EDF APPROACH FOR FOULING MITIGATION

Michel DIJOUX, Francis NORDMANN, and Agnès STUTZMANN. *Electricité de France - Groupe Des Laboratoires 2, rue Ampère - F 93206 St-Dénis Cedex 1.*

~~This paper describes~~ the situation and evolution of fouling of steam generator tubing in the 58 French PWR units and the different studies and actions carried out to try to solve the problem and avoid any power output reduction associated to pressure drop. The remedies include the selection of the best secondary water treatment with amines such as morpholine in order to minimise corrosion product transport as well as mechanical remedies such as sludge lancing or chemical cleaning. Other options like dispersant addition are under evaluation.

1. INTRODUCTION

Electricité de France is operating 58 PWRs units representing almost 80% of its electricity generation. The list of these units, as well as several of its characteristics (name of the plant, date of commercial operation, steam generator and condenser tubing material, secondary water treatment) are given in Table 1.

This is why the correct operation of French PWRs at full power is of utmost importance. Steam generator tubes fouling is one of the parameters which may influence steam pressure drop and, in case of large deposits, induce a power reduction. Moreover, production and transport of corrosion products from feedwater to steam generator (SG) tubing has a detrimental influence on the risk of Intergranular Stress Corrosion Cracking (IGA/SCC) of Inconel 600 SG tubes. In addition to fouling and thermal transfer decrease, corrosion products may partially plug flow holes, leading to flow instability.

According to the identification of fouling problems initiation on some of its units, EDF launched a comprehensive programme of studies and remedies to restore the units performances.

2. FOULING STATUS OF FRENCH PWRs

At the present time, a significant number of French units have some difficulties to adjust their electrical output to the power system request due to the pressure drop of steam at SG outlet as compared to nominal value. The kinetics of pressure drop decrease is ranging from 150 to 200 mbar per cycle, slightly less than in other countries (~ 280 mbar in USA and up to 400 mbar in Japan). This may be fully compensated by turbine inlet control valves for the 6 CP0 units and 18 CP1 units, but the exercisability of the valve reaches its limit of optimum output for the 10 CP2 units and the 20 units of 1300 MW.

Without any proper action on maintenance, these units will have to decrease their thermal output before the end of their estimated life.

As an example, Figure 1 shows the pressure drop decrease versus time at 2 different units :

- Chinon B1 - 900MW - CP2 unit, under morpholine treatment at pH 9.2,
- Blayais 2 - 900 MW - CP1 unit under morpholine treatment at pH 9.6.

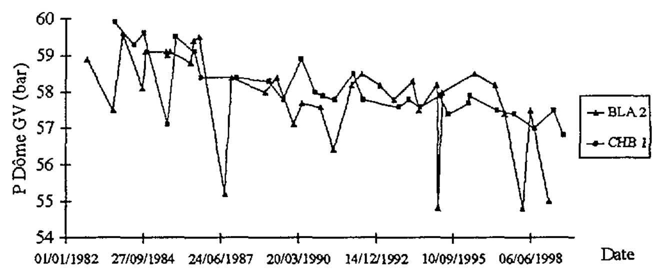

Figure 1 : Example of steam pressure drop at SG outlet of Chinon B1 CP2 unit and Blayais CP1 unit.

3. PRESSURE DROP CAUSES

In order to define the appropriate remedies able to recover the expected performances, it is important to clearly investigate the causes of steam pressure drop at SG outlet [1]. If fouling is obviously the main reason , other factors should be taken into account :

- number of SG plugged tubes (mainly for cracking of Inconel 600),

- presence of deposits on the primary side of SG tubes,
- modification of physical adjustment of the unit,
- uncertainty of physical measurements,
- potential influence of SG tubing thermal conductibility which is lower for Inconel 690 as compared to 600, after SG replacement inducing a power decrease if not compensated by a corresponding heat exchange surface increase.

4. IMPLEMENTED ACTIONS

Fouling mitigation is connected to secondary system corrosion actions which include :

- preventive actions on chemistry and corrosion,
- remedies such as sludge lancing or chemical cleaning, are directed towards main sources of fouling as well as on other sources such as the limitation of external pollutants ingress.

Table 1 - Main characteristics of French PWRs

Unit	Co Op	SG mat.	Cond. Mat.	Cool. Water	2 ry AVT
Fes 1	78	600M	CuZn	Rhin	M9.2 B
Fes 2	78	600M	CuZn	Rhin	M9.2 B
Bug 2	79	600M	316L*	Rhô	M9.6 B
Bug 3	79	600M	316L*	Rhô	M9.6 B
Bug 4	79	600M	316L*	T/Rh	M9.6 B
Bug 5	79	600T	316L*	T/Rh	Mo 9.6
Dam 1	79	690T	316L*	T/Lo	Mo9.6
Dam 2	81	600M	CuZn	T/Lo	M9.2 B
Dam 3	80	690T	316L*	T/Lo	Mo9.6
Dam 4	81	600M	CuZn	T/Lo	M9.2 B
Tri 1	80	690T	316L*	Rhô	Mo9.6
Tri 2	80	690T	316L*	Rhô	Mo9.6
Tri 3	81	600M	316L*	Rhô	Mo9.6
Tri 4	81	600M	316L*	Rhô	M9.6 B
Gra 1	79	690T	Ti	Sea	Mo9.6
Gra 2	80	690T	Ti	Sea	Mo9.6
Gra 3	81	600M	Ti	Sea	Mo9.6
Gra 4	81	690T	Ti	Sea	Mo9.6
Gra 5	85	600T	Ti	Sea	Mo9.6
Gra 6	85	600T	Ti	Sea	Mo9.6
Bla 1	81	600M	Ti	Estu	M9.6 B
Bla 2	83	600M	Ti	Estu	Mo9.6
Bla 3	83	600M	Ti	Estu	Mo9.6
Bla 4	83	600M	Ti	Estu	Mo9.6
SLB 1	83	690T	CuZn	T/Lo	Mo 9.2
SLB 2	83	600M	CuZn	T/Lo	M9.2 B
ChB 1	4	600M	CuZn	T/Lo	M9.2 B
ChB 2	84	600M	CuZn	T/Lo	Mo 9.2
ChB 3	87	600T	CuZn	T/Lo	Mo 9.2
ChB 4	88	600T	CuZn	T/Lo	Mo 9.2
Cru 1	84	600T	CuZn	T/Rhô	Mo 9.2
Cru 2	85	600T	CuZn	T/Rhô	Mo 9.2
Cru 3	84	600T	CuZn	T/Rhô	Mo 9.2
Cru 4	85	600T	CuZn	T/Rhô	Mo 9.2
Pal 1	85	600T	Ti	Sea	NH_3 9.7
Pal 2	85	600T	Ti	Sea	NH_3 9.7
Pal 3	86	600T	Ti	Sea	NH_3 9.7
Pal 4	86	600T	Ti	Sea	NH_3 9.7
Fla 1	85	600T	Ti	Sea	NH_3 9.7
Fla 2	87	600T	Ti	Sea	NH_3 9.7
SAL 1	86	600T	CuZn	T/Rhô	Mo 9.2
SAL 2	87	600T	CuZn	T/Rhô	Mo 9.2
Nog 1	88	600T	316L*	T/Se	Mo 9.6
Nog 2	89	600T	316L*	T/Se	Mo 9.6
Unit	MSI	SG mat.	Cond. Mat.	Cool. Water	2 ry AVT
Bel 1	88	600T	CuZn	T/Lo	Mo 9.2
Bel 2	89	600T	CuZn	T/Lo	Mo 9.2
Cat 1	87	600T	CuZn	T/Mo	Mo 9.2
Cat 2	88	600T	CuZn	T/Mo	Mo 9.2
Cat 3	91	600T	CuZn	T/Mo	Mo 9.2
Cat 4	91	600T	CuZn	T/Mo	Mo 9.2
Pen 1	90	600T	Ti	Sea	NH_3 9.7
Pen 2	92	690T	Ti	Sea	NH_3 9.7
Gol 1	91	600T	304L	T/Ga	Mo 9.6
Gol 2	97	690T	304L	T/Ga	Mo 9.6
Cho 1	00	690T	304L	T/Me	Mo 9.6
Cho 2	00	690T	316L	T/Me	Mo 9.6
Civ 1	00	690T	316L	T/Vie	Mo 9.6
Civ 2	00	690T	316L	T/Vie	Mo 9.6

(see detail explanations at §9)

4.1 Secondary water chemistry control

The optimisation of the best secondary water chemistry relies on all volatile treatment (AVT) with amines (morpholine) which is limiting flow assisted corrosion (erosion-corrosion) of carbon steel in the steam/water system.

Thus, the quantity of corrosion products entering the steam generators is minimised. The selection of the AVT options is a compromise between corrosion of the various components of the system [2]. It can be seen from Table 1 that :

- ammonia treatment at pH 9.7 is still applied in 8 sea water cooled units without copper alloys,
- morpholine treatment at pH 9.6 is selected on 28 units without copper alloys,
- morpholine treatment at pH 9.2 is used on 22 units still having copper alloys where it is not acceptable to operate at a higher pH due to copper dissolution.

As shown on Figure 2, morpholine treatment looks more favourable for minimising corrosion products transport and deposition, with about twice less sludge eliminated during refueling outages than when ammonia treatment is applied.

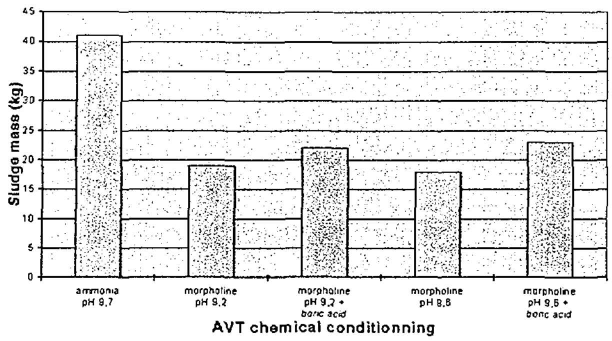

Figure 2 : comparison of sludge removed by lancing in some EDF PWRs units with various treatments.

It may be noted that 10 units also add boric acid in their secondary water in order to neutralise sodium hydroxide pollution and to decrease the secondary side corrosion of Inconel 600 MA tubing, very sensitive to stress corrosion cracking even in slightly alkaline environment.

The possibility of switching the 8 units still under ammonia treatment to morpholine treatment is under investigation, for decreasing flow assisted corrosion in some part of the system and quantity of corrosion products generated in the system.

Finally, after a test with ethanolamine (ETA) treatment on 1 unit during one fuel cycle, it appears that this is a viable alternative to morpholine with some little advantages and other disadvantages.

The main advantages and disadvantages of ETA versus morpholine are:

- a lower release of nitrogen compounds to the environment with ETA, due to a higher alkalinity and thus a lower molar concentration,
- a better protection of SG internals and MSR drains to Flow Assisted Corrosion with ETA, due to the lower partition coefficient and thus a higher concentration in liquid phase,
- a potential lower fouling of SG tube with ETA for the same iron concentration in feedwater, due to the difference of surface charges of magnetite,
- a lower protection of feedwater train against Flow Assisted Corrosion with ETA.

Before any changing of reagent, an official approval of French Ministers for Environment is requested to allow the corresponding release of the considered amine into the environment.

4.2 Materials replacement

A policy for progressively replacing copper alloys from condenser and low pressure heaters tubing by stainless steel (or other materials in some condenser cases) is implemented. The replacements occurs either during the same refueling as when some steam generators are replaced (already 9 units) or when the condenser tightness and integrity is not any more sufficient. The presence of copper has the main disadvantage for fouling of imposing an operation at a low pH (9.2 at 25°C) for avoiding ammoniacal corrosion. Such a low pH does not provide a sufficient protection of carbon steel against flow assisted corrosion. The progressive replacement of copper alloys allows an increase of room temperature pH up to about 9.5 - 9.8, depending on the reagent, which decreases the generation of corrosion products and subsequent SG fouling.

4.3 Elimination of sludge and deposits

The conventional lancing of the tubesheet in the bottom part of the steam generators, sometimes using a specifically more efficient process (CECIL tool) is one way of keeping a good cleanliness of the lower part of SG. CECIL is a registred name (Consolidated Edison Combined Inspection & Lancing system) corresponding to an improved system of lancing with access to an increased part of the bottom part of the steam generator.The lancing device is going inside the tube bundle, on the top of the tubesheet.

However, the efficiency for fouling is limited since 80% of deposits are located in the upper part of the tubing which is not cleaned by mechanical lancing.

Thus, only low amounts of sludge (< 20 kg) are typically eliminated. Based on such statement, the frequency of lancing on units with 600 TT or 690 TT, less sensitive to IGA/SCC SG tubing corrosion, is lower if the lanced mass during the past two refueling outages is lower than 12 kg of dry sludge [3]. Up to now, lancing of upper bundle part of SG is not expected to be implemented due to difficulties in introducing the corresponding tools in the SG.

The chemical cleaning of steam generators has been applied in 3 French PWR units with the EDF process.

It was applied first in Nogent 1 in 1989 and Saint-Alban 2 in 1990 for elimination of metallic particles which had been left from manufacturing. These metallic balls, at high temperature, even in the absence of contamination, have been normally oxidised by water, inducing a volume increase in the bottom part of the SG and denting (tubing diameter reduction) plus circumferential cracking from associated stress on the tubing. The chemical cleaning allowed the elimination of the oxides and then of the metallic particles. For the following units, a proper mechanical elimination of metallic balls before start up of the unit avoided the problem to occur again.

In 1992, the chemical cleaning of Fessenheim 2 has been carried out for mitigating secondary side corrosion (IGA/SCC) of SG tubing with sensitive Inconel 600 MA.

The purpose was to eliminate deposits of oxides in tube-tube support plates crevices and sludge pile above tubesheet where under heat flux, the contaminants may easily concentrate due to restricted flow.

In each case of chemical cleaning, several tons of iron oxides have been eliminated from the steam generators, allowing Fessenheim 2 to recover its initial pressure. In addition, the chemical cleaning has been of significant benefit on tubing corrosion mitigation.

Nevertheless, an insufficient control of chemicals velocity in some SG locations during Fessenheim 2 cleaning induced a too high corrosion of carbon steel. In addition, the length of the process, the quantity of wastes and the associated costs led EDF not to decide any other chemical cleaning up to now on French PWRs.

4.4 Limitation of contaminants ingress

Specific purification systems have been added in several plants in order to reduce important peaks of suspended solids introduced into the steam generators. This mobile system is used during start-up of each unit of a plant up to 20% nominal power for purification of the feed water by filter, ion exchange resins and fines filters.

The make-up water to the steam/water system is a significant source of soluble contaminants. Thus, additional polishing mixed beds, non regenerated, have been installed in the demineralisation station of the plants having units with sensitive SG tubing (Inconel 600 MA) to secondary side corrosion (IGA/SCC). The sodium content of make-up water is consequently lower.

The chemical quality of the reagents used either for resin regeneration or for secondary water treatment and the quality of the ion exchange resins for SG blowdown purification comply with particular chemistry specification labelled as PMUC (French initials for Products and Materials Used in Power Plants). This is a guaranty of soluble or insoluble contaminant ingress limitation.

5. NEW ACTIONS

The SG pressure drop led EDF to look for fouling indicators, to characterise deposits present in SG, to study deposition mechanisms and their influence on heat transfer in order to prepare its maintenance strategy [4].

5.1 Fouling indications

The main information is obtained from physical data during operation : SG temperature and pressure. The follow of hydrazine ratio (SG blowdown/feedwater), as proposed by the German, has been examined. Due to hydrazine reaction with oxides in SG, a ratio < 1 should be representative of a significant fouling while a clean SG tubing should show a ratio of about 2.

After measurements on 30 units in 1998 and 1999, contradictory results did not allow us to reliably identify which units were or not affected by fouling. However, ratios > 1 (low fouling) have been observed on units with morpholine treatment and limited hydrazine concentration in feedwater. The results representativeness may be affected by load follow which is frequent in French units, and by low hydrazine content in units with copper alloys.

5.2 Deposits characterisation

SG tubes have been pulled in the past for correlation between secondary side corrosion and deposit chemical composition. A new programme of pulled tubes examination and of sludge analyses has been started for preparing a potential chemical cleaning of Chinon B1 SG in 2003 (see § 5.5).

In addition to chemical composition, the deposit structure will be investigated : number and thickness of layers, porosity, density, oxide form so as to better understand deposition mechanism, evaluate its impact on heat transfer and prepare a chemical cleaning, if necessary.

5.3 Non destructive examination

An Eddy Current control at low frequency will be studied in order to try an evaluation of fouling localisation on the tube bundle and of deposits thickness. The results will be cross-checked by TV inspection.

5.4 Modelisation

From corrosion product transport into SG, a loop study of mechanism for deposit formation is expected. Feedback from operating units is limited due to the absence of regular analysis of suspended solids and soluble iron and copper. These parameters are only measured occasionally since their representativeness is poor in case of load follow with flow transients. Results with various secondary water treatments will be compared with additional measurements, if necessary.

The results from deposits analyses on pulled tubes and from non destructive examination will be used to validate the calculation codes from modelisation and to evaluate the influence on heat transfer.

The final objective is to provide the plant operators with a predictive tool on fouling allowing to schedule appropriate maintenance remedies. The study will go on with the evaluation of the most important parameters for fouling : secondary water treatment selection (pH reagent) and hydrazine concentration influence on oxides production and deposition.

5.5 Chemical cleaning

The progression of secondary corrosion (IGA/SCC) on Inconel 600 MA SG tubing at tube support plate level and the evolution of fouling led EDF to reconsider its position of non implementing chemical cleaning after Fessenheim 2 operation in 1992 [5].

Thus, a chemical cleaning is scheduled at Chinon B1 in 2003 with the double objective of IGA/SCC corrosion mitigation under broached tube support plates and SG pressure recovery. EDF chemical cleaning process having been given up, an evaluation of various available processes all over the world has been made. The high temperature on line process during cold shutdown [6] having many advantages (short time, good corrosion control and low waste quantity) is in the list of the considered processes. In France, environmental regulation does not allow any release of complexing reagents such as EDTA, which is the base of chemical cleaning solutions for iron oxides dissolution.

The study and implementation of treatment methods for elimination or transformation of EDTA containing wastes is of absolute necessity. The results of this first chemical cleaning with another process than the EDF one applied in the past, will be a test for potential other chemical cleaning operations in other French PWR units.

6. FUTURE ACTIONS

The already initiated programme will be extended with alternative ways of fouling mitigation. Among these, on-line addition of dispersant [7 - 8] is a promising mean. It has the advantage of being done on-line, without spending time for cleaning, preventively, at low cost, without associated waste problem. The principle is to use a PAA (polyacrylic acid) which keeps the iron oxide in the SG water with more efficient elimination through SG blowdown, drastically decreasing the proportion of iron oxide able to deposit on SG tubing. A decision of potential application on French plants will be taken after trial tests expected in other countries.

The improvement of secondary water treatment specification, mainly the optimisation of hydrazine concentration during operation and shutdown (SG lay up) will be a potential way of decreasing oxides production.

Other soft cleaning methods for elimination of deposit and fouling of slightly affected SG will be examined. The soaking methods already tested in USA are the PMC (Preventive Maintenance Cleaning) and the SCA (Scale Conditioning Agent). Standard Chemical cleaning process remains the most efficient remedy but the implementation cost is higher and the management of wastes is more difficult.

7. CONCLUSION

As observed on Nuclear Power Plants in other countries, the French PWR units are progressively affected by secondary side fouling of their steam generator tubing. The heat transfer decrease induces a SG pressure drop. The output adjustment flexibility is already reaching zero in about 50% of the units. This led EDF to keep implementing remedial actions for secondary system corrosion mitigation which also contribute to fouling limitation and to start a specific comprehensive programme of study for recovering output performances.

The following actions have been decided :

- define a SG fouling indicator,
- characterise physico-chemical composition of deposits present in SG, localise them and estimate their thickness by non destructive low frequency Eddy Current method,
- study and modelise deposition mechanism in loop test,
- optimise secondary water treatment (reagent and hydrazine content),
- carry out maintenance activities such as mechanical sludge lancing and chemical cleaning,
- evaluate alternative methods like on-line dispersant addition in the secondary system.

Hopefully, the programme implementation should be able to keep a high output with sufficient adjustment flexibility at the lowest possible cost and with limited undesirable wastes.

8 - REFERENCES

[1] Steam generator thermal performance degradation - Case studies EPRI TR 110018 - July 1998.

[2] F. Nordmann. EDF. Approach on steam-water chemistry and corrosion - ESKOM International Conference on Process Water Treatment and Power Plant Chemistry - Midrand, South Africa, 26-28 November 1997.

[3] P. Lemaire - M. Dijoux. Impact of sludge at EDF plants - EPRI Sludge management workshop – Scottsdale, USA, October 1999.

[4] A. Stutzmann - L. Viricel - M. Dijoux. French experience on OD IGA SCC and fouling of SG tubes BNES Bournemouth Conference, UK October 2000.

[5] F. Nordmann - A. Stutzmann, P. Lemaire. La maîtrise de la corrosion secondaire des tubes GV à EDF. Fontevraud IV International Symposium, SFEN, France - September 1998.

[6] S. Odar. Crevice cleaning experience with a KWU chemical cleaning process SFEN International Conference on "Chemistry in Water Reactors" - Nice, France, 24-27 April 1994

[7] A. Gryscavage - D. Jones - BetzDearborn Dispersing iron in nuclear Steam Generators - EPRI condensate polisher workshop June 2000.

[8] P Frattini - EPRI Dispersants Trial at ANO 2 : qualification for replacement SGs with Alloy 690 - « EPRI Meeting of Steam Generator Project », Albuquerque, USA, December 2000.

9. NOTES FOR TABLE 1

Plant & Unit names:
Fessenheim, Bugey, Dampierre, Tricastin, Gravelines, Blayais, Saint-Laurent B, Chinon B, Cruas, Paluel, Flamanville, Saint-Alban, Nogent, Belleville, Cattenom, Penly, Golfech, Chooz B, Civaux.

Co. Op = Year of Commercial Operation

SG Mat. = Steam Generator tubing material
600M = Alloy Inconel 600 Mill Annealed
600T = Alloy Inconel 600 Thermally Treated
690T = Alloy Inconel 690 Thermally Treated

Cond. Mat. = Condenser tubing material
CuZn= Copper Zinc Alloy (Brass)
316 L = Stainless Steel 18 %Cr – 10 % Ni + Mo
304 L = Stainless Steel 18 %Cr – 10 % Ni
Ti= Titanium
316L* : * means that 316L replaced original brass.

Cool. Water = Condenser Cooling water
Rhin = Rhine River
Rhô = Rhône River
Lo = Loire River
Sea = Sea Water
Estu = Estuary Water
Se = Seine River
Mo = Moselle River
Ga = Garonne River
Me = Meuse River
Vi = Vienne River
T/ = with Cooling Tower

2ry AVT = Secondary Water Conditioning with All Volatile Treatment
M9.2 B = $pH_{25°C}$ of 9.2 with Morpholine + Boric acid addition.
M9.6 B = $pH_{25°C}$ of 9.6 with Morpholine + Boric acid çaddition.
Mo9.2 = $pH_{25°C}$ of 9.2 with Morpholine.
Mo9.6 = $pH_{25°C}$ of 9.6 with Morpholine.
NH_3 9.7 = $pH_{25°C}$ of 9.7 with Ammonia.