THE THIRST CHEMISTRY MODULE AS A TOOL TO DETERMINE OPTIMAL STEAM GENERATOR CORROSION CONTROL STRATEGIES

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ABSTRACT

As a coordinated project, AECL is developing a set of tools to aid with the prediction and management of steam generator (SG) performance. THIRST (**T**hermal **H**ydraulic Analysis **I**n **R**ecirculating **ST**eam Generators) is a computational tool used for the prediction of SG thermalhydraulic performance. THIRST results have been applied successfully to predict thermal degradation, tube vibration and fretting, and flow-accelerated corrosion (FAC) degradation. A new chemistry module has been added to THIRST, which now makes this code useful for the prediction of local secondary side water chemistry parameters in the SG.

The THIRST chemistry module is comprised of a multicomponent, multiphase mass transport model coupled with a multiphase chemical equilibrium model. As input, the module requires amine and hydrazine concentrations in the feedwater and reheater drains. The module predicts local distributions of amine and hydrazine concentration in the secondary side. The concentration predictions of the module are used to compute the pH by assuming equilibrium between the liquid and gas phases. Predictions of the chemistry module compared reasonably well with plant data.

The module was used to perform corrosion control assessments for a SG with an internal preheater. Four different amines – ammonia, ethanolamine, dimethylamine, and morpholine – and hydrazine were tested for their ability to maintain high pH, i.e., above 9, to protect carbon steel against flow-accelerated corrosion. These amines and hydrazine were compared for their effectiveness in SGs designed with internal preheaters.

1. INTRODUCTION

Steam generator components may be subjected to corrosive solutions in turbulent flow. Under such conditions, actual component lifetimes may be significantly reduced from their original design lifetimes. Premature replacement of SG components before their expected lifetime can be very expensive. Furthermore, degradation of essential components can reduce the SG efficiency, thus reducing net profits. The rate of some SG corrosion mechanisms is a strong function of the secondary side water chemistry. Therefore, understanding and predicting secondary side chemistry in SGs is important for nuclear power generation.

THIRST is a three-dimensional thermalhydraulics code for calculating coupled momentum and heat transfer in recirculating SGs. Because proper chemistry control in SGs is very important to maximize equipment life, THIRST has been augmented with a chemistry module to predict species distributions in the SG that affect pH. The extent to which a particular species may raise the pH depends upon its concentration, volatility, and base strength. The pH distribution is of particular importance to stations as this helps identify areas of the SG with increased susceptibility to FAC. The information provided by the THIRST chemistry module can be used as a basis for prioritizing FAC-susceptible locations in the SG for inspections during shutdowns.

2. BACKGROUND

2.1. Assumptions of the Mathematical Model

The following assumptions have been used:

1. The flow, and all boundary conditions are steady. Boundary conditions for the concentration field are at the feedwater nozzle and the reheater drains, where the inlet concentrations are specified.
2. The liquid and vapour phases are in thermal and chemical equilibrium:
   2.1. This means that the temperature of the liquid and vapour phases are equal, the ratio of the liquid to vapour mass concentrations of the non-ionized species is equal to the partition coefficient, K_D, and that the base in the liquid is partially ionized such that $m_B m_{H^+} / m_{BH^+} = K_A$.
3. The tubesheet, shell and shroud walls are adiabatic, meaning that no heat is lost to the environment through the walls.
4. The effect of diffusion is negligible compared to convection.
5. The effect of corrosion products and other impurities in water on solution chemistry is neglected.
6. The liquid and vapour are modelled as a homogeneous fluid of varying density and void fraction.
7. Symmetry is assumed about the vertical plane containing the largest radius U-tube.
8. There is no carry-under or carry-over in the SG.
9. The solutions are very diluted.
10. Hydrazine decomposes exclusively by disproportionation to ammonia and nitrogen.

3. DESCRIPTION OF THE CHEMISTRY MODULE

The chemistry module calculates species distributions within the SG using thermalhydraulic data calculated by THIRST. pH-controlling agents are added to the SG through the feedwater and/or the reheater drains. These chemicals will exit either with the blowdown or the steam. Depending upon the volatility and base strength of a species, as well as the local steam quality, the concentrations of each species will vary throughout the boiler. For any species, an overall species mass balance for the whole SG requires that the total mass of base entering must equal the mass of base leaving, either as blowdown or with the steam, i.e.:

$$C_{B,steam}F_{steam} + C_{B,blowdown}F_{blowdown} = F_{feed}C_{B,feed} + F_{reheater}C_{B,reheater} \qquad \text{Eq. 1}$$

where each C_B and F in equation Eq. 1 are mass concentrations and mass flowrates.

3.1. Mass transport

Mass transport of the i^{th} species in the SG at high Reynolds numbers can be described by the following equation [1]:

$$\frac{\partial(\rho\varepsilon C_i)}{\partial t} = -\nabla \cdot (\rho\varepsilon C_i \mathbf{u}) + R_i \qquad \text{Eq. 2}$$

All symbols in Eq. 2 are described in the nomenclature. Eq. 2 states that mass must be conserved everywhere in the SG. Although a steady state solution is sought, the transient term is retained as a means of controlling the rate of convergence, thereby avoiding oscillations. This equation was discretized using the upwind scheme and solved using an alternating direction implicit (ADI) three-dimensional solver [2]. The velocity and density fields were determined using heat and momentum balances similar to Eq. 2.

Boundary conditions at the feedwater inlet and reheater drains for mass transport are supplied by the concentration of species in the feedwater and reheater drains, $C_{B,DC}$ and $C_{B,feed}$ respectively, which affect the pH.

A special treatment is required to calculate the concentration of base at the top of the downcomer (DC) from the concentration of base in the separators. The concentration at the top of the DC is dependent upon the temperature, steam quality, and composition of the two-phase mixture at the top of the riser. A species mass balance at the top of the riser yields:

$$C_B F_{riser} = C_{B,DC}F_{DC} + C_{B,Steam}F_{Steam} \qquad \text{Eq. 3}$$

Thus, the base concentration in the DC is related to the concentration in the riser by a mass balance. Furthermore, because the vapour and liquid are assumed to be in equilibrium, the following relationship can be written:

$$K_D = \frac{C_{B,Steam}}{C_{B,DC}(1-\alpha)} \qquad \text{Eq. 4}$$

Here, α is the mass fraction of the species in the liquid which is ionized and it is a function of pH. Substitution of equation Eq. 4 into equation Eq. 3 and subsequent isolation of the liquid concentration yields the following formula:

$$C_{B,DC} = \frac{C_B F_{riser}}{F_{DC} + K_D(1-\alpha)F_{Steam}} \qquad \text{Eq. 5}$$

The concentration of base in the DC is a function of the temperature of the top of the riser and the concentration of base in the steam. In turn, the steam composition is determined by the mass balance. Thus, the DC boundary condition is intercoupled with the mass transport equation. SG geometry and boundary conditions are illustrated in Figure 1.

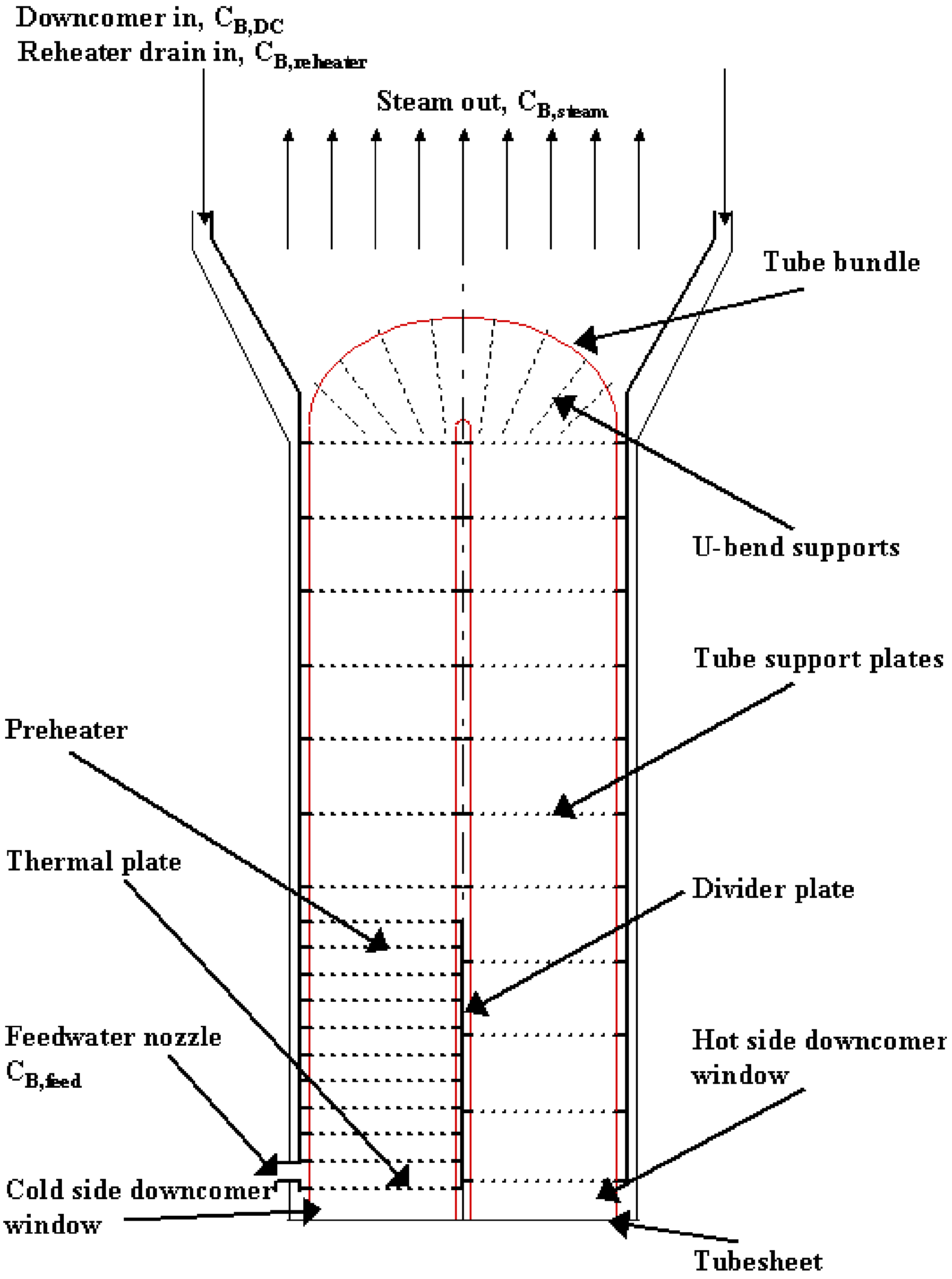

Figure 1 SG geometry and boundary conditions.

3.2. Hydrazine Decomposition

At typical SG conditions, hydrazine decomposes to form ammonia and nitrogen by the following reaction:

$$3N_2H_4 \rightarrow 4NH_3 + N_2 \qquad \text{Eq. 6}$$

Ammonia affects the pH while nitrogen is an inert gas. The rate of reaction is expressed as an Arrhenius function of the absolute temperature of the bulk water. This rate of hydrazine decomposition was obtained from data collected at AECL. Other hydrazine decomposition models are available in McKay [3] and Gundel [5]. This model assumes that the production of ammonia from hydrazine is homogeneous. It is valid for the following conditions:

- Hydrazine concentration between 10 and 430 µg/kg;
- pH at 25°C between 9.15 and 9.65 due to ammonia;
- Stainless steel system;
- Surface to volume ratio of 160 m^{-1}; and,
- 7,000 < Re < 100,000.

Using the convention introduced in Eq. 2, the mass transport source term for ammonia and sink term for hydrazine due to hydrazine decomposition is:

$$R_i = r_i \rho C_i \qquad \text{Eq. 7}$$

3.3. pH Calculation

Due to their volatility, the pH-controlling amines and hydrazine distribute between water and steam. The partitioning is pH dependent because both amines and hydrazine are chemical bases, and only the non-ionized portion of the species are volatile. To calculate the pH, the steam quality profile and the base concentrations in the mixture must be known. Therefore, mass, heat and momentum transport equations are solved prior to calculating the pH. The steam quality, x, is calculated by the heat transport equation and the concentration of base in the mixture, C_B, is calculated by the mass transport equation, Eq. 2. Consider a single base in the solution, B, whose ionic product is BH^+. The ionic product divides into a hydrogen ion H^+ and a neutral compound B. The ionization (or protonation) equilibrium is given by:

$$\frac{m_B m_{H^+}}{m_{BH^+}} = K_A \qquad \text{Eq. 8}$$

Equation Eq. 8 implies molal concentration. Electroneutrality in the water requires that:

$$m_{BH^+} + m_{H^+} - m_{OH^-} = 0 \qquad \text{Eq. 9}$$

Concentrations of [H^+] and [OH^-] are related as follows through the water ionization equilibrium:

$$m_{H^+} m_{OH^-} = K_w \qquad \text{Eq. 10}$$

The total base concentration in the water is:

$$m_{B,tot} = m_B + m_{BH^+} \qquad \text{Eq. 11}$$

The steam water distribution equilibrium for a base is given by:

$$\frac{m_{B,vap}}{m_B} = K_D \qquad \text{Eq. 12}$$

The pH-controlling agent concentration of the two-phase mixture can be related to its liquid and vapour phase concentrations by a mass balance using the mass steam quality:

$$m_{B,tot}(1-x) + m_{B,vap}\,x = \frac{C_B \cdot 10^{-3}}{MW_B} \qquad \text{Eq. 13}$$

The ionization and gas-liquid distribution of the base, *B*, is described by the above set of equations. There are six unknowns, namely m_{H^+}, m_{BH^+}, m_{OH^-}, $m_{B,tot}$, $m_{B,vap}$, and m_B. Because there are also six equations, equations, Eq. 8-Eq. 13, this system of equations is readily solvable to determine the dissociation and partitioning of a single base along with the solution pH. For multiple pH-controlling agents, equations Eq. 8, Eq. 11, Eq. 12, and Eq. 13 are written for each pH-controlling agent while equation Eq. 9, is modified to account for each ionic species in the system. The THIRST chemistry module calculates species distribution and partitioning, as well as solution pH, when multiple pH-controlling agents are present using the above model.

4. MODEL VERIFICATION

In this work, THIRST simulations were performed using a grid of 88 axial nodes, 30 radial nodes, and 30 circumferential nodes. The predictions of the THIRST chemistry module were verified by comparison with the predictions of ChemSolv^{TM}, a predictive SG crevice and bulk water chemistry software package developed by AECL which is part of the ChemAND^{TM} suite of tools. The ChemSolv^{TM} model calculates ionization and partitioning of pH-controlling agents in bulk and crevice water using a thermodynamic equilibrium model. Table 1 compares the predictions of the blowdown concentration and pH of the two models. The predictions of the THIRST chemistry module closely match the predictions of the ChemSolv^{TM} model. Discrepancies in the hydrazine and ammonia concentration predicted by the two models are predominantly due to hydrazine decomposition, which is modelled by THIRST. The blowdown concentrations as predicted by THIRST are expected to be similar to those predicted by ChemSolv^{TM} because liquid in the blowdown is assumed to be in chemical equilibrium with vapour leaving the SG.

[TM] ChemSolv and ChemAND are trademarks of Atomic Energy of Canada Limited (AECL)

Table 1
Comparison of Blowdown Concentrations Predicted Using the THIRST Chemistry Module with Predictions of ChemSolv™

Chemical	THIRST	ChemSolv™
Ammonia	0.23 ppm	0.21 ppm
Hydrazine	101 ppb	123 ppb
Morpholine	18.2 ppm	18.3 ppm
pH	6.3	6.3

The model was further verified to ensure that mass conservation was obeyed over the whole SG. The THIRST chemistry module outputs a mass balance summary report that shows total inflow and outflow of pH-controlling agents. This report should be inspected as a check to ensure that mass conservation is adhered to. For the simulation performed here, the mass balance over the whole SG, Eq. 1, was satisfied to less than 0.3% error for hydrazine and less than 0.05% for ammonia and morpholine. The error is defined as:

$$\in = \frac{F_{feed}C_{B,feed} + F_{reheater}C_{B,reheater} - C_{B,steam}F_{steam} - C_{B,blowdown}F_{blowdown}}{F_{feed}C_{B,feed} + F_{reheater}C_{B,reheater}} x100\% \qquad \text{Eq. 14}$$

5. COMPARISON WITH PLANT DATA

The THIRST chemistry module was used to predict the SG ammonia, hydrazine, and morpholine species distribution for a nuclear generating station for which plant data was available. Pertinent SG operational variables predicted by THIRST are shown in Table 2. Plots of species concentrations, as well as calculated absolute pH and pH relative to the neutral point predicted for this SG using the THIRST chemistry module, are shown in Figure 2 through Figure 6. A comparison of the predictions of the chemistry module with plant data is shown in Table 3. In the simulation, the feedwater concentrations shown in Table 3 were used as input to predict the blowdown concentrations. These predicted blowdown concentrations are compared with plant measurements in Table 3. Relative volatilities and dissociation constants of these three species were obtained from [4] and other sources.

Table 2
Thermalhydraulic Operating Parameters Used by Chemistry Module

Parameter	Unit	Value
Feedwater flowrate	kg/s	277.2
Reheater drain flowrate	kg/s	19.9
Blowdown flowrate	kg/s	0.9
Secondary side pressure	MPa (absolute)	5.096
Recirculation Ratio	-	4.97
Steam flowrate	kg/s	296.2
Flowrate in riser	kg/s	1774
Average outlet steam quality	%	16.7
Power Output	MWt	593.1

Table 3
Comparison of Blowdown Concentrations and pH Predicted using the THIRST Chemistry Module with Plant Data (92% power level). Mean values were used in the simulation. Reheater drain concentrations were assumed to be equal to feedwater concentrations.

Chemical	Concentrations From Plant Data		Predicted Concentrations
	Feedwater (Mean ± Std. Dev.)	Blowdown (Mean ± Std. Dev.)	Blowdown
Ammonia	0.919 ± 0.111 ppm	0.139 ± 0.141 ppm	0.231 ppm
Hydrazine	24 ± 3 ppb	39.6 ± 10.5 ppb	101 ppb
Morpholine	22.4 ± 2.39 ppm	20.0 ± 3.83 ppm	18.2 ppm
pH at 25°C		9.41 ± 0.0949	9.42

As shown in Table 3, the morpholine concentration predicted using the THIRST chemistry module is in very good agreement with plant data. For ammonia however, even though the predicted composition falls within one standard deviation of the measured composition, the standard deviation is greater than the value. Because of significant scatter in the ammonia concentration data, this alone cannot validate the predictions of THIRST. One explanation for this discrepancy is that the rate of decomposition of hydrazine is underpredicted. The rate constant used in this work is approximately one order of magnitude smaller than the rate predicted by Gundel [5]. Increased hydrazine decomposition would increase the ammonia concentration and lower the hydrazine concentration. Thus, increasing the rate of hydrazine decomposition would bring both the hydrazine and ammonia concentration closer to plant data. The predicted hydrazine concentration in the blowdown does not agree well with the plant data. The hydrazine concentration is predicted to be 101 ppb at the blowdown while the plant data reports around 40 ppb. This discrepancy may be due to the hydrazine decomposition model not being refined for this particular generator. Because hydrazine decomposition is electrochemical in nature, it is catalysed by metal surfaces in the generator. As a result, its rate is influenced by the SG design and the degree of fouling, whereas the experimental correlation employed was developed for stainless steel with the specific surface area of 160 m^2/m^3. To confirm this possibility, a sensitivity analysis of the blowdown hydrazine concentration on the rate of thermal decomposition was performed. The thermal decomposition rate was artificially increased by 10% and this resulted in very minimal changes to the blowdown concentration. When the rate was increased by an order of magnitude, the blowdown composition was reduced by 50%. Because reported decomposition rates vary by an order of magnitude, this could be a reason for the discrepancy between THIRST predictions and plant data. A smaller factor is that oxygen scavenging is not accounted for. However, because the chemistry specifications for the feedwater require less than 5 ppb of oxygen, this should not be a significant contribution to the discrepancy. Another possible source of the discrepancy is that carry-over is not accounted for. Carry-over would slightly lower the predicted hydrazine concentration in the blowdown because additional hydrazine would exit the SG with the steam.

To further test the results, the THIRST simulation was run at a lower power to determine if the effect of power level on the chemistry was as expected. For the concentrations predicted by THIRST to be realistic, the predictions should not be a strong function of the power level. At lower power levels, the recirculation ratio is increased. However, the temperature at the top of the riser, which determines the equilibrium partitioning and ionization of pH-controlling agents, will remain the same. It is expected that the compositions will reduce slightly because the reheater drain flow, the concentration of which is higher than the recirculation from the riser, remains constant while the recirculation flow from the riser increases. Thus, the composition of pH-controlling agents in the DC, and thus the blowdown, should reduce slightly but remain approximately constant.

Table 4 shows that this is the case. As the reactor power is reduced from 100% to 30%, the concentrations of ammonia and morpholine in the blowdown, as well as the blowdown pH, remain approximately constant. However, the hydrazine concentration changes more than the concentrations of the other chemicals with changing power level. This is also an expected result. As the feedwater flowrate and steam flowrate decreases, the residence time of the hydrazine in the SG increases. A larger residence time will result in increased thermal decomposition of hydrazine, and thus, its concentration in the blowdown decreases more than the two amines as power level decreases.

Table 4
Predicted Composition of Blowdown when the Reactor is Operating at Different Power Levels

Power Level	Recirculation Ratio	Hydrazine Blowdown Conc.	Ammonia Blowdown Conc.	Morpholine Blowdown Conc.	Blowdown pH at 25°C
100%	4.53	101 ppb	0.231 ppm	18.1 ppm	9.42
70%	6.85	98.9 ppb	0.230 ppm	18.2 ppm	9.42
50%	9.78	91.6 ppb	0.231 ppm	18.2 ppm	9.42
30%	15.74	69.7 ppb	0.232 ppm	17.9 ppm	9.42

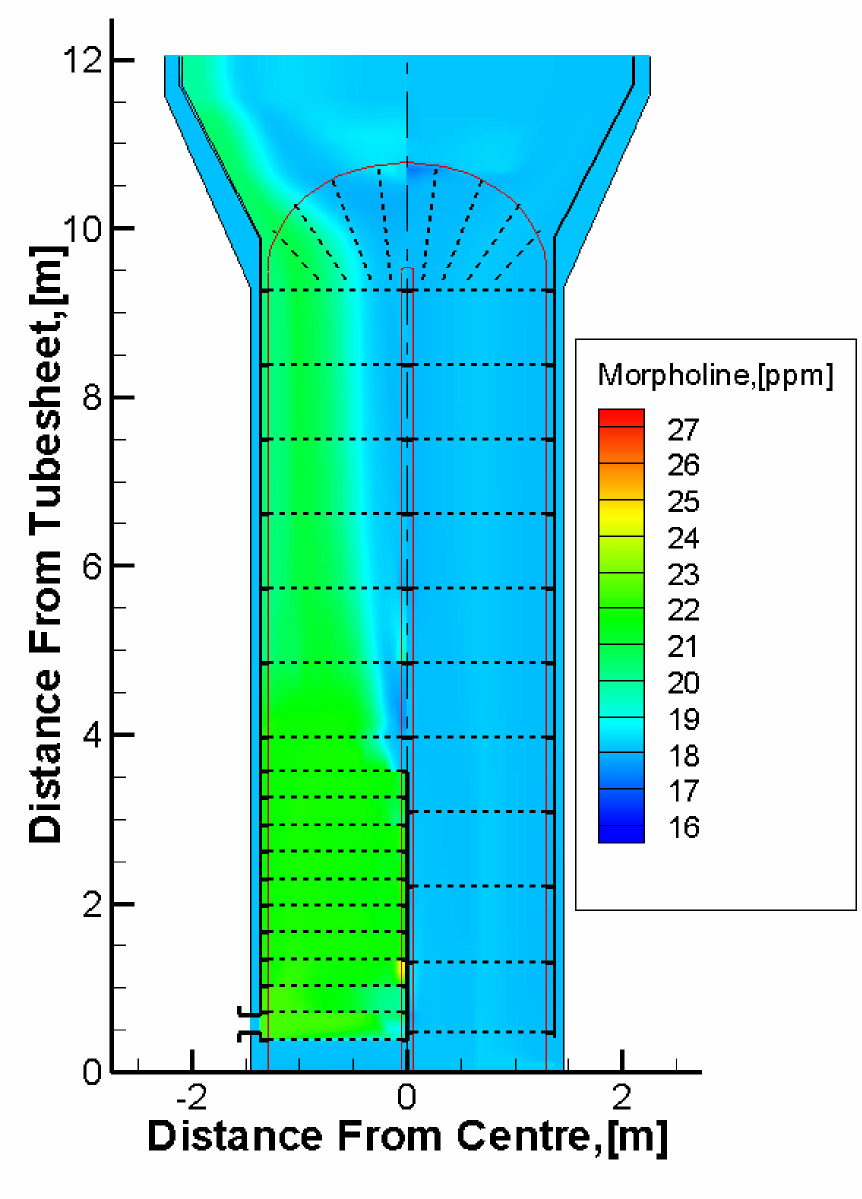

Figure 2 Morpholine distribution in the SG. Inlet concentrations are in Table 3.

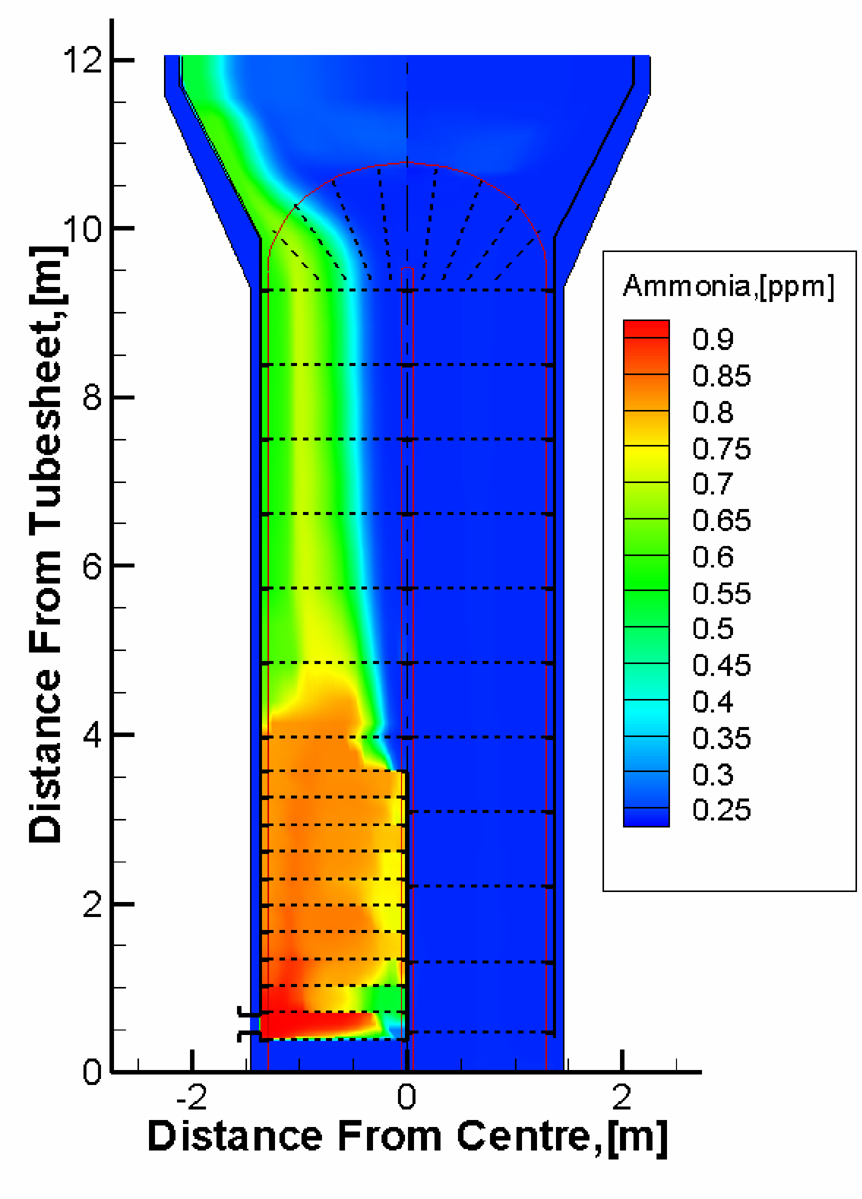

Figure 3 Ammonia distribution in the SG. Inlet concentrations are in Table 3.

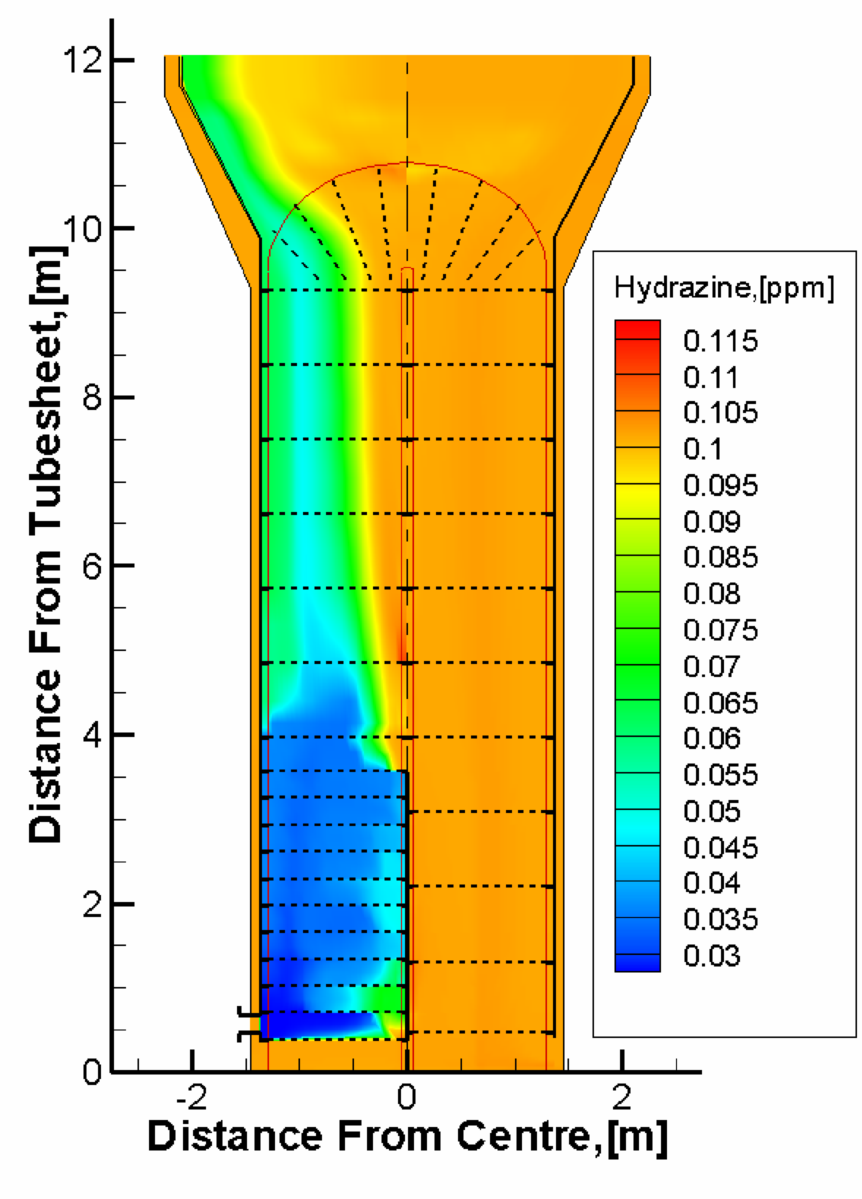

Figure 4 Hydrazine distribution in the SG. Inlet concentrations are in Table 3.

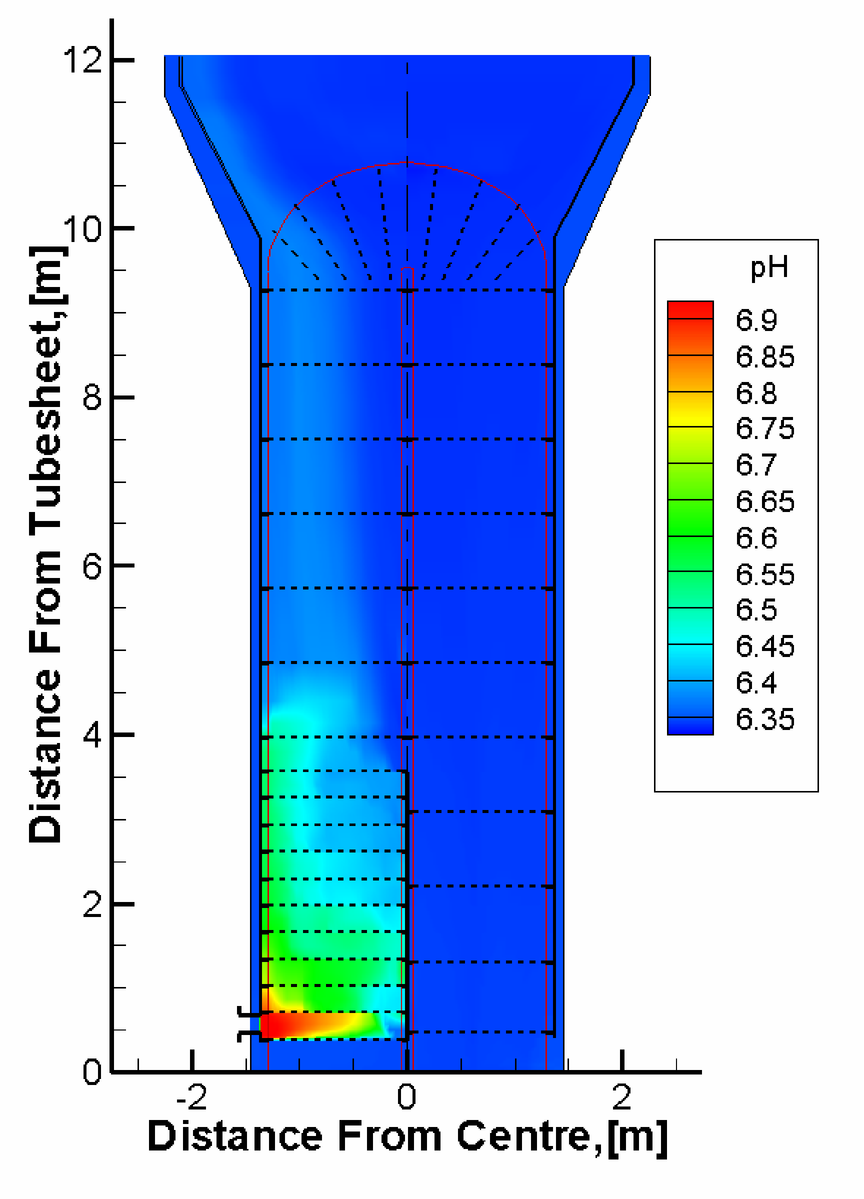

Figure 5 High temperature pH distribution in the SG. Inlet concentrations are in Table 3.

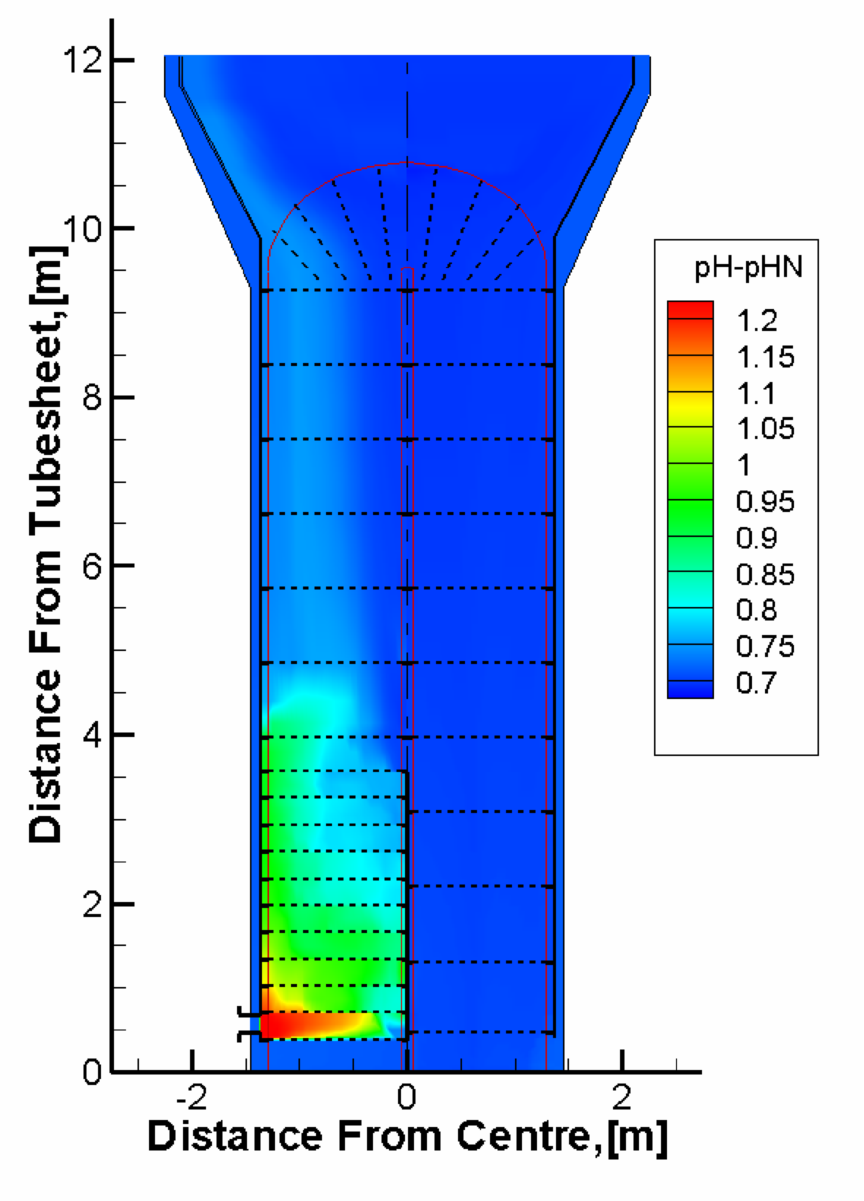

Figure 6 **High temperature pH distribution relative to high temperature neutral pH in the SG. Inlet concentrations are in Table 3.**

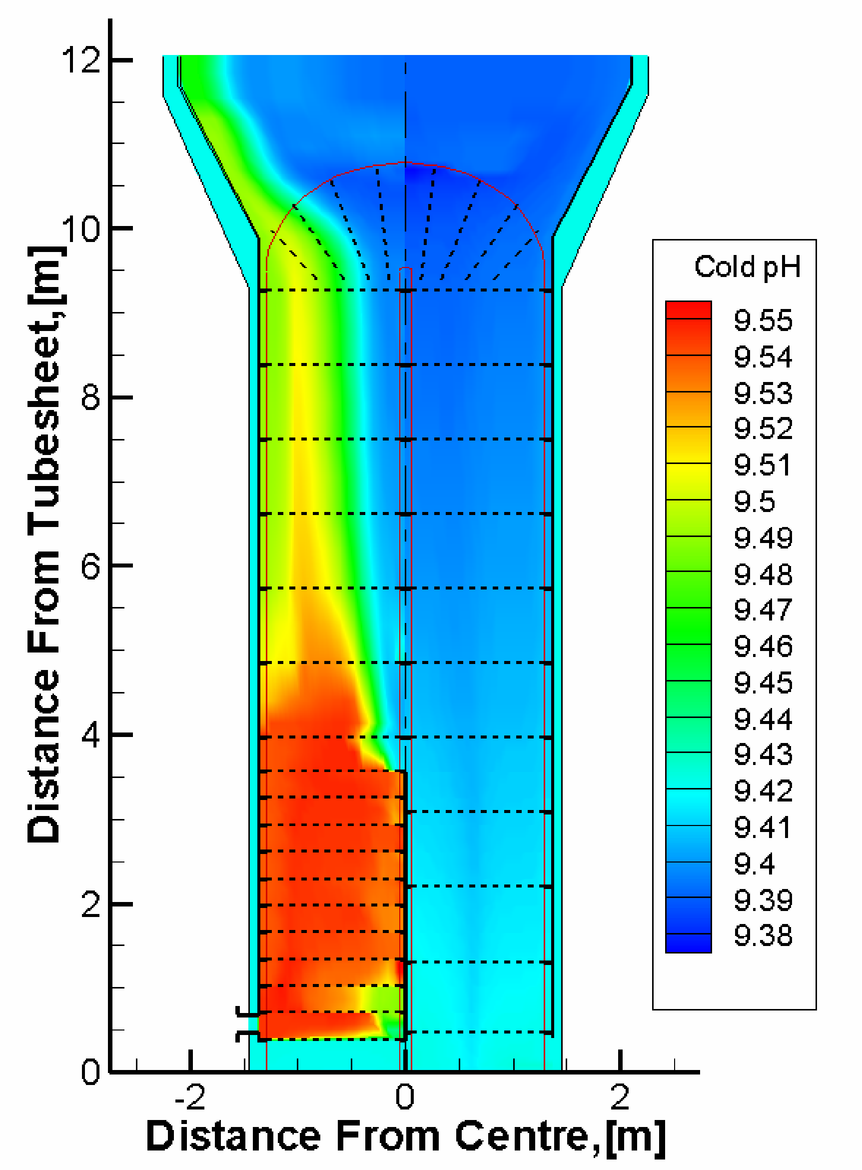

Figure 7 pH distribution at 25°C in the SG. Inlet concentrations are in Table 3.

7. APPLICATION OF CHEMISTRY MODULE TO PREDICT EFFECT OF pH-CONTROLLING AGENTS

The THIRST chemistry module was then applied to determine the effectiveness of amine and hydrazine mixtures for pH control. Several THIRST simulations were performed to assess the effect of different combinations of amines and hydrazine on the pH in different parts of the SG. The flow input parameters were the same as for the previous simulation at 100% power. Table 5 summarizes the predicted pH relative to the neutral pH in both the SG blowdown and separators.

Table 5
Calculated Average pH and Neutral Point pH in the Separators and Blowdown for Different Feedwater Concentrations of pH-controlling Agents (NH_3 = Ammonia, MPH = Morpholine, ETA = Ethanolamine, N_2H_4 = Hydrazine, DMA = Dimethylamine)

N_2H_4 (ppb)	MPH (ppm)	NH_3 (ppm)	ETA (ppm)	DMA (ppm)	Separators		Blowdown	
					pH	pH_N	pH	pH_N
0	10	0	5	5	6.58	5.63	6.58	5.63
20	0	0	10	0	6.61	5.63	6.63	5.63
0	10	10	0	0	6.30	5.63	6.33	5.63
0	20	5	0	10	6.49	5.63	6.53	5.63

8. CONCLUSIONS

A three-dimensional chemistry module for a recirculating SG has been developed. The module includes a 3-D mass transport model and a multiphase chemical equilibrium model. The module receives input from the feedwater and reheater drains concentrations and calculates species and pH distributions in the SG. Based upon this work, the following conclusions can be made:

- The predicted and measured morpholine concentrations are very similar. In addition, the predicted blowdown ammonia concentration is within one standard deviation of the mean measured value. The blowdown hydrazine composition did not compare as well with plant data, but this may be due to the hydrazine decomposition model not being properly refined for this particular SG.
- The model predictions show expected trends for lower power levels. The ammonia and morpholine concentrations in the blowdown do not change significantly. This is because their blowdown concentrations are primarily affected by the secondary fluid temperature, which remains constant for constant secondary side pressure. However, the decreased feedwater flow at lower power levels increases the residence time of the hydrazine in the SG and this increases the extent of thermal decomposition. Thus, for lower power levels, the concentration of hydrazine in the blowdown decreases.

9. ACKNOWLEDGEMENTS

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- Stan Klimas for providing input and data on amine and hydrazine properties and hydrazine decomposition, as well as review comments; and,
- Carl Turner for review comments.

10. NOMENCLATURE

α	Mass fraction of species that is dissociated, dimensionless
C	Mass concentration, ppm
ρ	Density, kg/m^3
ε	Porosity, dimensionless
F	Flowrate, kg/s
K_D	Gas-liquid partitioning coefficient
K_A	Ionization, or dissociation, constant
m	Molal concentration, mol/kg
MW_B	Molecular weight of base, g/mol
$\mathbf{u}$	Velocity vector, m/s
r	Chemical reaction rate, s^{-1}
R	Chemical reaction source term, mg/(m^3 s)
T	Temperature, K
x	Steam Quality, dimensionless

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