Hideout of Sodium Phosphates in Steam Generator Crevices

By

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Abstract

Sodium phosphates were at one time commonly used as additives in the secondary coolant of nuclear steam generators to buffer the effects of impurity ingress and to minimise corrosion. However, sodium phosphates tend to sequester or to "hideout" in the crevices and sludge piles in the secondary side of steam generators during operation. During transients they may then be released or "returned" to the bulk water – often as aggressive species. This hideout-return phenomenon of sodium phosphates is well known and documented and the fact that tube degradation such as pitting or wastage can occur has led to its falling into disuse in the industry. Point Lepreau is planning to switch from phosphate dosing to AVT (all volatile treatment). It is of interest to understand the chemistry changes that are likely to occur so steps can be taken in the event that corrosive conditions result. This report discusses a two-dimensional mathematical model that describes the transport processes involved; it also discusses the proposed experiments to validate the model.

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Introduction

Steam generators in CANDU and PWR power plants use the heat produced in the reactor to produce steam. The steam generator is a u-tube heat exchanger with the steam being produced on the outside or secondary side of the tubes. The tubes at Point Lepreau nuclear generating station are made of Alloy 800 and are held in place with tube support plates made of type-410 stainless steel. Chemicals are added to the secondary water for two reasons: to minimise corrosion of the metal components by creating an alkaline environment at a pH of approximately 9.8 and to reduce the oxygen concentration in the water.

Point Lepreau is presently adding sodium phosphates, based on Na_3PO_4, to the secondary water to minimise corrosion. Over time it has become evident that sodium phosphates can cause metal degradation, especially in the crevices and under sludge. During plant operation, sodium phosphates migrate into the crevices between the tube and the tube support plate (TSP) as well as the tubesheet crevices and become trapped. This can cause corrosive environments that are detrimental to the integrity of the materials. Point Lepreau is planning to switch from phosphate dosing to AVT (all volatile treatment).

Hideout and its Study

The term hideout refers to the migration of chemicals from the bulk water into the restricted regions of the steam generator, such as the sludge piles and the crevices, that develops into an aggressive solution. These restricted areas have thermal and hydraulic conditions different from those of the bulk. According to Baum, the various corrosion mechanisms observed in the steam generator include: stress corrosion cracking (SCC), intergranular attack (IGA), pitting, wastage of the heat transfer tubing, and general wastage of the various support structures [1]. The accumulation of these chemicals and the extent of accumulation are a complex function of local geometry, applied thermal and hydraulic conditions, and the solubility characteristics of the dissolved chemicals [1].

Crevice geometry is important in determining the thermal and hydraulic characteristics. Mechanical crevices are those crevices located in the tubesheet and between the tube support plate (TSP) and the tubes. These crevices vary in that the tubesheet crevices are single ended and the TSP crevices are double ended. Crevices may also refer to porous deposits and sludge. Most porous deposits and sludge consist primarily of magnetite. Most mechanical crevices, such as the tube support plate crevice, become filled with porous corrosion products over time [2]. This contributes to transport processes similar to those found in sludge deposits.

Corrosion of the steam generator materials is an important concern; it is, therefore, of interest to be able to predict the effects of impurities and sodium phosphates in the system with respect to localised corrosion. To do this, a mathematical model is required to describe the physical system.

In the U.N.B. study an experimental apparatus, shown in Figure 1, is set up in an autoclave to simulate a steam generator crevice. The apparatus involves a sludge cup forming an annulus around a section of Alloy 800 steam generator tube to simulate a double ended crevice. Magnetite powder is used to simulate sludge. Heat is transferred from the steam generator tube through the magnetite particles in the sludge cup. The flow through the porous magnetite is induced by capillary pressure. Boiling occurs in the sludge cup, resulting in a two-phase flow. During boiling, the sodium phosphates and impurities concentrate in the pores and crevices. Our approach to modelling this situation is similar to that of Millett and Fenton [3].

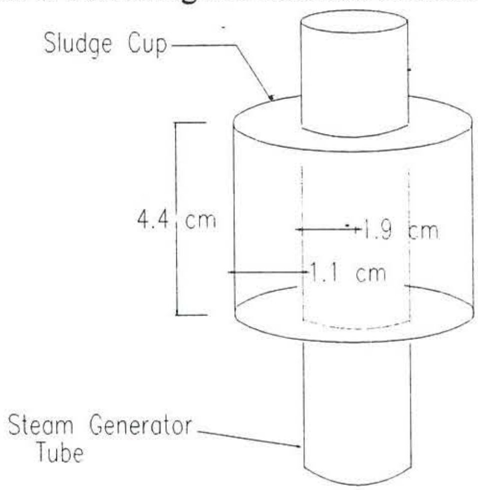

Figure 1. Steam Generator Tube With Sludge Cup

Mathematical Modelling

The transport processes involved in the sludge cup are key to the concentration of chemicals and subsequently the corrosion of the steam generator materials. Diffusion and convection of both heat and chemicals need to be considered in the development of the model. The equations shown here assume that things remain constant with time, or that the system is at steady state. Steady state is assumed to be the maximum concentrations that will be reached in the system.

Two other important assumptions are made with regard to the geometry of the sludge cup. The first assumption is that the sludge cup is axisymmetric. The second assumption that the sludge cup is symmetric about the middle in the axial direction. That is to say that the top half of the sludge cup exhibits the same profile as the bottom half of the cup.

Heat is transferred from the steam generator tube through the sludge to cause boiling. This boiling is a result of both the heat transfer properties of the liquid and the sludge as well as the solute concentration within the sludge. The following equation describes the heat transfer in the sludge cup.

$$2\pi r_{sg} H\left(T_{tube} - T_s\right) - k_{eff}\left(\frac{\partial^2 T}{\partial r^2} + \frac{1}{r}\frac{\partial T}{\partial r}\right) = \frac{\partial\left(\rho_l u_l h_{fg}\right)}{\partial z} \qquad (1)$$

The first term describes the heat being added to the sludge from the steam generator tube. The heat flux is a temperature-controlled process. The driving force for the heat transfer is a result of the difference in temperature between the steam generator tube and the saturation temperature of the fluid. The saturation temperature of the fluid will change with the concentration of dissolved chemicals. This will differ with both radial and axial position. The saturation temperature will increase as the concentration increases as shown here. The number five in the equation describes the increase in temperature as a result of concentration.

$$T_s = T_{so} + 5C \tag{2}$$

The second term refers to the heat that is removed from the steam generator tube by conduction. This considers only conduction in the radial direction since the conduction in the axial direction is considered negligible as it is the direction in which convection occurs. It is assumed that convection is the more dominant form of heat transfer.

The term on the right hand side of the heat transfer equation (1) represents the evaporation of the liquid as it passes through the sludge. The rate of evaporation changes as the liquid moves through the sludge as a result of the concentration of chemicals. As the concentration of chemicals increases the saturation temperature, it also increases the heat of evaporation.

The fluid flow equations are crucial to both the heat transfer and the concentration equations. Boiling occurs as the solution passes through the sludge; however, not all the liquid evaporates at once. This results in a two-phase flow through the sludge. Darcy's Law is assumed to apply in this situation; it assumes laminar flow with a Reynolds number less than one. The resulting equations for the liquid and vapour, respectively, are as follows:

$$u_l = -\frac{K_{rl}}{\mu_l}\left(\frac{\partial P_l}{\partial z} - \rho_l g\right) \tag{3A}$$

$$u_v = -\frac{K_{rv}}{\mu_v}\left(\frac{\partial P_v}{\partial z} - \rho_v g\right) \tag{3B}$$

The liquid and vapour flows are related by capillary pressure. Capillary pressure is the driving force that causes the liquid to flow through the medium. It is the difference between the vapour and liquid pressure and is a function of saturation, defined below. The vapour-liquid pressure difference can therefore be defined by:

$$P_C = P_v - P_l = f(S) \tag{4}$$

The relative permeability of each phase is an important parameter in the velocity equation. The relative permeability is a function of the overall permeability of the medium and the saturation. The saturation is the ratio of liquid trapped or flowing through the porous medium in comparison to the amount of vapour in the medium. The relationship between the relative permeability with the saturation and the overall permeability is as follows:

$$K_{rl} = kS \tag{5A}$$

$$K_{rv} = k(1 - S)^3 \tag{5B}$$

The final equation that describes the flow of both phases is the continuity equation. The continuity equation describes the flow of the vapour and liquid with respect to each other:

$$\frac{\partial(\rho_l u_l)}{\partial z} = -\frac{\partial(\rho_v u_v)}{\partial z} \tag{6}$$

Finally, the most important equation involves the concentration of chemicals. The chemicals concentrate in the crevice as a result of their inability to diffuse out of the sludge, efficiently. For this case, it is assumed that the solute will diffuse in both the axial and radial direction. Convection, however, will only occur in the axial direction due to the sludge cup design. This assumption is also valid for a double-ended tube support plate crevice. The mass transfer for this system is described by the following equation:

$$
-D_e\left(\frac{\partial^2 C}{\partial r^2}+\frac{1}{r}\frac{\partial C}{\partial r}+\frac{\partial^2 C}{\partial z^2}\right)-\frac{\partial (Cu_l)}{\partial z}=0 \tag{7}
$$

The first term refers to diffusion through the sludge in both the radial and axial directions. The second term refers to convection, which is assumed to occur in the axial direction only.

Model Results

From the solution of the equations, radial and axial profiles can be made for temperature and concentration factor. The concentration factor is defined as the concentration in the sludge cup divided by the bulk concentration of the chemical species. The axial profiles are needed for only half of the sludge cup, due to symmetry.

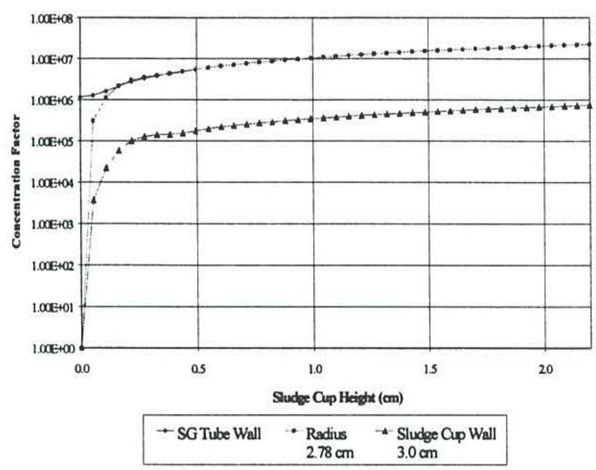

Figure 2. Concentration Factor Vs. Height

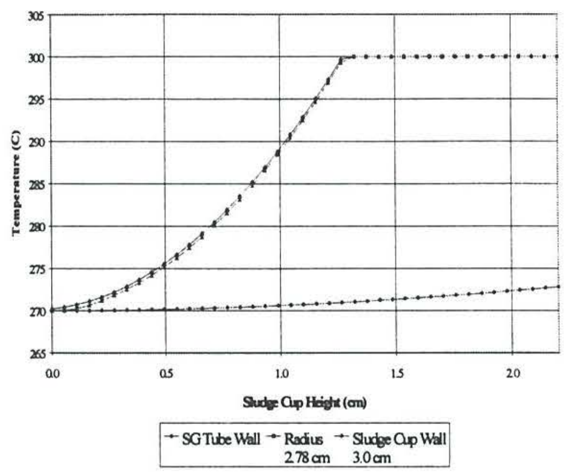

Figure 3. Temperature Vs. Height

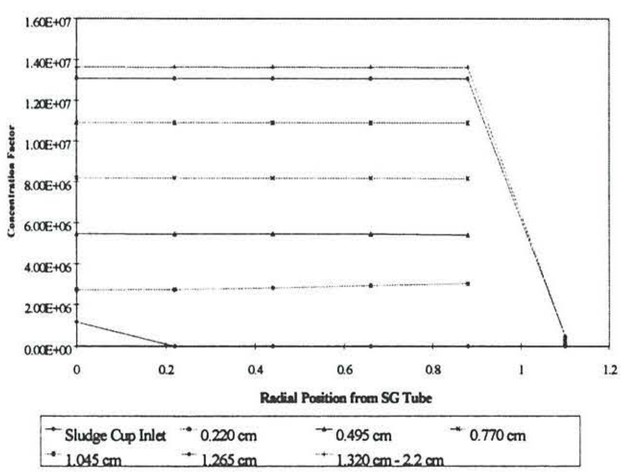

Figure 4. Radial Concentration Factor Profile

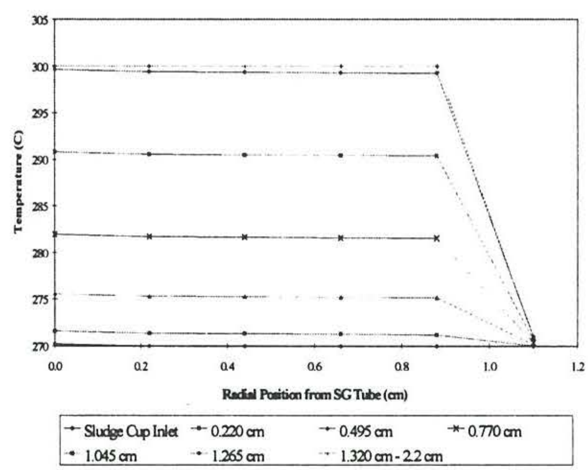

Figure 5. Radial Temperature Profile

As expected, the temperature and the concentration are highest at the tube wall at the centre of the sludge cup. The bulk water is saturated as it enters the sludge cup. This saturation temperature is lower than the temperature of the steam generator tube. As the solution flows through the sludge cup it becomes more concentrated increasing the saturation temperature. This creates the subsequent temperature and concentration factor profile in the sludge cup.

The lowest temperatures and concentrations occur at the sludge cup wall while the higher temperatures and concentrations occur at the steam generator tube surface. The bulk water, which is at the lower saturation temperature, flows around the sludge cup. This means that the outside wall of the sludge cup is also at the lower saturation temperature, causing the temperatures and the concentrations against the sludge cup wall to be lower than in the rest of the sludge cup.

Gonzalez and Spekkens examined the sludge piles found in a steam generator [4]. Their findings show that the highest concentrations occurred next to the steam generator tube and decreased as the distance from the tubes increased. This supports the model.

There are limitations to the model in describing the hideout for sodium phosphates. It has been documented that when transients occur in the operation of steam generators, the species return to the bulk water. However, in the case of sodium phosphates, it has also been noted that not all the phosphates return. Tremaine et al., in their work, have shown that the sodium phosphates tend to react with the magnetite and other chemicals in the sludge [5]. Such chemical reactions will be included in the model when experimental results are available.

Future Experimental

The model developed will be compared with experimental data obtained from the apparatus. The sludge cup will be filled first with carbon fibre. Samples will be taken from the sludge cup to determine the concentration of the phosphates. The sludge cup will be emptied and re-filled with magnetite powder and the loop operated under the same bulk chemistry conditions. More sampling will be done and compared with both the results from the model and the concentrations obtained in the carbon fibre. In accordance to the possible chemical reactions noted by Tremaine [5], it is expected that hideout will be greater in the magnetite powder than in the carbon fibre.

Conclusion

The model presented here provides a reasonable estimate of the temperature and concentration gradients that may occur in the sludge cup. The model shows that the temperature and concentration gradients are greatest halfway up the cup at the steam generator tube surface. One can see that this could lead to an aggressive environment and attack the materials in the steam generator tube leading to failure. The effectiveness of the model has yet to be corroborated with experimental evidence, though it is supported by information from the literature. Once accomplished, it will be one step closer to minimising this type of corrosion in steam generators.

Nomenclature

C concentration
D_e effective diffusivity
H heat transfer coefficient
K_r relative permeability
P pressure
S saturation
T temperature
T_s saturation temperature
T_{so} initial saturation temperature
T_{tube} steam generator tube temperature
h_{fg} heat of evaporation
k permeability
k_{eff} effective thermal conductivity
r radius
r_{sg} radius of steam generator tube
u velocity
μ viscosity
ρ density

Subscripts
l liquid
v vapour
c capillary

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