 mg/kg/day (IAEA 2011a), though it is slightly more conservative. The hydrazine concentration remained constant under a nitrogen gas phase indicating no other reaction consumes hydrazine besides that with oxygen. Under an

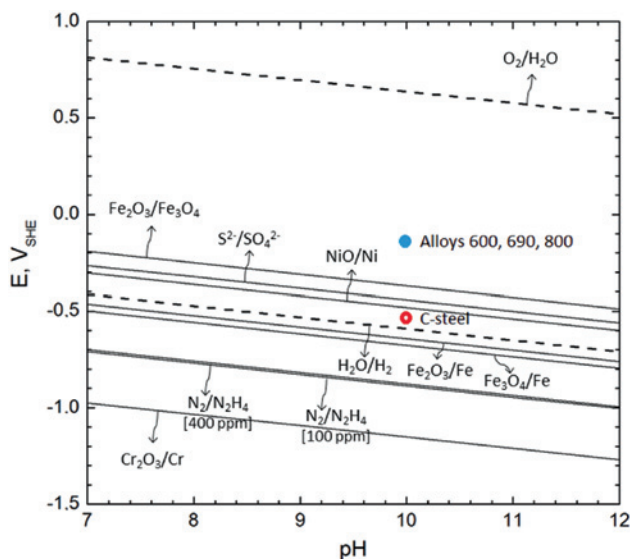


Figure 12: Potential vs. pH for various half cells at 25 °C in the pH range of interest for wet lay-up. Data extracted from (Latimer 1952; Pourbaix 1974) Open circuit potentials for alloys of interest are included (Rodríguez and Kappes n.d.).

air gas phase, oxygen concentration remained between 4 and 5 mg/kg in the absence of hydrazine. This value is below 8.3 mg/kg , which is the saturation concentration of oxygen in air-saturated water, at 25 °C and air pressure of 1 atm (Baboian 2002). Hydrazine concentrations of 75 and 200 mg/kg initially lowered the oxygen concentration in solution but they were not enough for effective oxygen scavenging in a 500-h period. Only 400 mg/kg of hydrazine provided an oxygen concentration below 1 mg/kg at the end of the 500-h test. However, the most efficient oxygen scavenging was reported under a nitrogen blanket which resulted in oxygen concentrations between 0.1 and 0.7 mg/kg after 24 h irrespective of the presence of hydrazine (Rabeau et al. 2002). In such conditions, the equilibrium oxygen concentration in solution depends on the oxygen partial pressure in the gas phase, which is given by the residual oxygen concentration in the nitrogen blanket. Figure 13 shows the average oxygen concentration in water as a function of the residual hydrazine concentration. In the presence of an air gas phase, hydrazine concentrations between 75 and 180 mg/kg are needed to keep the concentration of dissolved oxygen in the range from 1 to 2 mg/kg . Under a nitrogen gas phase hydrazine addition is not needed (Rabeau et al. 2002).

Long et al. (2002) carried out a testing programme aiming at reducing the dosage of hydrazine and eliminating the nitrogen blanket due to the environmental and safety restrictions described above. The metal surface to water volume ratio was $70 \text{ cm}^2/\text{L}$, and the gas phase to liquid phase volume of the cell was 0.5. Ammonia was added to set pH values of 9.7 and 10.0. Uncatalysed hydrazine was used at concentrations of 30 and 80 mg/kg , under air or argon gas phase, in stagnant conditions. Alike Rabeau et al. (2002), these authors report a constant hydrazine concentration over the 3-week period under argon gas phase. Under air gas phase, hydrazine concentration decreased to 50% of its initial value in 4.8–8 days. Authors suggest that metal surfaces

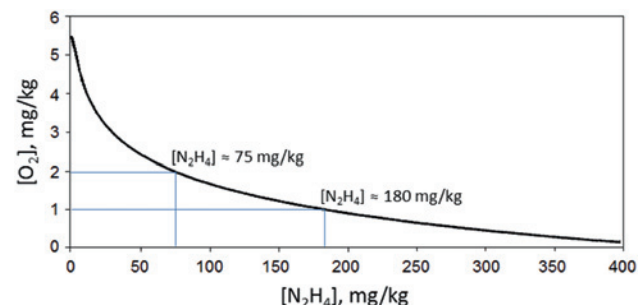


Figure 13: Evolution of oxygen content in water as a function of residual hydrazine concentration under air gas phase. Adapted from (Rabeau et al. 2002).

uncovered by oxides better catalyses hydrazine decomposition (Eq. (6)) than oxidized surfaces. Solution pH was reported to drop quickly in aerated conditions due to hydrazine consumption, carbonation and possibly metal hydrolysis. Under argon gas phase, solution pH remained fairly constant. Tests performed in initially oxygen-saturated solutions under argon blanket showed a rapid decrease of oxygen concentration until reaching 0.5 mg/kg.

5.6.3 Elimination of hydrazine after wet lay-up

Rabeau et al. (2002) performed a comprehensive analysis on the elimination of hydrazine that is needed in French NPPs before releasing the waste produced by wet lay-up. A concentration of hydrazine of 300 mg/kg results in approximately 100 kg of hydrazine to be disposed after lay-up while French regulations allowed a maximum of 7.5 kg. They looked for a cost-effective method to reduce hydrazine concentration in water from 300 mg/kg to a few mg/kg in 72 h. Two feasible treatments were selected among several options: 1) catalysed reaction of hydrazine and oxygen at room temperature and 2) catalysed/non-catalysed reaction of hydrazine and hydrogen peroxide (H_2O_2). The catalyst was copper sulphate ($CuSO_4$) in both cases. Laboratory tests indicated that hydrogen peroxide additions were more efficient than air sparging. The efficiency of hydrogen peroxide increased with the use of catalyst resulting in a decrease of hydrazine from 160 to 10 mg/kg in less than 4 h. The optimal catalyst concentration in water was 500 μ g/kg. On-site tests were carried out at Paluel and Flamanville NPPs by adding hydrogen peroxide directly into the waste tanks. A minimum copper sulphate concentration from 100 to 200 μ g/kg was needed for the reaction to take place in lay-up wastes. These very small amounts of copper may be safely released into the environment according to regulations. The addition of hydrogen peroxide to waste tanks may increase the open circuit potential of materials leading to the increase of general corrosion rates of active metals and/or the localized corrosion of passive metals. Studies on this regard considering the presence of stainless steels, carbon and low alloy steels, cast iron, coated concrete and composites indicated that corrosion risk for materials was not increased by peroxide additions. The effect of Cu^{2+} from the catalyst on materials corrosion was not studied. Rabeau et al. (2002) concluded that the addition of 700–800 L of 30% H_2O_2 enable the elimination of 100 kg of hydrazine in about one day. If copper is not present in the wastes it should be added as copper sulphate up to a concentration of 100–200 μ g/kg to catalyse the reaction. The amount of

hydrogen peroxide added in each case should be tailored according to the amount of hydrazine to be eliminated since the excess of peroxide cannot be released to the environment.

5.6.4 Alternates to hydrazine

Alternates to hydrazine have been tested in laboratory for both lay-up and operating applications (Andries and Couturier 2000; EPRI 2005; Huang et al. 2004; Millet et al. 2002; Tsubakizaki et al. 2009). Carbohydrazide (CBH) and diethyl-hydroxylamine (DEHA) have been used in steam-generating systems since 1981. They are considered acceptable alternates to hydrazine for NSG wet lay-up (Kawamura et al. 2019). CBH and DEHA need the addition of a stronger base, such as ammonia or ethanolamine, to reach the target pH (> 9.5). They are also catalysed for better oxygen scavenging, the same as hydrazine.

EDF has studied the possibility of replacing hydrazine by CBH for NSGs wet lay-up by laboratory tests. Above 100 °C, replacement of hydrazine by CBH is not possible since CBH hydrolysis produces hydrazine. EDF determined that for obtaining the same reduction in oxygen concentration the required amount of CBH is 20 times higher than that of hydrazine, by weight. Thus, the use of CBH would be costly and it would release more waste to the environment. Moreover, there is not a comprehensive study ensuring the carcinogenic innocuousness of CBH (Millet et al. 2002).

DEHA is more effective than hydrazine under laboratory conditions (Andries and Couturier 2000). DEHA and CBH were tested as replacements for hydrazine in CANDU NSGs lay-up. DEHA was preferred over CBH since the latter was unstable in the presence of simulated sludge that forms in thermal crevices. Secondary circuits of some CANDU units use copper-bearing alloys. These alloys promote copper-containing sludge which produces the breakdown of CBH in the wet lay-up environment. Typical specification for lay-up was a DEHA concentration of 250 mg/kg and pH of 10.2, to reach an oxygen concentration of 30 μ g/kg (EPRI 2005).

Even when some hydrazine substitutes may be effective, due to cost criteria and abundant lay-out experience hydrazine is still the most favourable scavenger (Andries and Couturier 2000).

5.6.5 Corrosion of carbon steel under wet lay-up conditions

Corrosion of carbon steel, the least corrosion-resistant material of the secondary circuit, in wet lay-up environments depends on many variables. Below, there is a

comprehensive list of these variables, though they are not independent but interrelated (EPRI 1992; Long et al. 2002).

- Solution pH
- Type and concentration of scavenger and presence of a catalyst in the scavenger formulation
- Type and concentration of alkalizing agent (ammonia or amines)
- Concentration of oxygen
- Concentration of chlorides and other anions (*e. g.* sulphate).
- Solution conductivity
- Gas phase: air or inert gas (nitrogen/argon)
- Agitation: stagnant/flowing solution or agitation by bubbling with an inert gas stream
- Temperature
- Other materials in the system (galvanic effect, cations release)
- Presence of a protective film normally formed in operation above 200 °C.
- Metal surface area to water volume ratio (catalysing effect due to the presence/absence of some surface films)
- Duration of the lay-up (consumption of scavenger).

Equation (9) states the minimum concentration of hydrazine to prevent carbon steel corrosion in aerated lay-up environments as a function of solution pH (Marks 2000). The corrosion rate of carbon steel in lay-up solutions in contact with an air gas phase, at the lowest pH and $[N_2H_4]$ boundaries given by EPRI lay-up guidelines (9.5 and 75 mg/kg, respectively), is approximately 230 $\mu\text{m}/\text{yr}$ (EPRI 2005).

$$[N_2H_4, \text{mg/kg}] > -210 \cdot \text{pH} + 2200 \text{mg/kg} \quad (9)$$

Studies of Rabeau et al. (2002) and Long et al. (2002) previously described report corrosion rates of carbon steel obtained by weight loss tests in simulating wet lay-up conditions. Figure 14 summarises data from Framatome

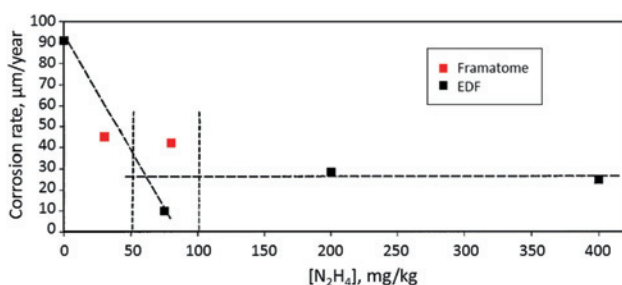


Figure 14: Corrosion rate of carbon steel as a function of hydrazine concentration at 25 °C, pH 10 in aerated conditions. Adapted from (Rabeau et al. 2002).

and EDF in aerated solutions of pH 10, at 25 °C (Rabeau et al. 2002). The general corrosion rate of carbon steel in aerated lay-up solutions is 90 $\mu\text{m}/\text{yr}$ and it decreases to 30 $\mu\text{m}/\text{yr}$ upon addition of 75–400 mg/kg hydrazine. Significant data scatter is observed. Initial oxygen concentration in EDF tests was not controlled and it varied from 2 to 6 mg/kg, which may account for this data scatter. In deaerated conditions, corrosion rates lower than 3 $\mu\text{m}/\text{yr}$ are reported disregarding the presence of hydrazine in solution (Rabeau et al. 2002). Note that reported corrosion rate of carbon steel in aerated lay-up solutions with $[N_2H_4] = 400 \text{ mg/kg}$ is 10 times higher than in deaerated conditions (30 $\mu\text{m}/\text{yr}$ vs. 3 $\mu\text{m}/\text{yr}$, respectively). Even though the final oxygen concentration at the end of the 500-h period was below 1 mg/kg in both cases, the initial concentration of oxygen in the aerated solution was higher than 1 mg/kg in the first 100 h. Consequently, the observed discrepancies may be due to an initially higher corrosion rate in the aerated solution.

Long et al. (2002) tested carbon steel coupled and uncoupled to alloy 600 in conditions of full and partial immersion, in simulating lay-up water. Galvanic coupling of carbon steel with alloy 600 did not have any significant effect on its corrosion rate. The main corrosion product deposited on steel for 30 mg/kg hydrazine was maghemite ($\gamma\text{-Fe}_2\text{O}_3$), and for 80 mg/kg hydrazine was lepidocrocite ($\gamma\text{-FeO(OH)}$) along with some magnetite. The authors report that the part of specimens above the water level, under air gas phase, did not show any corrosion even when significant corrosion occurred in the part of specimens below the water level. Long et al. (2002) conclude that even a deficient dry lay-up is better than a wet lay-up with inadequate hydrazine concentrations or absence of nitrogen blanket. However, note that the effect of the differential-aeration cell between the submerged (anodic) and the aerial (cathodic) parts of the specimens is disregarded. In the absence of a submerged part, the aerial part of the specimen would not be cathodic and thus, it would corrode more. Among studied variables (pH, concentrations of hydrazine and oxygen and atmosphere) the presence of an inert atmosphere had the largest impact on the reduction of corrosion rate of carbon steel. The hydrazine concentrations used by Long et al. (2002), 30 and 80 mg/kg, were too low to protect carbon steel from corrosion in aerated conditions. They suggest a hydrazine concentration threshold of 190–220 mg/kg on the basis of an acceptable corrosion rate of 6 $\mu\text{m}/\text{yr}$, in aerated conditions.

Rabeau et al. (2002) report that pits only nucleated and grew on carbon steel when significant concentrations of dissolved oxygen were present. This situation occurred in aerated solutions when hydrazine was absent or when its

concentration was sufficiently low. In deaerated conditions, pits only initiated at the beginning of the nitrogen sparging when the oxygen concentration was still high. This type of pitting is due to varying degrees of localization of the general corrosion of carbon steels. It is not necessarily associated with the presence of a particular detrimental anion, such as chloride, which is absent in the present case. Rabeau et al. (2002) conclude that a sufficiently high hydrazine concentration is paramount to ensure protection of carbon steel components under an air atmosphere. They also support the concept of the amount of hydrazine injected being proportional to the outage duration.

EPRI (2005) studied the corrosion performance of materials used in NSGs under wet lay-up conditions by weight loss tests. Tested materials included those used for tubing in American PWRs: alloys 600 and 690; stainless steel 405 (UNS S40500), and carbon steels 1010, SA-569 and SA-36, used in internal non-pressure parts; and two types of weld metals: ER70S-GMAW and E7018-A1SMAW. Results from tests on carbon steels and weld metals are discussed in this section while those of passive alloys are discussed in the following one. Allowable corrosion rates for carbon steels and weld metals are $58 \mu\text{m/yr}$ (2.28 mpy) and $170 \mu\text{m/yr}$ (6.75 mpy), respectively. These values result from considering the maximum corrosion penetration that can be tolerated in NSG environments for a 40-year operating life, with periodical chemical cleaning. This criterion is purely based on corrosion allowance limits. Therefore, it does not consider any effect of the generated corrosion products when they are released in the secondary circuit. Simulating lay-up conditions were as follows: pH > 9.0 obtained by ammonia addition when necessary, $[\text{O}_2] < 20 \mu\text{g/kg}$ at the beginning of tests, and 25°C of temperature. Tested specimens were exposed for 20–29 days to the testing environment. Studied scavengers included hydrazine, CBH and DEHA. It is assumed they are not catalysed since it is not reported. This report did not include the study of any type of localised corrosion or galvanic interactions of carbon steels and passive alloys. Such effects are within the latest results from this EPRI research line, but they are still proprietary and licenced material which remains undisclosed for the general public.

EPRI (2005) study included tests in the following control environments:

- Air-saturated demineralised water with pH of approximately 5.5 (uncontrolled), in fully immersed conditions and in the vapour phase,
- Demineralised water with an average pH of 9.4 (controlled) with continuous nitrogen sparging, under full immersion,

- Demineralised water with an average pH of 9.85 (controlled) with initial and periodic nitrogen sparging, in fully immersed conditions and in the vapour phase.

Figure 15 shows average corrosion rates of carbon steels 1010, SA-569 and SA-36 in the control environments. Specimens tested in the vapour phase, above air-saturated and initially deaerated water, showed corrosion rates of 14.5 ± 7.0 and $14.5 \pm 3.6 \mu\text{m/yr}$, respectively. These corrosion rates apply to aerial parts (not submerged in the lay-up solution) and also they could be used as reference values for a deficient dry lay-up. Specimens under full immersion in pH 9.4 water with continuous nitrogen sparging showed a corrosion rate of $14.4 \pm 7.3 \mu\text{m/yr}$. Immersion in air-saturated water and initially deaerated water led to corrosion rates of 73 ± 27 and $79 \pm 11 \mu\text{m/yr}$, respectively. These values are above the allowable corrosion rate for carbon steel. Initial and periodic deaeration of testing solution did not have any effect on corrosion rates since the solution saturated with oxygen within one day.

Before analysing the effect of selected scavengers, it is worth noting that continuous nitrogen sparging was applied throughout the entire length of these tests. Oxygen concentration was monitored periodically resulting in values below $20 \mu\text{g/kg}$, not only at the beginning of the tests but for most of the testing time. In such conditions, the tested scavengers may have reacted with residual amounts of oxygen without any other clear effect. Another effect to consider is the transport of the scavenger from the water to the gas phase depending on its distribution ratio coefficient. The continuous flux of nitrogen carried the scavenger away from the testing vessel. This effect is the most important for volatile species, such as DEHA, and the least important for CBH (Andries and Couturier 2000). These results apply for

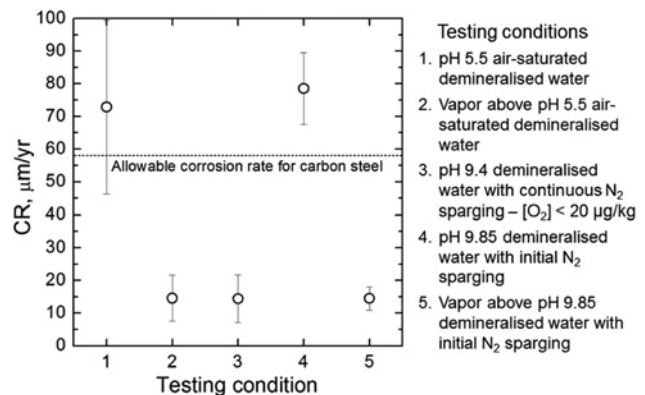


Figure 15: Average corrosion rate of carbon steels in various control environments without any scavenger addition. Error bars: standard deviation. Data from (EPRI 2005).

the use of scavengers in wet lay-up under a nitrogen blanket but not under an air phase. The corrosion rate of carbon steel in pH 9.4 water with continuous nitrogen sparging ($14.4 \pm 7.3 \mu\text{m/yr}$) is used as a basis of comparison for analysing the effect of scavengers (Figure 16).

Figure 16 shows the corrosion rate of carbon steels 1010, SA-569 and SA-36 as a function of the scavenger concentration. Corrosion rate (CR) of carbon steel decreased as the logarithm of hydrazine concentration increased according to Eq. (10), where $[\text{N}_2\text{H}_4]$ is in mg/kg. Disregarding the data for $[\text{N}_2\text{H}_4] = 1 \text{ mg/kg}$, the scatter at each hydrazine concentration is relatively low but the general trend of the data displays a large scatter around the trend line (Eq. (10)). As an example, $\text{CR} = 10.6 \pm 2.7 \mu\text{m/yr}$ is obtained for $[\text{N}_2\text{H}_4] = 25 \text{ mg/kg}$, and a higher value of $\text{CR} = 36.4 \pm 4.6 \mu\text{m/yr}$ is obtained for $[\text{N}_2\text{H}_4] = 50 \text{ mg/kg}$. This is attributed to the run-to-run variation in tests. For every tested hydrazine concentration, tests were performed in the same test vessel with the same solution composition and materials. The authors indicate that if multiple tests were repeated in different test vessels, with the same solution composition and materials, the obtained results would be less repeatable. This effect might be associated with different oxygen ingress rates to the various test vessels. However, oxygen concentration was below $20 \mu\text{g/kg}$, as stated previously, due to continuous nitrogen sparging. It is noticeable that, according to Eq. (10), 1555 mg/kg of hydrazine are needed for obtaining the same average corrosion rate ($14.4 \mu\text{m/yr}$) measured in pH 9.4 water with continuous nitrogen sparging and no added scavenger. Apparently, hydrazine effect is detrimental for the corrosion rate of carbon steel in solutions with $[\text{O}_2] < 20 \mu\text{g/kg}$ when added in low concentrations.

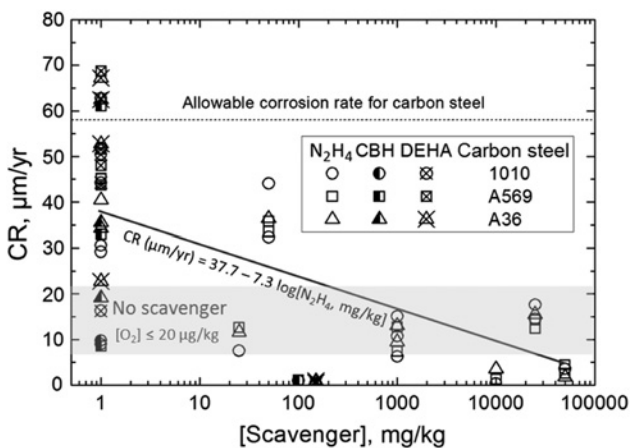


Figure 16: Corrosion rate of carbon steels as a function of scavenger concentration at 25°C , $\text{pH} > 9$, and initially $[\text{O}_2] = 20 \mu\text{g/kg}$. Data from (EPRI 2005).

$$\text{CR} (\mu\text{m/yr}) = 37.7 - 7.3 \log [\text{N}_2\text{H}_4, \text{mg/kg}] \quad (10)$$

EPRI (2005) assessed the effect of solution pH in the range from 9.2 to 10.6 on the corrosion rate of carbon steel in hydrazine-containing solutions with $[\text{O}_2] \leq 20 \mu\text{g/kg}$. No correlation was found between solution pH and corrosion rates of carbon steels in the tested conditions.

Figure 17 shows the reported corrosion rates of weld metals ER70S-GMAW and E7018-A1SMAW as a function of the concentration of tested scavengers (EPRI 2005). Average corrosion rate of E7018-A1SMAW fully immersed in air-saturated water is also shown. Even though corrosion rates of weld metals are higher than those of carbon steels 1010, SA-569 and SA-36 (Figure 16), they are all below the corrosion allowance threshold for welded material in all tested conditions.

Hydrazine was tested at 7 concentrations from 1 to 50,000 mg/kg, CBH was tested at concentrations of 1 and 100 mg/kg, while DEHA was tested at 1 and 150 mg/kg. CBH and DEHA led to very low corrosion rates for carbon steels at the highest tested concentrations (100 and 150 mg/kg, respectively). In such conditions, they outperformed hydrazine at 1000 mg/kg (Figure 16). Marks (2000) stated a minimum CBH concentration of 150 mg/kg in wet lay-up conditions to prevent carbon steel corrosion. Figure 18 shows the corrosion rates of carbon steels and weld metals in lay-up solutions with 1 mg/kg of tested scavengers. The scatter of data was significant. CBH led to lower corrosion rates than hydrazine for carbon steels. There is no data reported for weld metals in 1 mg/kg hydrazine lay-up solutions. DEHA led to the highest corrosion rates among tested scavengers at 1 mg/kg. Average corrosion rate in water with continuous nitrogen sparging was lower in the absence of any scavenger than with 1 mg/kg additions of hydrazine, CBH or DEHA. Data considered for building

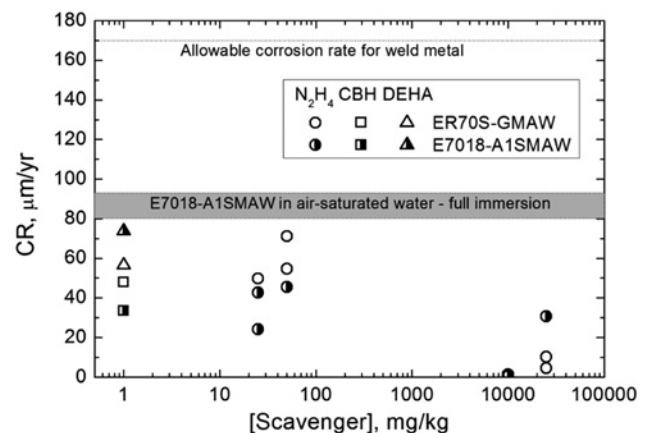


Figure 17: Corrosion rate of weld metals as a function of concentration of different scavengers at 25°C , $\text{pH} > 9$, and initially $[\text{O}_2] = 20 \mu\text{g/kg}$. Data from (EPRI 2005).

Figure 18 included 6 tests with no scavenger, 7 tests with hydrazine, 7 tests with CBH and 12 tests with DEHA, for carbon steels, and 2 tests with CBH and 2 tests with DEHA, for weld metals (EPRI 2005).

Reviewed research suggests that corrosion kinetics of carbon steel in wet lay-up conditions is under cathodic control. Oxygen reduction reaction, which governs the overall kinetics, is generally limited by diffusion. Equation (11) shows the dependence of the limiting current density (i_{LIM}) with the oxygen diffusion coefficient (D_{O_2}), $[O_2]$ and the thickness of the diffusion layer (δ), where n is the charge number of the cell reaction and F the Faraday constant (IUPAC 2019). Although circulation loops and nitrogen sparging help to homogenize concentration of additives in large volumes of lay-up solution, they also increase the rate of oxygen reduction by decreasing δ in Eq. (11).

$$i_{LIM} = n \cdot F \cdot D_{O_2} \cdot [O_2] / \delta \quad (11)$$

The main effect of scavengers is the oxygen removal while other effects are of second order. Efficient oxygen removal from water may be also attained by nitrogen sparging/blanket. The use of both scavengers and nitrogen sparging/blanket may be redundant in some cases. Analysis of reviewed experiments is complicated by various facts:

- Boundary conditions, such as $[O_2]$ in the gas phase or if it is an open or closed system, are not well defined.
- Nitrogen sparging may remove not only dissolved oxygen but also volatile scavengers when applied in conjunction.
- Scavenger and oxygen concentrations are not measured over time.
- The origin of data scatter is unclear. Reproducibility of results is not granted.

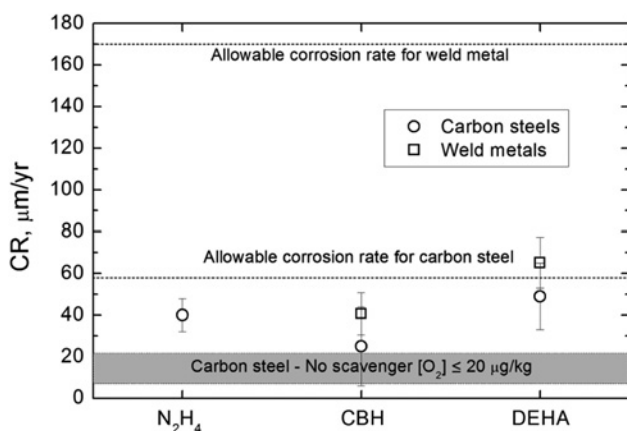


Figure 18: Average corrosion rate of carbon steels and weld metals for 1 mg/kg of different scavengers at 25 °C, pH > 9, and initially $[O_2] = 20 \mu\text{g/kg}$. Error bars: standard deviation. Data from (EPRI 2005).

- Electrochemical measures of corrosion rate, which provide instantaneous values, are not easy to implement due to the poor conductivity of the lay-up solution. Reviewed studies use weight-loss tests which provide an average corrosion rate over testing time, have low detection limits and a significant experimental error.

5.6.6 Corrosion of passive alloys under wet lay-up conditions

EPRI (2005) reports corrosion rates of alloys 600 and 690, and stainless steel 405 in simulating lay-up conditions and in air-saturated conditions. The allowable corrosion rate stated for these passive alloys, according to the above mentioned criterion, is $4.4 \mu\text{m/yr}$ (0.175 mpy). Figures 19–21 show the corrosion rates of alloys 600, 690 and stainless steel 405, respectively as a function of scavenger concentration. Overall, most of data are below detection limits without any clear dependence with scavenger type and/or concentration. Alloy 600 shows two extreme data points of corrosion rates above the allowable threshold, but they are attributed to experimental error (Figure 19). Tests in air-saturated demineralised water led to the following results:

- Two data of high corrosion rates (8.53 and $8.31 \mu\text{m/yr}$) and four data below the detection limit for alloy 600
- Two data of high corrosion rates (26.19 and $35.97 \mu\text{m/yr}$), one data of acceptable rate ($2.34 \mu\text{m/yr}$) and three data below the detection limit for alloy 690
- One data below the detection limit for stainless steel 405.

Alloys 600 and 690 were tested in the vapour phase above air-saturated water showing nil or acceptable corrosion rates. It is unlikely that general corrosion poses a risk for chromium-rich passivating alloys. However, localised corrosion in the forms of pitting or crevice corrosion, and galvanic effects should be analysed in more detail.

Nickel alloys used for NSG tubing may be prone to pitting and/or crevice corrosion in the presence of chlorides, at room temperature (Maristany et al. 2016). Chloride and sulphate are present as impurities in the secondary circuit and they concentrate within HTCs in operation. Impurities concentration within crevices decreases at reactor shutdown due to the hideout return process. However, even small amounts of chlorides may lead to crevice corrosion especially if the environment is not sufficiently reducing. This situation may occur during NSG wet lay-up.

In the early 1980s, pitting corrosion of alloy 600MA tubes was observed in some American PWRs which used seawater as a tertiary coolant. Damage occurred on the cold-leg tubes near the sludge pile at the TTS. Pits were

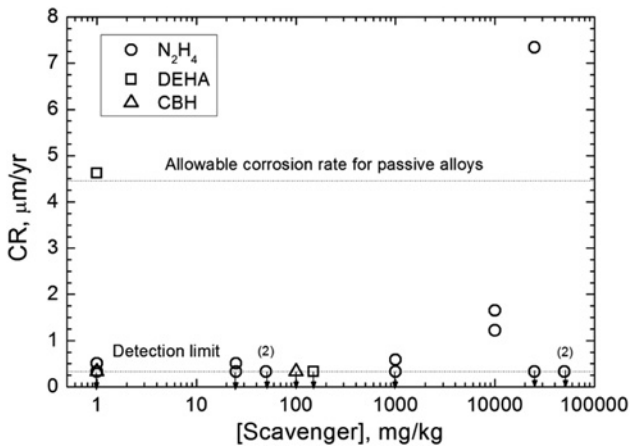


Figure 19: Corrosion rate of alloy 600 as a function of concentration of different scavengers at 25 °C, pH > 9, and initially [O₂] = 20 µg/kg. Data from (EPRI 2005).

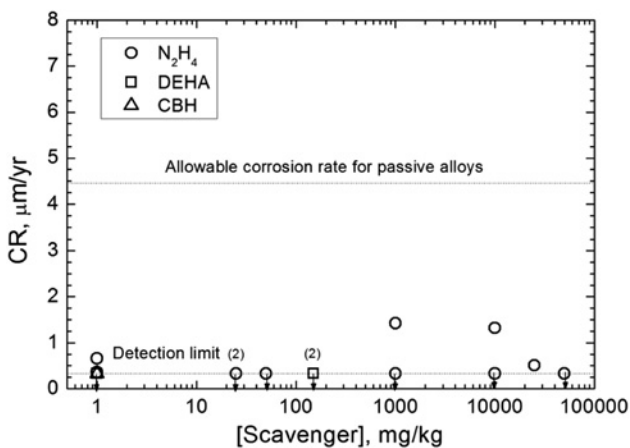


Figure 20: Corrosion rate of alloy 690 as a function of concentration of different scavengers at 25 °C, pH > 9, and initially [O₂] = 20 µg/kg. Data from (EPRI 2005).

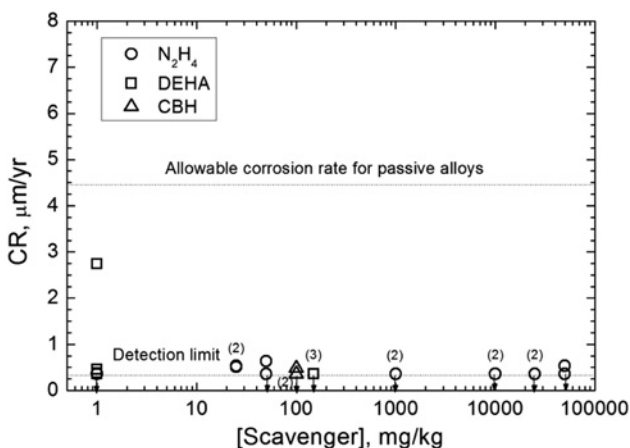


Figure 21: Corrosion rate of stainless steel 405 as a function of concentration of different scavengers at 25 °C, pH > 9, and initially [O₂] = 20 µg/kg. Data from (EPRI 2005).

filled with corrosion products which contained copper and chloride, besides the alloy constituents. Laboratory tests were performed to determine the effect of lay-up periods on the pitting corrosion of alloy 600MA tubes. Results showed that pitting corrosion of alloy 600MA may occur at ambient temperature in solutions with chloride concentrations as low as 700 mg/kg, when chloride is present as CuCl₂. In air-saturated seawater, pitting corrosion was observed for chloride concentrations of 6000 mg/kg or higher. In all cases, a copper-containing sludge was present. Presence of cupric ion (Cu²⁺) greatly accelerates the rate of pitting corrosion compared with sodium chloride solution of the same chloride concentration. In the absence of Cu²⁺, pitting corrosion only occurred above a threshold oxygen concentration of 10 µg/kg. Low pH solutions are required to initiate pitting corrosion of alloy 600MA. Ammonia additions to reach pH > 8.5 stop or retard pitting corrosion. Pure and commercial hydrazine additions did not have any effect on the pitting corrosion in CuCl₂ solutions and had a slightly beneficial effect in seawater. Pits observed in lay-up simulating environments were open and do not show corrosion products. Corrosion products found in tubes pulled from NSGs may have resulted from additional corrosion in operation, since oxides are less soluble at high-temperatures (EPRI 1983).

Atomic Energy of Canada Limited (AECL) studied the pitting corrosion susceptibility of nuclear grade alloy 800 tubing in NSGs lay-up, start-up and operating conditions (Lu 2012). The lay-up simulating conditions consisted of solutions with a mixture of NaCl, KCl and CaCl₂ with total chloride concentrations of 0.01, 0.1, 0.65, 1 or 4 mol/kg plus 0.15 mol/kg Na₂SO₄. The solution pH was fixed at 6.83 by small HCl or NaOH additions. Testing temperature was 40 °C. Pitting potential (E_p) of alloy 800 obtained by potentiodynamic polarisation decreased with increasing chloride concentrations according to Eq. (12). Alloy 800 did not suffer pitting corrosion in 0.01 mol/kg chloride solutions.

$$E_p [mV_{SCE}] = -61 + 141/[Cl^-] - 4.87/[Cl^-]^2 \text{ for } [Cl^-] \geq 0.1 \text{ mol/kg} \quad (12)$$

Maristany et al. (2016, 2018) report crevice corrosion repassivation potentials of alloys 600, 690 and 800 in as-received (solubilised) and thermally-aged conditions as a function of chloride concentration and temperature. They tested the tubing alloys in chloride solutions of concentrations ranging from 0.01 to 5 mol/L, at 30, 60 and 90 °C. The corrosion susceptibility increased as the chloride concentration and temperature increased. Thermal ageing of tubing alloys did not produce a significant decrease on their resistance to crevice corrosion. Unexpectedly, alloy

690 was the least resistant to crevice corrosion in spite of having the highest chromium content among tested alloys, while alloy 800 was the most resistant. Although the lower resistance to crevice corrosion of alloy 690 with regard to alloy 600 is apparently at odds with field experience, it should be considered that the chloride-induced crevice corrosion mechanism differs from those involved with corrosion damage in thermal crevices in operation. Crevice corrosion might occur under deficient wet lay-up conditions, *i. e.*, high chloride concentrations and oxidizing conditions (high $[\text{Cu}^{2+}]$ and/or $[\text{O}_2]$). To evaluate this possibility, Maristany et al. (2018) compared the open circuit potential of thermally-aged alloys 600 and 690 in simulating lay-up conditions with the corresponding crevice corrosion repassivation potential of these alloys. They considered a chloride concentration of 0.01 mol/L, which is 1000 times higher than that expected in bulk lay-up solutions after hideout return. In deaerated conditions, the open circuit potential of the alloys were 240–400 mV below their repassivation potentials, which represents a wide safety margin for avoiding crevice corrosion. However, in aerated conditions the open circuit potentials of the alloys were very close or even above the corresponding repassivation potentials (Maristany et al. 2018). Although this latter result does not imply the occurrence of crevice corrosion, it indicates that crevice corrosion of nickel alloys is not precluded under deficient wet lay-up conditions.

Beside chloride, another impurity usually present in the secondary circuit is sulphate. In a reducing environment, sulphate may be reduced to aggressive lower-valence sulphur species, such as thiosulphate or sulphide (Figure 12). Thiosulphate has shown to be particularly detrimental for tubing alloys in conjunction with chloride (Xia et al. 2013). Becerra Araneda et al. (2018) reported that small additions of thiosulfate to chloride solutions produce a significant decrease of the pitting potential of alloys 600, 690 and 800. The detrimental effect of thiosulphate on pitting corrosion of alloy 600 is reported for concentrations as low as 10^{-4} mol/L in a 1 mol/L NaCl solution. Alloys 690 and 800 may show two different types of localized corrosion processes called low potential and high potential pitting corrosion depending on the thiosulphate to chloride concentration ratio. In wet lay-up conditions, low potential pitting corrosion is the most likely process since it may happen at potentials slightly higher than the open circuit potential of these alloys. Thermally-aged alloys, such as those used for NSG tubing, are more prone to pitting corrosion than fully-solubilized alloys. However, if the concentration of thiosulphate is relatively large with respect to that of chloride, pitting corrosion is inhibited (Becerra Araneda et al. 2018).

5.6.7 Film-forming amines

FFAs belong to the oligo-alkyl-amino fatty amine family. Their general chemical formula is $R_1\text{-}[\text{NH}(\text{R}_2)]_n\text{-NH}_2$, where n is an integer between 0 and 7, R_1 is an unbranched alkyl chain (12–18 carbon atoms) and R_2 is a short chain alkyl group (1–4 carbon atoms). The most common FFA used for the protection of industrial condensate systems is octadecylamine, with $n = 0$ and $R_1 = \text{C}_{18}\text{H}_{37}$. FFAs are volatile so film formation occurs both on the steam and condensate system. The pH of the condensate must be controlled to ensure the formation of the film; pH from 8.0 to 8.5 is recommended for ODA. An alkalinizing amine is added to the commercial formulation of FFAs products to meet this requirement. FFAs are applied as solutions, emulsions, or suspensions in water with the exception of Russian WWERs which use pure ODA. Once the protective film has formed it remains intact even after the dosage has been stopped. Free FFAs in water form micelles. Although the concentration of FFAs in water may be analytically determined it is not a measure of the amine bonded to the metal surfaces. Overdosing of FFAs leads to the formation of clumps of gel-like material which may block vessels or tubes. For avoiding this problem free FFAs concentration must be kept constantly low (Betova et al. 2014; The International Association for the Properties of Water and Steam 2016).

Liao et al. (2007) studied the corrosion protection of ODA films formed on iron when tested in a solution containing chlorides, sulphates and carbonates by electrochemical impedance spectroscopy (EIS) and auger electron spectroscopy (AES). An ODA concentration of 25 mg/L provided the best corrosion resistance. The ODA film was made up of three layers: the inner layer consisted of iron oxides, the middle layer was mixed ODA iron oxides and the outer layer was pure ODA. The thickness of the outer layer varied with ODA concentration (Liao et al. 2007). The ODA treatment was applied for shut down protection of 125 and 300 MW power plants. Application of an emulsion containing 2–3 wt % ODA did not produce any change in pH and water and steam conductivity. Economiser, water-wall and superheater tubes were cut and examined to determine the effect of ODA treatment on their surfaces. The economiser and water wall tubes showed a black inner surface while the superheater tubes showed a dark grey colour. ODA concentration in the steam phase was higher than in the water phase which resulted in a better (more hydrophobic) film formed in the superheater. The corrosion resistance of the ODA treated tubes was studied by EIS in a solution of chlorides, sulphates and carbonates. ODA-treated economiser, water-wall and superheater tubes of both power plants showed better corrosion resistances than their analogous without ODA treatment (Liao et al. 2008).

Baux et al. (2018) studied the properties of the ODA film that forms on carbon steel surface by EIS, contact angle measurements and X-ray photoelectron spectroscopy (XPS). They used a testing solution of Na_2SO_4 0.001 M plus ammonia additions to reach a target pH of 10, at 80 °C. These conditions were close to those of a PWR secondary circuit. The authors confirmed that the steel surface is modified after the ODA treatment due to the adsorption of an organic hydrophobic thin film. Iron oxide/hydroxide is formed beneath the ODA film. The film thickness was estimated between 2 and 10 nm by *ex-situ* XPS analysis. The thickness indirectly obtained by analysis of *in-situ* EIS tests was about 16 nm. Approximately 10% of the carbon steel surface was accessible to the electrolyte after the ODA treatment (Baux et al. 2018).

Bäßler et al. (1999) studied the inhibiting effect of ODA on the pitting corrosion of stainless steel 321 (UNS S32100) by electrochemical and surface analytical techniques. They tested the effect of the ODA film formed on the metal surface at temperatures between 150 °C and 250 °C in deaerated chloride solutions. ODA-containing solutions led to lower open circuit potentials which results from the formation of a fine crystalline oxide layer. This layer acts as a diffusion barrier. In the absence of ODA, a porous oxide layer is formed on the metal. Stainless steel shows higher pitting potential and higher polarization resistance in the ODA-containing solution (Bäßler et al. 1999).

Mao et al. (2015) studied the inhibiting effect ODA on the corrosion of stainless steel 316 (UNS S31600) by electrochemical techniques. They performed tests in deaerated acetate buffer solutions, with and without chloride additions, at 75 °C. Lower corrosion rates and higher pitting potentials result from increasing ODA concentration in solution or from extending immersion time. The steel/solution interface comprises an inner barrier layer (passive film) and an outer inhibitor layer. The outer layer contains adsorbed ODA, it is porous and becomes more protective with increasing ODA concentrations up to a certain limit. The observed improvement of protective properties with immersion time is attributed to the slow restructuring of the outer layer. ODA film does not affect the properties of the barrier layer (Mao et al. 2015).

Hater et al. (2014) studied the adsorption of different FFAs on copper, carbon steel and stainless steel. FFAs adsorption on metals substrates follows a first order kinetic law and its rate increases at higher temperatures. Equilibrium is reached within 24 h. FFAs adsorb faster on copper than on carbon steel being the slowest on stainless steel. Surface coverage also follows the same trend being the highest for copper and the lowest for stainless steel. For a constant carbon chain length of 18, surface coverage of monoamine is higher than that of diamine which in turn is higher than coverage of triamine. Tested FFAs with longer

carbon chains show higher surface coverage. Authors stated that the surface coverage increases as the hydrophily of the molecule decreases. However, corrosion protection of the film is not directly derived from surface coverage. After the application of FFAs, metal coupons were dried and exposed to oxygen-containing deionized water, at 60 °C. The removal of FFAs after 24 h was nil (close to detection limit). No signs of corrosion were reported after a 120-h exposure (Hater et al. 2014).

6 Summary and conclusions

Steam generators are key components of (NPPs) since their reliability affects the overall plant performance. Steam generator tubing represents more than 50% of the reactor coolant pressure boundary which separates the non-radioactive water of the secondary circuit from the radioactive water of the primary circuit. Corrosion control of steam generators under operation and during plant outages is attained by proper design, adequate material selection and control of water chemistry in the entire secondary cooling circuit.

Alloys 600, 400, 690 and 800 and stainless steels have been used as steam generator tubing materials. Successive improvements in water chemistry control, steam generator designs, tubing alloy metallurgy and materials selection have resulted in a decreasing incidence of degradation modes, namely: wastage, denting, pitting corrosion, intergranular corrosion and the various forms of SCC and mechanically-aided damage. Most of tube failures results from the formation of a locally aggressive chemistry on the tube external surface in HTCs. Currently, alloys 690TT and 800NG are selected for the steam generator tubes of PWR/PHWRs and austenitic stainless steel 08Ch18N10T for the steam generator tubes of WWERs.

Preservation of steam generators and balance-of-plant equipment from corrosion during outages is of main importance for the safe and efficient operation of the plant in subsequent power cycles. Corrosion of carbon steel, the least resistant material of the secondary cooling circuit, is mitigated by maintaining a reducing and sufficiently alkaline environment (wet lay-up) or by excluding moisture (dry lay-up). After plant shutdown, the secondary circuit is separated in suitable subsystems and different lay-up strategies are applied for each one. The selected strategy depends on the outage length, type of materials to be protected from corrosion, maintenance activities during the outage, radiation protection, authorised methods and available systems and devices. Wet lay-up relies on ammonia/amines to maintain a sufficiently alkaline pH

and an oxygen scavenger, which is generally hydrazine, to remove oxygen. Dry lay-up uses dry and hot air to remove moisture from equipment. Alternative or complementary lay-up strategies involve the use of surface-active agents such as polymeric dispersants and FFAs. They may be applied in operation or at shutdown of the plant. NPPs follow industry lay-up guidelines based on control parameters that trigger some action when they are above/below their corresponding threshold values. However, overall duration of outages has decreased and less stringent requirements than those prescribed in guidelines may be applied for short lay-up periods.

Nowadays, NSGs are a mature technology. Their design, material selection and water chemistry have evolved to minimise, rule out or delay most of the corrosion processes that frequently appeared in the past. In this context, SCC of tubes in operation is the most complex and pervasive corrosion mode that affect steam generators as NPPs age. This is due to the many submodes it displays and the lack of precise understanding of the underlying mechanisms involved.

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Abbreviations

AcSCC	acidic stress corrosion cracking
AECL	Atomic Energy of Canada Limited
AES	Auger electron spectroscopy
AkSCC	alkaline stress corrosion cracking
AVB	anti-vibration bar
AVT	all-volatile treatment
AVT(O)	oxidising all-volatile treatment
AVT(R)	reducing all-volatile treatment
BAT	boric acid treatment
BOP	balance of plant
BWR	boiling water reactor
CANDU	Canada deuterium-uranium
CBH	carbohydrazide
DEHA	diethyl-hydroxylamine
DMA	dimethyl-amine
DSSCC	doped-steam stress corrosion cracking
EDF	Électricité de France
EIS	electrochemical impedance spectroscopy
EPRI	Electric Power Research Institute
ETA	ethanol-amine
FAC	flow-assisted corrosion
FFA	film-forming amine
HTC	heat-transfer crevice
HPSCC	high-potential stress corrosion cracking
IAEA	International Atomic Energy Agency
LPSCC	low-potential stress corrosion cracking

LTSCC	low-temperature stress corrosion cracking
MPA	methyl-propanol-amine
MRC	molar ratio control
NPP	nuclear power plant
NSG	nuclear steam generator
ODA	octadecylamine
ODSCC	outer diameter stress corrosion cracking
OgSCC	organic stress corrosion cracking
PAA	polyacrylic acid
PbSCC	lead stress corrosion cracking
PHWR	pressurized heavy water reactor
PWR	pressurized water reactor
PWSCC	primary water stress corrosion cracking
SCC	stress corrosion cracking
SySCC	reduced-sulphur stress corrosion cracking
TTS	top of the tubesheet
TSP	tube support plates
WWER	water-moderated water-cooled energy reactor
XPS	X-ray photoelectron spectroscopy

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