SECONDARY SIDE IGA/IGSCC OF SG ALLOYS 600, 690 AND 800 : R&D PROGRAM IN EDF LABORATORIES

F. VAILLANT[1], O. DE BOUVIER[1], M. BOUCHACOURT[2], A. STUTZMANN[3], P. LEMAIRE[4]

ABSTRACT

Many steam generators (SGs) equipped with "mill-annealed" (MA) Alloy 600 tubings suffer significant secondary side corrosion. Until now, no degradation has been observed with either Alloy 600 TT or Alloy 690 for new SGs. The understanding of IGA/SCC of Alloy 600 MA in plants and the development of predictive models have become an important challenge to assess the life span and to reduce the maintenance costs of SGs.

As degradation occurs in crevice environment,s which are varied and little known, EDF has undertaken an important program to improve the knowledge of crevice environments which lead to cracking. Corrosion tests are performed on Alloys 600 MA (also on 600 TT) in various environments in order to reproduce the deposits and the cracking observed on pulled tubes in laboratory conditions. Other corrosion tests are conducted in environments containing some pollutants identified by analyses of secondary water after hideout-return (sulfates) or oxidizing compounds,... : the influences of pH and potential are evaluated on Alloy 600 (MA or TT) and also on Alloys 690 and 800.

A comprehensive model is proposed using IGA/SCC results of Alloy 600 in caustic environments. The thermomechanical parameters of the tubes and the field environmental conditions, introduced in the model, confirm some important features of SGs tubings. The model will be improved to include other detrimental environments. It will provide a usefull tool to predict the life span (then steam generator replacements) and to optimize the maintenance policy of SGs still equipped with Alloys 600 MA and particularly with 600 TT (frequency and best locations of inspections). Margins will also be assessed for new SGs equipped with Alloy 690, and a comparison will be performed with Alloy 800.

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OBJECT

Hot legs of mill-annealed (MA) Alloy 600 tubings are affected by Intergranular General Attack (IGA) and Intergranular Stress Corrosion Cracking (IGSCC) on the secondary side of EDF steam generators. Some transgranular cracking has also been observed in relation to lead. All the cracks occur in flow-restricted areas (crevices between tubes and drilled tube-support plates (TSPs) in the sludge pile above the tubesheet (TS) or under the top of the TS) where chemical compounds are able to concentrate.

The local environment is varied and little known, so the influence of the main chemical parameters on the different types of corrosion is misunderstood. The crack propagation rates - which are of major concern for the maintenance policy of SGs - are also not clearly determined particularly for circumferential cracking at the TS, since plugging is carried out as soon as a crack is detected.

With regard to SGs equipped with tubings in thermally-treated (TT at 700°C) Alloy 600, no cracking has been reported but the margins in preliminary laboratory tests with respect to MA-Alloy are not so important and some corrosion could occur in the future.

Since 1984, the new SGs hace been equipped with Alloy 690 TT (30% chromium) : no corrosion was reported from field experience. Other countries use Alloy 800 (40% iron, 33% nickel, 20% chromium) successfully. With regard to Alloy 600 MA, the margins with these alloys are of course substantial in terms of initiation for corrosion but they cannot be quantified since no cracking has been observed in any plants.

So EDF has undertaken an important R&D program in order to help to :

- plant operation by identification of crevice environments responsible for IGA/SCC of tubes in Alloy 600 MA and by a contribution to the improvement of water chemistry requirements (sulfates..., hydrazine).

- the optimization of the maintenance policy by reduction of costs for SGs equipped with 600 MA or TT (location and frequency of controls, sludge lancing, planification of steam generator replacements (SGRs)).

- the assessment of the margins in terms of life duration with Alloys 690 and 800.

CURRENT STATUS ON SECONDARY SIDE IGA/SCC

A general overview [1] has been performed, including field experience (chemistry and corrosion), corrosion tests in laboratory during the last 20 years - the greatest part involving experiments in caustic environments - and a first step of a model for initiation and propagation has been proposed from tests in caustics. The results of the model have been compared to SGs behaviour [2].

Field experience

Secondary side corrosion on Alloy 600 MA occurs in flow-restricted areas where pollutants could concentrate. The local environment is varied and little known. During the first years of the operation with the oldest SGs, the local enironments in the crevices were thought to be mainly alkaline. But the improvement of the water chemistry - AVT treatment, no regeneration of resins, use of mixed beds for water purification - has led to less caustic environments (analyses of secondary water after hideout-

return (HOR) at Saint-Laurent B1, the most affected unit by IGA/SCC before SG replacement [3]). Analyses of deposits and films on pulled tubes have revealed that corrosion could be related to aluminosilicates in the deposits together with a brittle underlying chromium-rich layer [4].

Laboratory tests

Most of the corrosion tests were conducted in caustic environments. Though some questions may arise about their representativity of local chemistry, these conditions have reproduced the main degradations and material effects observed in service. It was found that the lower the yield stress of the tube the higher the sensitivity to IGA/SCC in caustic solutions, as it has been observed in Saint-Laurent B1 (figure 1, [3]). Tests in sodium hydroxide have also proved the beneficial effect of TT at 700°C [5,6]. Alloys 690 and 800 had a higher resistance to SCC in caustic environments than Alloy 600 and lead was always detrimental [6].

Complex acidic environments ($pH_T < 5$) could also induce severe cracking of Alloys 600 and 800, while Alloy 690 had the best resistance to corrosion in non-oxidizing conditions [6, 7].

But very few results were available for pH_T 5 to 9,(figure 2), [1, 8]. The local chemistry was probably very complex ; some cracking has been reported in laboratory with Alloy 600 in environments containing pollutants observed in SGs (aluminosilicates with organic species and phosphates) [4]. These degradations are still poorly understood, not easy to reproduce and the behaviour of Alloys 690 and 800 in these conditions are not known.

First proposed model of IGA/SCC

There are two possible ways for the development of predictive models of IGA/SCC applied to plants.

The first relies on the observation of damages as measured by inspections (eddy currents) on Alloy 600 MA at TSP elevations. A wide range of numerous damages (in millivolts) is required to get a conservative prediction of corrosion. This approach is of course not possible on Alloys 600 TT and 690 (no detected damage in SGs) or when the kinetics of corrosion cannot be measured (circumferencial cracking at the TS on 600 MA).

The other, a mechanistic model, relies on the corrosion behaviour in laboratory. The initiation time and the crack propagation rates are a function of pH, temperature, stress and tube characteristics as determined by laboratory tests. The first approach based on results in caustic environments is very attractive [2]. CGRs deduced from the model are consistent with CGRs from plants at pH_T about 10 for IGSCC (at TS and TSP elevations) and at pH_T about 10.5 for IGA at TSP elevation. In these conditions, the location and the orientation of the cracking, the influences of the yield stress and TT(700°C) are explained, and the location of first possible cracks of Alloy 600 TT can be predicted. This model will be fully predictive when the improvement resulting from the proposed program has been achieved.

R&D PROGRAM

Help to plant operation

Identification of the environments responsible for the cracking in SGs

Chemistry in flow-restricted areas can hardly be obtained from in-situ measurements. Only indirect information is available from analyses of deposits and films on pulled tubes and from analyses of secondary water after HOR.

Reproduction in laboratory of deposits, films and corrosion damages observed in SGs

The program proposes reproducing in laboratory conditions the aluminosilica gel with the underlying brittle Cr-rich layer and the cracking observed on pulled tubes. Complex environments are fabricated with the main pollutants (silica, alumina, phosphates, acetates as a result of thermal decomposition of morpholine) which could be detrimental to Alloy 600 MA or sensitized according to [4].

- The conditions leading to the formation of the deposits and of a brittle Cr-rich on Alloy 600 MA are investigated (pH, temperature, water treatment (morpholine or ammonia together with hydrazine)). The influence of pollutants is examined separately or with interactions during short-term tests (200 h). The ability of a crevice environment to destroy a protective film (preformed in pure ammonia) is also studied. During the surface analysis, the ratio Ni/Cr in the film is examined in relation to pH and redox conditions.

- Corrosion tests (2500 h) are also performed on C-rings stressed at 0.8YS, YS and more than YS in static autoclaves at 320°C, particularly in environments which have produced the deposits and the brittle Cr-rich layer. Alloys 600 MA, TT or sensitized and 690 are investigated. The matrix of the deposits and corrosion tests is provided in table 1.

Effect on IGA/SCC of the main chemical species identified by analyses after HOR

The detrimental effect of sulfate - which is one of the main pollutants at the blowdown of SGs after HOR[1] - is investigated on Alloy 600 MA : this species could not be observed on deposits and films, due to its solubility at low temperature. Some interactions with different redox conditions are also examined. They could lead to surface films and damages different from those examined in 3.1.1.1. Surface analyses (Ni/Cr ratio) and corrosion tests of 2500 h on C-rings are performed at 320°C in static autoclaves at corrosion potential in the following conditions :

- <u>Sulfates</u> : The influences on IGA/SCC of pH_T and sulfate concentration are investigated at pH_T of 5, 6, 8 and 9.5 and sulfate concentration 100, 5000 and 57000 ppm. The highest concentration is calculated code from HOR concentration in secondary water using MulteQ code.

Available results demonstrate that Alloy 600 (MA or TT) is very sensitive to IGSCC above 5000 ppm in some conditions, Alloy 800 is susceptible to IGSCC at pH 5 and 6 at 57 000 ppm and Alloy 690 is immune to SCC in all the investigated conditions.

- <u>Reduced-S species</u> as a consequence of the reduction of sulfates into thiosulfate and sulphide by hydrazine[2]) : corrosion tests on C-rings (as previously) are performed at pH_T = 5 and 8, 320°C. The thermodynamical stability of the different S-species are examined as a function of the potential.

- <u>Sulfates + oxidizing species</u> : in order to examine whether oxidizing conditions during start-up after shutdown could explain the damages observed in SGs, corrosion tests on C-rings are conducted in a weakly detrimental solution (5000 ppm sulfate) containing Cu or $Cu(NH_3)_4^{2+}$ or CuO or magnetite), table 2.

<u>Help to the chemical requirements of secondary water</u>

Hydrazine is added in the feedwater of SGs in order to obtain reducing conditions : its content is limited to 25 ppb for plants with copper alloys, but it can be higher for plants without copper. Nevertheless, the

[1] Lead is one of the most detrimental pollutants in plants with respect to IGA/SCC at any pH. In order to avoid hidden effects with other pollutants, lead is not introduced in this program. In addition, the study will not account for any specific effect of sodium, since it has been widely investigated during the two past decades.

[2] An increase of hydrazine content in secondary water is investigated in order to obtain reducing conditions in plants. A decrease of the amount of sludge is also expected from this increase of hydrazine, but other studies are also performed to assess the influence of hydrazine on flow-assisted corrosion on carbon steel in SGs.

hydrazine content has to be limited because flow-assisted corrosion could occur on the TSPs in carbon steel.

The program contributes to determine the maximum concentration of sulfates together with hydrazine content in order to avoid SCC of Alloy 600 with reduced-S species. Tests are performed in autoclave with a refresh device to control the hydrazine content. Of course, the results will require a validation in representative conditions in the future.

Optimization of maintenance ; life span

A precise model for initiation is necessary to assess life span of SGs equipped with Alloy 600 MA or TT. In the case of Alloy 600 TT, a predictive approach from field experience is not possible since corrosion has not been observed until now. Moreover, a model for propagation would be useful to help with the operation and maintenance of SGs.

The development of the corrosion model will use the laboratory data generated in 3.1, and will require :

- a comprehensive study of IGA/SCC to allow the determination of the parametric functions in laboratory conditions,

- a thermomechanical analyse of SG tubings,

- the development of the model itself in order to ensure that the life duration of remaining SGs in Alloy 600 MA and the more recent SGs in Alloy 600 TT will be at least 40 years. Margins will be assessed with Alloys 690 and 800.

<u>Comprehensive study of IGA/SCC</u>

Environmental conditions (potential, pH, concentration) : *The question arises as to whether the detrimental effect of the various pollutant is the result of potential or pH. This approach is useful in order to conclude whether cracking in SGs was mainly the consequence of the start-up conditions, until the oxidizing compounds were consumed. The corrosion tests at free potential with the investigated pollutant are described in 3.1 and the potential of the specimen is measured. Then this potential is applied on a C-ring without the pollutant at 320°C ; the CGRs with and without pollutant are compared to conclude on a purely potential effect.*

The influence of the concentration of pollutant (sulfates, ...) and pH will be assessed using the measurement of the dissolution rate by polarization resistance. This approach will be very usefull to take into account the great variability of local chemistries in plants. It will also save some long-term tests of corrosion.

Material parameters : *One basic objective of this program is to assess the life span of SGs equipped with 600 TT, in comparison with 600 MA. Safety margins with Alloys 690 and 800 are also evaluated. In any case, initiation time and crack growth rates are measured together on each alloy during the tests performed in 3.1. The detrimental effect of a low yield stress will be examined on Alloy 600 MA in 2 typical environments.*

Stress : *During the tests performed in 3.1 at 320°C, the stress levels are 0.8YS, YS and higher than YS for Alloy 600, YS and higher than YS for Alloys 690 and 800. The stress intensity factor threshold K_{ISCC} is also assessed in two typical environments in order to reach the critical size defect[3] (transition between slow propagation rate to rapid propagation rate).*

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[3] The critical size defect is related to the stress intensity factor threshold K_{ISCC}. It is defined as the crack depth transition between the slow (stable) propagation rate and the rapid propagation rate.

Temperature : *The influence of temperature on IGA/SCC is evaluated by a few corrosion tests on C-rings from each alloy at 290°C in 2 environments found to be very detrimental to Alloy 600 MA (minimum duration 3000 h).*

Development of the corrosion model

This is the main objective of the present program in order to propose help with maintenance of SGs.

Improvement of the first approach of the model

The first approach of the model [2] based on corrosion tests in sodium hydroxide solutions includes :

- the parametric functions of corrosion (IGA and IGSCC) in laboratory condition : initiation (time and stress threshold), slow-propagation rate and critical size defect versus temperature, stress, environment parameters (pH, potential) and material parameters (Alloys 600 MA and TT).

- an thermomechanical analysis of the tubes at the crevice locations (TSP, TS) during operation for each alloy/SG system.

- a predictive application of the model : local pH calculated from analyses after HOR, stresses and temperature of the main investigated locations will be introduced in the model for the remaining SGs with Alloy 600 MA and particularly for locations without CGRs from field experience (circumferential cracking under the top of the TS). The predictive approach will be performed also on Alloys 600 TT[4] and 690.

- a probabilistic approach will improve the model by including distributions of YS from plants and of stresses in operation.

- a software application will facilitate the use of the model based on caustic environments.

Extension of the model to other environments

A second important improvement of the model will be realized, similarly based on corrosion data from laboratory performed in neutral to mildly alkaline environments.

Global model

The global model will provide initiation, slow CGRs and critical size defects in all the environmental conditions mentioned above. The environmental conditions in SGs will be introduced with calculated pH after HOR and the main concentration of pollutants. The CGRs will be expressed in micrometers per hour (or angular sector /h) and an attempt to get a translation into millivolt per operating cycle will be proposed in case of validation.

The model will be improved by including a statistic / probabilist approach to account for the variety of field experience (materials (YS), stresses,...). A software application from this model will be developed for users.

CONCLUSION

An important R&D program to investigate IGA/SCC of steam generator (SGs) tubings is under way for 3 years. The main results of this program will provide a better understanding of crevice environmens and will contribute to the future improvement of the chemical requirements of the secondary water.

It will also provide a useful tool for operation and help with the maintenance policy of SGs : life span of SG (essential for scheduling of SG replacements) and crack propagation rates (for prediction and

[4] Life duration will be assessed as the time to reach a crack depth of 400 μm for a circumferential crack, on the basis of examinations of pulled tubes in Alloy 600 MA. This crack depth is suitable to ensure the mechanical resistance of the tube with safety margins.

control of corrosion) as a function of the main environmental and thermomechanical operating conditions of SGs equipped with Alloy 600 in the MA and TT conditions.
Margins with Alloy 690 will be assessed, and a comparison will be performed with Alloy 800.
At the end of the 3 year-period, the predictions of corrosion evolution from the developed mechanistic approach and from inspections of the tubing in Alloy 600 MA will be compared. If the approaches are in accordance, they could be linked together. Another prospect could be a coupling of a corrosion code with a chemistry code - as MulteQ - in order to obtain a direct input of the crevice chemistry of a given unit into the predictive model of corrosion.

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Table 1 - Reproduction in laboratory of deposits / films and cracking observed on pulled tubes : matrix of the tests

	Reference environm^t^ = R	R + Al_2O_3	R + $Ca_3(PO_4)_2$	R + acetate	R + Al_2O_3 + $Ca_3(PO_4)_2$ + acetate	R + Al_2O_3 + $Ca_3(PO_4)_2$ + acetate + sulfate	morpholine + silica
Objectives	Nature of the tests						
Effect of pollutants	-depos./film - IGA/SCC	-depos/film - IGA/SCC **	-depos./film - IGA/SCC **	-depos./film - IGA/SCC **	-depos./film - IGA/SCC	-depos./film - IGA/SCC	-
Effect of preoxidation in AVT	depos./film						
Effect of pH						-depos./film at pH 5, 6, 8	
Effect of water treatment							depos./film

* reference environment : AVT (ammonia + 2 ppm hydrazine pH_{20} 9.3) + 2 g/l SiO_2, 320°C

** corrosion tests with Alloy 600 only

Table 2 - Matrix for the tests performed with oxidizing compounds

Environment	Reference R' : sulfates (5000 ppm), pH_T 5	R' + Cu	R' + $Cu(NH_3)_4^{2+}$	R' + 0.01% Cu_2O + 0.01% CuO	R' + 1% Cu_2O + 1% CuO	R' + Fe_3O_4
Electrochemical tests	yes	yes (galvanic effect)	yes	yes	yes	yes
Corrosion tests (C-rings)	yes	yes	yes	yes	yes	yes

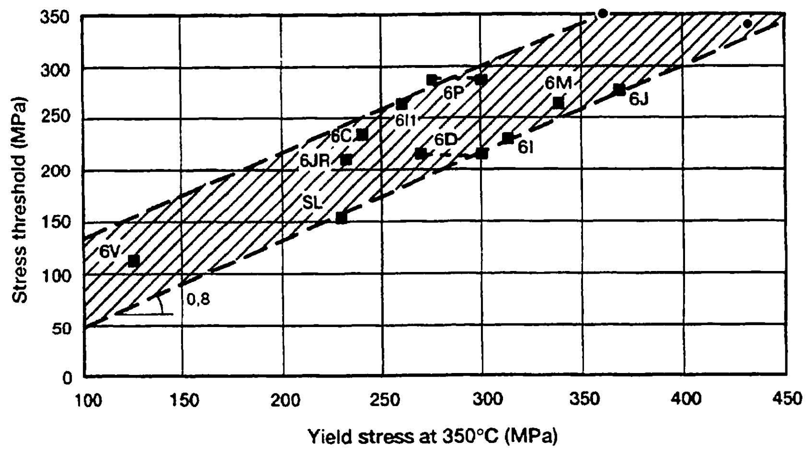

Figure 1 - Relationship between the stress threshold and YS_{350} of Alloy 600MA in sodium hydroxide 100 g/l, 350°C [1, 3, 6] (each point represents a tube)

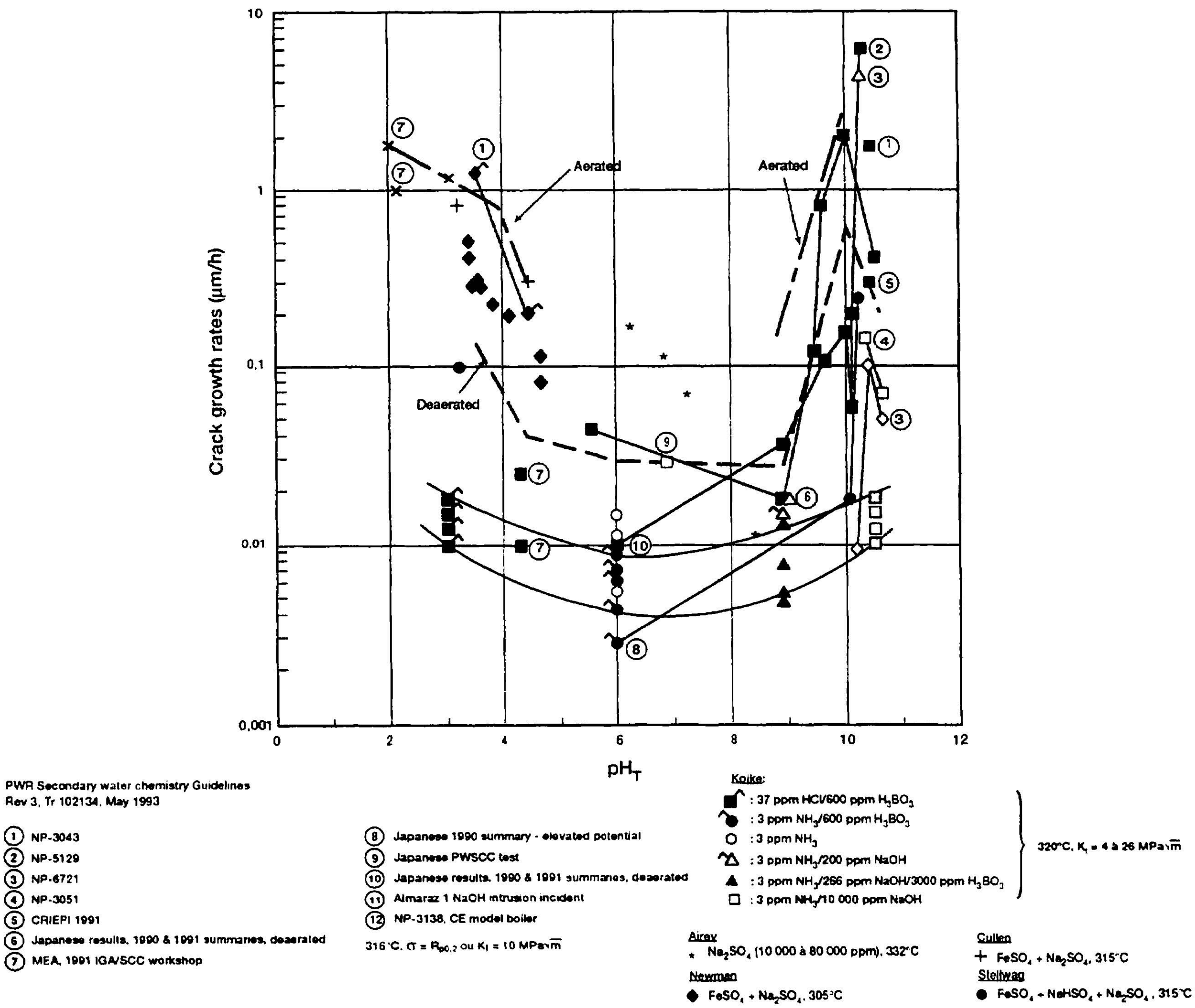

Figure 2 - Crack growth rates of Alloy 600MA versus pH at temperature [1, 8]

DISCUSSION

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Paper: Secondary Side IGA/IGSCC of SG Alloys 600, 690 and 800: R&D Program in EDF Laboratories

Questioner: J. Gorman

Question/Comment:

Will lead be included in your model? If not, why not?

Response:

We do not intend to include lead in our model in a first approach, because we do not wish to modify the response of other parameters that could be hidden due to the high detrimental effect of lead in many environments.

Though lead could be present in several circumstances in SGs, very few cases were attributed to Pb SCC in EDF plants. Transgranular or mixed cracking were scarcely observed (Bugey 3 Unit). In most of the investigated conditions in laboratory, lead has induced TG or mixed cracking or deep general corrosion. Environments without lead have generally induced IGA/IGSCC.