APPLICATION OF MODELING TO LOCAL CHEMISTRY
IN PWR STEAM GENERATORS

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ABSTRACT

Localized corrosion of the SG tubes and other components is due to the presence of an aggressive environment in local crevices and occluded regions. In crevices and on vertical and horizontal tube surfaces, corrosion products and particulate matter can accumulate in the form of porous deposits. The SG water contains impurities at extremely low levels (ppb). Low levels of non-volatile impurities, however, can be efficiently concentrated in crevices and sludge piles by a thermal hydraulic mechanism. The temperature gradient across the SG tube coupled with local flow starvation, produces local boiling in the sludge and crevices. Since mass transfer processes are inhibited in these geometries, the residual liquid becomes enriched in many of the species present in the SG water. The resulting concentrated solutions have been shown to be aggressive and can corrode the SG materials. This corrosion may occur under various conditions which result in different types of attack such as pitting, stress corrosion cracking, wastage and denting. A major goal of EPRI's research program has been the development of models of the concentration process and the resulting chemistry. An improved understanding should eventually allow utilities to reduce or eliminate the corrosion by the appropriate manipulation of the steam generator water chemistry and or crevice conditions. The application of these models to experimental data obtained for prototypical SG tube support crevices is described in this paper. The models adequately describe the key features of the experimental data allowing extrapolations to be made to plant conditions.

INTRODUCTION

One of the most persistent challenges facing utilities with pressurized water reactors is environmental degradation of steam generators to the point where premature replacement becomes necessary. Environmental degradation will limit the useful life of many steam generators unless ongoing research discovers ways to manage it. Various forms of damage, most involving some form of corrosion, have been experienced. These include stress corrosion, intergranular attack and wastage. Some of these problems have been successfully managed, others have not yet been brought under control. Secondary side stress corrosion cracking is not yet controlled. This form of degradation occurs most often at or near tube support plates or tube sheets where impurity concentration mechanisms can lead to an environment conducive to tube cracking.

The feed water to the steam generators contains small concentrations of impurities (ppb) such as sodium, chloride or calcium. Outside the tubes, boiling and dryout can occur in the occluded regions in the tube sheet or support plate. As a result, dissolved impurities may become concentrated up to a millionfold or more in the tube/tube support plate crevices, creating an aggressive environment.

Access to actual steam generator cervices, for sampling and monitoring purposes is not possible. Thus, laboratory simulation and modeling are necessary to predict and explain the environment located within the crevice.

PRESENTATION OF THE MODEL

A detailed model of the transport processes that produce concentrated solutions locally in pressurized water reactor steam generators has been developed [1, 2, 3, 4]. The model is used to describe the concentration process in regions where deposits accumulate in deep crevices between the tube and tubesheet (Figure 1).
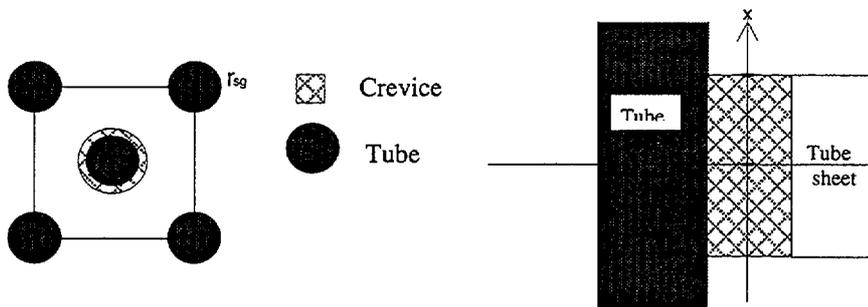

Figure 1 : Schematic of the crevice.

The model is based on the application of energy, mass, and momentum conservation laws for transport processes within fouled crevices and sludge.

Equation (1) describes the conservation of mass. It gives the relationship between the liquid and vapor velocities.

$$0 = \frac{\partial \rho_l v_l}{\partial x} + \frac{\partial \rho_v v_v}{\partial x}$$ (1)

ρ_l and ρ_v represents the liquid and vapor densities.

The heat flux is due to a gradient of temperature between the steam generator tube (T_p) and the porous deposit. The pore solution temperature is approximated by the saturation temperature of the crevice pore solution T_s. this heat flux causes water to be continuously evaporated by a nucleate boiling mechanism. The conservation of energy is expressed in Equation (2).

$$\frac{2\pi H r_{sg}}{A_c}(T_p - T_s) = \frac{\partial \rho_l v_l h_{fg}}{\partial x} \qquad (2)$$

The volumetric heat source term can be determined using an overall heat transfer coefficient H. r_{sg} is the outside radius of the steam generator tube. A_c is the cross sectional area of the pore matrix. h_{fg} represents the latent evaporation energy.

Within the liquid phase, each species accumulates as a result of the decrease in mass of liquid. The conservation of the chemical specie is reproduced by Equation (3).

$$\varepsilon\frac{\partial CS}{\partial t} + \frac{\partial Cv_l(1 - K_{v-l})}{\partial x} = -\frac{\partial D_{es}\frac{\partial C}{\partial x}}{\partial x} \qquad (3)$$

C is the concentration of the specie and S is the saturation (void fraction of pore space occupied by the liquid phase). ε is the porosity of the crevice. Two mechanisms can limit the concentration process: the chemical specie may diffuse (D_{es} represents the diffusion coefficient) or exit with the vapor (k_{vl} is the liquid vapor distribution coefficient).

The liquid and vapor relative permeabilities k_{rl} and k_{rv} can be determined if the saturation is known from correlations of the form given in equations (4) and (5).

$$k_{rl} = k_0 S^3 \qquad (4)$$

$$k_{rv} = k_0(1-S) \qquad (5)$$

The liquid and vapor velocities are related to pressure gradient (Equations (6) and (7)). μ_l and μ_v are the liquid and vapor viscosities.

$$v_l = -\frac{k_{rl}}{\mu_l}(\frac{\partial P_l}{\partial x} - \rho_l g) \cong -\frac{k_{rl}}{\mu_l}\frac{\partial P_l}{\partial x} \qquad (6)$$

$$v_v = -\frac{k_{rv}}{\mu_v}(\frac{\partial P_v}{\partial x} - \rho_v g) \cong -\frac{k_{rv}}{\mu_v}\frac{\partial P_v}{\partial x} \qquad (7)$$

A pressure gradient defined as the capillary pressure P_c exists at the interface between the vapor and the liquid phases. P_c is related to saturation (Equation (8)).

$$P_c = P_v - P_l = f [S] \qquad (8)$$

As shown in Equation (9), the saturation temperature is a linear function of the crevice solution's composition because of the vapor pressure depression of the aqueous phase by the accumulated solute.

$$T_s = T_{s0} + \alpha\, C \qquad\qquad\qquad (9)$$

Heat transfer from the inside of the SG tube to the porous deposit causes saturated water to be drawn into the deposit voids by capillary forces. . If sufficient liquid to maintain nucleate boiling cannot be drawn into the porous medium, a steam blanketed region will exist below the nucleate boiling region. The liquid influx rate will dictate whether the liquid phase can penetrate the entire depth of the crevice. The liquid penetration is called the wetted length W_l. It is assumed that nucleate boiling exists throughout the wetted length. Within the wetted length, nonvolatile species continually accumulate in the liquid phase because of evaporation of the incoming water. Appropriate boundary conditions should also be written. At the mouth of the crevice, the concentration is the concentration of the bulk water. The liquid and vapor pressure and the saturation are known.

$$x = 0 \quad \begin{aligned} C &= C_0 \\ P_l &= P_v = P_0 \\ S &= S_0 \end{aligned}$$

At the wetted length, the liquid doesn't penetrate anymore so the liquid and the vapor velocities equal zero.

$$x = L \quad \begin{aligned} v_l &= v_v = 0 \\ \frac{\partial C}{\partial x} &= 0 \end{aligned}$$

The differential equations and appropriate boundary conditions are written in finite difference form and solved using the Newman's technique. The major objectives of the model is to predict the mass of impurities accumulated within the crevice as a function of time and the concentration profile for a given species A. In previous work, the model has been benchmarked against experimental data from Mann [5]. In this work, the results given by the model have been benchmarked to two sets of experimental values : Those values were obtained by Lumsden [6] and Rogers [7].

LUMSDEN'S RESULTS [6]

Rockwell International has constructed a device which mimics the geometry and operating conditions of a Tube / Tube support plate crevice in a pressurized water reactor steam generator. A schematic of the Rockwell crevice is shown in Figure 2.
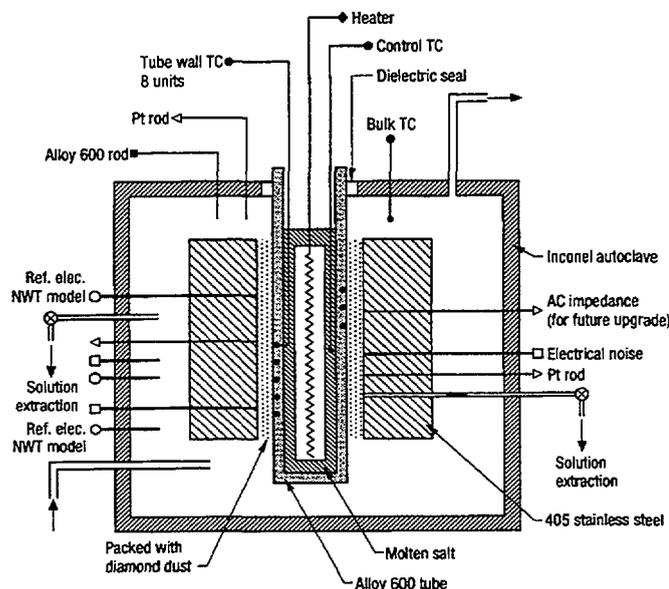

Figure 2 : Schematic of the heated crevice

The crevice is filled with diamond powder to simulate the corrosion products packed in a steam generator tube/ tube support plate crevice. This apparatus is instrumented to measure the crevice chemistry as a function of time. There are ports through which sensors can be inserted into the autoclave bulk water or through the TSP to monitor the crevice environment. The temperature profiles indicated that the whole crevice was initially steam blanketed. Hideout kinetics were determined for Na^+ using feedwater having 20ppm and 2ppm Na. Na^+ was extracted from the crevice after various exposure periods. The results are presented in Table1.

Table 1 : Mass of Sodium accumulated in heated crevice for feedwater containing 2ppm and 20ppm of Sodium.

time (hrs)	mg sodium Co=2ppm	time (hrs)	mg sodium Co=20ppm
4	1.15	1	1.94
8	0.66	2	3.73
22.75	2.12	4.75	6.53
24.3	2.5	7	8.64
72	6.08	16.6	23.75
96	9.96	20.0	31.5
144	16.5	20.5	28.3

Using experimental conditions, the model parameters were calculated. The model predictions are in excellent agreement with the diamond powder packed crevice data as shown in Figure 3.
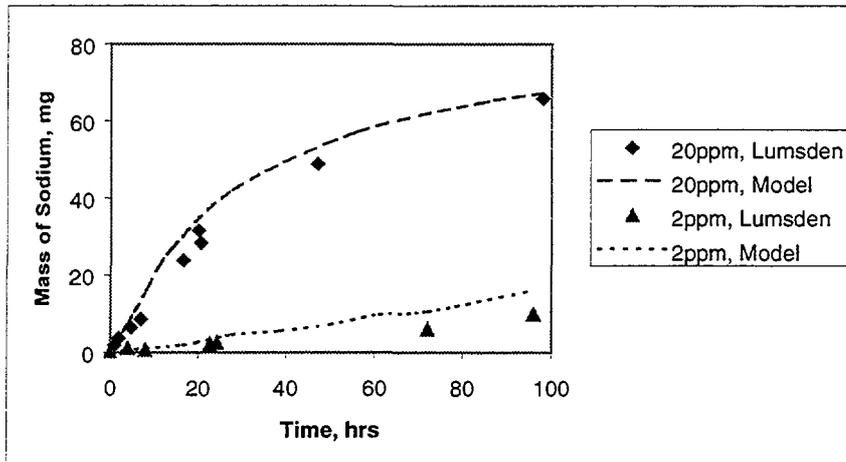

Figure 3 : Comparison between the experimental values given by Lumsden and the results obtained by modeling.

The evolution of the distribution of the impurities in the crevice as a function of time is presented in Figure 4. In the model, symmetry at the middle of the support plate is assumed.
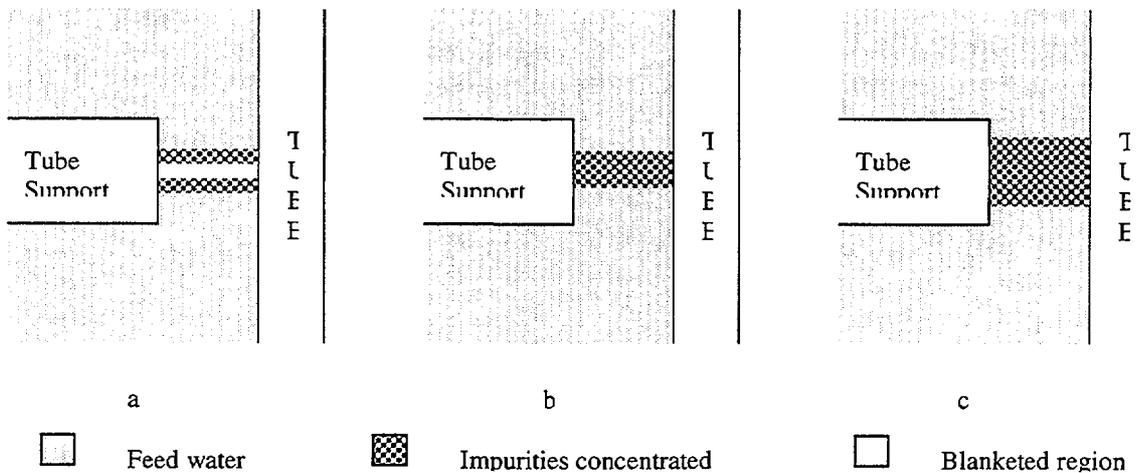

Figure 4 :Repartition of impurities in the crevice as time proceeds.

The model predicts the existence of a blanketed region initially (a). The crevice slowly fills with a concentrated solution that is in equilibrium with the available superheat, so the wetted length increases (b). Once the crevice is fully wetted, the concentration profile first limited deep in the crevice reaches its thermodynamic limit at the mouth of the crevice (c).

ROGERS' RESULTS [7]

Another facility built by Rockwell International has been utilized by Rogers at San Jose State University. One of the main differences between this device and the previous device is that the fouled crevice was packed with inert carbon fibers instead of diamond powder. The porosity in this case is double that of the porosity of the diamond powder case (0.6 instead of 0.3). Using feed solutions of 30, 60 and 120ppm sodium chloride and crevice powers of 85, 150 and 230 Watts, Rogers has measured the mass of sodium chloride in the packed crevice as a function of time.

Table 2 shows results from the runs that were performed for the characterization of the autoclave. Two runs were performed to illustrate repeatability.

Table 2 : Mass and rate of accumulation of Sodium Chloride in the crevice for 7 experimental runs.

Run	1	2	3	4	5	6	7
Heater Power (W)	85	230	85	85	230	150	150
Feedconcentration (NaClppm)	30	30	120	120	120	60	60
NaCl Hideout (mg)	8.95	54.7	16.6	17	87	26.4	26.9
Accumulation rate (mg/min)	0.023	0.087	0.101	0.103	0.42	0.077	0.088

Based on the data obtained there is a direct relationship between accumulation rates and the amount of heat flux across the crevice. As the heat flux is increased the rate of accumulation increased. The data also indicates that as the bulk water concentration increases the rate of accumulation increases. This is consistent with model predictions. However in the experiments performed, the data obtained show that the bulk water concentration has a linear effect on the crevice equilibrium concentration. A quadrupling of bulk water concentration typically led to a doubling of the equilibrium mass of sodium accumulating in the crevice.

In order to model those results, an additional term was introduced in the model in the conservation of species. Equation (1) was replaced by equation (1').

$$\varepsilon\frac{\partial CS}{\partial t} + \frac{\partial Cv_l(1-K_{v-l})}{\partial x} = -\frac{\partial D_{es}\frac{\partial C}{\partial x}}{\partial x} - \Gamma(C-C_0) \qquad (1')$$

The last term accounts for all the steady state processes for sodium chloride release. The constant Γ can be viewed as an overall mass transport coefficient, which is added to the diffusion term. It was fixed at a value of 2.0e-5 for all the runs performed by San Jose State University. The model predictions were then in good agreement with the experimental results as shown in Figure 5.
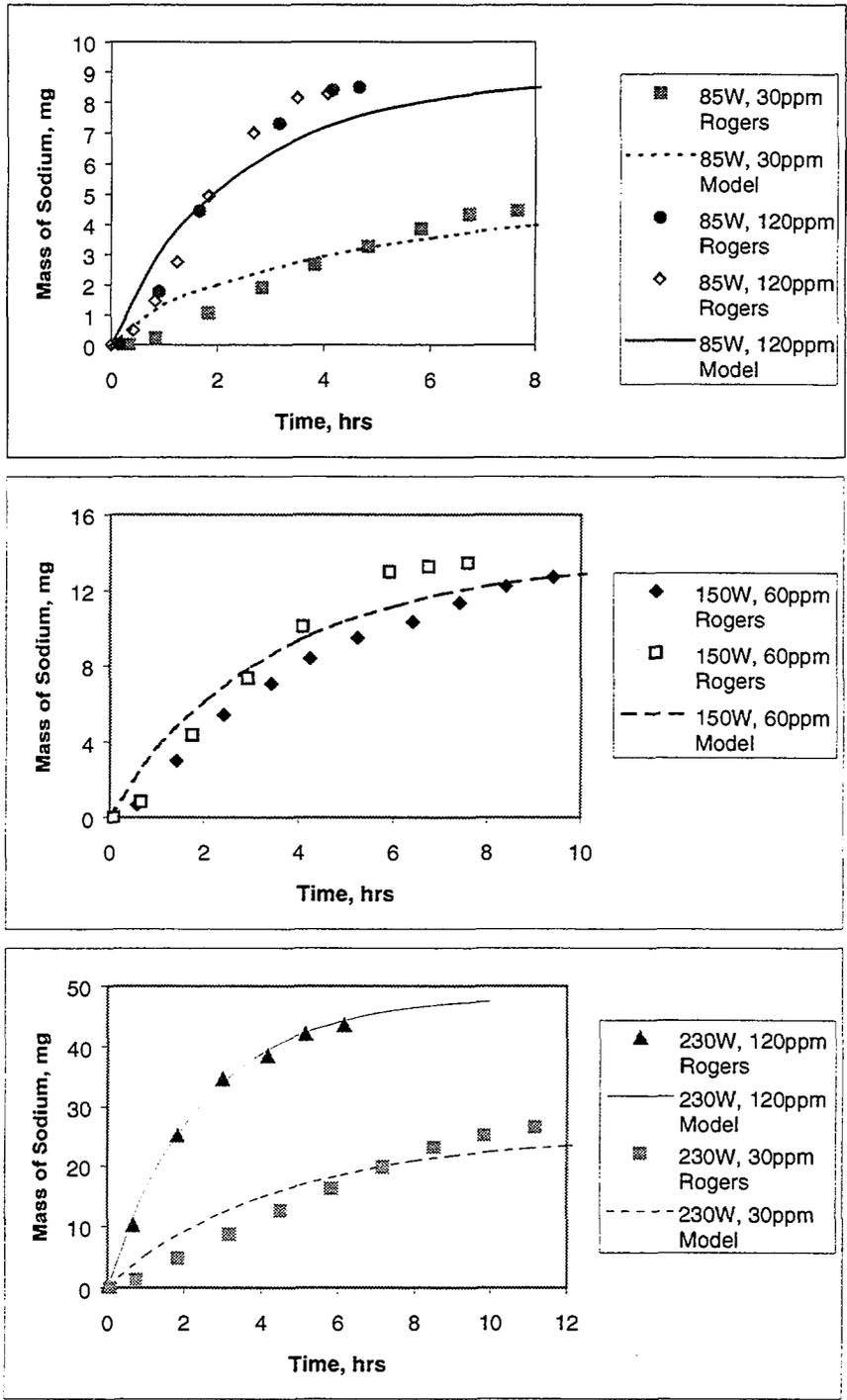
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Figure 5 : The accumulation of sodium was plotted against time for the different runs sorted by heat power. The lines correspond to the predictions of the model and the markers to the experimental data.

The model doesn't predict the presence of a blanketed region. The crevice packed with carbon fiber is initially fully wetted as the permeability of the carbon fibers is much greater than assumed for the diamond packing. The impurities slowly fill the entire crevice reaching maximum mass of sodium accumulated.

DISCUSSION

In both cases, the modeling predictions are in good agreement with the experimental results. The model predicts the crevice to be fully wetted and entirely filled with impurities at steady state. However, major differences exist between those two crevices. When the crevice is packed with diamond powder, a steam blanketed region initially exists When the crevice is packed with carbon fibers, the crevice is originally fully wetted. An additional term of overall mass transport was integrated in the conservation law.

In fact, the porosity of carbon fiber packing is twice the porosity of diamond powder so the permeability of carbon fiber crevice is also much greater. In the case of the carbon fiber, it is believed that the high permeability causes back mixing within the crevice. The need to incorporate an overall mass transfer coefficient into the model in order to fit the experimental data supports this assumption.

In Lumsden's work, the model predictions of a steam blanket initially in the crevice, seem to be confirmed by both temperature measurements and electrochemical measurements. In the case of electrochemical measurements, an initial high impedance path was interpreted as a steam blanket.

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DISCUSSION

Authors: C. Fauchon, P.J. Millett, P. Ollar, EPRI and EDF

Paper: Application of Modeling to Local Chemistry in PWR Steam Generators

Questioner: Al McIlree, EPRI

Question/Comment:

Is porosity modeled? And if so, at what porosity does concentration stop?

Response:

Porosity is not considered as a function of concentration. It is assumed to remain constant.

Questioner: R.F. Voelker, Lockheed-Martin

Question/Comment:

What is the mechanism in the model that allows the concentration/dryout interface to move into the crevice with time?

Response:

The process is the diffusion of concentrated solution towards the center of the crevice.

Questioner: Y. Lu, AECL

Comment:

Since the device condition and bulk conditions are quite different, an electrochemical concentration cell is formed. This modelling work probably should also consider the migration process of anions and cations.

Questioner: M. Rootham

Comment:

It was demonstrated several years ago that a "porous" packed crevice acts as a pure concentrator. Your model needs to take into account the chemistry changes occurring in the scale that is external to the crevice.