

WATER CHEMISTRY IN SECONDARY SIDE OF CNE CANDU STEAM GENERATORS AND THEIR RELATED DEGRADATION PROCESSES

S. MOGOSAN, D. LUCAN, D. STEFANESCU, M. FULGER

Institute for Nuclear Research, Pitesti, Romania, mogosansimona@yahoo.com

ABSTRACT

This paper presents a brief overview of steam generator functional parameters of nuclear power plants how use PWR (Pressurized Water Reactor) and PHWR (Pressurized Heavy Water Reactor) reactors, followed by a description of fundamental aspects on steam generator degradation and water chemistry in the secondary side, and also, water chemistry improvement by controlling pH. During operating life, cooling radioactive contamination occurs, but water conditions must be maintained inside specific ranges. Feedwater must be maintained as free from impurities as possible. This requirement involves careful attention to the entire system through which the water flows, either in the form of steam or water, for even though water is used as feedwater be pure at the same time of its entry into the system, it may absorb impurities from the various parts of the installation. Specific attention should be directed to possible points of water leakage from the service water system, as in the main and auxiliary condensers. Feedwater must be treated to maintain the required water conditions. As the concentration of the impurities in deposits increase, the pH can shift locally in these areas to acidic or alkaline conditions, entering in a pH range where initiation of corrosion phenomena cannot be longer excluded. By maintaining of sufficiently reducing conditions, the occurrence of certain corrosion mechanisms will be excluded (like pitting), but certain forms of SG tube corrosion may still occur.

Introduction

The functional connection between the two circuits of nuclear power plants it is made by the steam generator. Complexity and diversity of steam generators and their functional parameters led to numerous construction types. Generally for PWR and PHWR reactors are used vertical steam generators with U-tubing. **Figure 1**[1] shows a schematic section through a typical steam generator for a CANDU nuclear power plant. As a whole, optimization of the steam generator by implementing a comprehensive program for monitoring degradation processes, periodic inspection and preventive maintenance, involve savings of hundreds of millions of dollars, during the service life of a CANDU reactor.

This equipment raises several issues of safety operating, especially due to the presence of corrosion and damage of mechanical nature. Steam generators pose problems during enforcement inspection operations by reason of limited access to various components and the presence of high radiation field on the primary circuit. Because for manufactory of steam generators are used several types of steels, the coexistence under the generator environmental conditions involve high general problems in terms of corrosion.

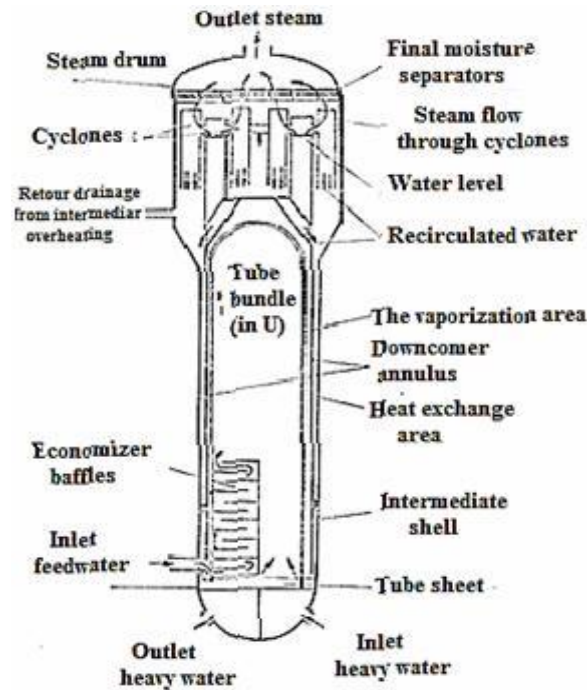


Figure 18 Schematic design of CANDU steam generator [1]

Chemistry description of secondary system

The structural materials achieving steam generator components are presented in **Table 1** [2] and the chemical composition of cooling water it is shown in **Table 2** [2]. During operation, corrosion reactions lead to accumulation of magnetite or other ferrous /ferric compounds as adherent films on the metal surfaces and also as mobile particles in these circuits. The corrosion of secondary side of Nuclear Power Plant (NPP) steam generator materials can be minimized, by judicious design materials selection and a rigorous chemistry control of aqueous in contact with them. [4 ÷ 6].

Table 3 Structural materials of steam generator [2]

Nr. Crt.	Components	Materials
1.	Water Chamber	SA 533 gr.B cl.I
2.	Divider sheet	SA 516 gr. 70
3.	Tube sheet	SA 5085 cl. II
4.	Tube sheet plate	Inconel 600
5.	Heavy coating(outside)	SA 516 gr. 70 (G 52-58)
6.	Intermediaries tube supports	SA 240-410S
7.	Grid support rings	SA 516 gr. 70
8.	Tube bundle	Incoloy-800
9.	Secondary casing	SA 516 gr. 70
10.	Cone, Shell, Steam drum	SA 516 gr. 70
11.	Upper cover	SA 516 gr. 70
12.	Supports	SA 516 gr. 70
13.	Cyclones	SA 516 gr. 70

The chemical control of the fluid which performs heat transport in the secondary circuit is necessary for the following reasons:

- minimizing corrosion of immersed components in steam and cooling water, including steam generator components;
- minimizing the systems contamination, particularly the heat transfer surfaces;
- minimization of transportation of insoluble chemical species resulting especially from the corrosion processes through the second side of SG;
- mitigation of corrosion in steam generator during periods of maintenance and/or accidental shutdowns.

Table 4 Chemical composition of cooling water [2]

Chemical parameters	Feed water	Water steam generator
Fe	<20 ppb	Max.50ppb
Cu	<2 ppb	Max.10ppb
pH	10-10,5 (to degasification)	9,5-10
Cyclohexylamine		5—10ppm
Morpholine		15-25 ppm
Sodium	<5ppb(condensate purification)	<20ppb
Chlorides	<5ppb	<20ppb
Cationic conductivity		<0,3mS/m
Si		<1ppm
Magnesium		<1ppb
Oxygen	<5ppb	<5ppb
Hydrazine	20-60ppb	20-60ppb

The secondary system steam generators degradations related to water chemistry regime

The degradation mechanisms that occurred in steam generators have a great variety [3, 7 and 8]. They are very extensive, affecting both primary and secondary side, from which the secondary side degradation has been the main problem. These SG problems often forced the plants to perform unscheduled or extended outages for preventive and/or corrective maintenance measures. In addition many SG replacements were necessary, which were costly in terms of repair work, personnel radiation exposure and loss of power [8, 9]. Numerous descriptions of the damage mechanisms have been published [10]. They are shown in a summarized form in **Figure 2** [7], identifying degradation sites for PWR steam generators.

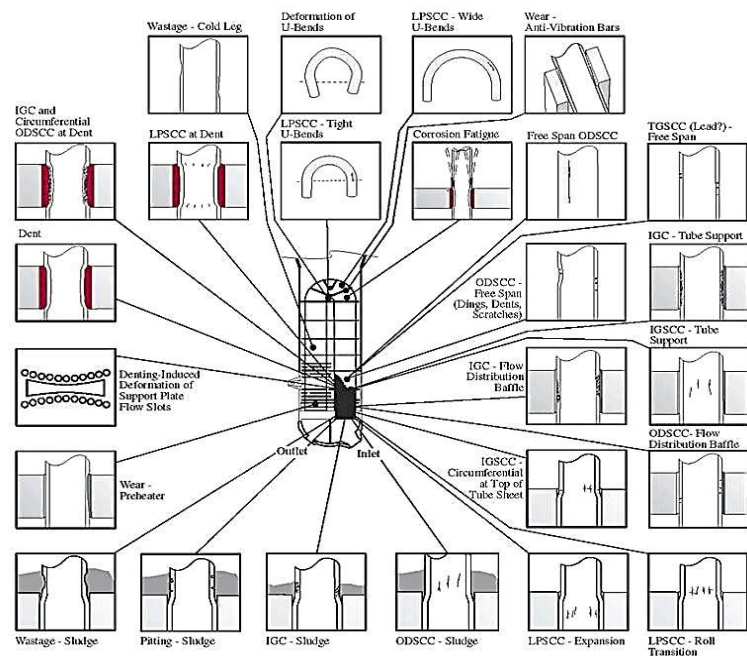


Figure 19 Failure types that have occurred in recirculation steam generators [7]

Water chemistry optimisation in secondary side of CANDU steam generator

pH control

The water chemical control is achieved by maintaining in certain limits the parameters which influence corrosion behaviour of steam generator materials: pH, oxygen content, quantity and composition of corrosion products, impurities (dissolved salts) and oxidizing agents. **Figure 3** [11] presents the report of steel corrosion rate at high temperature in acid and alkaline environment.

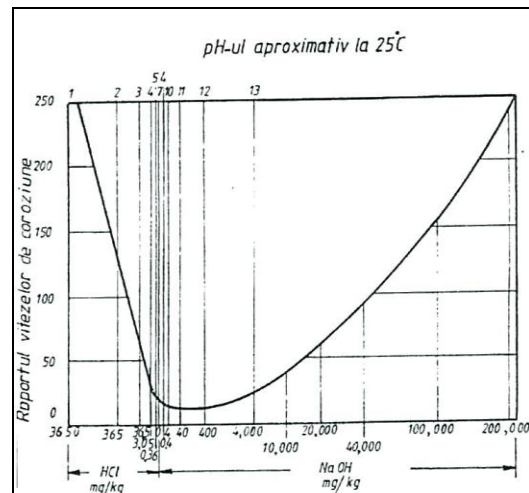


Figure 20 The report of steel corrosion rate, at high temperature in acid and alkaline environment [11]

The AVT (All Volatile Treatments) is now the worldwide treatment for the secondary water chemistry with two main options, ammonia at $\text{pH}_{25\text{ }^\circ\text{C}}$ of 10 (High-AVT) or an amine (Morpholine, ETA, DMA, MPA) [12]. Each reagent has its own advantage and inconveniences for protection of a defined material or component of the system and for operation easiness (costs, resins life duration, wastes).

It is also necessary to add sufficient quantity of hydrazine to get a reducing environment and minimize risks of SG tubes cracking. However, it is not useful and even inappropriate (cost, hazard) to add too much hydrazine ($>100\mu\text{g}/\text{kg}$) as some utilities may have done. If the pH is insufficient with or without amine, it is better to also add ammonia rather than increasing hydrazine concentration $>100\mu\text{g}/\text{kg}$. There is an international consensus for a target value of $\text{N}_2\text{H}_4 > 20\mu\text{g}/\text{kg}$ and > 8 times the oxygen concentration. The ANTI (Advanced Nuclear Technology International) reports proposed range from 20 to $100\mu\text{g}/\text{kg}$ in Feed Water, with a target value of $50\mu\text{g}/\text{kg}$. The rationale for AVT reagent selection will depend on the presence or not of copper alloys, as shown on **Tables 3** and **4**[12].

It can be concluded that:

- Ammonia is a viable option for operation at $\text{pH}_{25\text{ }^\circ\text{C}}$ of 9.9 - 10 and is easy to implement and monitor, but can only be used in plants without copper alloys and normally without condensate polishers in service and if the blow down resins are regenerated.
- Morpholine is a good selection when the blow down resins are not regenerated to avoid any risk of chemical or resin fines contamination, to limit liquid chemical effluents, when the condensate polishers are not permanently in operation. It also provides a uniform protection to all parts of the secondary system against FAC (Flow Accelerated (assisted) Corrosion).
- ETA (ethanolamine) is a good selection when condensate polisher are in continuous service or if specific parts of the secondary system must be protected against FAC (Flow Accelerated (assisted)

Corrosion) or if nitrogen release into the environment must be decreased or finally, if the reagent cost is in favour of ETA(ethanolamine).

If CPS (Condensate Polishing System) is present, it is highly advisable to keep it in by-pass mode, ready for use only in case of need for a limited period of time (condenser leak, start up). A less expensive option is to only have a CPS (Condensate Polishing System) with lower flow rate specifically aimed at eliminating contaminants before and during start-up.

Table 5 Advantages and inconveniences of two amines in the presence of copper alloys [12]

		Morpholine	Ethanolamine
Advantages		Distribution coefficient of 1 → constant concentration throughout the secondary system → good protection of many parts of the system against CS FAC (F low A ccelerated (assisted) C orrosion of C arbon S teel).	High alkalinity → lower concentration → more favourable for the environment and good compatibility with the use of condensate polishers.
		Good feedback experience for SG fouling and corrosion.	Low concentration of organic acids produced by thermal decomposition
Disadvantages		Compatibility with the operation of BD resin beyond breakthrough in its exhausted form (after saturation): ~1 year for the cation	Good protection against FAC (F low A ccelerated (assisted) C orrosion).in some parts of the system, where the pH is higher than with morpholine.
		Low alkalinity→ high molar content not always compatible with the use of condensate polishers.	Partition coefficient <1→ non-homogeneous protection for the various parts of the secondary system.
		Limited stability →presence of some organic acids, increasing the cation conductivity in the Steam Generator Blow Down(SGBD) and decreasing the detection sensitivity of other impurities.	Lower possibility of BD(blow Down) resin operation beyond breakthrough in the exhausted form, due to the higher affinity of ETA for cation resins compared with morpholine → lower Na elimination

Table 6 Advantages and inconveniences of two amines in the absence of copper alloys [12]

		Morpholine	Ethanolamine	Ammonia
Advantages		Coefficient distribution of 1 → constant concentration all over the secondary system	High alkalinity → lower concentration → more favorable for the environment	Easy treatment and monitoring, with potentially only hydrazine added if the ammonia is recycled.
		Good protection against FAC (F low A ccelerated (assisted) C orrosion) and corrosion transport throughout the system at high pH.		No organic acids produced as by products. Thus, no impact on cation conductivity and impurity detection.
Disadvantages		Low alkalinity → very high molar content hardly compatible with condensate polishers	Partition coefficient < 1 → nonhomogeneous protection for the various parts of the secondary system.	Requires a high pH25 °C (almost 10) to give sufficient protection against FAC (F low A ccelerated (assisted) C orrosion) and for corrosion product transport. High nitrogen release into the environment.
		Limited stability →presence of some organic acids, increasing the cation conductivity in the Steam Generator Blow Down(SGBD).	Lower possibility of BD resins operation in exhausted form (relative affinity) → lower Na elimination or more frequent regeneration or replacement.	Limited possibility of BD resins operation in exhausted form (relative affinity) and high frequency of regeneration required. Not compatible with condensate polishers.

For Steam Generator Blow Down (BD) purification, various options are possible but it may be interesting to also consider keeping the Ion Exchange Resin (IER) in operation past the break through by the alkaline reagent, allowing to easily operating at a sufficient pH without too much release of wastes into the environment. This also decreases the operating cost and avoids the burden and risks associated with resin regeneration.

With new materials, Condensate Polishing System (CPS) is more a burden and a pH limitation than an opportunity to eliminate pollution. Laboratory studies and plant experience have shown that decomposition products of resin fines, giving reduced sulphur compounds, or that sodium hydroxide throw, may constitute a very detrimental hazard for steam generators (SGs) integrity. Since reliable condensers exist and low leak detection with helium is carried out, it looks more desirable to avoid continuous operation of CPS. It appears that Feed Water corrosion product transport (iron oxides) is finally higher in units with CPS (Condensate Polishing System) than without. The CPS operation is hardly compatible with a sufficiently high pH (regeneration frequency, liquid wastes, and costs) and its benefit does not compensate the inconveniency of these lower pH values.

The concentration of impurities in the Steam Generator secondary circuit

The steam generator degradation problems arise from the continuous ingress of non-volatile contaminants, i.e. corrosion products and salt impurities accumulated in the steam generators. These impurities have their origin in the entire secondary circuit. The corrosion products generally accumulate in the steam generators and form deposits not only in the flow restricted areas, such as on top of tube sheet and tube support plates, but also build scales on the steam generator heating tubes. The most effective ways of counteracting all these degradation problems, and thus of improving the steam generator performance is to keep them in clean conditions [13]. The steam generation causes all the non-volatile compounds present in traces in the feedwater flow to be concentrated in the steam generator water, achieving concentrations quite higher than those of feedwater. To keep the impurities concentrations at a reasonable level, the steam generators are regularly cleaned by continuous blow down. At a steam generator blow down rate of for example 0.5% of the feedwater flow rate, the equilibrium concentrations of dissolved impurities in the bulk SG water are in principle expected to be therefore 200 times of the feedwater concentration for a non-volatile compound [10].

In fact ingress by feed water = elimination by blow down + elimination by main steam [g/h]

$$C_{fw} F_{fw} = C_{bd} F_{bd} + C_{ms} F_{ms} \approx C_{bd} F_{bd} \text{ [g/h]}$$

$$C_{bd} = C_{fw} F_{fw} / F_{bd} = C_{fw} 200 \text{ [}\mu\text{g/kg]}$$

where:

C_{fw} - the impurity concentration in feedwater

F_{fw} - the feedwater flow rate

C_{bd} - the impurity concentration in SG blow down

F_{bd} - the SG blow down flow rate

C_{ms} - the impurity concentration in main steam

F_{ms} - the main steam flow rate.[10]

That means, for the usual concentration of impurities in feed water (in the rule below the limits of detection, i.e. quite below 1 $\mu\text{g/kg}$ for most of the non-volatile impurities), the concentrations of these impurities in the SGs are expected to be few $\mu\text{g/kg}$ only, provided that these substances are soluble and homogeneously distributed in the SG bulk water.

However, there is also a permanent ingress of corrosion products, mainly magnetite into the steam generators, and deposits will be accumulated on the steam generator tubing surfaces at top of tube sheet or in the tube to tube support crevices. If the accumulated corrosion product deposits are sufficiently thick there is a risk of local concentration of impurities beneath these deposits. **Figure 4** [13] represent the case of tube sheet concentration of impurities. These high impurity concentrations, associated to the locally

higher temperatures (overheating) may be responsible for initiation of corrosion processes on the involved metal surfaces, especially on the steam generator tubing.

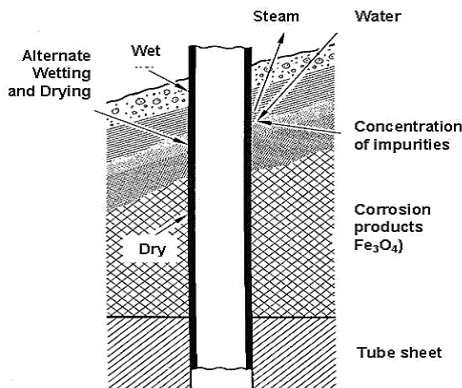


Figure 21

Impurities concentration mechanism beneath deposits at the SG tube sheet (schematic) [13]

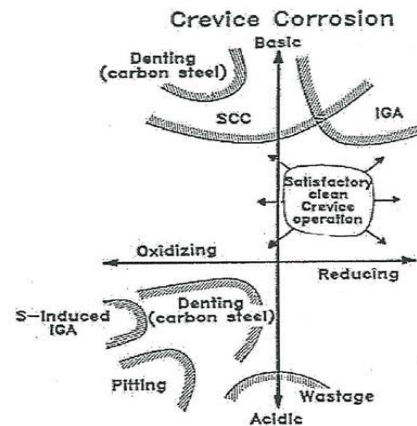


Figure 22

Illustration of SG tube corrosion depending of environmental conditions [3, 14, 15, 16]

Depending on the composition of the impurities in question, a series of physic-chemical changes will occur, like hydrolysis, precipitation of compounds after achievement the solubility product, etc.

These processes are very complex and strongly dependent on the composition rather than the concentration present in the bulk SG water. The composition of the bulk impurities will be given by the impurity sources, mainly:

- Ingress via make-up water (output quality of the water treatment plant),
- Condenser leaks (composition of cooling water),
- Consumables and auxiliary products which may enter into contact with inner surfaces (montage aids, for example),
- Impurities in the conditioning chemicals,
- Others.

As the concentration of the impurities in deposits increase, the pH can shift locally in these areas to acidic or alkaline conditions, entering in a pH range where initiation of corrosion phenomena cannot be longer excluded. By maintaining of sufficiently reducing conditions, the occurrence of certain corrosion mechanisms will be excluded (like pitting), but certain forms of SG tube corrosion may still occur. If these concentration mechanisms are considered, together with the redox condition of the system, a variety of possible corrosion mechanisms may appear [3, 14, 15, 16], including denting, SCC (Stress Corrosion Cracking), IGA (Inter Granular Attack) or the combination of both (IGA-SCC), pitting, among others, which are schematically shown in the **Figure 5** [13] where the possible corrosion mechanisms at different pH-redox conditions are graphically shown.

Worldwide performed investigations show clearly the SG tube material lack of stability against corrosion in the case of extremely acidic and/or alkaline conditions. Even with reducing conditions, stress corrosion cracking (SCC) of SG tubes cannot be excluded, if pH_T values of < 5.0 or > 9.5 prevail (**Figure 6** [10] and **Figure 7** [10]). That means that ensuring a local pH_T value within the range of 5.0 up to 9.5 under reducing conditions would minimize the risk of stress corrosion cracking, according to this source. However, the safe pH range at operation temperature shall be considered to be roughly 4 to 8.5 based on available experience.

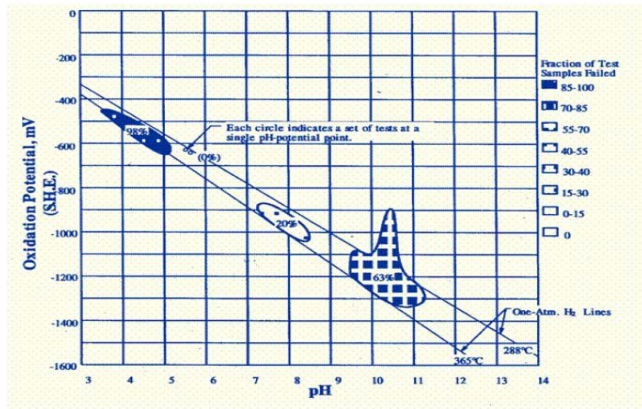


Figure 23

Stress corrosion cracking of Iy 800 as a function of pH [10]

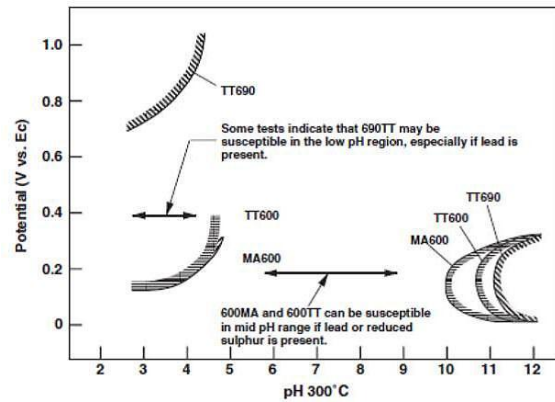


Figure 24

Stress corrosion cracking susceptibility of Alloy 600MA/TT and 690TT as a function of pH_T [10]

Some examples of experimental results for the testing of the Incoloy-800 samples for different times in demineralised water environments with pH=7.5, pH=8.5 and pH=9.5 (AVT) at secondary circuit steam generator specifically parameters (260°C and 5.1MPa) are presented in the **Figures 8-10** [17]

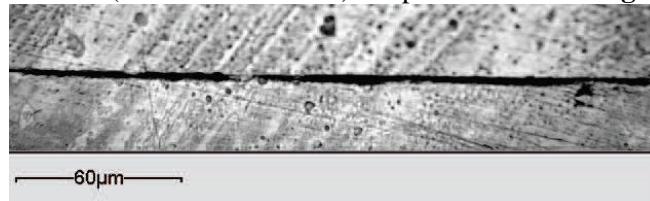


Figure 25

Aspect of the superficial layer for Incoloy-800 exposed 1680h in demineralised water, pH=7.5, T=260°C and p=5.1MPa (x1000)

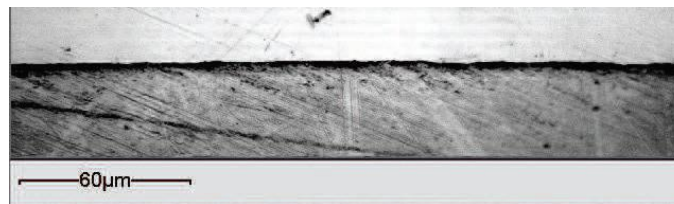


Figure 26

Aspect of the superficial layer for Incoloy-800 exposed 3600h in demineralised water, pH=8.5, T=260°C, and p=5.1MPa(x1000)

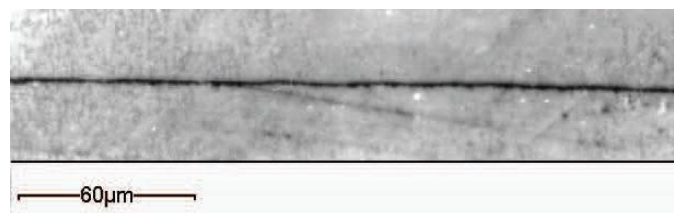


Figure 27

Aspect of the superficial layer for Incoloy-800 exposed 3192h in demineralised water, pH=9.5, T=260°C, and p=5.1MPa(x1000)

Conclusions

- Avoid the enrichment of impurities by avoiding at the maximum possible extent the accumulation of corrosion products inside the steam generators (SGs):
 - Copper free secondary system is required;
 - High pH chemistry by use of high hydrazine concentration;
 - Use of Advanced Amines (e.g. Morpholine, ETA) to reduce FAC in wet steam areas materials.
- Avoid at the maximum extent the ingress of impurities;
- Molar ratio control(The basis for this approach is that the molar ratio of strong cations (e.g. sodium, potassium)to strong anions (e.g. chloride, sulphate) in the crevice is considered to define the pHT (pH at temperature) in the crevice during operation);
- System conditioning with hydrolysable substances able to buffer locally enriched impurities(Phosphate treatment (PT) or Boric acid treatment (BAT)):

Intensification of impurity removal from SG (Impurity removal can take place during normal operation through the SG blow down; that so, increasing the blow down rate will decrease the bulk water concentration and slow down the enrichment process.

References

- [1] Bratianu,C., Bendeac, V., Georgescu, VI, „ Nuclear Energetics Strategies And Specifications”, Technical Publishing (published in Romanian), Bucharest, 1992
- [2] Lucan, D. „Specific Proceses For Steam Generator”, Paralela 45 Publishing (published in Romanian), Pitesti, 2009
- [3] Odar, S., Nordmann, F. „PWR and VVER Secondary System Water Chemistry” ANT International, 2010
- [4] Godfrey, M.R., etc., „On-Line Corrosion Monitoring in Boiler Systems” CORROSION/95 Paper No.621, 1995
- [5] Sweeton, F.H., Baes, C.F., etc., Trans.Amer.Nucl.Soc. 12 no.1, 1969
- [6] Barton, J.W., Arkless, F. „Experience with Ferritic and Austenitic Steel of PWR Circuits” IAEA-SM-264/10, 1983, p.35-148
- [7] Staehle, R.W., et al., „Progress in Understanding and Mitigating Corrosion on the Secondary Side in PWR Steam Generators”, Proceedings of the 10th International Symposium on Environmental Degradation of Materials in Nuclear Power Systems, Lake Tahoe, 2001
- [8] Electric Power Research Institute „Steam Generator Progress Report Revision 20061030”, EPRI, Palo Alto, 2006
- [9] Electric Power Research Institute „Steam Generator Progress Report”, Rev. 15 EPRI, Palo Alto, 2000
- [10] IAEA-TECDOC-1668, „Assessment and Management of Ageing of Major Nuclear Power Plant Components Important to Safety: Steam Generators”, International Atomic Energy Agency, Vienna, 2011
- [11] Lister, D.H. „Corrosion Products in Power Generating Systems”, AECL 6877, Canada, 1980
- [12] Normann, F., Odar, S., Venz, H., Kysela, J., Rühle, W., Riess, R. „International Conference on Water Chemistry of Nuclear Reactor Systems”, Advanced Nuclear Technology International, 2010
- [13] Odar, S. “Water Chemistry Measures to Improve SG Performance” 14th Intern. Conference on the Properties of Water and Steam –Kyoto, 2003
- [14] Tsujikawa, S., Yashima, S., Results of Steam Generator Reliability Test, p. 673 in Proceedings of a Conference on Steam Generators and Heat Exchangers, Vol. 2, Canadian Nuclear Society, Toronto, 1994
- [15] Electric Power Research Institute, Steam Generator Integrity Assessment Guidelines -Revision 2, EPRI TR 1012987, Final Report, EPRI, Palo Alto, 2006
- [16] Electric Power Research Institute, Steam Generator Integrity Assessment Guidelines, EPRI Report 1007346, TR-107621-R1, EPRI, Palo Alto, 2006
- [17] Lucan D.,” Degradations of Incoloy 800 Steam Generator Tubing” "Steam Generator Systems: Operational Reliability and Efficiency", InTech, March 3, 2011