

CC/9088

A-44 - P.1

SCECF

FR9302248

CICA

CEA-CONF--11381

## ELECTROCHEMICAL MEASUREMENTS IN PWR STEAM GENERATORS TO FOLLOW CREVICE CHEMISTRY

FERON Damien, Commissariat à l'Énergie Atomique  
Laboratoire d'Essais Technologiques de Corrosion,  
BP 508 50105 CHERBOURG CEDEX - FRANCE  
Phone : (33) 33 03 68 17 FAX : (33) 33 03 75 24

### ABSTRACT

In PWR steam generator crevices, the evolution of chemistry is important for the understanding of corrosion phenomena. Electrochemical measurements have been performed in high temperature simulated crevice environments in order to follow hideout processes and remedial actions (on-line addition of boric acid). Reported tests have been conducted with model boilers of AJAX facilities. Eccentric and concentric tube support plate crevices have been instrumented with platinum electrodes. Electrochemical measurements have been collected when model boiler was under nominal conditions (primary temperature 335°C, secondary temperature : 280°C). They include Electrochemical Impedance Spectroscopy (EIS) and potential measurements : with EIS, sodium and boric acid hideouts have been detected and followed. Potential measurements have been performed in an attempt to measure crevice pH evolution.

### INTRODUCTION

In recirculating Steam Generator (SG) of Pressurized Water Reactors (PWR), degradations of alloy 600 tubing from secondary side may occur in flow restricted regions such as in support plate crevices. In these crevices, contaminants that are at  $\mu\text{g.kg}^{-1}$  concentrations in the steam generator water may concentrate to weight percent concentrations. Concentration process is possible because there is a temperature difference, called superheat, between the tube surface and the bulk water. Contaminants concentrate until the boiling point of the crevice liquid is elevated to the tube wall temperature or the contaminants precipitate in crevice. In the case of soluble

species like sodium hydroxide, solutions up to 40 weight percent can form in the crevice. These concentrated sodium hydroxide solutions lead to tubing degradation such as stress corrosion cracking or intergranular attack [3].

In these PWR steam generator crevices, the evolution of chemistry is closely related to the corrosion phenomena which may affect tubes. In order to follow crevice chemistry, electrochemical measurements have been performed in high temperature simulated crevice environments. They include crevice potential and crevice resistance measurements. Crevice resistance measurements have been performed in order to follow the evolution of the crevice solution concentration (evolution of the solution resistance). Crevice potentials have been measured in an attempt to follow the pH evolution during hideout processes or remedial actions.

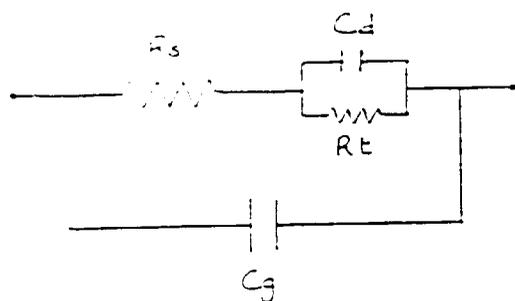
### TECHNICAL APPROACH

#### Crevice resistance

To perform conductivity measurements inside a tube support plate crevice, the electrochemical cell was composed of :

- a platinum electrode set in the support plate ;
- the tube itself which was the second electrode.

The characteristic of this design is that the measurements were made through the whole crevice medium. This electrochemical probe with two electrodes is a conductivity cell which is electrically similar to the electric circuit shown in figure 1 : the transfer resistance,  $R_t$ , and the double layer capacity,  $C_d$ , are correlated to electrode properties (corrosion).  $C_g$  is the geometrical capacity (cell parameter) and  $R_s$  is the electrolyte resistance i.e. the crevice medium resistance.



$C_g$  = geometrical capacity     $C_d$  = double layer capacity  
 $R_s$  = electrolyte resistance     $R_t$  = transfer resistance

Fig. 1: Electrical equivalent of a conductivity cell [2].

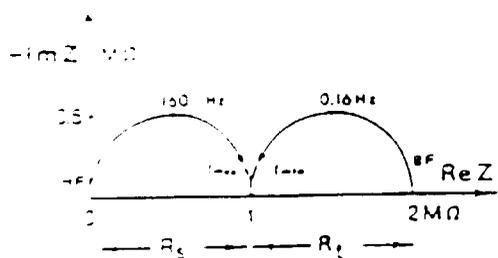


Fig. 2: Theoretical impedance diagram for a conductivity cell. Nyquist representation - ( $R_s = R_t = 10^6 \Omega$ ;  $C_g = 10^{-9} F$  and  $C_d = 10^{-6} F$ ) [2].

In order to measure  $R_s$ , Electrochemical Impedance Spectroscopy (EIS) is needed: as an example, figure 2 represents the EIS diagram for the equivalent circuit of figure 1 calculated with the following resistance and capacitance values:

$$R_s = R_t = 10^6 \Omega \text{ and } C_g = 10^{-9} F, C_d = 10^{-6} F$$

In this case, two half circles are obtained for the EIS diagram. The solution resistance  $R_s$  is found at the intersection of the 2 half-circles on the real axis, that is to say at frequencies between 1 and 10 Hz. It is obvious from this diagram that the measured resistance will not be the true solution resistance  $R_s$  if measurements are done at lower or higher frequencies. Of course, the shape of the EIS diagrams is function of the relative values of the parameters  $R_s$ ,  $R_t$ ,  $C_g$  and  $C_d$  and only one circle or one part of a circle may be obtained [2].

In order to link the evolution of crevice resistance with hideout process, theoretical calculations

and associated tests have been performed for a previous work and are reported in [3]. The main conclusions were: when hideout occurs with sodium hydroxide, the crevice resistance decreases; but when hideout occurs with boron, the crevice resistance increases in caustic preloaded crevices.

#### Crevice pH

To follow pH evolution inside tube support plate crevice, two platinum electrodes were used: one inside the crevice and the other one in the bulk water [1]. The following assumptions need also to be done:

- platinum electrodes can serve as hydrogen electrodes (there is a small amount of dissolved hydrogen in S.G. water);
  - redox potentials in the bulk water and in the crevice are controlled by the half reaction
- $$H_2 \rightleftharpoons 2H^+ + 2e^-$$
- all parameters are hold constant during the test, except  $H^+$  (or their effects on platinum potential are lower than the  $H^+$  influence);
  - temperatures are the same inside and outside the crevice (or the temperature influence is not important).

Thus the platinum potential difference between the crevice ( $E_c$ ) and the bulk ( $E_b$ ) corresponds to:

$$E_c - E_b = -2,3 \frac{RT}{F} (pH_c - pH_b) \quad [1]$$

with  $pH_c = pH$  inside the crevice and  $pH_b = pH$  in the bulk.

$$pH_c = pH_b - 8,8 (E_c - E_b)$$

So, if the above assumptions are correct, it is possible to follow the evolution of  $pH_c$  (inside the crevice) by the measurement of the platinum potential difference  $E_c - E_b$ .

#### EXPERIMENTAL DEVICE

The platinum electrodes (figure 3) are composed of a short platinum wire welded to a zircaloy wire of the same diameter (1 mm). A zircaloy sleeve surrounds the weld to get a better mechanical resistance. The electric insulation is made by a zirconia layer produced by oxydation in air. These electrodes were put inside the crevice or outside, in the bulk water.

Two types of tube support plate (TSP) crevices were used :

- a concentric and open TSP crevice (gap : 0.2 mm) was instrumented with one internal electrode and one external electrode (figure 4) ;
- an eccentric TSP crevice with 3 platinum electrodes : one near the contact point, another one in front of the largest gap (0.4 mm) and the third one in front of the standard gap (0.2 mm), as shown in figure 5.

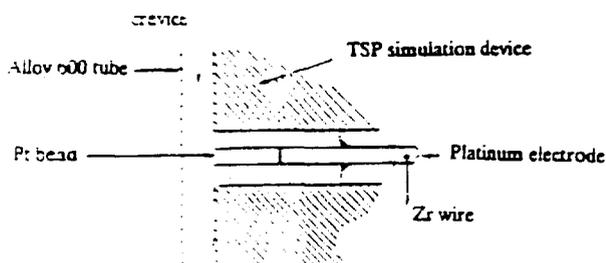


Fig. 3 : Platinum electrode in the TSP crevice

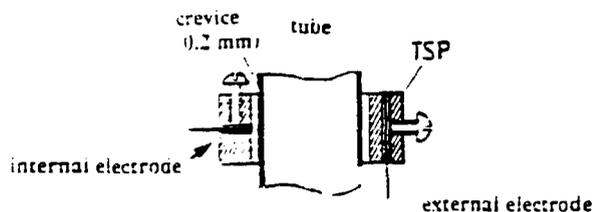


Fig. 4 : Platinum electrodes at the concentric and open TSP crevice

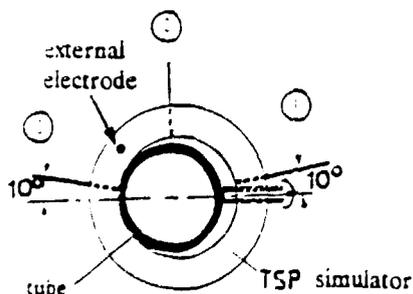


Fig. 5 : Schematic of the positions of platinum electrodes at the eccentric TSP crevice (1, 2 and 3 : internal electrodes)

## EXPERIMENTAL CONDITIONS

One model boiler of AJAX loop was equipped with the two TSP simulators described above and instrumented with platinum electrodes. On primary side, the temperature was held constant at 335°C during the test and a lithium-boron chemistry was used with addition of hydrogen (30 cm<sup>3</sup> H<sub>2</sub>/kg H<sub>2</sub>O). On secondary side, the temperature was 280°C and the All Volatile Treatment (AVT) was used : 0.27 mg.kg<sup>-1</sup> NH<sub>4</sub><sup>+</sup> with 0.05 mg.kg<sup>-1</sup> N<sub>2</sub>H<sub>4</sub> and less than 10 µg.kg<sup>-1</sup> O<sub>2</sub> in the feed water. The test can be divided into four periods following the secondary chemistry :

- a first period, at the beginning, without pollution (0 h to 240 h) ;
- a second period with caustic pollution (1 mg.kg<sup>-1</sup> NaOH in the feed water) between 240 h and 1267 h in order to study sodium hideout ;
- a third period with caustic pollution and boric acid addition (1 mg.kg<sup>-1</sup> NaOH and 10 mg.kg<sup>-1</sup> B added as H<sub>3</sub>BO<sub>3</sub>) ;
- a last period, at the end of the test, without pollution (2328 h to 2524 h).

In the table 1, the results of chemical analyses of S.G. feed water and of S.G. Blowdown are reported for the main elements which were added : ammonium, sodium and boron.

## RESULTS AND DISCUSSION

### Crevice resistance

EIS measurements have been performed with the 4 platinum internal electrodes during each period. Figure 6 illustrates the shape of diagrams obtained with a crevice gap of 0.4 mm : the crevice resistance is measured at low frequencies, between 400 Hz and 1 Hz. At higher frequencies, the contribution of the geometrical capacity is not negligible and explains the part of the half circle observed on figure 6. But with a very narrow crevice gap (less than 0.1 mm), the shape of the EIS diagrams is very different as shown in figure 7 : the crevice resistance is measured at high frequencies (~ 60 KHz) and the depressed semi-circle (the center of which is below the real axis) is due to the contribution of R<sub>f</sub> and C<sub>f</sub>. So the crevice electrolyte resistance had to be measured at the right frequency which is a function of the crevice gap as shown in figures 6 and 7. These results are in agreement with previous results obtained in tubesheet crevices [3]. The crevice resistances between the electrodes and the

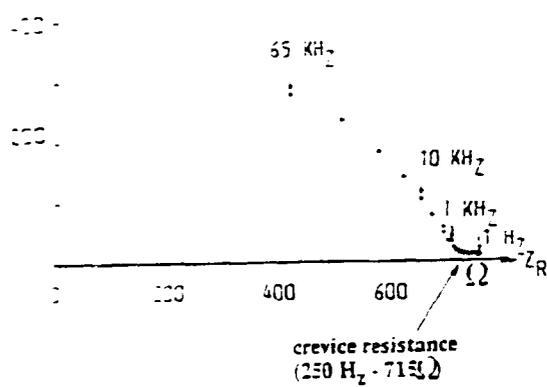
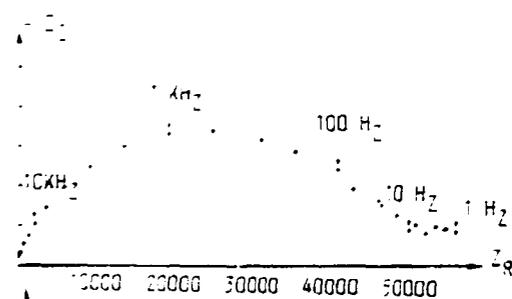


Fig. 6 : Impedance diagram obtained with the electrode n<sup>1</sup> (gap 0.4 mm, t = 835 h)



crevice resistance (60 KHz - 220 Ω)

Fig. 7 : Impedance diagram obtained with the electrode n<sup>3</sup> (gap <0.1 mm, t = 165 h)

Table 1 : Secondary Chemistry  
Mean values (standard deviations) mg.kg<sup>-1</sup>

	Feed Water	Blowdown
H <sub>2</sub> <sup>-</sup>	0.27(0.07)	0.27(0.08)
Second Period : Caustic pollution		
Na <sup>-</sup>	0.50(0.08)	0.44(0.12)
Third Period : Caustic and boric acid addition		
Na <sup>-</sup>	0.51(0.10)	0.52(0.12)
B	8.1(0.5)	7.4(1.1)

Table 2 : Frequencies at which the crevice resistances had been measured

TSP crevice	Electrode	gap	Frequency
eccentric	1	0.4 mm	250 Hz
	2	0.2 mm	2.5 KHz
	3	<0.1 mm	60 KHz
concentric	5	0.2 mm	2.5 KHz

Table 3 : Evolution of crevice resistance (Ω)

TSP	Gap	Before pollution	NaOH	NaOH + H <sub>3</sub> BO <sub>3</sub>
eccentric	0.4 mm	725	715	715
	0.2 mm	760	34	5000
	<0.1 mm	220	13	800
concentric	0.2 mm	3000-2500	2500-2000	4000

tube have been measured during the test at the frequencies reported in table 2. The evolution of these crevice resistances is shown in table 3 where the values obtained at the end of each test period are reported.

With the larger gap (0.4 mm, eccentric TSP) there is no evolution of the crevice resistances : no sodium concentration occurs during caustic pollution. The same result is obtained with the concentric and open crevice (gap 0.2 mm) where the variations of crevice resistances are small.

But near the contact point of the eccentric TSP (gap <0.1 mm), the variations of the crevice resistances are large : during caustic pollution, the decrease of crevice resistance is important (220 Ω to 13 Ω) and it means that a concentrated caustic solution has formed in that part of the crevice. This is in agreement with the chemical analyses performed during the test on feed water and on blowdown water and which showed that sodium hideout occurred during the second period of the test (table 1). When boric acid was added, the crevice resistance increased (13 Ω to 800 Ω - gap < 0.1 mm) which means that boron hideout occurred in front of the electrode n<sup>3</sup>, near the contact point of the eccentric TSP.

The same results were obtained with the electrode 2 (gap 0.2 mm, eccentric TSP) which is located in the middle of the eccentric crevice (figure 5). It means that concentrated solutions were present at that location and not only near the contact point between the tube and the TSP.

These results on crevice resistance evolution give informations on the dynamic behaviour of sodium hydroxide and boric acid in TSP crevices :

- with open concentric TSP, results confirm that the concentration of sodium and boron is very slow, with no significant evolution of crevice resistance ;
- in the case of eccentric TSP, concentration of sodium and boron begins near the contact point and then concentrated solutions spread in the crevice : significant evolutions of crevice resistance have been reported near the contact point and in the middle of the crevice.

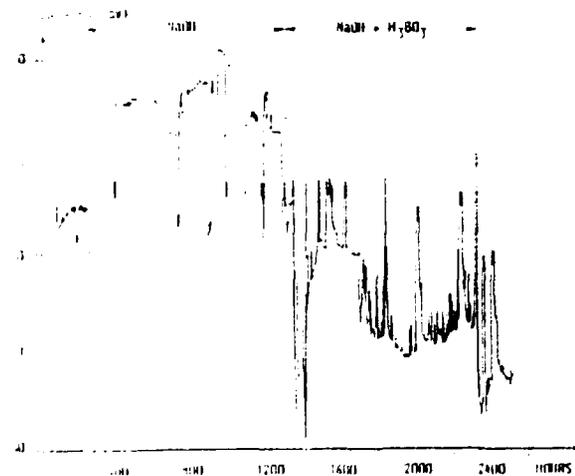


Fig. 8 : Evolution of the platinum potential difference  $E_c - E_b$ , during the AJAX test (electrode 3 - eccentric TSP, gap < 0.1 mm).

#### pH evolution

The potential differences between the crevice ( $E_c$ ) and the bulk ( $E_b$ ) has been recorded during the test. An example of the observed potential changes is shown in figure 8 : there were large fluctuations of the potential difference  $E_c - E_b$  throughout the test. They could be explained by the instability of the crevice medium : boiling and hideout processes might affect the electrochemical measurements and specially potential measurements. Mean values of  $E_c - E_b$  have been calculated at the end of the three first periods of the test and are reported in table 4. If the measurements

Table 4 : Evolution of platinum potential differences between the crevice and the bulk ( $E_c - E_b$ , mV)

TSP	Gap	Before pollution	NaOH	NaOH + $H_3BO_3$
eccentric	0.4 mm	+27(18)	-57(36)	-61(15)
	0.2 mm	+31(15)	+83(49)	+24(25)
	<0.1 mm	-58(12)	+33(35)	-159(41)
concentric	0.2 mm	+20(28)	-2(11)	51(33)

(Mean values calculated during the last 150 hours of the considered period with standard deviations)

performed where concentrated caustic solutions are localized (electrode 2 and 3) are compared to those performed where there is no concentrated solution (electrodes 1 and 4), it is obvious that the  $E_c - E_b$  measurements are in the same order of magnitude and that no clear evolution is observed. So crevice potential measurements with platinum electrodes in and out the crevice are not really indicative of crevice pH evolution during this experiment. It means that the assumptions done for the crevice pH evolution are not correct : platinum electrodes probably do not act as hydrogen electrodes in the bulk water and/or in the crevice solution.

#### CONCLUSIONS

This electrochemically instrumented test in model boiler gave informations on the dynamic behaviour of sodium hydroxide and boric acid in TSP crevices :

- with open concentric TSP, results confirm that the concentration of sodium and boron is very slow, with no significant evolution of crevice resistance (crevice solution resistivity) and potential (pH).
- in the case of eccentric TSP, concentration of sodium and boron occurs and begins near the contact point where significant evolution of crevice resistance has been reported.

Crevice resistance measurements appear to be a good way to follow hideout, provided that measurements are performed at the right frequency.

Potential difference measurements with platinum electrodes in and out the crevice are not sensitive to hideout due probably to the fact that platinum electrodes do not act as reference electrodes during this experiment.

## ACKNOWLEDGEMENTS

These experiments were carried out in the framework of an agreement between CEA, EdF, FRAMATOME and WESTINGHOUSE. We thank our partners for permitting publication.

## REFERENCES

- 1- "Attempts for the Measurement of pH in High Temperature Simulated PWR Steam Generator Crevice Environments at the On-Site Model Boiler Facilities".  
Kishida, Takamatsu, Isobe, Sato, Arioka and Tsuruta  
Symposium on Chemistry in High Temperature Aqueous Solutions, Provo, Utah, August 25-27, 1987
- 2- "Impedance de cellules de conductivité - Application à l'étude d'un nouveau matériau de cellule".  
Lu Dac Tri, Thèse de docteur - ingénieur, Institut National Polytechnique, Grenoble, France, November 10, 1983.
- 3- "Intergranular Attack of Alloy 600 : Simulation and Remedial Action Tests".  
J. DARET, D. FERON, EPRI NP 6115-SD, February 1989.