NUCLEAR ENERGY EDUCATION RESEARCH (NEER)
FINAL TECHNICAL PROGRESS REPORT

Electrochemistry of Water-Cooled Nuclear Reactors

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Digby D. Macdonald (PI), Mirna Urquidi-Macdonald (Co-PI), John H Mahaffy (Co-PI)
Amit Jain (Graduate Assistant)*, Han Sang Kim (Graduate Assistant***),
Vishisht Gupta (Graduate Student**), Jonathan Pitt (Graduate Assistant*)

* Graduate with a Master degree under this program; ** International undergraduate student; *** Graduating 08 with a Ph. D. under this program.

Pennsylvania State University
201 Steidle Building
University Park, PA 16802

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Tel: (814) 863-7772, Fax: (814) 863-4718, Email: ddm2@psu.edu

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I. BACKGROUND

This project seeks to develop a comprehensive mathematical and simulation model for calculating thermal hydraulic, electrochemical, and corrosion parameters, viz. temperature, fluid flow velocity, pH, corrosion potential, hydrogen injection, oxygen contamination, stress corrosion cracking, crack growth rate, and other important quantities in the coolant circuits of water-cooled nuclear power plants, including both Boiling Water Reactors (BWRs) and Pressurized Water Reactors (PWRs). The model will also help in assessing the three major operational problems in Pressurized Water Reactors (PWR), which include mass transport, activity transport, and the axial offset anomaly, and provide a powerful tool for predicting the accumulation of SCC damage in BWR primary coolant circuits as a function of operating history. Another objective of the project is to develop a simulation tool to serve both as a training tool for plant-operators and as an engineering test-bed to evaluate new equipment and operating strategies (normal operation, cold shut down and others). Once the model is developed and fully implemented, we plan to add methods to estimate the activity transport or “radiation fields” around the primary loop and the vessel, as a function of the operating parameters and the water chemistry.

The work on the project was started in the spring semester (January) of 2003 and during the past 42 months the work has involved the following tasks.

II. OBJECTIVES AND ACCOMPLISHMENTS

Task 1. Modification of the Boiling Crevice Model (BCM)

Objectives: In this initial task, we will modify the Boiling Crevice Model to describe the evolution of the environment in CRUD pores and hence in contact with the Zircaloy surface under low super heat (nucleate boiling, PWRs) and high super heat (sustained boiling, BWRs). Because the BCM also contains the Mixed Potential Model [35, 36, 37], it will be possible to calculate the pH and the ECP (corrosion potential) at the Zircaloy/environment interface within the pores. These values, which are expected to be significantly different from the bulk values, will then be used to model the oxidation of zirconium.

Task Status: The BCM has been modified to more accurately simulate boiling in porous CRUD (“Chalk River Unidentified Deposit”). The modifications include the incorporation of multiple, solution phase species (particularly for the BWR case) and heat flow through the pore base. (The original BCM assumed heat flow through the walls). Our objective is to first obtain an approximate analytical solution to the coupled thermal hydraulic/chemistry problem, so the magnitude of the concentrating effect in the pores can be scoped, followed by a full numerical solution of the governing equations (a much more difficult task).

1.1 Boiling Crevice Model (BCM)

The Boiling Crevice Model calculates the evolution of the solution contained within a boiling cavity (e.g., within the pores of a porous CRUD layer on the fuel) by noting the solubility of electrolytes in steam is much less than in liquid water, so that as boiling occurs within the crevice the concentration of the electrolyte increases. However, the concentration process begins at the bottom of the pore where the temperature is highest. Thus, a concentrated solution is produced in the pore from the pore base and gradually expands to fill the pore, as shown in Figure 1.1 for a 1-cm deep pore. The concentration of the solution is determined by the super heat, such that the elevation in boiling temperature at the steady state concentration matches the super heat. Physically, the process produces a “simmering”, stationary fluid in the pores that can concentrate electrolytes by a factor of more than 10^7 . This process is of fundamental importance in PWR operation, because it is believed to be the mechanism for concentrating Li^+ and $\text{B}(\text{OH})_4^-$ in CRUD pores on the fuel and, ultimately, the precipitation of $\text{LiB}(\text{OH})_4$. The high boron concentration absorbs neutrons to the extent that fission ceases and the power is drastically reduced. This phenomenon is known as the “axial offset anomaly.” As seen from Figure 1-1, the build-up can occur over extended periods of time, but we note the length of the pore chosen for these calculations is much greater than what exists in CRUD on the fuel (we have yet to determine the actual pore length in the CRUD).

Figure 1.1. Predicted build-up of a concentrated solution in a boiling, 1-cm long crevice with time for a bulk NaCl concentration of 10^{-7} M (5.8 ppb) and a superheat of 28°C . Note the concentrated, stationary phase progressively fills the crevice as time increases and, ultimately, (in the steady state) occupies the entire crevice, except for a small region at the crevice mouth [1].

Figure 1.2. Comparison between theory and experiment for the average volume concentration of Na^+ in a boiling crevice in contact with a bulk solution containing 40 ppm NaOH [1].

1.2 BCM in Steam Generators of Pressurized Water Reactors

That the BCM produces realistic results is shown by the data plotted in Figure 1.2, where the mass of Na^+ concentrated in the crevice is compared with experimental data published by Lumsden, et al. [2] for a crevice of identical dimensions. In performing this comparison, we fit the model to the first two experimental data points, in order to determine two model parameters, the values of which were unknown for this system. Comparison of the model with the experimental data for longer times shows excellent agreement, thereby lending great credence to the veracity of the model.

Figure 1.3. Volume averaged concentrations as a function of time for a heated crevice with a superheat of 28°C, a bulk concentration of NaCl of 10^{-7} M, and a bulk system temperature of 280°C. The iron species are formed by corrosion reactions in the crevice [1, 3].

In the work on PWR Steam Generator crevices, we developed an approximate analytical solution to the mass transport, electrolyte concentration mechanism that provides a fast method for performing the calculations. We tested the approximate method extensively, and shown it predicts crevice concentrations and electrochemical parameters within the crevice (e.g., the corrosion potential) to within a few tenths of one percent of the more time-consuming, numerical solution of the transport equations (Figure 1.3). This is an important development, because the eventual simulation of the processes which occur on the fuel, including those responsible for mass and activity transport and the axial offset anomaly, will require many thousands of runs of the algorithm in order to describe the evolution of the system over a typical operating history of a reactor.

Returning now to Figure 1.3, we see, for the assumed conditions of $[\text{NaCl}] = 10^{-7}$ M in the bulk solution, for a super heat of 28°C, and for a bulk temperature of 280°C, the crevice solution concentrates by a factor of about 10^7 and evolves toward an impure NaCl brine contaminated with Fe^{2+} species from corrosion (in this case). Note that 90% of the enhanced concentration within the crevice is predicted to occur within the first year.

1.2.1 Modeling of BCM

The cladding is normally covered with a layer of porous CRUD (“Chalk River Unidentified Deposit”). Thus, under boiling (BWR) and nucleate (PWR) operating conditions, electrolytes in the bulk coolant become concentrated in the pores. Accordingly, the environment in contact with the Zircaloy surface is considerably different from the bulk, as noted previously. By considering the “chemical amplifier” effects of these pores on the concentration in contact with the cladding surface, we proposed the modified boiling crevice model. The model is illustrated in Figure 1.4. In Figure 1.4, we consider a single pore and the crud in the immediate vicinity.

Figure 1.4. Schematic illustration of the modified boiling crevice model

The molar flux (in the x direction) of species k can be written as:

$$J_k = -D_s \frac{dC_k}{dx} + C_k v \quad (1-1)$$

where C_k is the concentration, D_k is the superficial diffusion coefficient; v is the superficial velocity for a given cross-section of the porous medium. By assuming the inlet and outlet fluxes in the pore are balanced, i.e., $J = 0$, Equation (1-1) can be written as

$$D_s \frac{dC_k}{dx} = C_k v \quad (1-2)$$

Rewriting the above equation in the format as $\frac{dC_k}{C_k} = \frac{v}{D_s} dx$ and integrate both sides, we get the concentration as a function of distance to the opening of pore.

$$C = C_0 \exp\left(\frac{vx}{D_s}\right) \quad (1-3)$$

At $X=L$, the concentration C_s in contact with the zirconium tubing can be obtained from above equation as:

$$C_s = C_0 \exp\left(\frac{vL}{D_s}\right) \quad (1-4)$$

The concentration factor can be obtained as:

$$CF \equiv \frac{C_s}{C_0} = \exp\left(\frac{vL}{D_s}\right) \quad (1-5)$$

where, only the velocity v is unknown, which can be calculated from the heat conservation:

$$q_v S_v = qS \quad (1-6)$$

as $V = SL$, $V_v = SL$, and $\varepsilon = \frac{V_v}{V}$, so

$$q_v = q \frac{S}{S_v} = q \frac{V}{V_v} = \frac{q}{\varepsilon} \quad (1-7)$$

and $q_v = h\rho v$ (1-8)

From Equations (1-7) and (1-8), we find the velocity as:

$$v = \frac{q_v}{h\rho} = \frac{q}{h\rho\varepsilon} \quad (1-9)$$

By substituting Equation (1-9) into Equation (1-5), we get the concentration factor as:

$$CF \equiv \frac{C_s}{C_0} = \exp\left(\frac{vL}{D}\right) = \exp\left(\frac{qL}{h\rho\varepsilon D}\right) \quad (1-10)$$

1.3 Conclusions

The concentrations of lithium and borate ions that govern whether a precipitate will form are the bulk concentrations multiplied by the respective concentration factors as determined from Equation (1-10). Non-volatile species tend to concentrate in a porous deposit layer overlaying a boiling surface. By using representative data (Table 1.1) available from literature, we calculate the concentrations of lithium and borate ions using the model described above. Determination of the concentration factor requires knowledge of the diffusion coefficients of these species. By assuming $D_{Li^+} = 1.11 \times 10^{-3} \text{ cm}^2/\text{s}$ for Li^+ and $D_{B(OH)_4^-} = 2.89 \times 10^{-4} \text{ cm}^2/\text{s}$ for $B(OH)_4^-$ at the in-core temperature (345 °C) of a PWR [5], we obtain

$$CF_{Li} = \exp\left(\frac{100 \times 10^{-2}}{1557.5 \times 0.755 \times 0.8 \times 1.11 \times 10^{-3}}\right) = 2.6 \quad (1-11)$$

$$CF_{B(OH)_4} = \exp\left(\frac{100 \times 10^{-2}}{1557.5 \times 0.755 \times 0.8 \times 2.89 \times 10^{-4}}\right) = 39.6 \quad (1-12)$$

Table 1.1 Base case input variables for the pores.

Parameter	Value	Source
h	1.557 J/g	(3)
ρ	0.755 g/cm ³	(3)
ε	0.8	(3,5)
L	100 μm	(4)
q	100 W/cm ²	(4)

Table 1.2. Bulk and pore concentration, and PH for this environment

	[B(OH) ₃] (ppm)	[LiOH] (ppm)	pH
C	1000	2	7.92
CF* C	39600	5.2	5.71

The concentration factor for the species $B(OH)_4^-$ is almost 40, which means the concentration of $B(OH)_4^-$ at the bottom of the pores is 40 times larger than that in the bulk. Typical PWR water primary coolant contains 1000 ppm [B(OH)₃] and 2 ppm [LiOH]. The concentrations of Li^+ and $B(OH)_4^-$ in the pores and pH calculated from the model are shown in Table 1-2. We can see that the concentration changed significantly for $B(OH)_4^-$ and the pH changed from 7.94 to 5.71 at 345°C, and hence this is the actual environment in contact with the Zircaloy cladding.

Issues and Concerns: None.

1.4 References

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Task 2. Calculation of Reactor Thermal Hydraulic and Electrochemical

Parameters

Objectives

We will obtain Thermal Hydraulic information from the new US Nuclear Regulatory Commission's Consolidated Safety Code (CSC), which is now known as TRACE. This is their replacement for the older RELAP 5 and TRAC series of safety codes. TRACE contains all of the modeling capabilities of the predecessor codes, including sub-cooled boiling models and a complete Heat Transfer package that has been partially validated against a database. It also includes an approximate 3-D neutronics model of the core. This enables the core to be analyzed in a coupled three-dimensional thermal hydraulic/kinetics basis. Thus local heat generation rates in each full assembly may be determined in a reasonable computational time.

The primary advantage of TRACE is it is designed to operate in a distributed parallel environment. Models for reactor components or physical processes may be added as independent programs coupled through the program's Exterior Communications Interface (ECI). Simple calls to ECI subroutines schedule transmission of thermal hydraulic variables to the chemistry code or boron deposition back to the consolidated code.

In this task, TRACE is being used to predict the local thermal hydraulic conditions that will then be input into the models for mass transport, activity transport and the axial offset anomaly (AOA). Since the code has 2-D kinetics capability the effects of AOA may be observed as the power shape is influenced by the buildup of boron compounds in a given core region.

Task Status

The first part of the task was to develop a good understanding of TRACE, and to be able to read parameters calculated in TRACE for a given reactor. Those thermo-hydrodynamic parameters (section characteristics, flow velocity, temperature, length, relative position to other sections, position, etc.) were used as input values to the model PWR_PC, which calculates the water radiolysis, pH, and electrochemical potential (steady state simulation) at each position of the primary coolant loop of a PWR.

The code is running correctly and can now be used for capability demonstration. But the calculations obtained have not been verified experimentally, because no independent check is currently available for a PWR primary circuit. This is due to the fact that the species concentrations are not measured in general. For example, concentration of oxygen, which is monitored on a routine basis in a BWR, is so low in a PWR primary circuit that it is not measured. Similarly, the hydrogen present in a PWR primary circuit is primarily the result of hydrogen additions and not radiolysis, so the $[H_2]$ measured in the circuit is not a viable indicator of the state of radiolysis. Finally, the ECP, which is now measured on a routine basis in BWRs[7], is not monitored in PWR primary circuit, to the PIs' knowledge, even on an experimental basis.

However, the results of these calculations are encouraging, because they suggest ECP control may be a practical way of mitigating environmentally induced fractures in the primary coolant circuits of PWRs, in much the same way as is being achieved in BWRs. [8-14]

2.1 The PWR-ECP Model

This is a quasi steady state model; i.e. transients are treated as a collection of steady state points. This model solves the mass transport in a simplistic way by assuming the velocity (and then the volume) of each of the sections analyzed in a nuclear reactor loop is constant. This model takes into account that the water-chemistry of PWRs is incumbent on three major factors. They are water radiolysis, chemical reactions, and convection of the injected chemicals like H₂ injection, boron and lithium (to maintain the proper pH). The combination of these three source terms, along with mass transport and conservation, is evaluated at each time and distance in the primary reactor loop to calculate the spatio-temporal concentration variation of 14 chemical species, ECP, and, later in this project, stress corrosion cracking growth rate and activity transport.

2.1.1 Water Radiolysis

The water that acts as the heat transport medium in the reactor core and primary circuit of nuclear power plants experiences, in the core, high doses of mixed field radiation. The resulting radiolysis produces radicals, ions, and molecular species which are highly reactive at the elevated temperatures corresponding to normal operating conditions. The highly oxidizing species like H₂O₂, O₂, e⁻ etc. are very corrosive to the primary circuit. The ability of these species to affect the corrosion properties of the coolant circuit components is reflected in the electrochemical corrosion potential ECP; generally a high ECP favors stress corrosion cracking (SCC), while an excessively low ECP is conducive towards (HIC), the two major failure modes in BWR and PWR primary coolant circuits, respectively. For this reason hydrogen is added to suppress their radiolytic generation and damaging action. To calculate the ECP, it is important that all the radiolytic species concentrations be determined, since all species are electro-active.

However, theory shows that the contribution any given species makes to the ECP is roughly proportional to its concentration, so accurate calculation of the most prevalent species like H₂, O₂ and H₂O₂ is very important. In order to calculate the species concentrations, the combined effects of the radiolytic yield of each species due to radiation, and the changes in concentration due to chemical reactions and fluid convection, must be carefully taken into account.

A number of radiolysis scientific considerations, measures, and codes have, also, been developed to determine the type of reactions occurring and the rate constants of those radiolytic species. These include data by Christensen at Studsvik AB in Sweden [17], Dixon and coworkers at Atomic Energy of Canada Limited [18], Burns and Moore at UKAEA Harwell [4], and by the present authors [1, 9]. All of the radiolysis research appears to confirm that hydrogen added at the 25 cc(STP)/kg level “suppresses radiolysis”, and the concentrations of the oxidizing radiolytic species (O₂, H₂O₂, OH) are very low compared with those of various reducing species, such as H₂ and H, although

differences do exist between the predictions and measures with respect to the actual values of the concentrations.

The ECP modeling work of Macdonald and coworkers [1] shows that under normal PWR primary circuit conditions [25 cc(STP)/kg] and in the absence of oxygen in the primary feed-water, the ECP is controlled primarily by the hydrogen electrode reaction (HER) according to the following equation

$$ECP = -(2.303RT / 2F) \log(f_{H_2}) - (2.303RT / F) pH_T \quad (2-1)$$

where R is the universal gas constant, f_{H_2} is the partial pressure of hydrogen, F is Faraday's constant, and pH_T is the pH at the operating Kelvin temperature (T).

2.1.2 Radiolytic Yield

The rate at which any primary radiolytic species is produced is given by

$$R_i^y = \left(\frac{G_i^{\gamma} \Gamma^{\gamma}}{100 N_V} + \frac{G_i^n \Gamma^n}{100 N_V} + \frac{G_i^{\alpha} \Gamma^{\alpha}}{100 N_V} \right) \tilde{F} \rho \quad (2-2)$$

where R_i^y has units of mol/cm³.s, G^n , G^{γ} , and G^{α} are the radiolytic yields for neutrons, gamma photons, and alpha particles, respectively, in number of particles per 100 eV of energy absorbed, N_V is Avogadro's number, F is equals 6.25×10^{13} (the conversion factor from Rad/sec to eV/gram-sec), and ρ is the water density in g/cm³. Γ^{γ} , Γ^n , and Γ^{α} are the gamma photon, neutron, and α -particle energy dose rates, respectively, in units of Rad/s. Table 2.1 shows compiled G values for 14 species.

Values for the radiolytic yields for various species considered in the radiolysis model were taken from Christensen [17]. A review of the literature revealed a wide variation in the G-values, even for a same author. As noted by Elliot [25], the current G-values should be regarded as being little more than rough estimates.

Table 2.1. G values for Primary radiolytic species

Species No.	Species	G^{γ} (No./100eV)	G^n (No./100eV)	G^{α} (No./100eV)
1	e ⁻	2.66	0.61	0.06
2	H	0.55	0.34	0.21
3	OH	2.67	2.02	0.24
4	H ₂ O ₂	0.72	0.65	0.985
5	HO ₂	0.00	0.05	0.22
6	HO ₂ ⁻	0.00	0.00	0.00
7	O ₂	0.00	0.00	0.00
8	O ₂ ⁻	0.00	0.00	0.00
9	H ₂	0.45	1.26	1.3

10	O ⁻	0.00	0.00	0.00
11	O	0.00	0.00	0.00
12	O ₂ ²⁻	0.00	0.00	0.00
13	OH ⁻	0.01	0.00	0.00
14	H ⁺	2.76	0.00	0.06

The radiolysis of water in a PWR core by α -particles, produced by $^{10}\text{B}_5(\text{n},\alpha)^7\text{Li}_3$ reaction, has recently been assessed, and we concluded that the contributions from α -radiolysis to the concentrations of the radiolytic species in most regions of the coolant circuit are small, when compared with those from neutrons and γ -photons at the prevailing dose rates. However, there are regions where α -particle radiolysis from the water radiolysis process contributes significantly to the formation of the radiolytic species ($> 10\%$), and hence the third term in Equation (2-2) is necessary. This term is absent in the case of a BWR.

2.1.3 Chemical Reactions

In the primary coolant components of the nuclear plant radiolysis is not prominent because of the distance from the core. The primary sources of chemical species are the governing reactions in the radiolysis mechanism. The reaction set used in this study is given in Table 2.2, along with the rate constants and the activation energies.

This reaction set is partly based on a published compilation [4], but has been modified to include hydrogen peroxide decomposition and additional species and reactions. Other radiolysis mechanisms, particularly those by Christensen [17] and Elliot [25], will be examined during the course of this work and the code has been written to facilitate, to the greatest extent possible, the inclusion of new mechanisms.

Table 2.2. Reaction set used in the radiolysis model

*Reaction No.	Rate Constant, k (l/mol.s)	Activation Energy (kcal/Mol)	Reaction
1	1.6D+1	3.0D0	$e^- + H_2O = H + OH^-$
2	2.4D+10	3.0D0	$e^- + H^+ = H$
3	2.4D+10	3.0D0	$e^- + OH = OH^-$
4	1.3D+10	3.0D0	$e^- + H_2O_2 = OH + OH^-$
5	1.0D+10	3.0D0	$H + H = H_2$
6	2.0D+10	3.0D0	$e^- + HO_2 = HO_2^-$
7	1.9D+10	3.0D0	$e^- + O_2 = O_2^-$
8	5.0D+9	3.0D0	$2e^- + 2H_2O = 2OH^- + H_2$
9	4.5D+9	3.0D0	$OH + OH = H_2O_2$
10	1.2D+10	3.0D0	$OH + HO_2 = H_2O + O_2$
11	1.2D+10	3.0D0	$OH + O_2^- = OH^- + O_2$
12	2.0D+7	3.0D0	$OH^- + H = e^- + H_2O$
13	4.5D+8	3.0D0	$e^- + H + H_2O = OH^- + H_2$
14	6.3D+7	3.0D0	$e^- + HO_2^- + H_2O = OH + 2OH^-$
15	1.44D+11	3.0D0	$H^+ + OH^- = H_2O$
16	2.6D-5	3.0D0	$H_2O = H^+ + OH^-$
17	2.0D+10	3.0D0	$H + OH = H_2O$
18	3.4D+7	4.6D0	$OH + H_2 = H + H_2O$
19	2.70D+7	3.4D0	$OH + H_2O_2 = H_2O + HO_2$
20	4.4D+7	4.5D0	$H + H_2O_2 = OH + H_2O$
21	1.9D+10	3.0D0	$H + O_2 = HO_2$
22	8.0D+5	3.0D0	$HO_2 = O_2^- + H^+$
23	5.0D+10	3.0D0	$O_2^- + H^+ = HO_2$
24	2.7D+6	4.5D0	$2HO_2 = H_2O_2 + O_2$
25	1.7D+7	4.5D0	$2O_2^- + 2H_2O = H_2O_2 + O_2 + 2OH^-$
26	2.0D+10	3.0D0	$H + HO_2 = H_2O_2$
27	2.0D+10	3.0D0	$H + O_2^- = HO_2^-$
28	1.3D+8	4.5D0	$e^- + O_2^- + H_2O = HO_2^- + OH^-$
29	1.8D+8	4.5D0	$OH^- + H_2O_2 = HO_2^- + H_2O$
30	1.9973D-6	14.8D0	$2H_2O_2 = 2H_2O + O_2$
31	1.04D-4	3.0D0	$H + H_2O = H_2 + OH$
32	1.02D+4	3.0D0	$H_2O + HO_2^- = H_2O_2 + OH^-$
33	1.5D+7	4.5D0	$HO_2 + O_2^- = O_2 + HO_2^-$
34	7.7D-4	7.3D0	$H_2O_2 = 2OH$
35	7.88D+9	3.0D0	$OH + HO_2^- = O_2^- + H_2O$
36	1.28D+10	3.0D0	$OH + OH^- = O^- + H_2O$
37	6.14D+6	3.0D0	$O^- + H_2O = OH + OH^-$
38	3.97D+9	3.0D0	$e^- + HO_2^- = O^- + OH^-$
39	6.42D+14	3.0D0	$O_2^- + O_2^- + H^+ = HO_2^- + O_2$
40	2.72D-3	15.0D0	$H_2O_2 = H_2O + O$
41	2.84D+10	3.0D0	$O + O = O_2$
42	1.1D+6	3.0D0	$O_2^{2-} + H_2O = HO_2^- + OH^-$
43	1.3D+10	3.0D0	$e^- + O_2^- = O_2^{2-}$
44	0.5D0	3.0D0	$H_2O_2 + HO_2 = H_2O + O_2 + OH$
45	0.13D0	3.0D0	$O_2^- + H_2O_2 = OH + OH^- + O_2$
46	2.56D-8	3.0D0	$H_2O_2 = H^+ + HO_2^-$
47	1.39D+10	3.2D0	$e^- + HO_2 + H_2O = H_2O_2 + OH^-$
48	1.39D+10	3.2D0	$e^- + O_2^- + H_2O = HO_2^- + OH^-$

The rate of change of each species at a given location is given by reaction rate theory as

$$R_i^c = \sum_{s=1}^N \sum_{m=1}^N k_{sm} C_s C_m - C_i \sum_{s=1}^N k_{si} C_s \quad (2-3)$$

where k_{sm} is the rate constant for the reaction between species s and m , k_{si} is the rate constant for the reaction between species s and i , and C_i , C_m , and C_s are the concentrations of Species i , m , and s , respectively. N is the number of reactions in the model (i.e., $N = 48$). Explicit expressions for the gain and the loss of each species are summarized in Table 2.3.

The rate constant, k_j (j denotes the reaction number in Table 2.2), is a function of coolant temperature. Since the temperature throughout the heat transport circuit is not constant, the actual rate constant for each chemical reaction must be calculated for each specific position using Arrhenius' law

$$k = k_o \exp\left[\frac{E_a}{R} \left(\frac{1}{T_o} - \frac{1}{T}\right)\right] \quad (2-4)$$

where k_o is the rate constant at temperature T_o , E_a is the activation energy (Table 2.2), R is the universal gas constant, and T is the temperature in Kelvin. The rate constant for Hydrogen peroxide decomposition (Reaction No. 30) was calculated separately using an experimentally derived relationship [6]:

$$k_{30} = 1.4096 \times 10^5 \cdot e^{-\left(\frac{14800}{RT}\right)} \quad (2-6)$$

Table 2.3. List of Coupled Differential Equations

$$\begin{aligned}
R_1 &= \frac{dC_1}{dt} = -C_1 [k_1 + k_2 C_{14} + k_3 C_3 + k_4 C_4 + k_6 C_5 + k_7 C_7 + 2k_8 C_1 \\
&\quad + k_{13} C_2 + k_{14} C_6 + k_{28} C_8 + k_{38} C_6 + k_{43} C_8 + k_{47} C_5 + k_{48} C_8] + \{k_{12} C_2 C_{13}\} \\
R_2 &= \frac{dC_2}{dt} = -C_2 [2k_5 C_2 + k_{12} C_{13} + k_{13} C_1 + k_{17} C_3 + k_{20} C_4 + k_{21} C_7 + k_{26} C_5 + k_{27} C_8 + k_{31}] \\
&\quad + \{k_1 C_1 + k_2 C_1 C_{14} + k_{18} C_3 C_9\} \\
R_3 &= \frac{dC_3}{dt} = -C_3 [k_3 C_1 + 2k_9 C_3 + k_{10} C_5 + k_{11} C_8 + k_{17} C_2 + k_{18} C_9 + k_{19} C_4 + k_{35} C_6 + k_{36} C_{13}] \\
&\quad + \{k_4 C_1 C_4 + k_{14} C_1 C_6 + k_{20} C_4 C_2 + k_{31} C_2 + 2k_{34} C_4 + k_{37} C_{10} + k_{44} C_4 C_5 + k_{45} C_8 C_4\} \\
R_4 &= \frac{dC_4}{dt} = -C_4 [k_4 C_1 + k_{19} C_3 + k_{20} C_2 + k_{29} C_{13} + k_{30} + k_{34} + k_{40} \\
&\quad + k_{44} C_5 + k_{45} C_8 + k_{46}] + \{k_9 C_3^2 + k_{24} C_5^2 + k_{25} C_8^2 + k_{26} C_2 C_5 + k_{32} C_6 + k_{47} C_1 C_5\} \\
R_5 &= \frac{dC_5}{dt} = -C_5 [k_6 C_1 + k_{10} C_3 + k_{22} + 2k_{24} C_5 + k_{26} C_2 + k_{33} C_8 + k_{44} C_4 + k_{47} C_1] + \\
&\quad \{k_{19} C_3 C_4 + k_{21} C_2 C_7 + k_{23} C_8 C_{14}\} \\
R_6 &= \frac{dC_6}{dt} = -C_6 [k_{14} C_1 + k_{32} + k_{35} C_3 + k_{38} C_1] + \{k_{48} C_1 C_8 + k_{46} C_4 + k_{42} C_{12} \\
&\quad + k_{39} C_8^2 C_{14} + k_{33} C_5 C_8 + k_{29} C_4 C_{13} + k_{28} C_1 C_8 + k_{27} C_2 C_8 + k_6 C_1 C_5\} \\
R_7 &= \frac{dC_7}{dt} = -C_7 [k_7 C_1 + k_{21} C_2] + \{k_{10} C_3 C_5 + k_{11} C_3 C_8 + k_{24} C_5^2 + k_{25} C_8^2 + 0.5k_{30} C_4 + k_{33} C_5 C_8 + \\
&\quad k_{39} C_8^2 C_{14} + k_{41} C_{11}^2 + k_{44} C_4 C_5 + k_{45} C_4 C_8\} \\
R_8 &= \frac{dC_8}{dt} = -C_8 [k_{11} C_3 + k_{23} C_{14} + 2k_{25} C_8 + k_{27} C_2 + k_{28} C_1 + k_{33} C_5 + 2k_{39} C_{14} C_8 + k_{43} C_1 \\
&\quad + k_{45} C_4 + k_{48} C_1] + \{k_7 C_1 C_7 + k_{22} C_5 + k_{35} C_3 C_6\} \\
R_9 &= \frac{dC_9}{dt} = -C_9 [k_{18} C_3] + \{k_5 C_2^2 + k_8 C_1^2 + k_{13} C_1 C_2 + k_{31} C_2\} \\
R_{10} &= \frac{dC_{10}}{dt} = -C_{10} [k_{37}] + \{k_{36} C_3 C_{13} + k_{38} C_1 C_6\} \\
R_{11} &= \frac{dC_{11}}{dt} = -C_{11} [2k_{41} C_{11}] + \{k_{40} C_4\} \\
R_{12} &= \frac{dC_{12}}{dt} = -C_{12} [k_{42}] + \{k_{43} C_1 C_8\}
\end{aligned}$$

Notice that $[H^+]$ and $[OH^-]$ are calculated from the pH and the dissociation of water.

2.1.4 pH

In general, the primary coolant in the PWRs of interest comprises a boric acid/lithium hydroxide solution with the boron concentration ranging from 2000 ppm at the beginning of a fuel cycle to about 10 ppm at the end. Lithium is injected as LiOH in the primary coolant via the RWCU and is in part produced via the $^{10}\text{B}_5(n,\alpha)^7\text{Li}_3$ reaction, but its actual concentration is controlled within the range of 0.4 to 2.2 ppm, using LiOH

injection or ion exchange column de-lithiation, so as to control the pH during operation. This is necessary, in order to minimize corrosion product transport and activation in the core region. Because oxide solubility and metal corrosion rate depend on pH, it is important to develop a model for the chemistry of the coolant from which the pH can be estimated for any given temperature, [B], and [Li]. The model used in the present work, subroutine pH value, makes use of the following reaction set [20]:

Values for the equilibrium quotients and constants for Reactions R1 to R8, together with the sources from which they were taken, are summarized in Table 2.4.

Table 2.4. Equilibrium constants* used in the Subroutine pH value

Equilibrium No.	Reaction Quotient/Constant	.
R1	$pQ_1 = -1573/T - 28.6059 - 0.012078*T + 13.2258*\log_{10}(T)$	20
R2	$pQ_2 = -2756.1/T + 18.966 - 5.835*\log_{10}(T)$	20
R3	$pQ_3 = -3339.5/T + 8.084 - 1.497*\log_{10}(T)$	20
R4	$pQ_4 = -12820/T + 134.56 - 42.105*\log_{10}(T)$	20
R5	$Q_5 = 0.0$	20
R6	$Q_6 = 1.99$	21
R7	$Q_7 = 2.12$	22
R8	$pK_w = -4.098 - 3245/T + 2.23 \times 10^5/T^2 - 3.998 \times 10^7/T^3 + (13.95 - 1262.3/T + 8.56 \times 10^5/T^2) \log_{10}(\text{Water Density})$	32

*N.B. T is in units of Kelvin. Q is the reaction quotient defined in terms of the molal concentrations.

The species concentrations are calculated by the solution of the mass action equations together with the elemental and charge balance constraints. The calculation is carried out iteratively with the activity coefficients being estimated at each step from extended Debye-Huckel theory.

2.1.5 Convection

Convection is considered as the only mode of transport, whereas diffusion and electro-migration are neglected. This assumption is adopted in all the other radiolysis models referred to above. It is assumed the coolant (water) flow is single-phase in all regions of a PWR primary coolant circuit and no trace of vapor is encountered. However, with

regard to nucleate boiling, the steam bubbles that form on the fuel collapse when they detach from the surface. Accordingly, any volatile radiolysis species that transfers to the steam phase is eventually returned to the primary coolant (liquid phase), so the net effect of nucleate boiling on the bulk concentrations is expected to be small, if it exists at all. This situation is in typical contrast with that in a BWR, where a continuous steam phase is formed that leaves the primary coolant. In case of BWR, the irreversible transfer of volatile species (H_2 , O_2) to the steam has an enormous impact on the electrochemistry of the primary circuit.

By adopting the rates of change of species mass from the various sources discussed above, we write the total rate as

$$R_i = \left(\frac{G_i^\gamma \Gamma^\gamma}{100N_V} + \frac{G_i^n \Gamma^n}{100N_V} + \frac{G_i^\alpha \Gamma^\alpha}{100N_V} \right) \tilde{F} \rho + \left[\sum_{s=1}^N \sum_{m=1}^N k_{sm} C_s C_m - C_i \sum_{s=1}^N k_{si} C_s \right] + \frac{d(uC_i)}{dx} \quad (2-7)$$

For a Steady State system the mass flow rate (dm/dt) in a single (un-branched) channel is constant at all points along the channel, the linear flow rate is given by

$$u = (dm / dt) / \rho A \quad (2-8)$$

where A is the cross-sectional area of the channel.

By solving the system of equations generated by Equation (2.7) numerically, we are able to calculate the concentrations of each species at any point in a PWR heat transport circuit.

This ordinary differential equations (ODE) system is “stiff” due to state variables evolving over time scales much shorter than others. If the governing reaction-convection equations were solved using an explicit scheme, the integration time step would be severely restricted by the shortest time scale and a large number of steps would be necessary to complete the simulation.

The approach used in this work to solve the set of coupled ODEs makes use of a publicly available subroutine (DVODE), which was developed by Hindmarsh at the Lawrence Livermore National Laboratory in California. This algorithm is designed to solve first degree, stiff ODE equation sets. Our system of equations is indeed coupled throughout via the concentrations of the 14 species considered. Notice that equation 2.7 represents a set of i -coupled differential equations coupled through the concentration of common species (equation 2.7). To solve the i -coupled differential equations (i = number of species), the DVODE subroutine needs to have the set of equations and the Jacobians described. We begin by assuming that the coolant is an incompressible fluid ($\bar{\nabla} \cdot \bar{v} = 0$) and the flow is turbulent (efficient mixing). Accordingly, the flux of each dissolved species is given by

$$\bar{N}_i = -Z_i U_i F c_i \bar{\nabla} \phi - D_i \bar{\nabla} C_i + C_i \bar{v} \quad (2.9)$$

Flux = migration + diffusion + convection

Because of efficient mixing and in the absence of an electric field, we may ignore diffusion and migration, respectively, and hence the material balance can be written as:

$$\frac{\partial C_i}{\partial t} = -\bar{\nabla} \cdot \bar{N}_i + R_i \quad (2-10)$$

(accumulation = net input + production) where R_i is the rate of production of the species in the fluid due to homogeneous reactions. Accordingly

$$\frac{\partial C_i}{\partial t} = -\bar{\nabla} \cdot (C_i \bar{v}) + R = -C_i \frac{\partial v}{\partial x} - v \frac{\partial C_i}{\partial x} + R_i \quad (2-11)$$

where $\bar{v}$ is the velocity vector and v the velocity for each considered section. Note that for the steady state model, the velocity is considered in one dimension and is considered to be constant in each section of uniform cross sectional area, accordingly

$$\frac{\partial v}{\partial x} = \frac{dv}{dx} \quad (2-12)$$

Noting that the concentration is a function of two independent variables (x and t), we may write the total differential as

$$dC_i = \frac{\partial C_i}{\partial x} dx + \frac{\partial C_i}{\partial t} dt \quad (2-13)$$

and hence

$$\frac{dC_i}{dt} = \frac{\partial C_i}{\partial x} \frac{dx}{dt} + \frac{\partial C_i}{\partial t} \frac{dt}{dt} \quad (2-14)$$

Therefore,

$$\frac{dC_i}{dt} - v \cdot \frac{\partial C_i}{\partial x} = \frac{\partial C_i}{\partial t} \quad (2-15)$$

By substituting equation (2-11) and (2-12) into equation (2-15) we then obtain:

$$\frac{dC_i}{dt} - v \cdot \frac{\partial C_i}{\partial x} = -v \cdot \frac{\partial C_i}{\partial x} - C_i \frac{dv}{dx} + R_i \quad (2-16)$$

and hence

$$\frac{dC_i}{dt} = -C_i \frac{dv}{dx} + R_i \quad (2-17)$$

This equation may be rewritten as:

$$\frac{dC_i}{dx} = \frac{dC_i}{\left(\frac{dx}{dt}\right)dt} = -\frac{C_i}{v} \frac{dv}{dx} + \frac{R_i}{v} \quad (2-18)$$

Thus, the calculation-strategy is to calculate dC_i / dx using equation (2-18) and dC_i / dt using the definition of local fluid velocity $\left(v = \frac{dx}{dt}\right)$ at different points in the system.

$$\frac{dC_i}{dt} = v \cdot \frac{dC_i}{dx} = -C_i \frac{dv}{dx} + R_i \quad (2-19)$$

Although DVODE is capable of computing J from the given system of ODEs, its performance is much improved when J is supplied. Hence, the Jacobean matrix was derived by analytically differentiating the system of ODEs and supplied to DVODE.

The elements of the Jacobean matrix used by DVODE for solving the set of twelve ODEs are given in Table 2.5. Note the Jacobean is only 12x12, because the activities of two of the species (H^+ and OH^-) are fixed by the $B(OH)_3/LiOH$ equilibrium where the numbers on R and C correspond to the species (14) and the number on the K corresponds to the 48 reactions considered.

2.1.6 Mixed Potential Model

After the concentration of each radiolysis species is calculated, the corrosion potential of the component can be calculated using a mixed potential model (MPM) [16]. The MPM is based on the physical condition that charge conservation must be obeyed in the system. Because electrochemical reactions transfer charge across a metal/solution interface at rates measured by the partial currents, the following equation expresses the charge conservation constraint

$$\sum_{j=1}^n i_{R/O,j}(E) + i_{corr}(E) = 0 \quad (2-20)$$

where $i_{R/O,j}$ is the partial current density due to the j-th redox couple in the system and i_{corr} is the metal oxidation (corrosion) current density. These partial currents depend on the potential drop across the metal/solution interface.

As we don't have any information for the MPM parameters for SS 316 and Zircaloy, we are using the current version of the MPM, which was developed for modeling the ECP of Type 304 SS in BWR primary circuits.

Table 2.5. Jacobean matrix elements used to solve the 12 coupled ordinary differential equations.

$$\begin{aligned} \frac{\partial R_1}{\partial C_1} &= -[k_1 + k_2 C_{14} + k_3 C_3 + k_4 C_4 + k_6 C_5 + k_7 C_7 + 2k_8 C_1 + k_{13} C_2 + k_{14} C_6 + k_{28} C_8 + k_{38} C_6 + k_{43} C_8 \\ &\quad + k_{47} C_5 + k_{48} C_8] - 2k_8 C_1 \\ \frac{\partial R_1}{\partial C_2} &= -k_{13} C_1 + k_{12} C_{13} \\ \frac{\partial R_1}{\partial C_3} &= -k_3 C_1 \\ \frac{\partial R_1}{\partial C_4} &= -k_4 C_1 \\ \frac{\partial R_1}{\partial C_5} &= -k_6 C_1 - k_{47} C_1 \\ \frac{\partial R_1}{\partial C_6} &= -k_{14} C_1 - k_{38} C_1 \\ \frac{\partial R_1}{\partial C_7} &= -k_7 C_1 \\ \frac{\partial R_1}{\partial C_8} &= -C_1 k_{28} - C_1 k_{43} - C_1 k_{48} \\ \frac{\partial R_2}{\partial C_1} &= -k_{13} C_2 + k_2 C_{14} + k_1 \\ \frac{\partial R_2}{\partial C_2} &= -[4k_5 C_2 + k_{12} C_{13} + k_{13} C_1 + k_{17} C_3 + k_{20} C_4 + k_{21} C_7 + k_{26} C_5 + k_{27} C_8 + k_{31}] \\ \frac{\partial R_2}{\partial C_3} &= -C_2 k_{17} + k_{18} C_9 \\ \frac{\partial R_2}{\partial C_4} &= -C_2 k_{20} \\ \frac{\partial R_2}{\partial C_5} &= -C_2 k_{26} \\ \frac{\partial R_2}{\partial C_7} &= -k_{21} C_2 \\ \frac{\partial R_2}{\partial C_8} &= -C_2 k_{27} \\ \frac{\partial R_2}{\partial C_9} &= +k_{18} C_3 \\ \frac{\partial R_3}{\partial C_1} &= -k_3 C_3 + k_4 C_4 + k_{14} C_6 \end{aligned}$$

$$\begin{aligned}
\frac{\partial R_3}{\partial C_2} &= -C_3 k_{17} + k_{20} C_4 + k_{31} \\
\frac{\partial R_3}{\partial C_3} &= -[k_3 C_1 + 2k_9 C_3 + k_{10} C_5 + k_{11} C_8 + k_{17} C_2 + k_{18} C_9 + k_{19} C_4 + k_{35} C_6 + k_{36} C_{13}] - C_3 2k_9 \\
\frac{\partial R_3}{\partial C_4} &= -k_{19} C_3 + k_4 C_1 + k_{20} C_2 + 2k_{34} + k_{44} C_5 + k_{45} C_8 \\
\frac{\partial R_3}{\partial C_5} &= -C_3 k_{10} + k_{44} C_4 \\
\frac{\partial R_3}{\partial C_6} &= -C_3 k_{35} + k_{14} C_1 \\
\frac{\partial R_3}{\partial C_8} &= -C_3 k_{11} + k_{45} C_4 \\
\frac{\partial R_3}{\partial C_9} &= -k_{18} C_3 \\
\frac{\partial R_3}{\partial C_{10}} &= k_{37} \\
\frac{\partial R_4}{\partial C_1} &= -k_4 C_4 + k_{47} C_5 \\
\frac{\partial R_4}{\partial C_2} &= -C_4 k_{20} + k_{26} C_5 \\
\frac{\partial R_4}{\partial C_3} &= -C_4 k_{19} + 2k_9 C_3 \\
\frac{\partial R_4}{\partial C_4} &= -[k_4 C_1 + k_{19} C_3 + k_{20} C_2 + k_{29} C_{13} + k_{30} + k_{34} + k_{40} + k_{44} C_5 + k_{45} C_8 + k_{46}] \\
\frac{\partial R_4}{\partial C_5} &= -C_4 k_{44} + 2k_{24} C_5 + k_{26} C_2 + k_{47} C_1 \\
\frac{\partial R_4}{\partial C_6} &= k_{32} \\
\frac{\partial R_4}{\partial C_8} &= -C_4 k_{45} + 2k_{25} C_8 \\
\frac{\partial R_5}{\partial C_1} &= -C_5 k_6 - C_5 k_{47} \\
\frac{\partial R_5}{\partial C_2} &= -C_5 k_{26} + k_{21} C_7 \\
\frac{\partial R_5}{\partial C_3} &= -C_5 k_{10} + k_{19} C_4 \\
\frac{\partial R_5}{\partial C_4} &= -C_5 k_{44} + k_{19} C_3 \\
\frac{\partial R_5}{\partial C_5} &= -[k_6 C_1 + k_{10} C_3 + k_{22} + 2k_{24} C_5 + k_{26} C_2 + k_{33} C_8 + k_{44} C_4 + k_{47} C_1] - 2C_5 k_{24} \\
\frac{\partial R_5}{\partial C_7} &= k_{21} C_2
\end{aligned}$$

$$\begin{aligned}
\frac{\partial R_5}{\partial C_8} &= -C_5 k_{33} + k_{23} C_{14} \\
\frac{\partial R_6}{\partial C_1} &= -C_6 k_{14} - C_6 k_{38} + k_{48} C_8 + k_{28} C_8 \\
\frac{\partial R_6}{\partial C_1} &= -C_6 k_{14} - C_6 k_{38} + k_{48} C_8 + k_{28} C_8 + k_6 C_5 \\
\frac{\partial R_6}{\partial C_2} &= k_{27} C_8 \\
\frac{\partial R_6}{\partial C_3} &= -C_6 k_{35} \\
\frac{\partial R_6}{\partial C_4} &= k_{46} + k_{29} C_{13} \\
\frac{\partial R_6}{\partial C_5} &= k_{33} C_8 + k_6 C_1 \\
\frac{\partial R_6}{\partial C_6} &= -[k_{14} C_1 + k_{32} + k_{35} C_3 + k_{38} C_1] \\
\frac{\partial R_6}{\partial C_8} &= k_{48} C_1 + 2k_{39} C_8 C_{14} + k_{33} C_5 + k_{28} C_1 + k_{27} C_2 \\
\frac{\partial R_6}{\partial C_{12}} &= k_{42} \\
\frac{\partial R_7}{\partial C_1} &= -C_7 k_7 \\
\frac{\partial R_7}{\partial C_2} &= -C_7 k_{21} \\
\frac{\partial R_7}{\partial C_2} &= -C_7 k_{21} \\
\frac{\partial R_7}{\partial C_3} &= k_{10} C_5 + k_{11} C_8 \\
\frac{\partial R_7}{\partial C_4} &= 0.5k_{30} + k_{44} C_5 + k_{45} C_8 \\
\frac{\partial R_7}{\partial C_5} &= k_{10} C_3 + 2C_5 k_{24} + k_{33} C_8 + k_{44} C_4 \\
\frac{\partial R_7}{\partial C_7} &= -[k_7 C_1 + k_{21} C_2] \\
\frac{\partial R_7}{\partial C_8} &= k_{11} C_3 + 2C_8 k_{25} + k_{33} C_5 + 2C_8 C_{14} k_{39} + k_{45} C_4 \\
\frac{\partial R_7}{\partial C_{11}} &= k_{41} 2C_{11} \\
\frac{\partial R_8}{\partial C_1} &= -[k_{28} + k_{43} + k_{48}] C_8 + k_7 C_7 \\
\frac{\partial R_8}{\partial C_2} &= -C_8 k_{27}
\end{aligned}$$

$$\frac{\partial R_8}{\partial C_3} = -C_8 k + k_{35} C_6$$

$$\frac{\partial R_8}{\partial C_4} = -C_8 k_{45}$$

$$\frac{\partial R_8}{\partial C_5} = -C_8 k_{33} + k_{22}$$

$$\frac{\partial R_8}{\partial C_6} = +k_{35} C_3$$

$$\frac{\partial R_8}{\partial C_7} = k_7 C_1$$

$$\begin{aligned} \frac{\partial R_8}{\partial C_8} = & -[k_{11} C_3 + k_{23} C_{14} + 2k_{25} C_8 + k_{27} C_2 + k_{28} C_1 + k_{33} C_5 + +2k_{39} C_{14} C_8 + k_{43} C_1 + \\ & k_{45} C_4 + k_{48} C_1] - C_8 [2k_{25} C_8 + 2k_{39} C_{14} * C_8] \end{aligned}$$

$$\frac{\partial R_9}{\partial C_1} = 2k_8 C_1 + k_{13} C_2$$

$$\frac{\partial R_9}{\partial C_2} = 2k_5 C_2 + k_{13} C_1 + k_{31}$$

$$\frac{\partial R_9}{\partial C_3} = -C_9 k_{18}$$

$$\frac{\partial R_9}{\partial C_9} = -k_{18} C_3$$

$$\frac{\partial R_{10}}{\partial C_1} = k_{38} C_6$$

$$\frac{\partial R_{10}}{\partial C_3} = k_{36} C_{13}$$

$$\frac{\partial R_{10}}{\partial C_6} = k_{38} C_1$$

$$\frac{\partial R_{10}}{\partial C_{10}} = -k_{37}$$

$$\frac{\partial R_{11}}{\partial C_{11}} = -4k_{41} C_{11}$$

$$\frac{\partial R_{11}}{\partial C_4} = k_{40}$$

$$\frac{\partial R_{12}}{\partial C_{12}} = -k_{42}$$

$$\frac{\partial R_{12}}{\partial C_1} = k_{43} C_8$$

$$\frac{\partial R_{12}}{\partial C_8} = k_{43} C_1$$

all others = 0

Table 2.6 lists the species considered and the number assigned to each of the species in the program.

Table 2.6. Chemical species and their Corresponding Index Numbers in the Equations

Number	Species
1	e^-
2	H
3	OH
4	H_2O_2
5	HO_2
6	HO_2^-
7	O_2
8	O^{2-}
9	H_2
10	O^-
11	O
12	O_2^-
13	OH^-
14	H^+

In the MPM for type 304 SS, the steel oxidation current density, i_{corr} , was modeled as an empirical function of voltage.

$$i_{corr} = \frac{e^{(E-E_o)/b_f} - e^{-(E-E_o)/b_r}}{384.62e^{4416/T} + X} \quad (2-21)$$

where

$$X = \frac{e^{(E-E_o)/b_f}}{2.61 \times 10^{-3} e^{-4416/T + 0.523(E-E_o)^{0.5}}} \quad (2-22)$$

and

$$E_o = 0.122 - 1.5286 \times 10^{-3} T \quad (2-23)$$

In these expressions, b_f and b_r are the forward and reverse Tafel constants, respectively, for the metal dissolution reaction, with values of 0.06 V being assumed for both. In actual fact, they are empirical constants assumed *a priori* in fitting Equation (2-20) to the current/voltage data. Again it is important to note that Equation (2-21) applies strictly to Type 304 SS in near neutral solutions [16] and, hence, this expression may not be a good empirical model for stainless steels in PWR primary circuits. More recently, one of the

authors has developed the Point Defect Model [26] for the oxidation of a passive metal. This model yields the passive current density in the form

$$i_{corr} = a * \exp(bE) + c \quad (2.24)$$

where the parameters a , b , and c are given in terms of fundamental parameters, as given in the original publication. The first term on the right side of Equation (2-24) arises from the transmission of cations (via cation vacancies) across the passive film from the metal/film interface to the film/solution interface, while the second term reflects the transmission of oxygen ions (via oxygen vacancies) in the reverse direction. We had hoped to fit Equation (2-24) to available experimental data from the literature for the alloys of interest (carbon steel, Alloy 600, and stainless steels, data for which are now being assessed) under the conditions that most closely approximate those present in the primary coolant circuits of PWRs. However, the required steady state current/voltage data are unavailable and this approach, which is more soundly based on the theory of passivity, had to be abandoned. It is our recommendation, however, that an experimental program be initiated to obtain the necessary data.

Because electrochemical kinetic data is available only for the hydrogen electrode reaction (HER, H_2/H^+), the oxygen electrode reaction (OER, O_2/H_2O), and the hydrogen peroxide electrode reaction (HPER, H_2O_2/H_2O), only H_2 , O_2 , and H_2O_2 can be considered as the redox species in the MPM. Furthermore, we currently have electrochemical kinetic data for these species only on Type 304 SS, so that only this substrate could be modeled with respect to the ECP. However, it is believed that Type 304 SS serves as a good analog for other stainless steels and, perhaps, also for nickel-based alloys, such as Alloys 600 and 718. This is based on the observation that all of these chromium-containing alloys form passive films which are essentially Cr_2O_3 and have the same thickness at any given potential. Because the exchange current density of a redox species is determined by resonant tunneling of charge carriers across the passive film, the exchange current densities for any given redox reaction on a wide variety of Fe-Cr-Ni alloys are expected to be similar. Furthermore, the electro-oxidation current densities for various Fe-Cr-Ni alloys in the same solutions and under the same conditions are also similar, again reflecting the essentially similar natures of the passive films. Accordingly, the ECP, which reflects a balance between the partial currents for the anodic reactions (substrate oxidation and hydrogen oxidation) and the cathodic reactions (reduction of oxygen and hydrogen peroxide) that occur on the substrate surface, should be similar. No electrochemical data is available for Zircaloy, so the ECP of this substrate could not be modeled. However, the code has been written so appropriate values are readily inserted when they become available.

The current density ($i_{R/O}$) for a redox couple (e.g. O_2/H_2O , H^+/H_2 , H_2O_2/H_2O)

$$R \rightleftharpoons O + ne \quad (R9)$$

(where R is the reduced species and O is the oxidized species) can be expressed in terms of a generalized Butler-Volmer equation as

$$i_{R/O} = \frac{e^{(E-E_{R/O}^e)/b_a} - e^{-(E-E_{R/O}^e)/b_c}}{\frac{1}{i_{0,R/O}} + \frac{1}{i_{i,f}} e^{(E-E_{R/O}^e)/b_a} - \frac{1}{i_{i,r}} e^{-(E-E_{R/O}^e)/b_c}} \quad (2-25)$$

where $i_{0,R/O}$ is the exchange current density, $i_{i,f}$ and $i_{i,r}$ are the mass-transfer limited currents for the forward and reverse directions of the redox reaction, respectively, and b_a and b_c are the anodic and cathodic Tafel constants. $E_{O/R}^e$ is the equilibrium potential for this reaction as computed from the Nernst equation:

$$E_{O/R}^e = E_{O/R}^0 - \frac{2.303RT}{nF} \log\left(\frac{a_R}{a_O}\right) \quad (2-26)$$

where a_R and a_O are the thermodynamic activities of R and O, respectively, and $E_{O/R}^0$ is the standard potential. Limiting currents are calculated using the equation:

$$i_{l,O/R} = \pm 0.0165 n F D C_{O/R}^b Re^{0.86} Sc^{0.33} / d \quad (2-27)$$

where the sign depends on whether the reaction is in the forward (+) or reverse (-) direction, F is Faraday's number, D is the diffusivity of the redox species, $C_{O/R}^b$ is the bulk concentration of O or R, as appropriate, Re is the Reynolds number ($Re = Vd/\eta$), Sc is the Schmidt number ($Sc = \eta/D$), d is the channel diameter, V is the flow velocity, and η is the kinematic viscosity.

The redox reactions of interest in this study are assumed to be:

as was found in the modeling of ECP in BWRs [10-16]. Using the data available from the published literature for the constants and the coefficients [9, 21-24], the ECP can be calculated.

An important point which needs to be emphasized is that the maximum contribution any given radiolytic species can make to the ECP is roughly proportional to its concentration. Thus, in BWR simulations the concentrations of H_2 , O_2 , and H_2O_2 are calculated to be orders of magnitude greater than any other radiolytic species and hence only these three need be considered. In the case of PWR primary HTC's, our previous modeling [1] suggests that equated electrons, H atoms, and OH radicals may be significant species in regions of very high-energy dose rate (e.g. near the fuel). However, no electrochemical kinetic data exist for these reactions and, hence, they cannot be incorporated at this time.

2.2 Background for TRACE

TRACE solves a fully conservative form of mass equations, but non-conservative forms of the energy and momentum equations. This was largely driven by convenience in solving with a “Semi-Implicit” method. For single phase flow these are in the form [34]

$$\frac{\partial \rho}{\partial t} + \nabla \cdot \rho \cdot \vec{V} = 0 \quad (2-28)$$

$$\frac{\partial \rho e}{\partial t} + \nabla \cdot \rho \cdot \vec{V} + p \nabla \cdot \vec{V} = q \quad (2-29)$$

$$\frac{\partial \rho \vec{V}}{\partial t} + \vec{V} \cdot \nabla \vec{V} + \frac{1}{\rho} \nabla p = -f |\vec{V}| \vec{V} + \vec{g} \quad (2-30)$$

In case of water chemistry calculations, the general form of the equation should be

$$\frac{\partial (1-\alpha) C_{i,j}}{\partial t} + \nabla \cdot (1-\alpha) C_{i,j} \cdot \vec{V} = \chi(C_{i1}, C_{i2}, C_{i3}, \dots) \quad (2-31)$$

(Similar to equation 2-27) where α represents the void fraction, C_{ij} represents the concentration of i^{th} species in j^{th} component and the right hand side represents the function of the source terms.

2.3 Integration of the PWR-ECP Model and TRACE

The program comprises of subroutines as shown in the diagram (2.1) below.

Figure 2.1. Algorithm of PWR-ECP Code

Description of the Functions

- Main – This subroutine loops over all the components of the nuclear reactor that are being analyzed.
- Calecp – Calculates the Electrochemical Potential

- Phvalue – Calculates the Ph
- F – This is the subroutine that evaluates all the source terms that involves Radiolysis, Chemical reactions and water chemistry
- Printing – This subroutine does generalized printing of all the input and output
- PrintEcp- This subroutine prints the Electrochemical Potential
- KMod1 – Modifies the Rate Constant using the Arrhenius' Law

The program reads the Input parameters from 3 different files

- The one containing Rate Constants for the governing chemical reactions
- The One containing the G values and K values for the radiolysis equations
- Thermal Hydraulic Data and Radiolytic Data (Gamma, Alpha and Neutron Dose Rates)

Note: The Gamma, Neutron and Alpha dose rates have been approximated by general literature survey and represent the typical values. We don't have any specific information as of now, but we expect it will be provided to us by DOE or Plant operators once the code is fully functional.

After reading the Input, the pH and Modified Rate Constant are calculated. Then DVODE evaluates the source equations and the Jacobean Matrix to give the concentration of different species in different parts of the circuit. Finally ECP is calculated using a Mixed Potential Model.

However, the existing code suffered from the following limitations:

- As the system of equations is stiff, the spatial integration scheme suffers from the drawback of being very slow. If more chemical species are added, then the numerical solution will become more complex.
- Transients could not be modeled in a Lagrangian Coordinate System.
- The velocity is assumed as constant; hence, a tapering cross section is modeled as a series of stepped cross sections.
- The modeling can be used for a wide range of PWR's and BWR's. It could be generalized but then would still not get rid of the above three limitations.

To take care of all this, the existing code was integrated with TRACE.

2.3.1 Integration with TRACE

Integration of the existing program with TRACE involved the following steps.

1. Reading the chemistry input files
2. Basic 1 D data Structure for chemical species

3. Basic 2 D data Structure for chemical species
4. Conversion of existing water chemistry code in Fortran 90 and its modularization
5. Changing the algorithm of the existing water chemistry code
6. Incorporating the water chem.-code in a new module in trace
7. Making subroutines for calling the water chemistry codes on a component by component basis in 1D and 2D
8. Making subroutines for writing the output
9. Changing the Graphical subroutines (the XTV routines) to generate graphics for water chemistry parameters like species concentration, pH and ECP.
10. Modifying the Fill component data structure to take care of injection of chemicals
11. Adding the advection terms to model the injection of species

Figure 2.2. Computational engine of trace/ consolidate code

Figure 2.3. Integration of trace and PWR-ECP.

2.3.2 Further Development of the PWR-ECP Code

Objectives

The most pressing needs in developing the advanced PWR-ECP Code is to incorporate kinetic parameters for the redox reactions which occur in the system, to incorporate the boiling crevice model, so the species concentrations at the site of precipitation in the porous deposit or on the fuel cladding surface under local boiling can be estimated and to modify the code so three-dimensional maps of species concentrations and ECP in the bulk coolant in the reactor core can be generated. The latter will involve considerable model and code development, since the present PWR-ECP models are one-dimensional.

Task Status

The current PWR-ECP was developed as a generic code to test a particular test problem. The code was hardwired for a particular plant (in this case, it was hardwired for the W4LOOP problem). Hence, the code was not flexible enough to analyze all PWRs, as well as, it did not have the flexibility to add or remove extra components from the case being considered.

So the need was felt to develop an object oriented code which would be flexible enough to test any kind of PWR. There were two options: a) develop an entirely new code using C++ or Fortran 90, or b) integrate the existing code with some other code which was already versatile. The second option seemed more efficient in terms of cost and time.

The reasons being:

1. Development of an object oriented code that will do the simulation and analysis of a system as complex as a Nuclear Power plant will require thousands of man hours.
2. The input decks to be prepared for each nuclear power plant system and test cases will also demand hundreds of man hours.

Hence, the PWR_ECP code was fully integrated with TRACE instead of partially integrated.

The present Algorithm involved spatial integration but TRACE worked in time domain. So the PWR_ECP algorithm was modified for time domain integration. The integration part is done and the following milestones have been achieved.

1. The program has been made flexible enough and can analyze any kind of PWR.
2. The program has been given tremendous graphical capabilities. It can now generate graphs for pH, ECP and concentration of all the chemical species being considered (currently they are 14) with respect to time. The code is flexible enough to add any number of species.
3. If injection of H_2 is not involved, then the program is already fully functional, however, we are including the injection of H_2 and O_2 (due to contamination on the water) in order to simulate “if then” scenarios. Additional work on injection is necessary. .
4. The program can model both the transients and steady-states, if the program has been made to run for a long time.

As of now, the injection modeling has been completed. Now the crack growth rate model is to be implemented.

Issues and Concerns: None

2.4. Test cases, Results and Discussions

2.4.1 Description of the Test Cases

1. A Simple Model (Fig. 2.3): Due to the complexities involved and the intensive calculation times in testing even the minor changes in code, a very simple case was modeled. This contains the following:
 - a. A reactor core
 - b. An Inlet Pipe to the core modeling the cold leg
 - c. Two Outlet Pipes from the core modeling the Hot leg
 - d. An injection fill has been added to inject oxygen at shut down.
2. The W4 LOOP Problem (Figure 2.4): W4LOOP test problem is the most popular test-problem used by code developers for initial testing of their update changes to TRAC. It is a quick running test problem that exercises the complexity and phenomena of a prototypic multiple-loop plant model for both steady-state and rapid transient conditions.

Figure 2.3: A simple test case with a short cycle (Table 2.7)

Description of Components:

Table 2.7 Listing of components of the Simple Test Case

1. liquid fill
2. inlet pipe for vessel 3
3. vessel component
4. Vessel Outlet
7. break $p = 1.01\text{e}5$ pa
9. Chemical Injection

Figure 2.4. The W4 Loop model (Table 2.8)

Figure 2.4.1. “Magnified View 1” of a section of W4 loop plant.

Figure 2.4.2. “Magnified View 2” of a section of W4 loop plant.

Figure 2.4.3. “Magnified View 3” of a section of W4 loop plant.

Figure 2.4.4. “Magnified View 4” of a section of W4 loop plant.

Table 2.8. List of all Hydraulic components of the W4 loop plant.

1. bkn-loop hot-leg pipe
2. bkn-loop st-gen primary
3. bkn-loop pump-suct pipe
4. bkn-loop pump
5. bkn-loop cold-leg & break

6. bkn-loop break valve
7. bkn-loop containment
8. bkn-loop sec-side feedwater
9. bkn-loop sec pressure bc
10. int-loop hot-leg & prizer
11. int-loop st-gen primary
12. int-loop pump-suct pipe
13. int-loop pump
14. int-loop cold-leg & accum
15. int-loop c-leg & hpi/lpi
16. int-loop c-leg flow split
17. bkn-loop sec-side downcom
18. int-loop sec-side downcom
19. int-loop hot-leg prizer
20. int-loop accum check valve
21. int-loop accumulator
22. int-loop prizer top
23. int-loop sec-side feed water
24. int-loop sec pressure bc
25. int-loop hpi & lpi
26. 3-d vessel
27. brk-loop sec boiler/stdom
28. int-loop sec boiler/stdom
31. int-loop accum top
41. int-loop c-leg vssl c6
42. int-loop c-leg vssl c7
43. int-loop c-leg vssl c8
44. int-loop c-leg vssl c8

Note: The missing numbers are for the hidden or internal components. Only hydraulic components are listed as corrosion parameters have been calculated for them only.

2.4.2 Results and Discussion

W4 Loop results: The following shows a glimpse of the result files generated from our code. This is a listing from the chemconpl.dat file which contains the results of the calculated chemical concentrations of the one-dimensional components.

```
Chemical concentrations in Moles/Liter
Cell Number = 1    time step= 79
Temp_In°C= 313.198    Temp_Out°C= 313.211
*****
***
e-    *    0.740E-07    H    *    0.387E-06
OH    *    0.357E-07    H2O2    *    0.509E-07
HO2    *    0.296E-10    HO2-    *    0.964E-07
O2    *    0.682E-09    O2-    *    0.435E-08
H2    *    0.759E-03    O-    *    0.252E-08
```

```

O      *      0.717E-08      O2      *      0.598E-10
OH-    *      0.294E-04      H+      *      0.417E-07

Cell Number = 2    time step= 79
Temp_In°C=  299.513    Temp_Out°C=  299.520
*****
***
e-      *      0.740E-07      H      *      0.387E-06
OH      *      0.357E-07      H2O2   *      0.509E-07
HO2     *      0.296E-10      HO2-  *      0.964E-07
O2      *      0.682E-09      O2-   *      0.435E-08
H2      *      0.759E-03      O-     *      0.252E-08
O       *      0.717E-08      O2     *      0.598E-10
OH-     *      0.294E-04      H+     *      0.417E-07

Cell Number = 3    time step= 79
Temp_In°C=  289.736    Temp_Out°C=  289.730
*****
***
e-      *      0.740E-07      H      *      0.387E-06
OH      *      0.357E-07      H2O2   *      0.509E-07
HO2     *      0.296E-10      HO2-  *      0.964E-07
O2      *      0.682E-09      O2-   *      0.435E-08
H2      *      0.759E-03      O-     *      0.252E-08
O       *      0.717E-08      O2     *      0.598E-10
OH-     *      0.294E-04      H+     *      0.417E-07

```

Figure 2.5. Steady state concentrations in W4 loop component 11.

Individual graphs can be plotted for chemical concentration, pH and ECP.

Figure 2.6. Concentration of H^+ in a pipe of the w4 loop (the steady state reaches after 25 seconds of running).

```

Time step=110
Problem Time= 0.977763E+02

Component: $28$ int-loop sec boiler/stdom

Cell Number = 2    PH= 6.68    ECP=-0.70
Temp_In°C= 262.547    Temp_Out°C= 262.547

Cell Number = 3    PH= 6.67    ECP=-0.70
Temp_In°C= 262.058    Temp_Out°C= 262.058

Cell Number = 5    PH= 6.67    ECP=-0.70
Temp_In°C= 262.060    Temp_Out°C= 262.060

Component: $1$ bkn-loop hot-leg pipe

Cell Number = 1    PH= 7.20    ECP=-0.36
Temp_In°C= 312.746    Temp_Out°C= 312.740

Cell Number = 2    PH= 7.20    ECP=-0.44
Temp_In°C= 312.744    Temp_Out°C= 312.738

```

Figure 2.7. Output screen shot for the w4 loop model

Figure 2.8. ECP variation in a pipe of the w4 loop.

2.4.3 Concentration of Species in Vessel

Figure 2.9. Concentration of HO₂⁻ at startup in reactor core

Figure 2.10. Concentration of O⁻ at startup in reactor core.

Figure 2.11. Concentration of O_2^- in reactor core (about to reach steady state).

2.4.4 Effect of Oxygen Injection.

Figure 2.12: Concentration of peroxide with different levels of oxygen

The Oxygen injection increases the rate of production of Hydrogen Peroxide, as shown above. Hydrogen peroxide is highly oxidizing and that results in very positive ECP, hence, aiding corrosion.

Figure 2.13. Concentration of peroxide with different levels of hydrogen.

2.4.5 Effect of Hydrogen Injection (Figure 2.13)

The injection of Hydrogen suppresses Hydrogen peroxide production and this is why it's a general practice to inject Hydrogen. It is important to note that too much hydrogen is not recommended as it leads to hydrogen embrittlement. The highlights of our code are that we can calculate the exact concentration of Hydrogen needed to suppress radiolysis and maintain the concentration of radiolytic species.

2.5 Model Future Capabilities

1. The program will have the functionality of analyzing BWRs.
2. The program gives Finite Element grid based distribution of ECP and pH. This will help in analyzing the corrosion at a molecular level in the structure. This capability has been achieved by modifying the *trcgrf* subroutines of the consolidated code and the SNAP (symbolic nuclear analysis package) will be able to read graphics data from it.
3. Mixing part has been taken care off and CVCS and RHRS can now be modeled
4. The program will have the capabilities of selecting any kind of material for its components. That way various simulations can be done and will aid in cost cutting of expensive experiments.
5. When fully functional the code will generate enough data to set up Design of Experiments (DOE) and Factorial experiments can be done. Based on this Optimization algorithms can be developed using Non Linear programming and Dynamic Programming to optimize plant parameters like pressure, temperature Velocity of the coolant and Concentration of chemical species for maximum output and minimum corrosion.

Issues and Concerns: None

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Task 3. The BWR-ECP Code Development

3.1 The ECP and CGR Models in BWR.

In 1983, hydrogen water chemistry (HWC), a remedial measure for mitigating intergranular stress corrosion cracking (IGSCC) in boiling water reactors (BWRs), was first introduced in a commercial BWR in the United States [38]. The purpose of HWC technology is to lower the electrochemical corrosion potential (ECP) and thus reduce the crack growth rate (CGR) or crack initiation probability of BWR components by injecting hydrogen into the reactor coolant through the feedwater line of a BWR. Once a sufficient amount of hydrogen is present in the reactor coolant, it is possible to reduce the concentrations of certain oxidizing species (i.e., oxygen and hydrogen peroxide) through their recombination with hydrogen in environments exposed to neutron and gamma radiation fields. However, because of the gas transfer process in the core boiling channels of a BWR, most of the injected hydrogen along with dissolved oxygen is stripped from the liquid phase. The high concentration of the other oxidizing species, namely, hydrogen peroxide, produced by radiolysis of water in the reactor core thus leads to high ECPs in regions near the core exit.

Intergranular Stress Corrosion Cracking (IGSCC) under normal BWR operating conditions ($T=288^{\circ}\text{C}$, pure water) is primarily an electrochemical process that occurs at potentials more positive than a critical value of $E_{\text{IGSCC}} = -0.23 \text{ V}_{\text{she}}$. However, the crack growth rate (CGR) at $E > E_{\text{IGSCC}}$ is also a function of potential, conductivity, degree of sensitization of the steel, flow velocity, mechanical load, and crack length. The dominance of electrochemical, solution, and hydrodynamic factors in controlling CGR has led to the development of various techniques for mitigating IGSCC in sensitized Type 304 SS by modifying the environment, such that the corrosion potential (ECP) is displaced to a value more negative than E_{IGSCC} . However, even in those regions of the heat transfer circuit (HTC) where the corrosion potential cannot be displaced sufficiently in the negative direction to satisfy the condition $\text{ECP} < E_{\text{IGSCC}}$, considerable benefit is obtained because of the roughly exponential dependence of the CGR on potential.

Macdonald et al.[3, 9, 10-12, 41] have developed powerful water chemistry and corrosion models for calculating radiolytic specie concentrations in the HTCs of BWRs and for predicting the damage that accumulates from the corrosion processes resulting from the presence of these species in the coolant. The original code (DAMAGE-PREDICTOR) incorporates deterministic modules for estimating the specie concentrations, the ECP, and crack growth rate (CGR) of stainless steel components at closely spaced points around the coolant circuit, as a function of coolant pathway geometry, reactor operating parameters (power level, flow velocity, dose rates, etc.), coolant conductivity, and the concentration of hydrogen added to the feedwater. DAMAGE-PREDICTOR, which has been used to model nine BWRs worldwide, has been validated by direct comparison with plant data (e.g. at the Leibstadt BWR in Switzerland), and is found to accurately simulate hydrogen water chemistry. The code has also been used to explore various enhanced versions of HWC and completely new strategies, such as those which employ noble metal coatings and dielectric coatings, respectively. Two of the component models of DAMAGE-PREDICTOR, in fact, predicted quantitatively the effectiveness of dielectric

coatings for inhibiting crack growth in stainless steels in high temperature water, and these predictions have been validated by direct experiment [39]. Even more advanced versions, including ECP-ALERT, CGR-ALERT, and DAMAGE-ALERT have now been developed, which provide fast simulation of the ECP and CGR in boiling water reactors, respectively.

Furthermore, the theory of crack initiation in the form of the Point Defect Model for the growth and breakdown of passive films is currently being incorporated into DAMAGE-ALERT. These enhanced codes allow an operator to explore alternate hydrogen water chemistry protocols (including the absence of HWC) and other remedial measures (e.g. surface modification by dielectric coatings, SMDC, and ultra-low conductivity operation, ULCO) over an envisioned operating period, in order to identify the most cost-effective operating strategy.

At present, we are describing the backgrounds of three main codes, DAMAGE-PREDICTOR, REMAIN, and ALERT, for calculating ECP and CGR of BWRs. The details of the ALERT code and the calculations results are showed in this chapter. The CEFM model incorporating the effects of sulfuric acid additions to the coolant and including thermal activation of the crack tip strain rate has been changed to incorporate the effects of caustic soda (NaOH) and hydrochloric acid (HCl). Therefore the calculation results of both codes are included in this chapter.

3.1.1 Background of DAMAGE-PREDICTOR

The original DAMAGE-PREDICTOR contained three principal sub-modules: (1) A water radiolysis code (RADIOCHEM) for calculating the concentrations of electroactive radiolytic species under steady-state conditions, at user-specified intervals around the coolant circuit. (2) A mixed potential model (MPM) for calculating the ECP from the concentrations of electroactive species. (3) A coupled environment fracture model (CEFM) for estimating the growth rate of standard cracks at the same locations. The distance between successive points is typically a few centimeters to a meter, depending on the component being considered. Not unexpectedly, the larger the number of points, the slower the code, because of the increase in the sizes of the matrices.

The radiolysis code, RADIOCHEM, is based on a model originally developed to describe the corrosion of high level nuclear waste canisters. This model was subject to quality assurance, which involved tracing the reactions contained in the model to their original sources and ensuring the model could reproduce the original observations. Few models, of which we are aware, satisfy this condition. Indeed, many radiolysis models simply combine reactions from other models and transpose the associated kinetic parameters without recognizing the fact that the values of the kinetic parameters are model-dependent. Thus, most importantly, the radiolysis model employed in DAMAGE-PREDICTOR was subjected to extensive analysis and critique, and has been found to accurately describe the radiolysis of water. Thus, over the past five years, RADIOCHEM has also been subject to extensive testing by comparing calculated oxygen and hydrogen concentrations in the recirculation and steam lines of BWRs with observed values. Excellent agreement has been obtained when using a single set of model parameters for

reactors at both extremes of the population defined by Ruiz et al. [2] with respect to HWC response.

To our knowledge, DAMAGE-PREDICTOR was the first BWR radiolysis code to contain a deterministic model for calculating ECP. The Mixed Potential Model (MPM), which others have now copied, makes use of the fact that, for a system undergoing general corrosion (which is the process that establishes the ECP), the sum of the current densities due to all charge transfer reactions at the steel surface must be zero. By expressing the redox reaction currents in terms of the generalized Butler-Volmer equation, which incorporates thermodynamic equilibrium, kinetic, and hydrodynamic effects, and by expressing the corrosion current in terms of either the Point Defect Model or as an experimentally-derived function (both have been used), it is possible to solve the charge conservation constraint for the corrosion potential (ECP). The MPM has been extensively tested against experimental and field data and has been found to provide accurate estimates of the ECP.

DAMAGE-PREDICTOR also contains a deterministic model (the CEFM) for calculating the rate of growth of a standard crack at any point in the coolant circuit. The CEFM is deterministic, in that it satisfies the relevant natural law, the conservation of charge. Furthermore, a basic premise of the CEFM, that current flows from the crack and is consumed on the external surface, has been demonstrated experimentally. To our knowledge, the CEFM is the only currently available model which satisfies the conservation of charge constraint explicitly. The high degree of determinism is demonstrated by the fact the model can be calibrated by a single CGR/ECP/Conductivity datum for a given degree of sensitization (DOS) of the steel.

3.1.2 Background of REMAIN

A second-generation code, REMAIN, has been developed to model BWRs with internal coolant pumps. This greatly enhanced code, which employs the same mathematical techniques as does the ALERT series of codes executes in about one fiftieth of the time required for DAMAGE-PREDICTOR. Accordingly, these second-generation codes provide for near real time simulations and have flexible architectures, in that they may be readily tailored to simulate a particular reactor. Some of our modeling work on simulating operating reactors using DAMAGE-PREDICTOR and the second-generation codes is discussed below.

The ECP and CGR are related to the concentrations of H_2 , O_2 , and H_2O_2 in a rather complex manner, in addition to depending on flow rate and temperature [40]. These complex relationships cannot be captured by empirical methods, simply because the responses of the ECP and CGR to each of the independent variables, and each combination of variables, are highly non-linear.

As noted above, both DAMAGE-PREDICTOR and REMAIN contain versions of the CEFM for predicting the crack growth rate. The deterministic nature of the CEFM means it requires minimal calibration. Accordingly, because it captures vital relationships between the CGR and various independent variables, it can be used to

model regions in a reactor for which insufficient data exist for reliable calibration. For example, the CEFM yields the crack growth rate as a function of crack length. This relationship, which is not captured by any empirical model, is essential for the prediction of integrated damage (i.e. crack length as a function of time for a proposed operating history), because the crack growth rate decreases as the crack length increases. This is due to an increase in the potential drop down the crack, even though the mechanical driving force (the stress intensity) is maintained constant. If the dependence of CGR on crack length is not recognized, the integrated damage function is over-predicted by several hundred percent, thereby leading to a much more pessimistic evolution of damage.

The MPM and CEFM contain the necessary facilities for modeling enhanced hydrogen water chemistry (EHWC), as affected by the use of catalytic coatings (i.e. noble metal coatings), and other advanced remedial measures, such as SMDC and ULCO. A considerable achievement of the MPM was the prediction that dielectric coatings represented a viable, and indeed an advantageous, alternative to noble metal coatings; a prediction that has been confirmed experimentally [40]. The effectiveness of both strategies arises from modification of the exchange current densities for the redox reactions (oxidation of hydrogen and the reduction of oxygen and hydrogen peroxide) which occur on the steel surface. In the case of the noble metal coatings, the exchange current densities are increased, with the greatest increase occurring for the hydrogen electrode reaction. This renders hydrogen to be a much more effective reducing agent than it is in the absence of the noble metal, thereby making it much more effective in displacing the ECP in the negative direction. In the case of dielectric coatings, the lower exchange current densities render the metal less susceptible to the ECP raising oxidizing species, with the result that the ECP is displaced in the negative direction, even in the absence of hydrogen added to the feedwater.

To our knowledge, the MPM and CEFM are the only models that could have predicted the effects of catalysis (i.e. NMEHWC) and inhibition (SMDC), because they are the only models which explicitly consider the electrochemical kinetics of the redox reactions that occur on the steel surface. Again, we emphasize the accumulation of damage due to stress corrosion cracking is primarily an electrochemical phenomenon, and any quantitative, deterministic theory must address the kinetics of the charge transfer processes in the system.

3.1.3 Background of ALERT

ALERT is a computer code for modeling water chemistry and estimating the accumulated damage from stress corrosion cracking in boiling water reactors. ALERT can predict water chemistry radiolysis, corrosion potential (ECP), crack velocity, and accumulated damage (crack depth in reactor components). The code contains two principal sub-modules which are a water radiolysis code (RADIOCHEM) for calculating the concentrations of electroactive radiolytic species under steady-state conditions and a mixed potential model (MPM) for calculating the ECP from the concentrations of electroactive species.

The algorithm of ALERT is shown in Figure 3.9. The main body of the algorithm of ALERT code is the water radiolysis model, which yields the concentrations of radiolysis products from the decomposition of water under neutron and gamma irradiation, coupled with homogeneous and heterogeneous chemical reactions, liquid /steam transfer of volatile species (H₂ and O₂), and fluid convection. After the species concentrations have been determined in the whole heat transport circuit under steady-state conditions, the ECP is calculated using an optimized mixed potential model (MPM).

Figure 3.9. Structure of the algorithm of alert.

ALERT code incorporates deterministic modules for estimating specie concentrations, the ECP, and CGR on natural laws governing material and electrochemical behavior. The MPM and CEFM contain the necessary facilities (explicit kinetic parameters, such as the exchange current densities) for modeling HWC and enhanced hydrogen water chemistry (EHWC), as affected by the use of catalytic coatings (i.e. noble metal coatings), and other advanced remedial measures, such as dielectric coatings and ultra-low conductivity operation.

3.1.4 ALERT Code

The speed afforded by the enhanced ALERT codes, which employ essentially the same optimized mathematical algorithms as does REMAIN, permits the prediction of the integrated damage function, which is the crack length vs. time for a preconceived operating history. The cracks are assumed to grow from an initial depth of 0.5 cm for a 40 year period of continuous operation. The crack length, x_N , over the anticipated service time of a component, T , is obtained by an accumulation of the crack advances over N periods of time $\Delta t_1, \dots, \Delta t_i, \dots, \Delta t_N$.

$$x_i = x_{i-1} + \text{CGR}_i \cdot \Delta t_i, \quad i = 1, \dots, N \quad (3-1)$$

$$T = \sum_{i=1}^N \Delta t_i$$

The crack growth rate, CGR_i , is presumed to be time-independent for each interval, Δt_i , in that it depends on the crack length (through K_I and because of changes in the current and potential distributions in the crack internal and external environments). The initial crack length, x_0 , corresponds to the depth of a pre-existing crack (as may have been detected during an inspection for an assumed safety analysis scenario).

Recognizing the crack opening displacement, a , and stress intensity factor, K_I , will grow with time as the crack advances, one can specify that failure of a component will occur during the i -th time interval, if the accumulated damage, x_i , exceeds a limiting value, x_{lim} , which is termed the critical dimension, or if the stress intensity, $K_{I,i}$, exceeds the critical value for fast, unstable fracture (K_{IC} , which for stainless steel is $60\text{-}65 \text{ MPa}\sqrt{m}$). We refer to these two cases as being “damage-controlled” and “stress-controlled” failures, respectively. The stress intensity is assumed to increase with $x^{1/2}$, short crack effects are ignored for simplicity, and the crack opening displacement is taken to be proportional to the length of the growing crack, x (i.e., we assume that the aspect ratio is independent of the crack length). Because the present calculations assume an active, preexisting crack of 0.5 cm length, no account of initiation is incorporated into the model.

ALERT can predict the concentration of hydrogen, oxygen, and hydrogen peroxide using the radiolysis model, RADIOCHEM. The specie concentrations calculated from RADIOCHEM are offered to inputs of the ECP model and the crack growth rate model calculations. The ECP model calculates the metal surface ECP using radiolysis results.

The crack growth rate model generates growth rates and crack depths as a function of time and the crack velocity depends on operating conditions, stress intensity, and crack depth. It is shown in Figure 3.10 that the crack growth is essentially non-linear due to crack depth dependence, such as deeper cracks grow more slowly than shallow cracks.

Figure 3.10. The Prediction of ALERT on Nonlinear Crack Growth

Diagram of Simulated Plant

The simplified BWR reactor diagram is shown in Figure 3.11. It is a part of the typical boiling water reactor. The BWR reactor typically allows bulk boiling of the water in the reactor. The operating temperature of the reactor is approximately 288°C producing steam at a pressure of about 68 bars. In the figure below, water is circulated through the reactor core picking up heat as the water moves past the fuel assemblies. The water eventually is heated enough to convert to steam. Steam separators in the upper part of the reactor remove water from the steam. The steam then passes through the turbine to rotate the turbine-generator.

A lot of electrochemical properties and the concentrations of species, such as the concentration of hydrogen, oxygen, and hydrogen peroxide, the electrochemical potential and crack growth rate, etc. can be calculated by the ALERT in the numbered points from 1 to 10.

Figure 3.11. Typical Coolant Flow in the BWR Primary System.

Calculation Results and Discussion

The predicted effect of hydrogen injection in feed water of a boiling water reactor is shown in Figures 3.12 and 3.13. It shows electrochemical potentials and crack growth rates which are variable as the operation period and reactor power. The ECPs are calculated by changing five different hydrogen concentrations, 0.5 ppm, 1 ppm, 3 ppm, and 5 ppm, in feed water which are the same values during the operation period in 20 months.

Figure 3.12. ECP Variation at the Top of Core Channel of a Typical Boiling Water Reactor.

As shown in Fig. 3.12, the ECP values are decreased as the concentration of hydrogen in the feed water is increased. During the normal operation, the ECP values are low and during the startup or low power operation, the ECP values are considerably high because of the effect of temperature and conductivities. Vankeerberghen et al. have published a paper on the effect of temperature on the electrochemical potential on the external surfaces during crack growth in Type 304 SS in dilute sulfuric acid solutions with a dissolved oxygen concentration of 200 ppb. Reactor coolant of BWR usually contains 200ppb of oxygen under steady state operation arising from radiolysis of water in the core of reactors. The ECP more or less decreases monotonically with increasing temperature from about 150 to -70 mV, as the temperature is increased from 50 to 300 .

During the normal operation, the ECP values are between 0.24 to 0.25 V_{SHE} . These values are so high compared to the critical potential of the intergranular stress corrosion cracking (E_{IGSCC}) of about -0.23 V_{SHE} at the operating temperature of 289°C. It is supposed that the injected hydrogen affects the suppression of the oxygen and hydrogen peroxide and it would be helpful to decrease the ECP value.

Figure 3.13 shows the relation between CGRs and operation times at the same reactor power and operational conditions. The CGR also changes monotonously as the variation of ECPs.

The calculated ECP and CGR data suggests hydrogen water chemistry (HWC) is effective in protecting the reactor internal equipment. For BWRs, this approach was pioneered by various Japanese workers, who showed that feed water hydrogen concentrations of 1 to 2 ppm should be sufficient to reduce the oxygen level in the recirculation system to an acceptable level.

Figure 3.13. CGR Variation at the Top of Core Channel of a Typical Boiling Water Reactor

3.2 CEFM Code Predicting Crack Growth Rate vs. Temperature Behavior of Type 304 Stainless Steel in Dilute Sulfuric Acid Solutions

The coupled environment fracture model (CEFM) for intergranular stress corrosion cracking of Type 304 stainless steel in BWR primary heat transport circuits containing relatively pure water has been extended to incorporate the effects of sulfuric acid additions to the coolant and to include thermal activation of the crack tip strain rate. These extensions allow comparisons to be made between theoretically estimated and experimentally determined crack growth rates (CGRs) over a considerable temperature range after calibration at a single temperature.

3.2.1 Introduction

The CEFM code has been used extensively and successfully to model crack growth rates (CGRs) of Type 304 stainless steel in BWR coolant environments [33], [41]. The medium in these coolant environments is basically pure water of low conductivity. Vankeerberghen et al. extended the CEFM to dilute sulfuric acid solutions over the temperature range 50-300°C [42]. The changes are the incorporation of the effects of sulfuric acid and its dissociated species (HSO_4^- and SO_4^{2-}) on the properties of the environment and the inclusion of a thermally activated crack tip strain rate. These modifications allow comparisons to be made of calculated and published experimental data on the effect of temperature on CGR in Type 304 SS in dilute sulfuric acid aqueous media over the temperature range of 50-300°C. Such a model for calculating CGR over an extended temperature range is required for use in codes, such as DAMAGE PREDICTOR, REMAIN, and ALERT, which are currently being used to predict the accumulation of damage due to SCC in BWR primary coolant environments.

3.2.2 Basis of the Coupled Environment Fracture Model

Crack advance is assumed to occur via the slip dissolution-repassivation mechanism, but the governing system equation is a statement of charge conservation,

$$i_{\text{crack}} A_{\text{crack_mouth}} + \int_S i_C^N ds = 0, \quad (3-2)$$

where i_{crack} is the net (positive) current density exiting the crack mouth, $A_{\text{crack_mouth}}$ is the area of the crack mouth, i_C^N is the net (cathodic) current density due to charge transfer reactions on the external surface, and ds is an increment in the external surface area. The subscript S on the integral indicates the integration is to be performed over the entire external surface. The CEFM performs its calculations in two steps. In a first step, it calculates the electrochemical potential of the external surface, and in a second step, the CGR is estimated. The electrochemical potential relatively far from the crack is assumed to be unchanged by the presence of the crack and, hence, is equal to the free corrosion potential (the ECP). The CGR calculation relies on splitting the crack environment into the crack-internal environment and the crack-external environment. To solve for the CGR, an electrochemical potential is assumed at the crack mouth, the boundary between the crack internal and external environments. This electrochemical potential is then

changed until the crack internal current and crack external current match. Hence, the crack internal and external currents are calculated given a particular electrochemical potential at the crack mouth and for the prevailing ECP. For the calculation of the internal crack current an electrochemical potential is assumed at the crack tip. This electrochemical potential is changed until electro-neutrality is satisfied at the crack tip. For the calculation of the external current, a non-iterative procedure is followed involving the solution of Laplace's equation. When Congleton's approach is used for calculating the crack tip strain rate, which is a function of the CGR, an additional iteration must be performed to obtain the CGR.

Here, only the extensions to the CEFM which are needed to calculate CGRs in dilute sulfuric acid solutions over the temperature range of 50-300°C are described.

3.2.3 Incorporation of the Effects of Sulfuric Acid and Temperature

The CEFM, in a first step, calculates the electrochemical potential at the external surface in the absence of a crack using the mixed potential model [16]. This entails the use of equilibrium potentials and charge transfer kinetic data (exchange current densities and Tafel constants), as contained in the general Butler-Volmer equation, for the hydrogen, oxygen, and hydrogen peroxide electrode reactions, together with the polarization characteristics of the steel, in order to calculate the potential at which the total interfacial current is zero. The equilibrium potentials and exchange current densities, at least, are functions of the pH of the aqueous medium. Furthermore, the hydrogen, oxygen, and hydrogen peroxide electrode reactions and the dissolution rate of the steel substrate participate in the charge transfer reactions on the surface close to the crack mouth and represent the processes that consume the current ejected from the crack mouth as the crack grows. Accordingly, the CGR is expected to reflect dependencies on pH in addition to those embodied in the equilibrium potentials. Any viable model for crack growth must take these effects into account. Note that in the original CEFM, the pH was calculated as that for pure water at all temperatures considered.

In a second step, CEFM solves for the effect of a crack being present in the system. Here, two environments, the crack-internal and the crack-external environments, are coupled by a common potential at the mouth of the crack and a common crack mouth current. The potential field in the external environment is calculated by using Laplace's equation. Hence, the current field in the external environment depends on the conductivity of the external environment and, hence, is influenced by the addition of sulfuric acid to pure water. Later in this paper, the change in conductivity, due to the addition of sulfuric acid to pure water, is calculated. The current exiting the crack is related to the crack tip current that results from film rupture and repassivation (slip/dissolution/repassivation) at the crack apex. This process is postulated here to be thermally activated.

3.2.3.1 The Effect of Sulfuric Acid on pH

The temperature dependence for the pH of pure water is given by Equation (3-3),

$$pH(T) = -\log_{10}(\sqrt{K_w(T)}) = pK_w/2 \quad (3.3)$$

where $K_w(T)$ is the water dissociation constant. The pK_w vs. T correlation of Naumov et al. [43],

$$pK_w(T) = \frac{4466.2}{T} - 5.941 + 0.016638T, \quad (3-4)$$

is sufficiently accurate, where T is the absolute temperature of the water in degrees Kelvin.

In the case of a dilute sulfuric acid solution, the activity of the hydrogen ion is determined by three equilibriums, namely

where HSO_4^- and SO_4^{2-} are the bisulfate and sulfate oxyanions of S(VI), respectively. The equilibrium constants for the two sulfuric acid dissociation reactions, K_1 and K_2 , are defined by equations as follows,

$$K_1(T) = \frac{a_{H^+} a_{HSO_4^-}}{a_{H_2SO_4}} = \frac{m_{H^+} m_{HSO_4^-}}{m_{H_2SO_4}} \frac{\gamma_{H^+} \gamma_{HSO_4^-}}{\gamma_{H_2SO_4}}, \quad (3-8)$$

and

$$K_2(T) = \frac{a_{H^+} a_{SO_4^{2-}}}{a_{HSO_4^-}} = \frac{m_{H^+} m_{SO_4^{2-}}}{m_{HSO_4^-}} \frac{\gamma_{H^+} \gamma_{SO_4^{2-}}}{\gamma_{HSO_4^-}}, \quad (3-9)$$

where m_i , a_i , and γ_i are the molal concentration, the activity and the activity coefficient of species i in the system. Because the solution is dilute, it may be assumed the first dissociation is complete and, hence, $K_1(T) \rightarrow \infty$. Accordingly, only the dissociation of the bisulfate anion needs to be considered. According to Naumov et al. [43], the second dissociation constant is given by

$$pK_2(T) = \frac{318.5}{T} - 4.146 + 0.01687T. \quad (3-10)$$

Thus, on adding sulfuric acid to water, four ionic species will be present in the solution: hydrogen ion, H^+ , hydroxyl anion, OH^- , bisulfate anion, HSO_4^- , and the sulfate anion, SO_4^{2-} . The composition of the system is readily determined by combining Equation (3-9) with the mass action statement for the dissociation of water,

$$K_w = \frac{a_{H^+} a_{OH^-}}{a_w} = \frac{m_{H^+} m_{OH^-} \gamma_{H^+} \gamma_{OH^-}}{a_w}, \quad (3-11)$$

and the electro neutrality

$$m_{H^+} - m_{OH^-} - m_{HSO_4^-} - 2m_{SO_4^{2-}} = 0, \quad (3-12)$$

and sulfur conservation constraints

$$[H_2SO_4]_{mol/kg, original} = m_{HSO_4^-} + m_{SO_4^{2-}}, \quad (3-13)$$

where a_w is the activity of water (equal to one for dilute solutions).

Calculation of the single ion activity coefficients was affected by using the extended form of Debye-Huckel theory, as given by Naumov et al. [43]

$$\log(\gamma_i) = -z_i^2 A \sqrt{I} / (1 + \hat{a}_i B \sqrt{I}), \quad (3-14)$$

where z_i is the ion charge, $\hat{a}_i$ is the distance of closest approach, $I = 0.5 \sum_i z_i^2 m_i$ is the ionic strength, and dielectric constant. Values for the latter two constants are given by Naumov et al.[43] as

$$A = 0.42041 + 0.00321t - 0.00002t^2 + 5.95143 \times 10^{-8} \times t^3, \quad (3-15)$$

and

$$B = 0.3237 + 0.00019t - 2.12586 \times 10^{-7} \times t^2 + 1.4241 \times 10^{-9} \times t^3, \quad (3-16)$$

where t is the temperature in degrees Celsius. The values used for $\hat{a}_i$ are listed in the table below.

Table 3.1. Values for $\hat{a}_i$ as used in the calculation of the activity coefficients [Equation (3-14)]

Species	$\hat{a}_i$
HSO_4^-	6.0
SO_4^{2-}	5.5
H^+	9.0
OH^-	3.5

The solution to the set of four non-linear equation (Equations (3-8), (3-10)-(3-12)) is given by the roots of a cubic equation in the bisulfate ion concentration, $m_{HSO_4^-}$, as shown

in Equation (3-17). This equation is derived by substituting Equations (3-8), (3-10)-(3-12) into the electro neutrality equation (Equation (3-11)). Thus,

$$m_{HSO_4^-}^3 + pm_{HSO_4^-}^2 + qm_{HSO_4^-} + r = 0, \quad (3-17)$$

where

$$p = \frac{K_w - \alpha\beta K_2^2 - 3\alpha\beta K_2 TS}{\beta K_2},$$

$$q = \frac{2TS(TS\beta K_2 - K_w)}{\beta K_2},$$

$$r = \frac{K_w TS^2}{\beta K_2},$$

$$\alpha = \frac{\gamma_{HSO_4^-}}{\gamma_{H^+} \gamma_{SO_4^{2-}}},$$

and

$$\beta = \frac{\gamma_{HSO_4^-} \gamma_{OH^-}}{\gamma_{SO_4^{2-}}}.$$

The solution to the cubic equation can be obtained by using modified Newton-Raphson algorithm,

$$\Delta m_{HSO_4^-} = -\frac{m_{HSO_4^-}^3 + pm_{HSO_4^-}^2 + qm_{HSO_4^-} + r}{3m_{HSO_4^-}^2 + 2pm_{HSO_4^-} + q} \quad (3-18)$$

and

$$m_{HSO_4^-} = m_{HSO_4^-}^0 + \Delta m_{HSO_4^-} \quad (3-19)$$

with iterative correction for the activity coefficients, as calculated using Equation (3-13), being made until no further change in pH is noted. The concentrations of the other ionic species are then readily obtained from

$$m_{SO_4^{2-}} = TS_4 - m_{HSO_4^-}, \quad (3-20)$$

$$m_{H^+} = \frac{m_{HSO_4^-}}{(TS - m_{HSO_4^-})} K_2 \frac{\gamma_{HSO_4^-}}{\gamma_{H^+} \gamma_{SO_4^{2-}}}, \quad (3-21)$$

and

$$m_{OH^-} = \frac{K_w}{\left(\frac{m_{HSO_4^-}}{TS - m_{HSO_4^-}} K_2 \frac{\gamma_{HSO_4^-}}{\gamma_{H^+} \gamma_{SO_4^{2-}}} \right) \gamma_{H^+} \gamma_{OH^-}}. \quad (3-22)$$

3.2.3.2 The Effect of Sulfuric Acid on Conductivity

The conductivity of pure water is determined only by the mobility of the hydrogen ion, H^+ , and the hydroxyl anion, OH^- . On adding sulfuric acid to water, two additional ionic species are present in the solution. As mentioned previously, they are the bisulfate anion, HSO_4^- , and the sulfate anion, SO_4^{2-} , and at even quite low stoichiometric concentrations of sulfuric acid, the conductivity becomes dominated by H^+ , HSO_4^- , and SO_4^{2-} , with the relative contributions of the two latter species being strongly dependent on temperature. According to dilute solution theory, the conductivity of the solution, σ (mS/cm), can be written as

$$\sigma = \sum_i |z_i| C_i \lambda_i. \quad (3-23)$$

where C is the molar concentration (mol/l), z_i is the ion charge, and λ_i is the equivalent conductivity of species i (Scm²). Equivalent conductivities are [44]

$$\lambda_{H^+}(T) = -2759.6378 + 17.5151T - 0.028435T^2 + 1.569794 \times 10^{-5} \times T^3, \quad (3-24)$$

$$\lambda_{OH^-}(T) = -929.116 + 3.3085T + 0.003754T^2 - 7.326785 \times 10^{-6} \times T^3, \quad (3-25)$$

$$\lambda_{HSO_4^-}(T) = 226.5884 - 2.7298T - 0.009082T^2 - 6.4037 \times 10^{-6} \times T^3, \quad (3-26)$$

$$\lambda_{SO_4^{2-}}(T) = 497.09 - 5.7410T - 0.018506T^2 - 1.32037 \times 10^{-5} \times T^3, \quad (3-27)$$

where T is the temperature in K.

3.2.3.3 The Thermal Activation Energy for the Crack Tip Strain Rate

The film rupture and repassivation processes are postulated to be temperature dependent. As described in [39], the poorly known parameters that describe the film rupture and repassivation processes can be lumped into one parameter. A value for this lumped parameter was obtained by calibration, but strictly speaking, the lumped parameter is

only valid at the calibration temperature, for the given geometry, etc. Here, we propose the temperature dependence of the film rupture and repassivation process could be included in the CEFM model by using temperature dependent crack tip strain rate, since it is the crack tip strain rate that controls the film rupture frequency, which in turn controls (along with the kinetics of the reactions that occur on the external surfaces) the average crack tip current and, hence, the CGR. The effect of temperature on the crack tip strain rate is expressed by an Arrhenius-type expression around a reference temperature of 288°C, i.e.

$$\dot{\epsilon}(T) = \dot{\epsilon}(288^{\circ}\text{C}) \exp \left\{ \frac{Q}{R} \left(\frac{1}{T} - \frac{1}{288 + 273.15} \right) \right\}. \quad (3-28)$$

In this expression $\dot{\epsilon}(T)$ and $\dot{\epsilon}(288)$ are the crack tip strain rate at temperature $T(\text{K})$ and 288°C , respectively. Q is the thermal activation energy for the crack tip strain rate in J/mol , and R is the universal gas constant in J/mol/K .

3.2.3.4 Experimental Data and Modeling Results

The extensions to the CEFM described were made in order to model the experimental CGRs given by Andresen for sensitized Type 304 in $0.27 \mu\text{S/cm}$ ($0.3 \mu\text{M}$, $T=25^{\circ}\text{C}$) H_2SO_4 [45]. We chose to use this set of data, because the dilute sulfuric acid solution is much more strongly (pH) buffered than is pure water, in which even quite low concentrations of contaminants (e.g. corrosion products) can adversely affect the pH. The input data for the CEFM calculations are shown in Table 3.2.

Table 3.2.: Input Parameters for the Calculation with the CEFM

Stress intensity factor ($\text{MPa} \sqrt{m}$) = 33
Oxygen concentration (ppb O_2) = 200
Hydrogen concentration (ppb H_2) $\ll 1$
H_2O_2 concentration (ppb H_2O_2) $\ll 1$
Concentration H_2SO_4 (ppb SO_4^{-2}) = 29

An ambient temperature, (25°C) molar concentration of $0.3 \mu\text{M}$ of sulfuric acid corresponds to ~ 29 ppb SO_4^{-2} . This yields a theoretical conductivity of $0.265 \mu\text{S/cm}$ as calculated using the equivalent conductivities stated above and the speciation of the system. A calibration of the CEFM was performed at 288°C . This gave calibration factors of 4000 when using the Congleton crack tip strain rate models. The activation energy for the crack tip strain rate was taken from [45] as 40 kJ/mol . The experimental and modeled CGR of Type 304 SS in dilute sulfuric acid solution is shown in Figure 3.14 over a temperature range $50\text{-}300^{\circ}\text{C}$. The results are in good agreement with the experimental data of Andresen. In order to obtain the observed agreement, the model was fitted to the experimental CGR data by determining a calibration factor at one temperature, 288°C , and using single thermal activation energy of 40 kJ/mol .

The form of the temperature dependence of the CGR is indeed well predicted by the CEFM, as can be seen by comparing the experimental and the modeled CGRs. An

important feature of the CEFM is that it provides a direct link between the properties of the external environment and the CGR. In the present work, we have extended the regime within which the CEGM is effective in predicting CGR to a wide temperature range that extends from 50 to 300°C.

3.3 Revised CEFM Model

A revised CEFM model has been developed to incorporate the effects of caustic soda (NaOH) and hydrochloric acid (HCl). It is mostly based on the model by Dr. Marc Vankeerberghen and Dr. Digby Macdonald “Predicting crack growth rate vs. temperature behavior of Type 304 stainless steel in dilute sulfuric acid solutions.” But, we have changed the species from sulfuric acid to caustic soda and hydrochloric acid. Concentrations of HCl and NaOH (ppb) are taken as input, and pH of the solution is calculated from seven simultaneous equations. The dissociation reactions occurring in the solution are the following:

3.3.1 Electro neutrality

The solution after dissociation should be electrically neutral as all the ingredients are neutral to begin with. This implies the sum of concentrations of all the charged species multiplied by their charged values should be zero. In our case, as the charge for each species is either 1 or -1, it means the sum of concentrations of positively charged particles should be equal to that of negatively charged particles. The equation becomes the following, where the symbols are taken from the reactions given above.

$$m_{H^+} + m_{Na^+} - m_{OH^-} - m_{Cl^-} = 0 \quad (3-33)$$

Figure 3.14. The Effect of Temperature on CGR in Type 304 SS in Dilute Sulfuric Acid Solution Having an Ambient Temperature (25 C) Conductivity of 0.27 $\mu\text{S/cm}$ and a Dissolved Oxygen Concentration of 200 ppb. Experimental data (curve) are taken from [45] and, the Model Curves are Calculated Using the CEFM Calibrated at 288°C and Assuming Crack Tip Strain Rate Thermal Activation Energy of 40kJ/mol.

3.3.2 Mass Balance

The sum of concentrations of the each species in the final solution should be equal to its concentration in the initial ingredients. If m_{NaOH}^0 and m_{HCl}^0 are the concentrations of HCl and NaOH which were mixed, then the equations become

$$m_{\text{Na}^+} + m_{\text{NaCl}} + m_{\text{NaOH}} = m_{\text{NaOH}}^0 \quad (3-34)$$

$$m_{\text{Cl}^-} + m_{\text{NaCl}} + m_{\text{HCl}} = m_{\text{HCl}}^0 \quad (3-35)$$

The equilibrium constants for the dissociation reactions mentioned above are defined as

$$K_w(T) = \frac{a_{\text{H}^+} a_{\text{OH}^-}}{a_w} = \frac{m_{\text{H}^+} m_{\text{OH}^-} \gamma_{\text{H}^+} \gamma_{\text{OH}^-}}{a_w} \quad (3-36)$$

$$K_1(T) = \frac{a_{\text{Na}^+} a_{\text{Cl}^-}}{a_{\text{NaCl}}} = \frac{m_{\text{Na}^+} m_{\text{Cl}^-} \gamma_{\text{Na}^+} \gamma_{\text{Cl}^-}}{m_{\text{NaCl}} \gamma_{\text{NaCl}}} \quad (3-37)$$

$$K_2(T) = \frac{a_{H^+} a_{Cl^-}}{a_{HCl}} = \frac{m_{H^+} m_{Cl^-} \gamma_{H^+} \gamma_{Cl^-}}{m_{HCl} \gamma_{HCl}} \quad (3-38)$$

$$K_3(T) = \frac{a_{Na^+} a_{OH^-}}{a_{NaOH}} = \frac{m_{Na^+} m_{OH^-} \gamma_{Na^+} \gamma_{OH^-}}{m_{NaOH} \gamma_{NaOH}} \quad (3-39)$$

where m_i , a_i and γ_i are molar concentration, activity and activity coefficient of species i in the system. The activity of water a_w can be assumed to be unity for dilute solutions. The activity coefficients are calculated using the extended form of Debye-Huckel theory, as given in Naumov et. al.

$$\log(\gamma_i) = \frac{-Az_i^2 \sqrt{\mu}}{(1 + Ba^0 \sqrt{\mu})} \quad (3-40)$$

where $\mu = 0.5 \sum (m_i z_i^2)$ is the ionic strength of the solution and z_i is the ion charge, a^0 is the distance of closest approach and A and B are constants which depend on temperature, density (pressure) and dielectric constant. Values for A and B are given by Naumov et al. as:

$$A = 0.4241 + 0.00321 t - 0.00002 t^2 + 5.95143 \times 10^{-8} t^3 \quad (3-41)$$

$$B = 0.3237 + 0.00019 t - 2.12586 \times 10^{-7} t^2 + 1.4241 \times 10^{-9} t^3 \quad (3-42)$$

where t is the temperature in degree Celsius. Value of a^0 has been taken as 4.5×10^{-8} cm.

In our case, it turns out that $\gamma_{H^+} = \gamma_{OH^-} = \gamma_{Na^+} = \gamma_{Cl^-}$. So, we denote them by a common symbol γ . Also, $\gamma_{NaCl} = \gamma_{HCl} = \gamma_{NaOH} = 1$. So, for notational convenience we will denote $\gamma_{H^+} \gamma_{OH^-} = \gamma_{Na^+} \gamma_{Cl^-} = \gamma_{H^+} \gamma_{Cl^-} = \gamma_{Na^+} \gamma_{OH^-} = \gamma^2 = G$.

The various dissociation constants were obtained as a function of temperature in Kelvin by curve fitting on experimental data from Naumov et al. and

$$pK_w = 4673.8604/T_K - 7.0269 + 0.0180xT_K \quad (3-43)$$

$$pK_1 = 483.7740/T_K - 5.0881 + 0.0091xT_K \quad (3-44)$$

$$pK_2 = 2684.0060/T_K - 16.4465 + 0.0226xT_K \quad (3-45)$$

$$pK_3 = 1324.6809/T_K - 8.2525 + 0.0120xT_K \quad (3-46)$$

So, on adding sodium hydroxide and hydrochloric acid to water four ionic species will be present in the solution; hydrogen ion, H^+ , hydroxyl ion OH^- , sodium ion Na^+ and chloride ion Cl^- . Also, there are some amounts of un-dissociated hydrochloric acid and

sodium hydroxide left in the solution. Na^+ and Cl^- combine to form some NaCl in the solution. So, there are seven species in the solution whose concentration is unknown. Also, we have seven equations to solve for these seven unknowns. By solving this set of seven non-linear equations, we can get the concentrations of all the species in the solution.

3.3.3 Solution of Non-linear Equations

These equations have been solved by using Newton-Raphson method for non-linear systems of equations. A typical problem gives N functional relations to be zeroed, involving variables, x_i , $i = 1, 2, 3, \dots, N$:

$$F_i(x_1, x_2, \dots, x_N) = 0 \quad i = 1, 2, \dots, N. \quad (3-47)$$

where $\mathbf{x}$ denotes the entire vector of variables x_i and $\mathbf{F}$ denotes the entire vector of functions F_i . In the neighborhood of $\mathbf{x}$, each of the functions F_i can be expanded in Taylor series

$$F_i(\mathbf{x} + \delta\mathbf{x}) = F_i(\mathbf{x}) + \sum (\partial F_i / \partial x_j) \delta x_j + O(\delta x^2) \quad (3-48)$$

where the summation is taken from $j = 1$ to N . The matrix of partial derivatives appearing in the above equation is the jacobian matrix $\mathbf{J}$.

$$J_{ij} \equiv (\partial F_i / \partial x_j) \quad (3-49)$$

In matrix notation, the above equation becomes

$$\mathbf{F}(\mathbf{x} + \delta\mathbf{x}) = \mathbf{F}(\mathbf{x}) + \mathbf{J} \delta\mathbf{x} + O(\delta x^2) \quad (3-50)$$

By neglecting the term of order δx^2 and higher and by setting $\mathbf{F}(\mathbf{x} + \delta\mathbf{x}) = 0$, we get a set of linear equations for the correction $\delta\mathbf{x}$ that move each function closer to zero simultaneously.

$$\mathbf{J} \delta\mathbf{x} = -\mathbf{F} \quad (3-51)$$

This set of linear equations can be solved using Gauss Elimination method and the new value of variables is given as

$$x_{\text{new}} = x_{\text{old}} + \delta x \quad (3-52)$$

and the process is iterated till the values converge.

In our case, the system of seven non-linear equations is reduced to four functions, which have to be zeroed. The matrix $\mathbf{F}$ so derived is given as

$$\mathbf{F} = \begin{bmatrix} m_{OH^-} - K_w / m_{H^+} G \\ m_{H^+} + m_{Na^+} - m_{OH^-} - m_{Cl^-} \\ m_{Na^+} + m_{Na^+} m_{Cl^-} G / K_1 + m_{OH^-} m_{Na^+} G / K_3 - m_{NaOH}^0 \\ m_{Cl^-} + m_{Na^+} m_{Cl^-} G / K_1 + m_{H^+} m_{Cl^-} G / K_2 - m_{HCl}^0 \end{bmatrix} \quad (3-53)$$

As G is also the function of concentrations, the above function $\mathbf{F}$ is quite complicated for the Jacobean matrix to be calculated analytically. The matrix was calculated using Mathematica. But, the results obtained even after full simplification were very long and complex to be coded in C. So, it was decided to use finite difference method to calculate the Jacobean matrix. The step value while calculating the Jacobean matrix using finite difference method has been taken as 10^{-8} , which is approximately square root of the machine precision.

δx gives the Newton direction in which the functions decrease. Full Newton step is taken first and the new value of the functions at x_{new} is compared to value of the function at x_{old} . If the new value is less than the old value, then full Newton step is taken, otherwise the step in the Newton direction is reduced until the value of the functions at the x_{new} is less than the value at x_{old} . This process is repeated till convergence.

It was observed that at very low concentrations of HCl and NaOH, the Newton-Raphson method fails to converge sometimes. However, changing the initial guess to a more appropriate value brought about the convergence. So, the initial guess value for H^+ ion was varied from very low to a maximum of m_{HCl}^0 .

3.3.4 Modeling Results

The revised CEFM described above were made to incorporate the effects of caustic soda and hydrochloric acid to the CGR. The input data for the calculations of revised CEFM are shown in Table 3.3. We used the same geometry and data as the calculation of the CEFM in chapter 3.3.3.4, except the concentrations of NaOH and HCl.

Table 3.3. Input Parameters for the Calculation with the Revised CEFM

Stress intensity factor ($MPa \sqrt{m}$) = 33
Oxygen concentration (ppb O_2) = 200
Hydrogen concentration (ppb H_2) $\ll 1$
H_2O_2 concentration (ppb H_2O_2) $\ll 1$
Concentration NaOH (ppb NaOH) = 100
Concentration HCl (ppb HCl) = 100

The results shown in Figure 3.15 show also the temperature dependency of the CGR. But the maximum value of the CGR is less, around 125, and the CGR increases again after 275.

Figure 3.15. The Effect of Temperature on CGR in Type 304 SS in Dilute Caustic Soda and Hydrochloric Acid Solution Having an Ambient Temperature (25) Conductivity of $0.27 \mu\text{S/cm}$ and a Dissolved Oxygen Concentration of 200 ppb.

3.4 Development New Computer Code using the Modified Functions

The existing code, ALERT, has now been superseded by a new code, FOCUS. This new code predicts water chemistry (radiolysis), electrochemical corrosion potential, crack velocity, and accumulated damage (crack depth) in BWR primary coolant circuits at many points simultaneously under normal water chemistry (NWC) and hydrogen water chemistry (HWC) operating protocols over specified operating histories. FOCUS includes the Advanced Coupled Environment Fracture Model (ACEFM) for estimating crack growth rate over a wide temperature range and, hence, is particularly useful for modeling BWRs that are subject to frequent start ups and shut downs. Additionally, a more robust and flexible water chemistry code is incorporated into FOCUS that allows for more accurate simulation of changes in coolant conductivity under upset conditions. The application of FOCUS for modeling the chemistry, electrochemistry, and the accumulation of intergranular stress corrosion cracking (IGSCC) damage in BWR primary coolant circuits is illustrated in this paper.

3.4.1 FOCUS Code

Code Structure

FOCUS is designed to predict water chemistry radiolysis, ECP, crack velocity, and accumulated damage deterministically (i.e., based on natural laws governing material and electrochemical behavior). The code contains four principal sub-modules: the water

radiolysis code (RADIOCHEM), an Advanced Mixed Potential Model (AMPM), an Advanced Coupled Environment Fracture Model (ACEFM), and a Damage Function Analysis (DFA) module that integrates the damage over the specified corrosion evolutionary path (CEP).

The algorithms employed in this code are shown in Figure 3.16 [46]. The main body of the algorithm is the water radiolysis model, which yields the concentrations of radiolysis products from the decomposition of water under neutron and gamma irradiation, coupled with homogeneous and heterogeneous chemical reactions, liquid/steam transfer of volatile species (H₂ and O₂), and fluid convection. After the species concentrations have been determined at every point around the heat transport circuit under steady-state conditions, the ECP is calculated using the AMPM.

Figure 3.16. Structure of the algorithm of the simulation code

Radiolytic Yield

The rate at which any primary radiolytic species produced is given by

$$R_i^y = \left(\frac{G_i^\gamma \Gamma^\gamma}{100 N_V} + \frac{G_i^n \Gamma^n}{100 N_V} + \frac{G_i^\alpha \Gamma^\alpha}{100 N_V} \right) \tilde{F} \rho \quad (3-54)$$

where R_i^y is the homogeneous rate having units of mol/cm³·s, G^γ , G^n , and G^α are the radiolytic yields for gamma photons, neutrons, and alpha particles, respectively, in number of particles per 100eV of energy absorbed, N_V is Avogadro's number, $\tilde{F}$ equals 6.25×10^{13} (the conversion factor from Rad/sec to eV/gram-sec), and ρ is the water density in g/cm³. Γ^γ , Γ^n , and Γ^α are the gamma photon, neutron, and α -particle energy

dose rates, respectively, in units of Rad/s. Table 3.4 shows compiled G values for the 13 radiolysis products.

Table 3.4. G Values for Primary Radiolytic Species [46]

Species	G ^r (No./100eV)	G ⁿ (No./100eV)
e ⁻	4.15	0.93
H	1.08	0.50
OH	3.97	1.09
H ₂ O ₂	1.25	0.99
HO ₂	0.00	0.04
HO ₂ ⁻	0.00	0.00
O ₂	0.00	0.00
O ₂ ⁻	0.00	0.00
H ₂	0.62	0.88
OH ⁻	0.00	0.00
H ⁺	4.15	0.93
O ₂ g	0.00	0.00
H ₂ g	0.00	0.00

The dose rate due to α -particle (⁴He₂ nuclei) is negligible and can be ignored, because these particles are effectively stopped by the fuel cladding. Accordingly, it is necessary to consider only gamma photons and neutrons when modeling BWR primary coolant circuits. A wide spectrum of gamma photon and neutron energies exist in a reactor core and any highly accurate simulation of the radiochemistry of the coolant should recognize these distributions. Furthermore, the core in any reactor is not homogeneous with regard to dose rate and, hence, the horizontal geometric dispersion of the dose rate should be incorporated in any accurate model. These factors are ignored in the present work, as they are in all, current models. Note the distributions in the gamma photon and neutron dose rates in the vertical direction through the core are incorporated in FOCUS.

Advanced Mixed Potential Model (AMPM)

The MPM, which was originally developed by Macdonald [47], is based on the physical condition that charge conservation must be obeyed at a metal surface when a corrosion process is in progress. The charge conservation constraint is

$$\sum_{j=1}^N i_{R/O,j}(E) + i_{corr}(E) = 0 \quad (3-55)$$

where $i_{R/O,j}$ is the partial current density due to the j^{th} redox couple in the system and i_{corr} is the corrosion current density of the material.

For the Type 304 SS, the steel oxidation current density, i_{corr} , was modeled as an empirical function of voltage.

$$i_{corr} = \frac{e^{(E-E_o)/b_f} - e^{-(E-E_o)/b_r}}{384.62e^{4416/T} + X} \quad (3-563)$$

where

$$X = \frac{e^{(E-E_o)/b_f}}{2.61 \times 10^{-3} e^{-4416/T + 0.523(E-E_o)^{0.5}}} \quad (3-57)$$

and

$$E_o = 0.122 - 1.5286 \times 10^{-3} T \quad (3-58)$$

b_f and b_r are the forward and reverse Tafel constants, respectively, for the metal dissolution reaction, with values of 0.06V being assumed for both.

The current density ($i_{R/O}$) for a redox couple (e.g. O_2/H_2O , H^+/H_2 , H_2O_2/H_2O)

(where R is the reduced species and O is the oxidized species) can be expressed in terms of a generalized Butler-Volmer equation as

$$i_{R/O} = \frac{e^{(E-E_{R/O}^e)/b_a} - e^{-(E-E_{R/O}^e)/b_c}}{\frac{1}{i_{0,R/O}} + \frac{1}{i_{l,f}} e^{(E-E_{R/O}^e)/b_a} - \frac{1}{i_{l,r}} e^{-(E-E_{R/O}^e)/b_c}} \quad (3-60)$$

where $i_{0,R/O}$ is the exchange current density, $i_{l,f}$ and $i_{l,r}$ are the mass-transfer limited currents for the forward and reverse directions of the redox reaction, respectively, and b_a and b_c are the anodic and cathodic Tafel constants. $E_{R/O}^e$ is the equilibrium potential for this reaction as computed from the Nernst equation:

$$E_{R/O}^e = E_{R/O}^0 - \frac{2.303RT}{nF} \log \left(\frac{a_R}{a_O} \right) \quad (3-61)$$

where a_R and a_O are the thermodynamic activities of R and O , respectively, and $E_{R/O}^0$ is the standard potential, which is readily calculated from the change in standard Gibbs energy for the cell reaction ($\Delta G_{R/O}^0$); $E_{R/O}^0 = -\Delta G_{R/O}^0 / nF$. Limiting currents are calculated using the equation:

$$i_{l,R/O} = \pm 0.0165 n F D C_{R/O}^b Re^{0.86} Sc^{0.33} / d \quad (3-62)$$

where the sign depends on whether the reaction is in the forward (+) or reverse (-) direction, F is Faraday's number, D is the diffusivity of the redox species, $C_{R/O}^b$ is the bulk concentration of R or O , as appropriate, Re is the Reynolds number ($Re = Vd/\eta$), Sc is the Schmidt number ($Sc = \eta/D$), d is the channel diameter, V is the flow velocity, and η is the kinematic viscosity.

The redox reactions of interest in this study are assumed to be:

and

as was assumed previously [10]. In this regard, it is important to note the maximum contribution that any given radiolytic species can make to the ECP is roughly proportional to its partial current [Eq. (3.62)] and hence concentration. Thus, in BWR simulations, the concentrations of H_2 , O_2 , and H_2O_2 are calculated to be orders of magnitude greater than any other radiolytic species and, hence, only these three need be considered.

Advanced Coupled Environment Fracture Model (ACEFM)

The Advanced Coupled Environment Fracture Model (ACEFM) differs from the Coupled Environment Fracture Model (CEFM) previously used in DAMAGE-PREDICTOR, REMAIN, and ALERT in two important respects [48]. Firstly, it incorporates thermally activated creep at the crack tip and, hence, includes a temperature-dependent crack tip strain rate that allows for more accurate simulation of the effect of temperature on the crack growth rate, as described by Vankeerberghen and Macdonald [49]. The model needs to be calibrated at only two temperatures, in order to calculate the activation energy and is then capable of reproducing the temperature dependence of the crack growth rate, including the existence of the maximum at about 150-200°C [50]. The model has also been modified to incorporate more accurate calculation of conductivity by employing NaOH and HCl as basic and acidic electrolytes, respectively. The stoichiometric concentrations of HCl and NaOH (ppb) are taken as input and the pH and conductivity of the solution are calculated from seven simultaneous equations, as described below.

The dissociation reactions occurring in the solution are the following:

and

The solution must be electrically neutral, which is expressed as

$$m_{H^+} + m_{Na^+} - m_{OH^-} - m_{Cl^-} = 0. \quad (3-70)$$

Furthermore, mass balance must be maintained for each chemical species in the solution. Thus, designating m_{NaOH}^o and m_{HCl}^o as the stoichiometric concentrations of HCl and NaOH results in the following mass balance equations

$$m_{Na^+} + m_{NaCl} + m_{NaOH} = m_{NaOH}^0 \quad (3-71)$$

and

$$m_{Cl^-} + m_{NaCl} + m_{HCl} = m_{HCl}^0 \quad (3-72)$$

The equilibrium constants for the dissociation reactions are defined as

$$K_w(T) = \frac{a_{H^+} a_{OH^-}}{a_w} = \frac{m_{H^+} m_{OH^-} \gamma_{H^+} \gamma_{OH^-}}{a_w} \quad (3-73)$$

$$K_1(T) = \frac{a_{Na^+} a_{Cl^-}}{a_{NaCl}} = \frac{m_{Na^+} m_{Cl^-} \gamma_{Na^+} \gamma_{Cl^-}}{m_{NaCl} \gamma_{NaCl}} \quad (3-74)$$

$$K_2(T) = \frac{a_{H^+} a_{Cl^-}}{a_{HCl}} = \frac{m_{H^+} m_{Cl^-} \gamma_{H^+} \gamma_{Cl^-}}{m_{HCl} \gamma_{HCl}} \quad (3-75)$$

and

$$K_3(T) = \frac{a_{Na^+} a_{OH^-}}{a_{NaOH}} = \frac{m_{Na^+} m_{OH^-} \gamma_{Na^+} \gamma_{OH^-}}{m_{NaOH} \gamma_{NaOH}} \quad (3-76)$$

where m_i , a_i and γ_i are the molal concentration, activity, and activity coefficient of species i in the system. The activity of water, a_w , can be assumed to be unity for dilute solutions. The activity coefficients are calculated using the extended form of Debye-Huckel theory, as given in Naumov et. al [43].

$$\log(\gamma_i) = \frac{-Az_i^2 \sqrt{\mu}}{(1 + Ba^0 \sqrt{\mu})} \quad (3-77)$$

where $\mu = \sum_{i=1}^I z_i^2 m_i$ is the ionic strength of the solution, z_i is the ion charge, a^0 is the distance of closest approach, and A and B are constants that depend on temperature, density (pressure), and the dielectric constant. Values for A and B are given by Naumov et al. as [43]:

$$A = 0.4241 + 0.00321 t - 0.00002 t^2 + 5.95143 \times 10^{-8} t^3 \quad (3-78)$$

and

$$B = 0.3237 + 0.00019 t - 2.12586 \times 10^{-7} t^2 + 1.4241 \times 10^{-9} t^3 \quad (3-79)$$

where t is the temperature in degrees Celsius. The value of a^0 is taken as 4.5×10^{-8} cm. Because the solution is dilute and, hence, because the activity coefficients are dominated by ion-solvent rather than ion-ion interactions, we may assure that: $\gamma_{H^+} = \gamma_{OH^-} = \gamma_{Na^+} = \gamma_{Cl^-} = \gamma$. Also, we assume that $\gamma_{NaCl} = \gamma_{HCl} = \gamma_{NaOH} = 1$. Accordingly, for notational convenience we will denote $\gamma_{H^+} \gamma_{OH^-} = \gamma_{Na^+} \gamma_{Cl^-} = \gamma_{H^+} \gamma_{Cl^-} = \gamma_{Na^+} \gamma_{OH^-} = \gamma^2 = G$. Values for the various dissociation constants were obtained as a function of temperature by using the $\log(K)$ versus T_K (Kelvin temperature) correlations given by Naumov et. al. [43]:

$$pK_w = 4673.8604/T_K - 7.0269 + 0.0180 \times T_K \quad (3-80)$$

$$pK_1 = 483.7740/T_K - 5.0881 + 0.0091xT_K \quad (3-81)$$

$$pK_2 = 2684.0060/T_K - 16.4465 + 0.0226xT_K \quad (3-82)$$

and

$$pK_3 = 1324.6809/T_K - 8.2525 + 0.0120xT_K \quad (3-83)$$

Because there are seven species in the solution whose concentrations need to be determined, we need to solve seven equations simultaneously to yield the composition of the system. These are Equations (3.70) to (3.76), which are solved iteratively using the Newton-Raphson technique with progressive updating of the activity coefficients. Once the concentrations have been obtained, it is a simple matter to calculate the conductivity of the solution using the limiting ionic conductivity data of Quist and Marshall [51]. We should note that the model for the solution chemistry is currently being extended to include other ionic impurities, including sulfate and carbonate.

The crack growth rate model (ACEFM) generates growth rates as a function of time and, hence, crack length for specific input parameters, including stress intensity, temperature, ECP, conductivity, pH, and flow velocity. Previous modeling work has shown [52] and experimental observations have confirmed that the crack growth rate depends upon crack length, independent of the stress intensity. Thus, Macdonald, et al. [48] have shown it is necessary to differentiate between the *mechanical crack length* (MCL), which, together with the stress, establishes the stress intensity, and the *electrochemical crack length* (ECL), which partly controls the potential distribution between the crack tip and the external surface. Because current flows through the path of least resistance, the electrochemical crack length may be defined as being, in many instances, the shortest distance between the crack tip and the external surface, where it is consumed by oxygen reduction. For a CT specimen, the ECL (distance between the crack tip and the side surfaces of the specimen) is independent of the mechanical crack length and remains approximately constant as the crack propagates through the specimen, even though the MCL increases.

On the other hand, for a thumbnail crack in a surface, the MCL and the ECL, both being distributed quantities, appear to be virtually identical. For a thumbnail crack in an infinite plate, the stress intensity is lowest at the edge of the crack and is highest in the center. Likewise, the ECL is smallest at the crack edge and is greatest in the center. As the ECL increases, the IR potential drops down, the crack reduces the potential drop across the external surface available for reducing oxygen, which consumes the coupling current between the crack and the external surface. Accordingly, the mechanical driving force for crack propagation decreases as one moves from the crack center to the crack edge, whereas the electrochemical driving force (potential drop across the external surface) increases. It is found that the crack growth rate is higher at the edge than in the center, resulting in the formation of elongated thumb nail geometry, thereby illustrating the dominance of electrochemical factors over stress (intensity) in controlling the rate of environmentally-induced crack growth. Thus, an important conclusion is the crack growth rate should decrease with increasing electrochemical crack length. This expectation is well illustrated in the calculated crack length plotted in Figure 3.22.

Damage Function Analysis (DFA)

The cracks are assumed to grow from an initial length of 0.1 cm and the crack length, x_N , over the anticipated service time of a component, T , obtained by an accumulation of the crack advances over N periods of time $\Delta t_1, \dots, \Delta t_i, \dots, \Delta t_N$.

$$x_i = x_{i-1} + \text{CGR}_i \cdot \Delta t_i, \quad i = 1, \dots, N \quad (3-84)$$

$$T = \sum_{i=1}^N \Delta t_i \quad (3-85)$$

The crack growth rate, CGR_i , is presumed to be time-independent for each interval, Δt_i . The initial crack length, x_0 , corresponds to the depth of a pre-existing crack (as may have been detected during an assumed inspection for a safety analysis scenario).

3.4.2 Simulation of Plant Operation

A simplified BWR coolant circuit diagram is shown in Figure 3.17. The reactor operates at approximately 288°C, producing steam at a pressure of about 68bar. FOCUS calculates the concentrations of chemical species, the corrosion potential, and the growth rate of a crack of any specified length at closely spaced points within each of the coolant circuit sections numbered from 1 to 10 in Figure 3.17 under NWC and HWC conditions. The code also integrates the crack growth rate along the corrosion evolutionary path (CEP) to yield the crack length at any specified point along that path.

Corrosion Evolutionary Path

To illustrate the application of FOCUS, in the present analysis, it is presumed the reactor was operated for 12 months from initial heat up and had one scram midway through that period of operation. The reactor was maintained at 95% of full reactor power or at full power, in order to consider normal reactor power fluctuations (Figure 3.18). The Corrosion Evolutionary Path (CEP), summarized in this figure, includes 24-hour start-up and outages (at 6 months) over which the reactor parameters (power level, flow velocity, temperature) were assumed to vary linearly with time. The electrolyte concentration (5ppb NaCl) was maintained constant during the start-up and outage with the conductivity varying according to the model presented above and shown in Figure 3.20 (see later). During NWC operation, no H_2 is added to the coolant while, under HWC operation, H_2 is injected into the feedwater to maintain the concentration at 0.5ppm. Cracks with initial lengths of 0.1cm were assumed to exist in all sections of the primary coolant circuit. Furthermore, for the present calculations, the cracks are assumed to be loaded to stress intensity factors of $15 \text{ MPa}\sqrt{m}$ (in the core) or $27.5 \text{ MPa}\sqrt{m}$ (out of core). Finally, the concentrations of HCl and NaOH during normal operation were set at 5ppb. The four main predicted parameters, ECP, conductivity, CGR, and the crack depth, are displayed in Figures 3.19-3.22.

Figure 3.17. Typical equipment and coolant flow in the BWR primary system.

Figure 3.18. Reactor power variation and feedwater H₂ concentration over a single cycle (12 months).

Table 3.5. Input Parameters for the Calculation with the FOCUS.

Stress intensity factor ($\text{MPa} \sqrt{m}$) = 15 (in core), 27.5 (other regions)
Concentration HCl during the normal operation = 5ppb
Concentration NaOH during the normal operation = 5ppb

3.4.3 Simulation Results and Discussion

During full power operation, the ECP values in the coolant circuit under NWC operation are in the range of $271\text{mV}_{\text{SHE}}$ in the core channels to $-36\text{mV}_{\text{SHE}}$ at the exit to the recirculation pipes. However, under HWC operation with 0.5 ppm H₂ in the feedwater, the ECP lies in the range from $270\text{mV}_{\text{SHE}}$ in the core channels to $-623\text{mV}_{\text{SHE}}$ at the

bottom of the lower plenum. The predicted ECP values in the core channels under both NWC and HWC are essentially identical, because H_2 is removed from the liquid (water) phase in the core by boiling transfer to the steam phase. RADIOCHEM predicts the H_2 concentrations in the core channels for both cases (NWC and HWC) are almost the same and are very low.

Figure 3.19. ECP values of NWC (A) and HWC ((B), 0.5 ppm H_2) operation.

The bulk conductivities for the reactor coolant involving HCl and NaOH species are shown in Fig. 3.20. The conductivity calculated from ACEFM is found to be a function of the HCl and NaOH concentrations and the bulk temperature with little contribution being apparent from the radiolysis products. Therefore, the difference in bulk conductivity for NWC and HWC operation is not significant. From a separate calculation performed to investigate the effect of changes in temperature, the CGR was found to pass through a maximum at around 150-200°C, as previously noted.

Figure 3.20. Bulk conductivity of NWC (A) and HWC ((B), 0.5 ppm H_2) operation.

Figure 3.21. CGR values of NWC (A) and HWC ((B), 0.5 ppm H₂ operation.

The predicted CGR in the coolant circuit components during NWC and HWC operation of the BWR is shown in Figure 3.21. The data presented in Figures 3.19 and 3.21 reveal a close correlation between the predicted ECP and CGR, no doubt recognizing the latter is a quasi exponential function of the former. Accordingly, it is expected that the core internal components at high ECP values have high CGR values, and vice versa.

FOCUS predicts the accumulated damage (crack length) in components in the reactor primary coolant circuit under any given set of operating conditions. In this way, it is possible to compare the accumulated damage (crack depth) between NWC and HWC operating conditions over identical corrosion evolutionary paths (operating histories). In doing so, it is important to note the damage is considered to develop from initial, 0.1 cm long cracks. This approach, of course, ignores the initiation process, which, in this case, is the time for the crack to nucleate and grow to a 0.1 cm length. Incorporation of the initiation process into FOCUS is underway, by introducing the deterministic Damage Function Analysis (DFA) for describing the dynamics of passivity breakdown and nucleus growth [53]. Because the crack growth rate in the fuel channels is virtually the same for both NWC and HWC (0.5ppm H₂ in the feedwater), the accumulated damage is expected to be similar, as observed. On the other hand, the accumulated crack growth in the core bypass for the one year of NWC operation is 0.21 cm, but is only 0.04 cm for the one year HWC operation. The accumulated damage (crack length) is distinctly lower as the result of HWC operation compared with NWC operation, at least for out-of-core components. Furthermore, because the ECP is much lower under HWC than under NWC in all components except those in the core and upper plenum, and assuming that passivity breakdown followed by micro pit growth is the precursor to IGSCC, DFA predicts the initiation time will be considerably longer under HWC conditions than under NWC conditions [53]. Accordingly, it is likely that FOCUS significantly underestimates the benefits of HWC, but only in those regions where the ECP is greatly reduced.

Figure 3.22. Crack depth versus operating time for NWC (A) and HWC ((B), 0.5 ppm H₂) operation of a BWR.

Focusing now on crack growth only, the calculated damage at various points around the primary coolant circuit under both NWC and HWC conditions is summarized in bar-graph form in Figure 3.23. This data again indicates the CGR values in the BWR internals are closely related to the ECP values during both NWC and HWC operations. In particular, they indicate only marginal benefit of HWC over NWC for cracks in the upper plenum (UP), the mixing plenum (MP), and the jet pumps, where “marginal” is taken to be a diminution in CGR of no more than 50%. The calculations also demonstrate the facility offered by FOCUS for estimating accumulated damage at many locations within the coolant circuit simultaneously, while the plant traverses a complicated Corrosion Evolutionary Path (CEP). Clearly, the inclusion of a viable crack initiation model is an important future development.

Figure 3.23. Comparison of the accumulated damage of the Rx. internals after 12 month NWC and HWC operation.

3.5 References

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Task 4. Model Integration and Development of BWR and PWR Primary Water

Chemistry Codes

Task Status: Completed.

4.1 Radiation Transport and Human Exposure

A major operating concern at every NPP is the spread of radiation to areas of the plant that do not have the necessary shielding to prevent human exposure. Areas with inadequate shielding may exist because the plant designs did not take into account the spread of radioactivity to these areas, or because it is not technically feasible to shield the area, possibly due to maintenance or structural requirements. Regardless of shielding, many areas of the plant that experience radiation accumulation are routinely subject to inspection for both operational and safety purposes. While many thorough safety precautions are considered and implemented, human exposure does occur. The US government regulates the limits of radiation exposure by setting maximum annual human exposure levels. The current acceptable level of radiation dosage for NPP employees and maintenance workers is the effective equivalent dose of 5 *rems* per year, where a *rem* is defined as the absorbed dose in *rads* multiplied by the quality factor [1]. A *rad* is a physical quantity defined as the absorption of one one-hundredth of a joule per kilogram; the *rad* is a measure of energy absorbed per unit mass. The quality factors used to define a *rem* are given in Table 4.1.

Although reducing radiation exposure to employees is always a concern, it is now of special concern because of possible future legislation that would reduce the maximum yearly exposure limits. Reducing exposure will certainly require a comprehensive analysis of NPP operating procedures. Clearly, regardless of the efforts made to block exposure to radiation, the best approach is to prevent the accumulation of radiation in areas where routine maintenance will be performed.

Table 4.1. Type of Radiation and Quality Factor [1].

Type of radiation	Quality factor (Q)
X-Ray, gamma, or beta radiation	1
Alpha particles, multiple-charged particles, fission fragments and heavy particles of unknown charge	20
Neutrons of unknown energy	10
High-energy protons	10

The scope of the discussion in this section has already been declared to contain only light water PWRs. The discussion will now be further restricted to examining the primary coolant loop of a pressurized water reactor. Figure 4.1 provides a diagram of a typical PWR primary coolant loop. Nearly all of the parts of the primary coolant loop are inspected or serviced at one time or another, but certain areas are of particular interest.

The steam generators of a PWR often need servicing, primarily due to tube cracking, and are very important when considering the spread of radiation to out-of-core areas. As shown in Figure 4.1, light water travels through the core where it is heated by the fuel elements and travels through the hot leg to a U-shaped steam generator, where it passes heat to the secondary coolant loop. The coolant is then re-circulated to the core via the cold leg. Two systems of importance are the Residual Heat Removal System (RHRS), which regulates coolant temperature during shutdown, and the CVCS system, which regulates the concentrations of chemicals in the primary coolant.

Figure 4.1. Diagram of a Typical PWR Primary Coolant Loop.

4.2 Problem Definition and Overview

The objective of this section is to quantify via a numerical model the accumulated radiation on the wet surfaces of the structures of the primary loop of a PWR, due to the activation and mass transport of dissolved corrosion products in the primary coolant.

From this point forward, in this report, the term activity transport refers to the accumulation of radioactivity on the interior surfaces of the primary loop structures of a PWR that are in contact with the primary coolant, due to the activation of dissolved corrosion products in the primary coolant. An overview of the physical process behind this phenomenon is now given.

1. The inner surfaces of the structures of the primary loop, such as the interior of the piping and steam generators, corrode as a consequence of their contact with the primary coolant.
2. The corrosion layers are dissolved into the primary coolant. The dissolution of the corrosion products is considered to be described by an equilibrium electrochemical and chemical system formed by primary loop structures and the primary coolant.
3. The dissolved corrosion products, now aqueous species of the elements found in the corrosion layers on the wetted surfaces of the primary loop structures, travel with the primary coolant through the reactor core, where some of them will absorb a neutron. The absorption process is also called neutron activation, and changes the atomic weight of the isotope in question. This change in atomic weight may cause the struck isotope to become unstable, and hence radioactive.
4. The normal and radioactive isotopes travel with the primary coolant out of the core and, through a change in saturation concentration of the isotope, deposit on the interior walls of the primary loop structures.

Clearly, as this chain of processes is repeated the amount of radioactive nuclides on the wetted surfaces of the primary loop structures will increase, leading to a build-up of radiation fields in that area of the plant. A central idea behind the proposed model is that electrochemical equilibrium exists between the primary coolant and the structures of the primary loop. This report will present a model to predict the accumulation on the interior surfaces of the primary loop structures, as a function of the operating parameters and the time of operation of the plant.

4.3 Review of Existing Models

Many models already exist to calculate the accumulation of radioactivity on the surfaces of the primary loop components of a PWR [2-4, 10, 13-17]. These models vary greatly in their origins and approach to describing this phenomena. A chart of the country of origin of each code reviewed in this chapter is given in Table 4.2, and a brief description of the nature of each code is given after that.

Table 4.2. Activity transport code country of origin [10]

Code	Origin Country
CPAIR-P	Pakistan
ACE-II	Japan
Crudtran	Korea
MIGA-RT	Bulgaria
Pactole-2	France
Diser	Czech Republic

4.3.1 CPAIR-P

Mirza et al. set forth a computer simulation model to describe the corrosion product activity in the primary coolant of pressurized water reactors [2]. Their model uses a modification of the CPAIR-P code developed by F. Deeba [3], but this work built off of previous work by Mirza [4]. The most recent modifications include the ability to simulate flow rate transients and account for linearly accelerating corrosion during the fuel cycle. The original model developed by Deeba is based on five physical processes: the production of activated CRUD products due to their passing through the neutron flux in the core, the removal of activated isotopes due to purification of the water, the removal of activated isotopes from the primary coolant due to deposition on the interior surfaces of the primary loop structures, leakage of coolant from the primary loop, and radioactive decay of these isotopes. Three major assumptions are made in their model. Uniform time independent corrosion has been assumed in Deeba's model, meaning the rate of corrosion is assumed to be constant. The concentration gradients are assumed to be zero at a given point along the primary loop, which signifies the effects of local concentration gradients have been ignored. Finally, the precipitation of CRUD and activated species onto the interior wetted surfaces of the primary coolant loop structures is assumed to occur in the same proportion as the species are found in the primary coolant. Figure 4.1 is a diagram of the many possible paths of how the generation and removal of activated corrosion products may occur in the primary coolant of a typical PWR according to this model.

The basic mathematical model underlying the above mentioned reports is now described. Mirza et al. define N_w , N_p and N_c to be the concentration of precursor nuclides in the primary coolant, on the interior surfaces of the primary loop surfaces, and the core surfaces, respectively. The precursor nuclides are the non-activated corrosion products found in the coolant, and the interior surface of the primary loop structures refers to the collective, out-of-core surfaces in the primary loop. Likewise, they define n_w , n_p , and n_c to be the concentration of activated corrosion products in the primary coolant, on the interior surfaces of the primary loop surfaces, and on the core surfaces, respectively.

Figure 4.2. Diagram of situations that can lead to the generation and removal of activated corrosion products in the primary coolant of a typical PWR, according to Mirza et al. [4]

The rate of change of a single activated corrosion product in the primary coolant is defined by Mirza et al. as:

$$\frac{dn_w}{dt} = \sigma \phi_\epsilon N_w - \left\{ \sum_j \frac{\epsilon_j Q_j g(t)}{V_w} + \sum_k \frac{l_k g(t)}{V_w} + \lambda \right\} n_w + \frac{K_p g(t)}{V_w} n_p + \frac{K_c g(t)}{V_w} n_c \quad (4-1)$$

The first term of Equation 4-1 quantifies the generation of radioactive nuclei, where, σ is a representative neutron capture cross-section and Φ_ϵ is the effective neutron flux for the corrosion product in question. The next term quantifies the removal of radioactive nuclei from the primary coolant due to coolant purification by ion exchangers, filters, deposition on pipes and deposition on core surfaces. In this term, each $\epsilon_j Q_j$ represents the corresponding rates of removal, l_k is the rate of coolant leakage from the k^{th} leak, $g(t)$ is a factor to account for time dependent flow perturbations, and λ is the decay constant for the isotope in question. The third and fourth term quantify the removal of activated isotopes from deposits on the primary loop out of core piping and the core, respectively. In these terms, K_p and K_c are the constant rates at which these events occur.

The expression used to determine the number of precursor nuclides in the coolant, N_w , is given as:

$$\frac{dN_w}{dt} = - \left\{ \sum_j \frac{\varepsilon_j Q_j g(t)}{V_w} + \sum_k \frac{l_k g(t)}{V_w} + \sigma \phi_\varepsilon \right\} N_w + \frac{K_p g(t)}{V_w} N_p + \frac{K_c g(t)}{V_w} N_c + \frac{C(t) S N_0}{V_w A} f_n f_s \quad (4-2)$$

Equation (4-2) is similar to Equation (4-1) in that it contains the same bracketed loss terms and the same consecutive release terms, from the corrosion already present on the piping and core, respectively. The primary difference is in Equation (4-1) there is a source term for activated isotopes, and in Equation (4-2) that term has been considered a loss term, due to the fact activation is a loss process from the point of view of the precursor isotopes. The precursor isotopes do have a source, however, and it is described by the last term in Equation (4-2). In this term, $C(t)$ gives the corrosion rate as a function of time, S the total wetted surface area of the primary coolant loop structures, N_0 is Avogadro's number and A is the atomic weight of the precursor in question, f_n the natural abundance fraction of the precursor isotope in the element, and f_s the fraction of the element in the material being corroded. The following four equations complete the model Mirza et al. set forth:

$$\frac{dN_c}{dt} = \frac{\varepsilon_c Q_c g(t)}{V_c} N_w - \left\{ \frac{K_c g(t)}{V_c} + \sigma \phi_0 \right\} N_c \quad (4-3)$$

$$\frac{dn_c}{dt} = \sigma \phi_0 N_c + \frac{\varepsilon_c Q_c g(t)}{V_c} n_w - \left\{ \frac{K_c g(t)}{V_c} + \lambda \right\} n_c \quad (4-4)$$

$$\frac{dN_p}{dt} = \frac{\varepsilon_p Q_p g(t)}{V_p} N_w - \frac{K_p g(t)}{V_p} N_p \quad (4-5)$$

$$\frac{dn_p}{dt} = \frac{\varepsilon_p Q_p g(t)}{V_p} n_w - \left\{ \frac{K_p g(t)}{V_p} + \lambda \right\} n_p \quad (4-6)$$

In Equations (4-3)-(4-6), as in (4-1) and (4-2), the subscripts c, w, and p stand for the core, coolant water, and piping (out-of-core areas), respectively. These equations all have the same basic form, linear combinations of source and loss terms. The system of Equations (4-1)-(4-6) forms a coupled set of first order differential equations. The authors solved these equations by implementing a fourth-order Runge-Kutta routine.

A major feature of this program is the mass balance approach to quantifying the number of nuclides, precursor and activated, by describing the source and loss terms. While these terms certainly represent physical processes occurring, the mechanisms for predicting these rates are not present. All of these rates are taken as empirical or previously calculated results, and are not derived from any sort of first principles in the code itself. Table 4.3 lists the constants used by Mirza et al. [2], which are cited from Jaeger [11] and Glasstone and Sesonske [12]. Even with this disadvantage, the code has merit in its consideration of many physical processes.

Table 4.3. Physical Constants used by Mirza et al. in the CPAIR-P Activity Transport Code [2]

Rate Type	Value
Deposition on Core ($\varepsilon_c Q_c$)	$8.0 \times 10^{-5} \text{ m}^3/\text{s}$
Deposition on Piping ($\varepsilon_p Q_p$)	$1.37 \times 10^{-5} \text{ m}^3/\text{s}$
Ion Exchanger Removal ($\varepsilon_I Q_I$)	$5.0\text{-}7.81 \times 10^{-4} \text{ m}^3/\text{s}$
Re-Solution Ratio for Core (K_c)	$4.0 \times 10^{-5} \text{ m}^3/\text{s}$
Re-Solution Ratio for Piping (K_p)	$6.9 \times 10^{-6} \text{ m}^3/\text{s}$
Volume of Primary Coolant (V_w)	13.7 m^3
Volume of Scale on Core (V_c)	9.08 m^3
Volume of Scale on Piping (V_p)	1.37 m^3
Total Corrosion Surface (S)	$1.01 \times 10^2 \text{ m}^2$
Average Corrosion Rate (C_o)	$2.4 \times 10^{-12} \text{ kg/ m}^2\cdot\text{s}$

4.3.2 ACE-II

The ACE-II code was developed to predict the residual radiation fields in the components of Japanese style PWRs. The code is largely empirical in nature [10]. The process of activity transport and diffusion of activated isotopes into the construction parameters is described by the following sequence of physical phenomena:

1. Inner and outer oxides form on the wetted surfaces of the primary loop components due to corrosion.
2. The corrosion is released into the primary coolant by dissolution and erosion of the outer oxide layer.
3. The dissolved and particulate corrosion products in the primary coolant are activated as they travel through the intense radiation fields in the core.
4. The particulate and dissolved corrosion products, both non-activated and activated are precipitated onto the wetted surfaced of the primary loop components, resulting in a buildup of CRUD.
5. Activated isotopes in the CRUD diffuse into the outer layer oxides, and then into the inner layer oxides, and eventually into the construction materials themselves by isotopic exchange. The authors of this code have named this process incorporation with corrosion of material.

The code also identifies that the corrosion products released from the core are to be activated before they are released, providing a source of activated corrosion products that do not occur by activation after being released into the coolant. The corrosion products accounted for are cobalt 58 and cobalt 60, with precursor isotopes of iron, nickel, and cobalt. The code uses solubility to describe mass transfer. It either calculates or uses experimentally determined solubility for nickel oxide, metallic nickel, and nickel ferrite (NiO , Ni , NiFe_2O_3). Cobalt's solubility is not calculated; instead the movement of cobalt is determined by the movement of the nickel ferrite.

All of the above listed processes are quantified through empirical measurements. None of the processes are quantified by fundamental principles, making the code difficult to

adapt to different styles of nuclear power plants; however, for the Japanese PWRs, the code works well [10]. The volume mesh for the code considers many segments of the primary loop, which allows for detailed calculation of radiation field buildup in a given area. Figure 4.3 shows a diagram of the processes described by the ACE-II code for a given element; Figure 4.4 shows the processes modeled for activity transport.

Figure 4.3. Logic diagram of the mass transport processes modeled in the ACE-II code. [10]

Figure 4.4. Logic diagram of the activity transport processes modeled in the ACE-II code. [10]

4.3.3 CRUDTRAN

The CRUDTRAN code was developed as an empirical code to describe activity transport in a PWR. Both soluble and particulate forms of corrosion products are considered when determining the release of corrosion products into the water. The code models the processes of ion dissolution in the steam generators and ion deposition in in-core areas, as well as particle nucleation in the core regions and particle breakdown in the steam generators. Particle deposition is modeled around the entire primary coolant loop. A summary of these processes is given in Figure 4.5, in which it is shown that the code models the release of ions from the steam generator tube surfaces and the deposition of these ions on the core fuel surfaces, where it is activated. Particle nucleation from dissolved crud is modeled in the core and particle disassociation is modeled in the steam generator, which describes the transport of activity. This model assumes deposition around the entire loop.

Figure 4.5. Mass transport of corrosion products modeled in CRUDTRAN. PD = Particle Deposition, PN = Particle Nucleation, PDA = Particle Disassociation, S/G = Steam Generator.

Figure 4.6. The 'Four Node Model' for corrosion product transport used by CRUDTRAN. CR = Corrosion rate in the Steam Generator, RS = CRUD release rate of soluble species in the Steam Generator, DS = CRUD deposition rate of soluble species in core, PR = CRUD precipitation rate in the coolant, DP1 = CRUD deposition rate as a particulate in the core, DP3 = CRUD deposition rate as particulate in the Steam Generator.

The empirical nature of the CRUDTRAN code enters through the determination of the rate constants shown in Figure 4.6. The rates that must be specified for the model are: the deposition of soluble species in the core (DS), the deposition of particulate corrosion products in the core and steam generator (DP1, DP3 respectively), the dissolution of

soluble species from the steam generator (RS), and the corrosion rate in the steam generator and rate of nucleation of particles from dissolved corrosion products (CR, PR respectively). These rate constants were determined using data obtained from the Massachusetts Institute of Technology's PWR Coolant Chemistry Loop. The model assumes the release of dissolved ions from the steam generators is governed by surface kinetics rather than mass transport. This means the dissolution of corrosion films on the wetted surfaces of the pipes is important to this model of activity transport.

Activity transport is modeled in CRUDTRAN by quantifying the number of cobalt 58 and cobalt 60 isotopes deposited in a given area of the primary coolant loop. The precursor isotopes considered are cobalt and nickel, but the mass transfer properties for these elements are not calculated directly. Instead, the mass transfer of iron is calculated and the cobalt and nickel are determined from set ratios to this amount.

Important predictions made by this code include comparing the quantified amounts of mass transport and activity transport, as well as the sensitivity of corrosion to radiation levels in the core. Lee [20] used this code to determine that mass transport outweighs activity transport by about ten times, and that an increase in reactor radiation will cause the code to predict that less CRUD will precipitate in the core.

4.3.4 MIGA-RT

The activity transport code MIGA-RT originated in Bulgaria and has been used by Dinov to make predictions about radiation fields in PWR and VVER type reactors [13, 14]. The most recent versions of this code focus on the use of particulate forms of corrosion products to predict the accumulation of radiation around the primary heat transfer loop. This approach was taken due to previous work by the author, Dinov, where he sets forth an analytical model to calculate mass transfer coefficients for particulate corrosion products [15]. The mass transfer of particles is assumed to be dependent upon the interior surface conditions of the coolant pipes and sticking probabilities. While the emphasis in this model is on particle deposition, the model still includes the effects of soluble corrosion products in the primary coolant.

The dissolved corrosion products are quantified by using a parabolic rate law for the first fuel cycle, and a constant release rate for subsequent cycles. Particulate forms of the corrosion products are assumed to be released into the coolant by erosion of the corrosion films on the wetted surfaces due to the primary coolant flow. The elemental solubility of iron and nickel and the ratio of these elements in the construction materials of the primary loop determine the release rates of the corrosion products. These products are magnetite, nickel ferrite, sub-stoichiometric nickel ferrite, metallic nickel, and nickel oxide. The activated isotopes considered by MIGA-RT are cobalt 58 and cobalt 60; they are characterized in the primary coolant in the same manner as their precursor isotopes. MIGA-RT is a FORTRAN code in which time does not appear explicitly. The change in time is simulated by changing the water chemistry conditions as appropriate for the duration of a normal fuel cycle [10].

Figure 4.7. Processes Modeled in MIGA-RT. Dotted lines represent mass transfer processes for soluble species; Solid lines represent particulate processes.

4.3.5 PACTOLE-2

According to Burrill and Menut (2001), the Pactole series of codes are considered to be the most developed and advanced activity transport codes. The current version of the code is Pactole-2, which uses analytic solution for many of its calculations, while the version under development, Pactole-3, uses numerical methods and object oriented languages to perform the calculations. This code has been under development in France for nearly 20 years, and is also considered by the aforementioned authors to contain all of the necessary and relevant mechanisms for predicting activity transport.

Pactole-2 works from the assumption that corrosion layers on the internal surfaces of the primary loop components release corrosion products directly into the primary coolant. Both the inner and outer oxide layers are considered to be composed of the same species, namely oxides of the elements found in the base metal. The thickness of the inner layer is used to determine the rate of release of dissolved ions into the coolant, while the thickness of the outer oxide layer, beyond a critical thickness, is used to determine the rate of erosion of particulate corrosion products into the coolant. Pactole-3 will also include the effects of dissolution kinetics on reaction rates as new parameter for determining the rate of release of ions into the coolant.

The mass transfer of magnetite is solved completely in this model, and is used to determine the mass transfer of other ferrites, including manganese ferrite, cobalt ferrite, and nickel ferrite. Precipitation of any of these ferrites is determined to occur when their concentration in the bulk coolant exceeds their saturation concentration in a given section of the primary loop. According to the model, precipitation can occur at any point around

the primary loop, including both in-core and out-of-core areas, the water chemistry of the loop will permit. The water chemistry of the primary coolant, in this model, is assumed to be dominated by the addition of boron and lithium to the system for the purposes of pH control. Other deposition methods, besides precipitation due to concentration gradients of dissolved species, are considered to occur as well; precipitation of particulate corrosion products can occur by turbulent diffusion, thermophoresis, and gravitational settling [16].

Figure 4.8. Logic Diagram of Processes Modeled in PACTOLE-2 Code. Note: Dotted lines denote processes that occur due to isotopic exchange [16]

Ten activated nuclides are modeled in the Pactole series of codes. They are isotopes of iron, nickel, manganese, chromium, cobalt, and zirconium created by neutron activation from both thermal and fast neutrons. Permanent radiation field growth due to isotopic exchange with both the base metal and inner oxide layers is also accounted for in this model. In terms of program mechanics, the Pactole codes incorporate a fixed water chemistry system, meaning the system conserves mass. The primary loop is divided into seventy sections, eight for the CVCS system, four for each steam generator, forty-two are included in the core, while the rest of the sections are other supporting structures of the primary loop [10].

4.3.6 DISER

At the heart of the DISER code is its careful treatment of the size distribution of the particulate forms of corrosion products in the primary coolant. This code models corrosion products in the coolant in three states: soluble, colloids, and particles. This makes it quite unique from the other codes summarized in this section, because it is the only one that produces a distribution of the corrosion products found in the primary loop.

The DISER code models release of dissolved corrosion products into the coolant by assuming a single oxide layer, whose thickness is determined by parabolic rate and surface kinetics, and the saturation concentrations of magnetite and nickel ferrite in the coolant. The elements considered in the mass transport are iron, nickel, chromium, and cobalt; the radioactive isotopes considered are Mn^{54} , Fe^{59} , Co^{58} , Cr^{51} , and Co^{60} . The generation of these isotopes is assumed to happen by thermal neutron activation [10]. While these characteristics are not unique to this code, the method for quantifying deposition is.

Precipitation of the dissolved corrosion products is predicted by this code to occur when the coolant in the diffusion boundary layer becomes supersaturated with the dissolved corrosion products. When the bulk solution becomes supersaturated with corrosion products, the DISER code models the formation of colloids. The deposition of colloids to the internal surfaces of the primary loop components is determined by the water chemistry of the reactor loop. If the colloid possesses enough energy, from Brownian motion, to overcome the repulsive electrostatic force of the oxide layers on the pipes, it will deposit onto the pipe wall [17]. The authors of the DISER code modeled the work needed for the colloid to be deposited onto the wall. Furthermore, if a colloid reaches a size above 0.8 microns in diameter, it is considered to behave as a particulate mass and is subject to the sticking probabilities predicted by Beal's theory [25]. In all, the code contains thirteen different scales for particles sizes, and can predict the distribution of these sizes as deposited around the primary loop [10].

For this code, the primary loop of a PWR is sectioned into 14 regions; five are for the steam generator, two are for the entrance and exit of the steam generator, two are for the hot and cold legs, and five are for the core, where both zirconium and iron based materials are modeled as base substrates. Each section must solve all forty-five mass balance equations, using the code's time-step of one day.

4.3.7 Summary

The review of codes in this chapter has demonstrated the diversity present in existing approaches to modeling activity transport in PWRs. The various approaches emphasized different processes which they consider important. Most models considered the mass transport of dissolved ions and particulate corrosion products, while one, MIGA-RT, looked between these two states and described the formation and deposition of colloids. The primary variation between codes is the area of detail present in each model. For example, Mirza et al. chose to identify and quantify many sources and deposits of mass transfer, while PACTOLE-2 focused on the microscopic model of the surface-coolant interface to describe the release of corrosion products into the coolant.

A common feature of many of the codes is the use of various empirically determined constants. This feature precludes them from being applied to primary circuits other than the ones they have been specifically designed to model, because the necessary constants may not be applicable to different loops or the data may not be available. The goal of this report is to take the modeling techniques, for activity transport, previously developed and use them in a model not dominated by empirical constants. More specifically, the

goal is to create a model that predicts the extent of activity transport from the physical properties of the primary coolant circuit, such as the temperature, chemical characteristics, hydro-dynamic properties, and, most importantly, the electrochemical properties.

4.4 PWR Electrochemistry

The calculation of the Electrochemical Corrosion Potential (ECP), at a given position along the primary loop of a PWR, requires the consideration of many processes and physical phenomena. Physically, an ECP exists between all metals and their environments. In the primary loop of a PWR, this quantity is significant because of its variance with position in the loop, due to changes in thermal-hydraulic parameters, temperature, pH, and the local concentration of electroactive species. The ECP is a function of these values, thus, they must be known in order to calculate it. The thermal-hydraulic parameters and temperature values are readily available from TRACE, the Nuclear Regulatory Commission's accident safety code. The local pH, as a function of temperature, and the local concentration of electroactive species must be calculated separately.

Calculation of the local pH is achieved by considering a system of chemical reactions involving the primary species responsible for determining pH, namely boron and lithium hydroxide. Quantifying the local concentrations of electroactive species is performed by first identifying the important species, and then determining their rates of production and consumption. Finally, the ECP is calculated using a Mixed Potential Model (MPM).

4.4.1 Calculation of pH

One standard method of controlling pH in a PWR is the injection of Lithium and Boron throughout the fuel cycle. The lithium is typically injected as LiOH, and is maintained in the range of 0.4 to 2.2 ppm [26]. Controlling the pH has shown to be very important in regards to PWR operation, as many phenomena, such as stress corrosion cracking, have been shown to vary in part due to the pH of the system [18]. Table 4.4 gives a list of the chemical reactions used to calculate the pH in the primary loop of a PWR. The equilibrium constants for these reactions are given in Table 4.5, and, can be seen to be functions of the temperature. This allows for the calculation of the pH as a function of temperature, which is denoted as pH_T .

Table 4.4. Reactions for pH calculation [9]

Reaction Number	Reaction
1	$B(OH)_3 + OH^- = B(OH)_4^-$
2	$2B(OH)_3 + OH^- = B_2(OH)_7^-$
3	$3B(OH)_3 + OH^- = B_3(OH)_{10}^-$
4	$4B(OH)_3 + 2OH^- = B_4(OH)_{14}^{2-}$
5	$5B(OH)_3 + 3OH^- = B_5(OH)_{18}^{3-}$
6	$Li^+ + OH^- = LiOH$
7	$Li^+ + B(OH)_4^- = LiB(OH)_4$
8	$H_2O = H^+ + OH^-$

Table 4.5. Rate Constant for pH calculation [9]

Reaction Number	Rate Constant
1	$pQ_1 = -1573/T - 28.6059 - 0.012078*T + 13.2258*\log_{10}(T)$
2	$pQ_2 = -2756.1/T + 18.966 - 5.835*\log_{10}(T)$
3	$pQ_3 = -3339.5/T + 8.084 - 1.497*\log_{10}(T)$
4	$pQ_4 = -12820/T + 134.56 - 42.105*\log_{10}(T)$
5	$Q_5 = 0.0$
6	$Q_6 = 1.99$
7	$Q_7 = 2.12$
8	$pK_w = -4.098 - 3245/T + 2.23 \times 10^5/T^2 - 3.998 \times 10^7/T^3 + (13.95 - 1262.3/T + 8.56 \times 10^5/T^2) \log_{10}(\text{Water Densité})$

4.4.2 Local Electro active Species Concentrations

We seek the steady state concentrations of the electroactive species listed in Table 4-6, in order to calculate the ECP. One can find these concentrations by quantifying the rate of change of the rate of change of each species and solving the consequent first order differential equation numerically. The rate of change of each of these species is determined by three factors: the generation of each species by water radiolysis, the production and consumption due to chemical reactions, and the mixing of the coolant by convection.

Table 4.6. Electro active species considered when calculating the ECP. [9]

Species Number	Species
1	e^-
2	H
3	OH
4	H_2O_2
5	HO_2
6	HO_2^-
7	O_2
8	O_2^{2-}
9	H_2
10	O^-
11	O
12	O_2^-
13	OH^-
14	H^+

4.4.2.1 Production by Water Radiolysis

The light water coolant of a PWR is subjected to an extremely high dose of radioactive energy, in the form of high-energy alpha particles, gamma photons, and neutrons. The breakdown of water into other ions and other radical species is known as radiolysis, and must be accounted for when describing the rate of change of the particles listed in Table 4.6. Quantification of the rate of generation by radiolysis, of the i^{th} species in Table 4.6, is given by Macdonald et al. as [9]:

$$R_i^y = \left(\frac{G_i^y \Gamma^y}{100 N_V} + \frac{G_i^n \Gamma^n}{100 N_V} + \frac{G_i^\alpha \Gamma^\alpha}{100 N_V} \right) \tilde{F} \rho \quad (4-7)$$

Where, in Equation 4-7, the rate of generation, R_i^y , is calculated in units of moles/cm³. The values Γ^y , Γ^α , Γ^n , denote the energy dose rate of gamma photons, alpha particles, and neutrons, while the values G_i^y , G_i^α , G_i^n denote the yield per unit energy of the i^{th} species, from gamma photons, alpha particles, and neutrons, respectively. Also, N_V is Avogadro's number, ρ is the water density, and $\tilde{F}$ is a unit conversion factor. The selection of the G -Values is very important, as they directly determine the ratio of generated species to energy adsorbed by the coolant. Due to the nature of the measurements required, it is difficult to obtain precise G -Values, especially at the temperatures needed for modeling a PWR, thus confining the model to a limited amount of accuracy in this respect. The G -Values used here are given in Table 4.7.

Table 4.7: G-Values – 293K [19]

Species	G^y (No./100eV)	G^n (No./100eV)	G^α (No./100eV)
e ⁻	2.66	0.61	0.06
H	0.55	0.34	0.21
OH	2.67	2.02	0.24
H ₂ O ₂	0.72	0.65	0.985
HO ₂	0.00	0.05	0.22
HO ₂ ⁻	0.00	0.00	0.00
O ₂	0.00	0.00	0.00
O ₂ ⁻	0.00	0.00	0.00
H ₂	0.45	1.26	1.3
O ⁻	0.00	0.00	0.00
O	0.00	0.00	0.00
O ₂ ²⁻	0.00	0.00	0.00
OH ⁻	0.01	0.00	0.00
H ⁺	2.76	0.00	0.06

4.4.2.2 Production by Chemical Reactions

As stated earlier, the rate of change of the electroactive species given in Table 4-6 is partly dependent on the production and consumption of these species by chemical reactions in the primary coolant. It is important to realize these reactions involve both the combining of other species to produce the species in question, and the consumption of the important species to create others that may not be considered important for calculating

the ECP. While chemical reactions play an important role in determining the local concentration of the electroactive species in Table 4.6, it is the radiolysis of the water which accounts for most of the generation and variance of their concentrations around the primary loop. A list of the reactions considered in this model is given in Table 4.9. Macdonald et al give the rate of change of a given species, due to the chemical reactions, as [9]:

$$R_i^c = \sum_{s=1}^N \sum_{m=1}^N k_{sm} C_s C_m - C_i \sum_{s=1}^N k_{si} C_s \quad (4-8)$$

In Equation 4-8, the rate of change due to chemical reactions of the i th species, R_i^c , is determined by the concentrations of the species, C_i , C_s , C_m , and the rate constants for the reactions between the species, k_{sm} and k_{si} .

4.4.2.3 Convective Transport

The third and final source of electro-active species, at a given position along the primary loop, is provided by accounting for the influx of ions due to the primary coolant flow. The rate at which species are delivered to a location by the flow is quantified by Macdonald et al. [9] as:

$$R_i^{flow} = \frac{d(uC_i)}{dx} \quad (4-9)$$

Where C_i is the concentration of the species, x represents the direction of the flow (always considered to be in the axial direction of the pipe of component in question), and u is the linear flow rate, defined by Macdonald et al. [10] as:

$$u = (dm / dt) / \rho A \quad (4-10)$$

The linear flow rate is a function of the rate of mass transfer (dm/dt), water density (ρ), and cross-sectional area of the flow at the location in question (A). The total source term of a species is given as:

$$R_i = \left(\frac{G_i^\gamma \Gamma^\gamma}{100N_v} + \frac{G_i^n \Gamma^n}{100N_v} + \frac{G_i^\alpha \Gamma^\alpha}{100N_v} \right) \tilde{F} \rho + \left[\sum_{s=1}^N \sum_{m=1}^N k_{sm} C_s C_m - C_i \sum_{s=1}^N k_{si} C_s \right] + \frac{d(uC_i)}{dx} \quad (4-11)$$

Because the flow is assumed to be turbulent, which creates an efficient mixing environment, and due to the fact that no electric field is present in the primary coolant, the rate of change of concentration of a species in the coolant can be quantified as the gradient of the flux plus the source terms mentioned above [9].

As done earlier, restricting the velocity to the axial direction of the section in question allows for the flux to be written as $C_i v$, where v is the velocity at the point in question [10]. This assumption leads to a final system of equations, given by Macdonald et al. as:

$$\frac{dC_i}{dt} = -C_i \frac{dv}{dx} + R_i \quad (4-12)$$

Table 4.8 Chemical Reactions used by Macdonald and Urquidi-Macdonald. [10]

Reaction No.	Rate Constant, k (l/mol.s)	Activation Energy (kcal/Mol)	Reaction
1	1.6D+1	3.0D0	$e^- + H_2O = H + OH^-$
2	2.4D+10	3.0D0	$e^- + H^+ = H$
3	2.4D+10	3.0D0	$e^- + OH = OH^-$
4	1.3D+10	3.0D0	$e^- + H_2O_2 = OH + OH^-$
5	1.0D+10	3.0D0	$H + H = H_2$
6	2.0D+10	3.0D0	$e^- + HO_2 = HO_2^-$
7	1.9D+10	3.0D0	$e^- + O_2 = O_2^-$
8	5.0D+9	3.0D0	$2e^- + 2H_2O = 2OH^- + H_2$
9	4.5D+9	3.0D0	$OH + OH = H_2O_2$
10	1.2D+10	3.0D0	$OH + HO_2 = H_2O + O_2$
11	1.2D+10	3.0D0	$OH + O_2^- = OH^- + O_2$
12	2.0D+7	3.0D0	$OH^- + H = e^- + H_2O$
13	4.5D+8	3.0D0	$e^- + H + H_2O = OH^- + H_2$
14	6.3D+7	3.0D0	$e^- + HO_2^- + H_2O = OH + 2OH^-$
15	1.44D+11	3.0D0	$H^+ + OH^- = H_2O$
16	2.6D-5	3.0D0	$H_2O = H^+ + OH^-$
17	2.0D+10	3.0D0	$H + OH = H_2O$
18	3.4D+7	4.6D0	$OH + H_2 = H + H_2O$
19	2.70D+7	3.4D0	$OH + H_2O_2 = H_2O + HO_2$
20	4.4D+7	4.5D0	$H + H_2O_2 = OH + H_2O$
21	1.9D+10	3.0D0	$H + O_2 = HO_2$
22	8.0D+5	3.0D0	$HO_2 = O_2^- + H^+$
23	5.0D+10	3.0D0	$O_2^- + H^+ = HO_2$
24	2.7D+6	4.5D0	$2HO_2 = H_2O_2 + O_2$
25	1.7D+7	4.5D0	$2O_2^- + 2H_2O = H_2O_2 + O_2 + 2OH^-$
26	2.0D+10	3.0D0	$H + HO_2 = H_2O_2$
27	2.0D+10	3.0D0	$H + O_2^- = HO_2^-$
28	1.3D+8	4.5D0	$e^- + O_2^- + H_2O = HO_2^- + OH^-$
29	1.8D+8	4.5D0	$OH^- + H_2O_2 = HO_2^- + H_2O$
30	1.9973D-6	14.8D0	$2H_2O_2 = 2H_2O + O_2$
31	1.04D-4	3.0D0	$H + H_2O = H_2 + OH$
32	1.02D+4	3.0D0	$H_2O + HO_2^- = H_2O_2 + OH^-$
33	1.5D+7	4.5D0	$HO_2 + O_2^- = O_2 + HO_2^-$
34	7.7D-4	7.3D0	$H_2O_2 = 2OH$
35	7.88D+9	3.0D0	$OH + HO_2^- = O_2^- + H_2O$
36	1.28D+10	3.0D0	$OH + OH^- = O^- + H_2O$
37	6.14D+6	3.0D0	$O^- + H_2O = OH + OH^-$
38	3.97D+9	3.0D0	$e^- + HO_2^- = O^- + OH^-$
39	6.42D+14	3.0D0	$O_2^- + O_2^- + H^+ = HO_2^- + O_2$
40	2.72D-3	15.0D0	$H_2O_2 = H_2O + O$
41	2.84D+10	3.0D0	$O + O = O_2$
42	1.1D+6	3.0D0	$O_2^{2-} + H_2O = HO_2^- + OH^-$
43	1.3D+10	3.0D0	$e^- + O_2^- = O_2^{2-}$
44	0.5D0	3.0D0	$H_2O_2 + HO_2 = H_2O + O_2 + OH$
45	0.13D0	3.0D0	$O_2^- + H_2O_2 = OH + OH^- + O_2$

46	2.56D-8	3.0D0	$\text{H}_2\text{O}_2 = \text{H}^+ + \text{HO}_2^-$
47	1.39D+10	3.2D0	$\text{e}^- + \text{HO}_2 + \text{H}_2\text{O} = \text{H}_2\text{O}_2 + \text{OH}^-$
48	1.39D+10	3.2D0	$\text{e}^- + \text{O}_2^- + \text{H}_2\text{O} = \text{HO}_2^- + \text{OH}^-$

The system of equations in 4-12 is solved numerically to provide the steady state concentrations of the electro-active species in Table 4.6 at many positions around the entire length of a PWR loop.

4.4.3 Mixed Potential Model

Previous discussions have shown how the values of the temperature, pH_T , and concentrations of electro-active species can be found at any location around the primary loop of a PWR. The mixed potential model combines the contributions of the potentials of all of the species listed in Table 4.6 to calculate the ECP, in proportion to their concentrations. Therefore, the species with the highest concentrations will have the greatest contribution and influence over the ECP. These species have been found by Macdonald et al. to be dissolved hydrogen and oxygen gas (H_2 and O_2 respectively) and hydrogen peroxide (H_2O_2) [27]. Enough empirical data about these species is available to accurately predict the corrosion potential, the ECP. The combination of these three potentials can be markedly different than the hydrogen potential alone, and is the basis for wanting the ECP of the system.

4.4.4 ECP Values

The results of four small studies are given in this section to demonstrate the effect oxygen and hydrogen injection have on the ECP in the primary loop of a PWR. The input values used and the corresponding figure for the study are listed in Table 4.9.

Table 4.9. Figures and Corresponding runs

Figure	O_2 Concentration	H_2 Concentration
4-9	0 pbb – 50 ppm	25 cc/kg
4-10	5 ppb	1 cc/kg – 35 cc/kg

All of these studies were completed using the previously developed code by Macdonald, Urquidi-Macdonald, and Mahaffy [9]. Figure 4.9 shows the influence of oxygen injection on the ECP. Increasing the oxygen levels increases the ECP, though slowly at first. The range of values here is roughly between -0.3 and -0.9 V_{SHE} . An interesting observation is the slump in ECP through the latter parts of the core, hot leg, and hot side of the steam generator. This shows the dependence of the ECP on temperature, a trend that is visible to some extent for each of the different oxygen concentrations.

In Figure 4.10 one can observe that adding hydrogen to the system produces the opposite effect on the ECP as injecting oxygen did. As the concentration of dissolved hydrogen gas is increased in the system, the ECP is lowered, especially in the areas where the temperature is elevated. It is important to recognize the difference in range in this graph; where as oxygen injection changed the ECP almost 0.6 V_{SHE} in some places, the addition of hydrogen has caused a change in ECP of at most 0.08 V_{SHE} .

Figure 4.9. Effect of varying Oxygen Concentration on ECP

Figure 4.10. Effect of varying Hydrogen Concentration on ECP

4.5 Electrochemical Model for Activity Transport

4.5.1 Model Development Overview

This section will fully describe the development and methods used in the model presented in this report. The first step is to identify which elements are likely to be found as corrosion products in the primary coolant of a PWR. To accomplish this, an inventory of PWR primary loop construction materials was performed. The composition of the construction materials will dictate the make-up of the corrosion films, and hence, control what species are released into the primary coolant. Following this inventory and analysis of corrosion layer composition, a nodalization of a typical PWR loop was created. By assuming electrochemical equilibrium, the rates of dissolution and precipitation were determined for each section of the primary loop. Knowing the rates allows for the calculation of the steady state concentrations of corrosion products in the primary coolant, and hence, the concentrations of activated species in the primary coolant. This information, together with the rates of precipitation, allow for the calculation of the accumulated activity in a given section of the primary loop as a function of time, hence, yielding the predictions that are the stated purpose of this report.

4.5.2 Material Inventory

The goal of this section is to summarize the common materials used to construct the Primary Heat Transfer Circuits (PHTCs) of PWRs. This information is necessary for the development of an accurate model of the activity transport in the primary coolant system of a PWR plant. The critical information that must be known is the type of materials in contact with the water, where in the PHTC that material is located, the composition of the material, and the wetted surface area of the material. The PHTC of a PWR is comprised of four general areas: the reactor core, the hot leg, the cold leg, and the steam generator. Each of these sections contains metals specifically chosen for the environment present in that section.

4.5.2.1 Reactor Core

The primary construction materials of the reactor core are stainless steels and zirconium based alloys. The zirconium alloys are used mainly in the fuel cladding, rod guides, and fuel grids. Stainless steels are used primarily in the reactor support structures, bypass, and upper/lower reactor regions [21, 22]. Zircaloy was chosen and developed for use in nuclear reactors because of its low neutron cross section and ability to resist corrosion in water temperatures common in PWRs [7].

The specific metals used in construction will vary in composition from plant to plant because of the difference in alloy specifications between nations and the availability of materials due to geography and cost constraints. However, by reviewing specific materials from various plants, a decent inventory can be made of the construction materials.

Fuel Cladding, Fuel Grid Assemblies, and Guide tubes/thimbles

A commonly used Zirconium alloy is Zircaloy-4 [7]. Zircaloy-4 is used in the fuel cladding, fuel grid assemblies, and in core tube guides of Cruas-1 [20] and GKN's Isar-2 [21], for example. The composition of Zircaloy-4 is given by Framatome as:

Table 4.10. Composition of Zircaloy-4 [20].

Fe	Ni	Co	Cr	Mn	Zr
0.18%	0.007%	0.002%	0.07%	0.005%	Remainder

The composition of Zircaloy-4 as given by the AMS handbook as [5]:

Table 4.11. Composition of Zircaloy-4 (AMS Handbook).

Sn	Fe	Cr	O*	Zr
1.4%	0.2%	0.1%	0.12%	Remainder

*Represents typical content

The total wetted area of Zircaloy-4 will also depend on the specific design of the plant in question. This information was found for Cruas-1, and was calculated approximately for the Siemens plant.

Table 4.12. Wetted Surface Area of Zircaloy-4 in Reactor Core of Specific Plants.

Cruas-1 (Framatome)	7047 m ² [20]
Isar-2 (Siemens)	8215 m ² (calculated from [21])

The difference in area seems appropriate when taken into account that Cruas-1 is a 900MW reactor while Isar-2 is a 1300MW reactor [20, 21].

Other Core/Pressure Vessel Structures - Fuel Supports/Grids/Spacers

The reactor contains many other structures besides the fuel rods, including supports for the fuel, regions above and below the fuel, and grids/spacers to properly position the fuel. These parts are often constructed from Type-304 austenitic stainless steels and/or Inconel [7]. The composition of these materials is given below.

Table 4.13. Composition of Type-304 SS and Inconel 600 – AMS Handbook [5].

	C	Cr	Ni	Fe	Mn	Si	Cu
304	0.08%	19%	10%	Remainder	-	-	-
Inconel 600	0.15%	14-17%	72%	6-10%	1.0%	0.5%	0.5%

The two materials reported above have many variants, such as Type-304H, 304L, and 304N stainless steels. These variances must be accounted for on a case by case basis for the plant in question. Specific information about Cruas-1 and Isar-2 is listed below.

Table 4.14. Composition of in-core/pressure vessel structures materials used in Cruas-1. [20]

	Fe	Ni	Co	Cr	Mn
Stainless Steel	72%	8%	0.06%	18%	2%
Inconel	8%	70.5%	0.08%	12.4%	0.7%

Note the slight difference in composition between the materials used in Cruas-1 and ASM standards.

Table 4.15. Wet Areas for Materials in Cruas-1 Core/Pressure Vessel

Stainless Steel	1674 m ²
Inconel	744 m ²

Table 4.16. Composition of in-core/pressure vessel structure materials used in Isar-2 [21]

	Cr	Ni	Nb	Fe
Stainless Steel	10%	18%	9%	Remainder

4.5.2.2 Steam Generator

Typical construction materials of PWR steam generators are nickel based alloys, such as 600, 690, or 800 and austenitic stainless steels [23]. The channel heads are usually clad with austenitic stainless steel and the tubes are often constructed of the nickel based alloys to prevent cracking. The AMS standards for Alloys 600, 690, and 800 are:

Table 4.17. Composition of Alloy 600 and 800 – AMS

	C	Cr	Ni	Fe	Mn	Si	Other
Alloy 600	0.15%	14-17%	72%	6-10%	1.0%	0.5%	0.5% Cu
Alloy 690	0.05%	27-31%	58%	7-11%	0.5%	0.5%	0.5% Cu
Alloy 800	0.1%	19-23%	30-35%	39.5%	1.5%	1.0%	.15-.60% Al,Ti

Comparison of these metals with materials reported to be in use at Cruas-1 and Isar-2 show that Framatome and Siemens chose to use similar alloys when fabricating their steam generators. Cruas-1 has Inconel 600 tubes and a nickel based channel head [21], while Isar-2 contains steam generators with tubes made of a material similar to Incoloy

800 (1.4558) and austenitic cladding on the other surfaces [22]. The details are listed below.

Table 4.18: Cruas-1 Steam Generator Materials Compositions [20]

	Fe	Ni	Co	Cr	Mn
Alloy 600	9.5%	71%	0.025%	17%	1.5%
Channel Head	28.2%	52.1%	0.08%	17.3%	1.65%

Table 4.19: Isar-2 Steam Generator Tube Material Composition [21]

	C	Mn	Si	P	Ni	Al	Fe	Cr	Ti
1.4558*	0.03%	1%	0.7%	0.02%	35%	0.45%	47.8%	23%	0.6%

* X2NiCrAlTi32-20 [23]

Table 4.20: Wet Areas of Steam Generator Materials – Single Steam Generator

Cruas-1 Tubes	4434 m ² *
Cruas-1 Channel Head	20 m ²
Isar-2 Tubes	5400 m ²

*Calculated from [21]

4.5.2.3 Hot and Cold Leg Piping

The piping loop connecting the reactor pressure vessel to a steam generator is generally constructed from austenitic stainless steel or from carbon steel clad with austenitic stainless steel [22]. The most commonly used steel for this is Type-316 stainless [7]. Its composition is reported below.

Table 4.21. Composition of Type-316 Stainless Steel [5]

C	Cr	Ni	Mo	Fe
0.08%	17%	12%	2.5%	Remainder

It was determined that Cruas-1 and Isar-2 do have austenitic stainless steel hot and cold legs [20, 21]. While there are many variations of these steels, it is important to note that as a whole their elemental makeup does not vary dramatically [5], thus the composition given here can be used as a good guideline for the piping in most plants.

Table 4.22. Wet Areas of Out of Core Piping – Single Loop

Cruas-1 Hot Leg	14 m ²
Cruas-1 Cold Leg	66 m ²
Isar-2 Hot and Cold Leg	245 m ² *

*Calculated from [20]

4.5.3 Primary Loop Nodalization

The chosen nodalization is primarily a result of the decision to use the existing PWR ECP code to calculate the ECP values used in this model. For the sake of consistency, the same nodalization was used, with the exception of the steam generators, where the ECP and temperature exhibited a gradient significant enough to warrant a refining of the mesh. Figure 4.11 gives a graphical representation of the nodes, while Table 4.23 lists the geometrical and physical properties. Each section of the loop is considered to be comprised of only one material. The flow is assumed to be constant, over a node, and only in the axial direction of the node.

Many of these parameters came from the existing ECP code written by Macdonald et al. This was done to ensure the ECP results from that program would be accurate in this model. Specifically, the node lengths and materials have been preserved in all cases except for the steam generator tubes, where a significant gradient in predicted ECP, temperature, and pH_T values existed, deeming it necessary to further refine the nodalization.

Figure 4.11. Graphical View of Primary Loop Nodalization

Table 4.23. Geometry and Physical Properties of the Primary Loop

Node	Material	Wet Area (m ²)	Volume (m ³)	Coolant Velocity (m/s)	Length (m)	d_h (m)
1	Zircaloy-4	1400	10.7	7.93	0.8540	0.004
2	Zircaloy-4	4200	31.74	5.06	2.5620	0.004
3	Zircaloy-4	1400	10.7	5.32	0.8540	0.004
4	Stainless Steel	235.2	11.05	5.00	0.3170	0.0111
5	Stainless Steel	452.96	4.46	4.00	3.5500	0.4000
6	Stainless Steel	50	15.83	15.98	6.8450	0.7360
7	Inconel 600	200	18.07	5.50	7.8150	0.7360
8	Inconel 600	1012.5	37.75	5.25	1.4240	0.0169
9	Inconel 600	1012.5	37.75	5.25	1.4240	0.0169
10	Inconel 600	1012.5	37.75	5.25	1.4240	0.0169
11	Inconel 600	1012.5	37.75	5.25	1.4240	0.0169
12	Stainless Steel	200	17.99	5.12	7.2740	0.7874
13	Stainless Steel	150	18.33	12.40	7.4110	0.7874
14	Stainless Steel	100	46.47	15.73	21.177	0.6985
15	Stainless Steel	911.94	22.5	5.50	13.769	0.5200

The composition of the materials used in the loop model takes into account only the percentages that include cobalt, nickel, iron, chromium, and zirconium. These percent weights are given below, in Table 4.24.

Table 4.24. Percent Weight of Materials in Primary Loop Model

Material	Fe	Cr	Zr	Co	Ni
304 SS	70.9%	19.0%	0%	0.1%	10.0%
Alloy 600	10.0%	17.0%	0%	0.1%	72.9%
Zircaloy-4	0.205%	0.1%	99.685%	0.01%	0%

The oxide layers on the materials listed in Table 4.24 are assumed to have the compositions given in Table 4.25. Both the Alloy 600 and stainless steels will have a barrier layer comprised of primarily chromium oxide [9], while the Zircaloy material has a barrier layer with multiple species, including zirconium oxide. The outer layers of both the Alloy 600 and stainless steels will have many species in them. The precipitated layer will include many species, even those not found in the construction materials, i.e. zirconium species depositing onto the Alloy 600 in the steam generators.

Table 4.25. Species Present in Oxide Layers

Material	Barrier Layer	Outer Layer	Precipitated Layer
Zircaloy	ZrO ₂ , ZrH _x	ZrO ₂	(Fe, Ni, Cr) _x O _y , ZrO ₂
Stainless Steel	Cr ₂ O ₃	(Fe, Ni, Cr) _x O _y	(Fe, Ni, Cr) _x O _y , ZrO ₂
Alloy 600	Cr ₂ O ₃	(Fe, Ni, Cr) _x O _y	(Fe, Ni, Cr) _x O _y , ZrO ₂

4.5.4 Dissolution and Precipitation of Oxide Layers

The dissolution/precipitation of corrosion products into/out of the primary coolant is determined by chemical and electrochemical processes. The saturation point, or surface concentration, of the corrosion products in the primary coolant is determined by considering the chemical and electrochemical reactions that reduce the species found in the passive corrosion films into aqueous ions. The approach used to calculate this was presented by M. Urquidi-Macdonald and D. D. Macdonald for the release of magnetite into the primary coolant of PWRs, in order to describe the mass transport of magnetite around the primary coolant loop [6]. Their approach has been broadened in this paper to include other species likely to be found in the primary coolant. These species are listed on the left hand side of Table 4.26, and were chosen because of the corrosion film composition. The reduction of each species on the left to the aqueous ions on the right is given by either a chemical reaction or electrochemical reaction, depending on the state of charge balance after the mass balancing of the reaction has been preformed.

Table 4.26. The corrosion products found in the primary loop and the aqueous species used to determine surface concentration at the coolant-metal interface.

Corrosion Products		Aqueous Species
Fe_3O_4		$M(OH)_i^{(2-i)+}$
Fe_2O_3		$M=Fe, Cr, Ni, Co$
Cr_2O_3	$\Rightarrow$	
ZrO_2		$M(OH)_i^{(3-i)+}$
NiO		$M=Fe, Cr, Co$
CoO	$\Rightarrow$	
Ni		$M(OH)_i^{(4-i)+}$
Co		$M=Zr$

4.5.4.1 Dissolution by Electrochemical Reactions

The dissolution of an oxide or metal is governed by an electrochemical or a chemical reaction. The general case for oxide (or metal) dissolution by electrochemical means will now be given. See Table 4.27 for a complete list of specific reactions considered. The electrochemical relation between an oxide, or metal, A, listed in Table 4.26, and the aqueous species of the element, B, is given by:

In Reaction (4-13), the coefficients are all real values. The Nernst equation for Reaction (4-13), under equilibrium conditions, is:

$$E = E^0 - \frac{2.303RT}{zF} \log \left[\frac{a_B^b a_{H_2O}^c}{a_A^a a_{H^+}^x} \right] \quad (4-14)$$

In Equation (4-14), a denotes the activity of the subscripted species, R the gas constant, T the temperature in Kelvin, and F Faraday's constant. By the properties of the logarithm, one can write:

$$E = E^0 + \frac{2.303RT}{F} \left[\frac{a}{z} \log a_A + \frac{x}{z} \log a_{H^+} - \frac{b}{z} \log a_B - \frac{c}{z} \log a_{H_2O} \right] \quad (4-15)$$

After some rearranging of Equation (4-15), substituting $E=ECP$ for the local electrochemical conditions, substituting $pH=-\log(a_{H^+})$ by definition, and letting $a_A=a_{H_2O}=1$ by convention, one obtains:

$$\frac{F}{2.303RT} (ECP - E^0) = -\frac{b}{z} \log a_B - \frac{x}{z} pH \quad (4-16)$$

Further rearrangement yields:

$$\log a_B = \frac{z}{b} \frac{F}{2.303RT} (E^0 - ECP) - \frac{x}{b} pH \quad (4-17)$$

Where the standard potential, E^0 , is given as:

$$E^0 = \frac{-\Delta G_{f,i}^0}{zF} \quad (4-18)$$

The Gibb's energy of formation values of the reactions were obtained using a commercially available database, and are also a function of temperature. See Appendix B for a list of these values. For dilute solutions, the activity of the solute may be replaced with the molar concentration of the solute; thus, Equation (4-17) becomes an expression for the concentration of the i^{th} hydrolyzed aqueous species of an element as a function of only ECP, temperature, and pH. For example, for Reaction 24 in Table 4.27, $z=2$, $x=6$ and $b=2$, thus Equation 4-17 becomes:

$$\log[Cr^{2+}] = \frac{F}{2.303RT} (E^0 - ECP) - 3pH \quad (4-19)$$

4.5.4.2 Dissolution by Chemical Reactions

If charge is conserved after the mass balance of the reaction, normal chemical methods can be employed to find the equilibrium surface concentration. To find the surface concentrations, we assume a general form of the chemical reaction as:

From reaction rate theory, we can find the rate constant as:

$$K = \frac{a_B^b a_{H_2O}^c}{a_A^a a_{H^+}^x} = e^{-\Delta G_{f,i}^0 / RT} \quad (4-21)$$

By convention, we can set the activity of water and the solid substance, A, to one. After rearrangement, this yields:

$$a_B = \left[a_{H^+}^x e^{-\Delta G_{f,i}^0 / RT} \right]^{-b} \quad (4-22)$$

Table 4.27. Reactions Describing the Dissolution of Corrosion Products into the Primary Coolant

Reaction	Index	Number
$Fe_3O_4 + (8-3i)H^+ + 2e^- = 3Fe(OH)_i^{(2-i)+} + (4-3i)H_2O$	[0,1]	0-1
$Fe_3O_4 + 2H^+ + 2e^- = 3FeO(s) + H_2O$	N/A	2
$Fe_3O_4 + 2H_2O + 2e^- = 3HFeO_2^- + H^+$	N/A	3
$3Fe(OH)_i^{(3-i)+} + (4-3i)H_2O + e^- = Fe_3O_4 + (8-3i)H^+$	[0,2]	4-6
$3HFeO_2^- + H^+ + e^- = Fe_3O_4 + 2H_2O$	N/A	7
$3FeO_2^- + 4H^+ + e^- = Fe_3O_4 + 2H_2O$	N/A	8
$Fe_2O_3 + (6-2i)H^+ + 2e^- = 2Fe(OH)_i^{(2-i)+} + (3-2i)H_2O$	[0,1]	9-10
$Fe_2O_3 + 2H^+ + 2e^- = 2FeO(s) + 2H_2O$	N/A	11
$Fe_2O_3 + H_2O + 2e^- = 2HFeO_2^-$	N/A	12
$Fe_2O_3 + (6-2i)H^+ = 2Fe(OH)_i^{(3-i)+} + (3-2i)H_2O$	[0,2]	13-15
$Fe_2O_3 + H_2O = 2HFeO_2^-$	N/A	16
$Fe_2O_3 + H_2O = 2FeO_2^- + 2H^+$	N/A	17
$Cr_2O_3 + (6-2i)H^+ = 2Cr(OH)_i^{(3-i)+} + (3-2i)H_2O$	[0,2]	18-20
$Cr_2O_3 + H_2O = 2HCrO_2^-$	N/A	21
$Cr_2O_3 + (6-2i)H^+ = 2Cr(OH)_i^{(3-i)+} + (3-2i)H_2O$	[4]	22
$Cr_2O_3 + (6-2i)H^+ + 2e^- = 2Cr(OH)_i^{(2-i)+} + (3-2i)H_2O$	[0,3]	23-26
$2CrO_4^{2-} + 10H^+ + 6e^- = Cr_2O_3 + 5H_2O$	N/A	27
$Cr_2O_7^{2-} + 8H^+ + 6e^- = Cr_2O_3 + 4H_2O$	N/A	28
$ZrO_2 + (4-i)H^+ = Zr(OH)_i^{(4-i)+} + (2-i)H_2O$	[0,2]	29-31

$ZrO_2 + H^+ = HZrO_2^+$	N/A	32
$ZrO_2 = ZrO_2(s)$	N/A	33
$ZrO_2 + H_2O = HZrO_3^- + H^+$	N/A	34
$Co(OH)_i^{(2-i)+} + (i)H^+ + 2e^- = Co + (i)H_2O$	[0,2]	35-37
$HCoO_2^- + 3H^+ + 2e^- = Co + 2H_2O$	N/A	38
$CoO + (2-i)H^+ = Co(OH)_i^{(2-i)+} + (1-i)H_2O$	[0,2]	39-41
$CoO + H_2O = HCoO_2^- + H^+$	N/A	42
$Co(OH)_i^{(3-i)+} + (i)H^+ + 3e^- = Co + (i)H_2O$	[0,4]	43-47
$Co(OH)_i^{(3-i)+} + (1-i)H_2O + e^- = CoO + (2-i)H^+$	[0,4]	48-52
$Ni(OH)_i^{(2-i)+} + (i)H^+ + 2e^- = Ni + (i)H_2O$	[0,1]	53-54
$NiO(s) + 2H^+ + 2e^- = Ni + H_2O$	N/A	55
$Ni(OH)_i^{(2-i)+} + (i)H^+ + 2e^- = Ni + (i)H_2O$	[3]	56
$NiO_2^{-2} + 4H^+ + 2e^- = Ni + 2H_2O$	N/A	57
$NiO + (2-i)H^+ = Ni(OH)_i^{(2-i)+} + (1-i)H_2O$	[0,1]	58-59
$NiO = NiO(s)$	N/A	60
$NiO + (2-i)H^+ = Ni(OH)_i^{(2-i)+} + (1-i)H_2O$	[0,1]	61
$NiO + H_2O = NiO_2^{-2} + 2H^+$	N/A	62

From the definition of pH, it follows that:

$$a_{H^+}^x = 10^{-xpH} \quad (4-23)$$

Which, when substituted into Equation (4-22) in conjunction with the fact that the solution is dilute, the expression for the surface concentration is:

$$m_i = \left[10^{-xpH} e^{-\Delta G_{f,i}^0 / RT} \right]^{-b} \quad (4-24)$$

4.5.4.3 Dissolution during Cold Shutdown

Special consideration has been taken in this model to accurately describe the rate of dissolution during cold shutdown due to scheduled outages, such as refueling. The special consideration is derived from a limitation of the existing model for the calculation of ECP. As stated in 4.4, the existing ECP model created by M. Urquidi-Macdonald and D. D. Macdonald is dependent on certain G-Values, which are experimentally observed constants that quantify the number of water radiolysis products generated per unit of absorbed energy. As discussed in 4.4, these values are not known precisely. Currently, this author and his advisors are not aware of any measurements that have been made to derive values for the radiolysis constants during times of PWR cold shutdown. Because of this, it has been decided that until the predictions of the ECP code can be validated against experimentally measured values for times at cold shutdown, the hydrogen

potential should be used instead of the predicted corrosion potential, the ECP. This change is subtle, and results in Equation 4-17 taking the form:

$$\log a_B = \frac{z}{b} \frac{F}{2.303RT} (E^0 - E_{H_2}) - \frac{x}{b} pH \quad (4-25)$$

Where the hydrogen potential is found from the hydrogen electrode reaction:

The standard potential for this reaction is zero, by convention, and after some rearranging, yields the Nernst Equation in the form:

$$E_{H_2} = \frac{-2.303RT}{2F} \left(\frac{1}{2} \log f_{H_2} + pH \right) \quad (4-27)$$

Equation 4.27 shows that the hydrogen potential is a function of the pH, temperature, and the fugacity of hydrogen; the fugacity of hydrogen is a function of the coolant concentration of hydrogen and the coolant temperature.

4.5.5 Mass Transfer of Ions

The equilibrium concentrations calculated above, which we will now call $C_{s,ij}$ where s represents surface, i is the ion index, and j is the node index, quantify the concentrations of corrosion products found in the coolant at the metal-coolant interface. The concentration of an ion in the bulk of the coolant is calculated from these values by examining the difference between surface and the bulk concentrations, and hence, determining rates of dissolution or precipitation. Figure 4.12 illustrates the condition when precipitation will occur, namely where the bulk concentration, $C_{b,i}$, is greater than the local equilibrium concentration of the coolant-metal interface.

Figure 4.12. Concentration gradient at the Coolant-Metal Interface, assuming linear transition. δ_N is the thickness of the Nernst Diffusion Layer.

The rate of release/deposition, $R_{i,j}$, for the i^{th} species in the j^{th} node of the loop, in mol/s is given as:

$$R_{i,j} = D_{i,j} \frac{\partial C_{i,j}}{\partial x} A_j = D_{i,j} \frac{C_{s,i,j} - C_{b,i}}{\delta_{N,j}} A_j = \frac{D_{i,j} Sh_j A_j c}{L_j} (C_{s,i,j} - C_{b,i}) \quad (4-28)$$

In Equation (4.25), the subscript i refers to the i^{th} hydrolyzed species of a given corrosion product listed in Table 4.27; $D_{i,j}$ is the diffusion constant for the species in question, Sh_j is the Sherwood number for the j^{th} section, and L_j is the characteristic length for the j^{th} section. The wet area of the j^{th} node is A_j , and c is unit conversion factor to give us the rate in moles per second. Note the diffusion constant will vary according to the temperature [18], where:

$$D_{i,j} = D_i^0 \exp[(-k_c / R)(1/T_j - 1/2.98.15)] \quad (4-29)$$

From the principles of mass transfer, the total rate of change of the ionic species in the bulk coolant is then given as:

$$\frac{dC_{b,ion,i}}{dt} = \sum_{j=1}^{15} R_{i,j} \quad (4-30)$$

In Equation (4-27), the rate of change is simply the sum of the rates of release/dissolution change from each section of the PWR primary loop. Applying the Euler-Method, and letting n denote our time step, we can rewrite Equation (4-27), in mol/L, as:

$$C_{b,ion,i}^{n+1} = C_{b,ion,i}^n + \left(\sum_{j=1}^{15} R_{i,j} \right) \left(\sum_{j=1}^{15} Vol_j \right)^{-1} \Delta t \quad (4-31)$$

4.5.6 Activation Theory

As described at the beginning of the previous section, the aqueous species of the corrosion products found in the primary coolant are activated as they travel through the core. Since the time it takes an atom to travel through the core and the neutron flux in the core are considered to be determined by the flow rate and core length, the rate of activation, in the j^{th} node of the loop of the i^{th} species is given as:

$$ACT_{i,j} = C_{b,isotope,i} \Phi_j \sigma_i \quad (4-32)$$

In this relation, $C_{b, isotope, i}$ is the number of isotopes present in moles per liter, Φ_j is the neutron flux in neutrons per second per square meter of the j^{th} section, and σ_i is the neutron capture cross-section in square meters; thus ACT is the rate of activation in moles per liter per second. At this time, the model only considers activation by thermal neutrons.

4.5.7 Mass Transfer of Isotopes

Calculating the accumulated activity at a given point in the primary loop of a PWR is the stated goal of this report. It is now possible to develop the algorithms that predict activity accumulation as a function of time. Table 4.28 lists the nuclear reactions that are considered in this model. These reactions were chosen based on the corrosion products dissolving into the system, a review of the isotopes modeled in existing codes and information about measurements taken by plant owners and operators.

We define the rate of release/precipitation of the isotopes of an element into the coolant in terms of the previously quantified rates of that element's ionic release. It must be clear that the mass transport of the ionic species is dependent on the electrochemistry of the system, and the isotope release is dependent on the ionic release.

Table 4.28. Modeled Nuclear Reactions

1	$^{54}\text{Fe}(n, \gamma)^{55}\text{Fe}$
2	$^{58}\text{Fe}(n, \gamma)^{59}\text{Fe}$
3	$^{50}\text{Cr}(n, \gamma)^{51}\text{Cr}$
4	$^{59}\text{Co}(n, \gamma)^{60}\text{Co}$
5	$^{94}\text{Zr}(n, \gamma)^{95}\text{Zr}$
6	$^{58}\text{Ni}(n, p)^{58}\text{Co}$
7	$^{58}\text{Co}(n, \gamma)^{59}\text{Co}$

The total rate of change of a precursor species in the bulk coolant ($C_{b,p}$) where p denotes the equation number above, can be written as:

$$\begin{aligned} \frac{dC_{b, isotope, p}}{dt} = & \mu_p \left(\sum_{element} \sum_{j=1}^{15} R_{i,j}^{n,+} \right) / \sum_{j=1}^{15} Vol_j - \sum_{j=1}^{15} C_{b,p}^n \Phi_j \sigma_p \\ & - (C_{b, isotope, p}^n / C_{b, element}^n) \left(\sum_{element} \sum_{j=1}^{15} R_{i,j}^{n,-} \right) / \sum_{j=1}^{15} Vol_j \end{aligned} \quad (4-33)$$

In Equation (4-30), we have quantified the rate of release of the p^{th} isotope as the sum of the rate of the release of all ions of the element, in all sections, along with the removal of precursor isotopes due to activation and precipitation. The natural abundance of the isotope is μ_p . The rate had to be separated into the positive (dissolution) and negative (precipitation) to account for the fact that a fixed percentage, the natural abundance, of

the dissolving isotopes are of the desired isotope, while the precipitating isotopes are assumed to do so as in the same fraction at which they are presently found in the coolant. We denote the p^{th} activated species and write the change in concentration, accounting also for radioactive decay, as:

$$\begin{aligned} \frac{d\tilde{C}_{b,isotope,p}}{dt} = & \sum_{j=1}^{15} C_{b,p}^n \Phi_j \sigma_p - \lambda_p \tilde{C}_{b,isotope,p}^n \\ & - (\tilde{C}_{b,isotope,p}^n / C_{b,element}^n) \left(\sum_{element} \sum_{j=1}^{15} R_{i,j}^{n,-} \right) / \sum_{j=1}^{15} Vol_j \end{aligned} \quad (4-34)$$

After discretizing these equations, and choosing n as the subscript to denote our time step, we can express these concentrations as recursive functions:

$$\begin{aligned} C_{b,isotope,p}^{n+1} = & C_{b,isotope,p}^n + \left[\mu_p \left(\sum_{element} \sum_{j=1}^{15} R_{i,j}^{n,+} \right) / \sum_{j=1}^{15} Vol_j - \sum_{j=1}^{15} C_{b,p}^n \Phi_j \sigma_p \right. \\ & \left. - (C_{b,isotope,p}^n / C_{b,element}^n) \left(\sum_{element} \sum_{j=1}^{15} R_{i,j}^{n,-} \right) / \sum_{j=1}^{15} Vol_j \right] \Delta t \end{aligned} \quad (4-35)$$

$$\begin{aligned} \tilde{C}_{b,isotope,p}^{n+1} = & \tilde{C}_{b,isotope,p}^n + \left[\sum_{j=1}^{15} C_{b,p}^n \Phi_j \sigma_p - \lambda_p \tilde{C}_{b,isotope,p}^n \right. \\ & \left. - (\tilde{C}_{b,isotope,p}^n / C_{b,element}^n) \left(\sum_{element} \sum_{j=1}^{15} R_{i,j}^{n,-} \right) / \sum_{j=1}^{15} Vol_j \right] \Delta t \end{aligned} \quad (4-36)$$

It should be noted in Equations (4-32, 33) the rates of dissolution and precipitation and the rates of activation have time indices. The time indices are necessary because these quantities depend on the concentration of a given isotope in the bulk coolant, which varies as time is run. Clearly, the model is fully explicit.

We can quantify the accumulated activity, due to the build-up of nuclide p in section j , in Becquerel per square meter, with the following equation, where N_v is Avogadro's Number and λ_p is the decay constant of the isotope in question.

$$\tilde{C}_{precip,p,j}^{n+1} = (1 - \lambda_p \Delta t) \tilde{C}_{precip,p,j}^n + \frac{\tilde{C}_{b,isotope,p} N_v \Delta t \lambda_p}{(C_{b,element}) A_j} \sum_{element} R_{i,j}^{n,-} \Delta t \quad (4-37)$$

4.6 Results and Analysis

As outlined in Chapter 4, the model set forth has dependencies on certain parameters, whose integrity is beyond the scope of this report. For example, the calculation of the ECP during cold shutdown conditions is not a topic of this report; however, future work must include an examination of how to properly calculate this value and validation of the calculations against observed values.

The most critical set of physical values to this model are the Gibb's Energies of Formation for the full cell reactions that correspond to the reactions listed in Table 4.27. During the course of developing this model, it was discovered that not all of the values contained in the available databases are entirely accurate. The task of seeking out other databases and collaborating with the database developers to correct these issues has been left as future work, largely because of time constraints. Interpretation of the following results should be mindful of the above statements, and include the realization this project is very much still at a 'work in progress' stage. An emphasis throughout the results will be on the sensitivity of the model to certain parameters, demonstrating where future work should be concentrated.

4.6.1 Ion Concentrations at The Metal-Coolant Interface

The first set of results that are important to present and analyze is the concentration of ions at the metal-coolant interface. These values will drive the dissolution and precipitation rates, and hence, the mass transfer of the entire system. Ionic concentrations at the interface are determined from the Nernst Equation, which requires us to assume electrochemical equilibrium. Figure 4.13 shows the surface concentrations, calculated using the Nernst Equation, and normalized in a fashion to show the trends of all the elements on one graph. The values graphed in Figure 4.13 are the concentration for a node, minus the average concentration from around the loop of that element, with that difference being divided by the average.

Figure 4.13. Surface Concentration Trends. $H_2=25$ cc/kg; $O_2=5$ ppb. The trends are given for each element as a whole, that is, the sum of all of the species of the same element.

Clearly, an inverse solubility is predicted for nickel; the change in concentration of nickel is the most pronounced of the elements. This implies that as the bulk concentration of nickel rises, one may expect to see precipitation occur in larger amounts in the higher temperature areas, such as the hot leg. However, caution should be given to this interpretation as the rates of precipitation, as shown in Equation (4-18), are also dependent upon the Sherwood number, and hence, the hydro-dynamic characteristics of the node. Furthermore, the rate of dissolution/precipitation is proportional to the surface area of the node.

Meanwhile, the Iron, Chromium, and Zircaloy trends all indicate a similar behavior; these elements increase in surface concentration with temperature. The case of predicted cobalt surface concentrations, however, is not describable by a general trend. This alludes to a strong dependence of the surface concentrations of cobalt on some parameter at the given location, or possibly inaccurate thermodynamic data skewing the values.

The surface concentrations are dependent on four quantities: the temperature, pH_T , electrochemical potential (hydrogen or corrosion), and the Gibb's energy values. Table 4.29 and Table 4.30 show the surface concentrations for cold shutdown and modified normal operation, where the Gibb's energy values have been changed by 5%,

respectively. Increases in the surface concentrations are observed in Table 4.29, indicating more corrosion products are likely to be found in the coolant during cold shutdown. This does not lead to a conclusion that activity transport should increase, however, because the cause of activation, the neutron flux, will be greatly reduced during this time. It should be noted the increase for Iron and Nickel in Table 4.29 are clearly too large, this problem is thought to be caused by the combination of using the Hydrogen Potential during cold shutdown and the previously mentioned issues with the Gibb's energy values.

The sensitivity to the Gibb's Energy values was studied by perturbing them slightly and examining the resulting change in surface concentrations and accumulated activity. Table 4.30 shows the percent change observed in the surface concentrations as a result of this study. One can clearly see the importance of obtaining accurate thermodynamic information. From this small study, a change in Gibb's Energy can result in a change in surface concentration between two and fifteen times the perturbation. This reinforces the importance of thermodynamic data to this model.

Table 4.29: Comparison of average surface concentrations during normal operation to surface concentrations during cold shutdown, which are the same around the entire primary loop because there is no temperature gradient, and hence no pH or ECP gradient.

	Fe (mol/L)	Cr (mol/L)	Zr (mol/L)	Co (mol/L)	Ni (mol/L)
Hot Average	2.60E-06	2.03E-05	2.08E-11	4.51E-06	8.21E-09
Cold Shutdown	4.26E-03	6.85E-05	2.57E-12	5.89E-05	4.43E-04

Table 4.30. Percent Change in Surface Concentrations as a result of a 5% increase in Gibb's Energy Values.

Node	Fe (%)	Cr (%)	Zr (%)	Co (%)	Ni (%)
1	72.47	74.21	70.98	49.40	15.59
2	74.86	74.63	70.75	50.23	18.39
3	76.12	75.07	70.57	50.63	19.19
4	76.17	75.11	70.54	50.64	18.69
5	76.13	75.11	70.54	50.77	18.46
6	76.15	75.11	70.54	50.82	18.94
7	76.13	75.11	70.54	50.66	18.67
8	75.68	74.97	70.61	50.59	18.26
9	74.67	74.70	70.70	50.33	17.07
10	73.57	74.46	70.84	49.79	16.08
11	71.53	74.17	71.00	49.30	13.48
12	71.56	74.07	71.06	49.09	14.20
13	71.56	74.07	71.06	49.09	14.20
14	71.65	74.07	71.06	49.16	14.56
15	72.04	74.12	71.02	49.19	14.96

4.6.2 Isotope Concentrations in the Bulk

The concentrations of isotopes are of true interest in this project, because it is these values that will ultimately determine the concentrations of activated isotopes deposited on the wet areas of the primary loop components. Figures 4.14 and 4.15 show the concentrations of the stable and activated isotopes approaching steady state, for the same water chemistry used in the last section, where the concentration of H₂ gas is set at 25 kg/cc and the concentration of O₂ gas is set to 5 ppb. These results are only for operation of an activity-free plant for one fuel cycle, not including a cold shutdown period at the end.

The primary distinctions between Figures 4.14 and 4.15 are the scales of concentration and time. The naturally occurring, or inactivated, isotopes reach steady state much more quickly than the activated isotopes, and in larger concentrations. This is expected, because the source terms for the naturally occurring isotopes are much greater in magnitude than the source terms for the activated species; the source terms for the stable isotopes are the rates of dissolution of corrosion products into the primary coolant. A table of the constants used for the reactions is given below.

Table 4.31. Thermal Neutron Capture Cross-Sections

Reaction	Cross-Section (m ²)
⁵⁴ Fe(n, γ) ⁵⁵ Fe	2.30 x 10 ⁻²⁸
⁵⁸ Fe(n, γ) ⁵⁹ Fe	1.30 x 10 ⁻²⁸
⁵⁰ Cr(n, γ) ⁵¹ Cr	1.50 x 10 ⁻²⁷
⁵⁹ Co(n, γ) ⁶⁰ Co	2.07 x 10 ⁻²⁷
⁹⁴ Zr(n, γ) ⁹⁵ Zr	4.90 x 10 ⁻³⁰
⁵⁸ Ni(n, p) ⁵⁸ Co	4.60 x 10 ⁻²⁸
⁵⁸ Co(n, γ) ⁵⁹ Co	1.90 x 10 ⁻²⁵

Figure 4.14. Stable Precursor Isotope Concentrations in the Bulk Coolant. Note that the steady state concentrations are reached after approximately 30 hours.

Figure 4.15. Activated Isotope Concentrations in the Bulk Coolant. Note the contrast in scale with the stable isotopes. The activated isotopes take much longer to reach steady state.

4.6.3 Accumulated Activity

Calculating the accumulated activity is the final goal of this report; these results are now presented. For continuity with earlier results, for ease of explanation and comparison, the same water chemistry scheme has been used to calculate these values. Figure 4.16 presents the accumulated activity in the primary loop after one fuel cycle of 18 months in length. Three distinct predictions are shown in Figure 4.16. Maximums are predicted in the hot and cold legs, with a substantial gradient through the steam generator. The core experiences the least accumulated activity, but still is affected.

A comparison cannot be made between the total element surface concentration and the bulk concentration of the element to determine if precipitation will occur, because while one species may be dissolving another may be precipitating. Hence, if the dissolution of species A is happening faster than the precipitation of species B, a net dissolution will be happening for the element, but activity will still be accumulating onto the metal.

Figure 4.17 shows a non-logarithm scale of the total accumulated activity in each node, after an operating period of eighteen months. Two distinct maximums occur at nodes 6 and 14, which are the hot and cold legs, respectively. Also of interest is the drop through the steam generator, although, in Figure 4.16, it is clear substantial accumulation will

occur in the steam generator tubes. Also note the activity due to Zirconium was so low it does not appear on the plots.

Figure 4.16. Accumulated activity in each node, by isotope, after 18 months of operation. This time span represents a typical fuel cycle or a PWR. The least accumulated activity was found to occur, for these water chemistry conditions, in the core; maximums occur in the Hot and Cold Legs.

Figure 4.17. Total accumulated activity in each node after 1 fuel cycle, 18 months. Clear maximums are present in the Hot Leg, at Node 6, and throughout the Cold Leg.

A breakdown by isotope of the time history of activity accumulation in the hot and cold legs is given in Figures 4.18 and 4.19. It is observed that some of the activity levels appear to reach steady state, while others continue to increase. As the concentrations of ions in the bulk coolant reach steady state, the rate of dissolution/ precipitation for a given species in a given section will converge to a single value as well. As this rate converges, we expect a constant increase in accumulated activity will occur, but, in some cases the half-life of the isotope is short, causing an equilibrium concentration to be reached very quickly. Table 4.25 gives the half-life of each of the species in Figures 4.18 and 4.19. From this table, we can see the two isotopes with the longest half-lives, Co^{60} and Fe^{55} , converge the least quickly in Figures 4.18 and 4.19. This is of particular importance, due to the fact cobalt dominates the primary loop activity levels, and hence, will continue to cause out-of-core radiation fields for a long time.

The composition of the accumulated activity is predicted to be different between the hot and cold legs. Figures 4.18 and 4.19 display this, where in the hot leg chromium dominates the local activity, while in the cold leg cobalt dominates. It is important to examine the composition of the accumulated activity because areas with higher concentrations of longer-lived isotopes will see higher levels of residual radiation fields for longer.

Table 4.32. Isotope Half-Lives

Isotope	Co^{60}	Co^{58}	Fe^{55}	Fe^{59}	Cr^{51}
Half-Life	5.271 years	70.88 days	2.73 years	44.51 days	27.7 days

Figure 4.18. Time history of activity accumulation in the Hot Leg, Node 6. Clearly, cobalt contamination is continuing to grow and chromium has reached its short-lived maximum. The zirconium products are so low in activity that they are not displayed.

Figure 4.19. Time history of activity accumulation in the Cold Leg, Node 14. The composition of the predicted accumulated activity is clearly different than that of Hot Leg.

4.6.4 pH_T Sensitivity

The responsiveness of this model to changes in primary coolant pH is an important attribute to explore because of the prevalent use of such methods in PWR operation. Controlling pH is already used for a variety of purposes in PWR operation, such as mitigating component wear, reactivity control, and for attempting to mitigate activity transport. Figure 4.20 shows the effect on pH of varying the lithium concentration in the primary coolant, which, along with the addition of boron is the most common means of pH control. The values in this figure were calculated using the pH subroutine of the existing ECP code, which has been shown to quite accurately predict pH and its dependence on temperature.

Figure 4.21 shows the response of the total accumulated activity to changes in the pH of the primary coolant. From Figure 4.20, we can see increasing the lithium concentration in the primary coolant causes the pH to rise, but does not alter the trend around the loop. Thus, we can conclude from Figure 4.21 that increases in the pH cause this model to predict that the accumulated activity will increase. The range of predicted values seems, for this water chemistry scenario, to fluctuate about an order of magnitude at most. There is a slight change in trend from the prediction when no lithium is used to the maximum concentration, most notably in the core. This suggests the pH may play a significant role in the trend of accumulated activity.

Figure 4.20. Calculated values of pH as a function around the primary loop. Lithium addition increases the pH, but does not alter the trend.

Figure 4.21. Accumulated Activity as pH is varied. Increasing the pH increases the Activity.

4.7 Conclusions

The modeling of activity transport in PWRs using electrochemical methods has been presented. The electrochemical properties of the system formed by the primary coolant and the structures that contain it are used to determine the rate at which corrosion products will dissolve into the system, and what the equilibrium concentrations of these dissolved products will be in the bulk coolant. From this information, concentrations of stable and activated isotopes are calculated, and ultimately, the accumulated activity on the surface of a node, or section, of the primary loop is found.

This model predicts cobalt and chromium are the dominating corrosion products in terms of activity transport in PWRs. Ultimately, by the sequence of the calculations described above, the corrosion products with the greatest collective surface concentrations around the loop will produce the highest steady state concentration in the bulk coolant, and hence, the largest concentration of activated isotopes, assuming the physical constants are not abnormally large or small for this isotope. In the case of this model, chromium and cobalt routinely have the greatest local concentrations; with the iron and nickel having the next highest concentrations. The first conclusion we can draw from this is that if a material is causing an activity transport problem, it is paramount to reduce the surface concentrations as much as possible. Clearly, the best answer for this is to use materials that possess either no or very small quantities of the problem precursor. In the case of the results from this model, it is shown that the creation of Cr^{51} from Cr^{50} plays a dominating role; however, the eradication of chromium from the primary circuit is not feasible. Steps have already been taken in some plants to reduce the amount of cobalt in some plants by the replacement of materials.

A second conclusion is that great care must be taken when calculating the surface concentrations of each ion. As said previously, these values determine the outcome of the entire model, and should certainly be studied to further improve the accuracy of this model. Surface concentrations are predicted by assuming electrochemical equilibrium and applying the Nernst equation for the dissolution reaction in question. This final expression is given in (4-17) as:

$$\log a_B = \frac{z}{b} \frac{F}{2.303RT} (E^0 - ECP) - \frac{x}{b} pH \quad (4-38)$$

It is clear that these concentrations, a_B , are dependent on four distinct quantities: the ECP, pH, temperature, and the standard potential of the reaction (E^0). By Equation (4-18), we know the standard potential to really be a measure of the Gibb's Energy of the reaction, which is also temperature dependent. The Gibb's Energies are empirically determined constants, and excellent data does not exist for all of the species considered here. In the case of iron, there is much variation in the values reported [24]. An extremely important caveat to the reader, when interpreting the results of this report, is that uncertainties have been discovered within the available database used to derive the Gibb's energies of formation. Much future study is needed to sure up these values, either through the use of a different database or more fundamental methods of calculating these values.

The implication from this discussion is that we are dependent on the existence of good thermodynamic data to achieve accurate results using the approach outlined in this report. While this is a fundamentally different problem than those existing models which are dependent on empirically measured values (of mass transfer, for example), it is still a serious limitation in the implementation of the model. As stated earlier in the text, a commercial program was used to establish Gibb's Energy values in this work, future work may include more comprehensive review of what values are known.

4.8 Future Work

While much has been considered in the construction of this model, some future work is certainly required. This includes:

- The transport of a greater number of activated isotopes can be considered. This involves identifying the isotopes, the construction materials in which these isotopes are present, and the dissolution reactions for the oxides and elements that release the isotopes into the coolant.
- Final finishings and treatments of the construction materials must be taken into account. Processes such as pickling, heat treatment, and polishing must be accounted for in the rates of release and precipitation of corrosion products. These processes, as well as the grain structures of the metals and alloys, need to be examined for their effect on the corrosion layers, and hence, the dissolution rates.
- More source and sink terms in the mass balance can be identified, such as sequential activation of already activated isotopes to other isotopes. Activation processes can also be extended to fast and epi-thermal neutrons, protons, alpha particles, and beta

particles. Also, a uniform flux is assumed in the core, a 3-D model of the core neutronics could improve accuracy of the model.

4.9 References for Task 4

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Task 5. Code Performance Evaluation

Objectives

The models and codes will be evaluated against plant data obtained from operating BWRs and PWRs in the United States. Several PWRs have now experienced Axial Offset Anomaly (AOA), and data from these plants will be particularly valuable in calibrating and benchmarking the codes. Likewise Mass Transport (MT) and Activity transport (AT) data for a variety of plants (BWRs and PWRs) are available, and hence, represent a convenient source of calibrating and benchmarking information.

5.1 Code Performance Evaluation for Boiling Water Reactors

5.1.1 Simulation of Plant Operation

A simplified BWR coolant circuit diagram is shown in Figure 5.1. The reactor operates at approximately 288°C, producing steam at a pressure of about 68 bar. FOCUS calculates the concentrations of chemical species, the corrosion potential, and the growth rate of a crack of any specified length at closely spaced points within each of the coolant circuit sections numbered from 1 to 10 in Figure 5.1 under NWC and HWC conditions. The code also integrates the crack growth rate along the corrosion evolutionary path (CEP) to yield the crack length at any specified point along that path.

5.1.2 Corrosion Evolutionary Path

To illustrate the application of FOCUS, in the present analysis, it is presumed the reactor was operated for 14 months operation cycles from refueling outages with initial heat up to normal operation. One scram is assumed midway through that period of operation. The reactor was maintained at 95% of full reactor power or at full power, in order to consider normal reactor power fluctuations (Figure 5.2). The Corrosion Evolutionary Path (CEP), summarized in this figure, includes a 48-hour hot stand-by by a reactor scram and start-up for normal operation (at 6 months) over which the reactor parameters (power level, flow velocity, temperature) were assumed to vary linearly with time. The electrolyte concentration (5ppb NaCl) was maintained constant during normal operation, but it increased during start-up and refueling outage with the conductivity varying according to the model presented above and shown in Figure 5.4. During NWC operation, no H₂ is added to the coolant while, under HWC operation, H₂ is injected into the feedwater to maintain the concentration at 0.5ppm. Cracks with initial lengths of 0.1 cm were assumed to exist in all sections of the primary coolant circuit. Furthermore, for the present calculations, the cracks are assumed to be loaded to stress intensity factors of 15 MPa $\sqrt{m}$ (in the core) or 27.5 MPa $\sqrt{m}$ (out of core). Finally, the concentrations of HCl and NaOH during normal operation were set at 5ppb as indicated in Table 5.2. The four main predicted parameters, ECP, conductivity, CGR, and the crack depth, are displayed in Figures 5.3 through 5.6 [see Fig. 5.8 through 5.12 in Extended Operation for 10 Rx. cycles (140 months)].

Legend	
1. Core Channel	(CC)
2. Core Bypass	(CB)
3. Upper Plenum	(UP)
4. Mixing Plenum	(MP)
5. Upper Downcomer	(UD)
6. Lower Downcomer	(LD)
7. Recirculation line	(RE)
8. Jet Pump	(JP)
9. Bottom of the Lower Plenum	(BLP)
10. Top of the Lower Plenum	(TLP)

Figure 5.1. Typical equipment and coolant flow in the BWR primary system.

Figure 5.2. Reactor operation scenario over a single Rx. cycle (14 months)

Table 5.1 Reactor operation scenario over a single Rx. cycle (14 months)

Time	Rx. Power	Operation condition
2 weeks	0.01%	Fuel unloading
1 week	0%	Rx. empty
2 weeks	0.01%	Fuel loading
1 week	0.01 → 100%	Heat up
3 months	100%	Normal operation
1 month	95%	Reduced operation
2 months	100%	Normal operation
1 week	10% → 100%	Rx. trip & Heat up
3 months	100%	Normal operation
1 month	95%	Reduced operation
2 months	100%	Normal operation
1 week	100 → 0.01%	Cool down for refueling

Table 5.2. Input Parameters for the Calculation with the FOCUS

Stress intensity factor ($\text{MPa}\sqrt{m}$) = 15 (in core), 27.5 (other regions)
Concentration HCl during the normal operation = 5ppb
Concentration NaOH during the normal operation = 5ppb

5.1.3 Simulation Results and Discussion

During full power operation, the ECP values in the coolant circuit under NWC operation are in the range of 271 mV_{SHE} in the core channels to -36 mV_{SHE} at the exit to the recirculation pipes, and 484 mV_{SHE} and 416 mV_{SHE}, respectively, during the refueling outage. However, under HWC operation with 0.5 ppm H₂ in the feedwater, the ECP lies in the range from 270 mV_{SHE} in the core channels to -623 mV_{SHE} at the bottom of the lower plenum. The ECP values in both NWC and HWC operations during the refueling outage are not much different, because hydrogen was not injected into the coolant in the HWC case. The predicted ECP values in the core channels under both NWC and HWC are essentially identical, because H₂ is removed from the liquid (water) phase in the core by boiling transfer to the steam phase. RADIOCHEM predicts the H₂ concentrations in the core channels for both cases (NWC and HWC) are almost same and are very low.

Figure 5.3. ECP values of NWC (A) and HWC (B) 0.5 ppm H₂ operation.

The bulk conductivities for the reactor coolant involving HCl and NaOH species are shown in Fig. 5.4. The conductivity calculated from the advanced coupled environment fracture model (ACEFM) [1] is found to be a function of the HCl and NaOH concentrations and the bulk temperature with little contribution being apparent from the radiolysis products. Therefore, the difference in bulk conductivity for NWC and HWC operation is not significant. From a separate calculation performed to investigate the effect of changes in temperature, the CGR was found to pass through a maximum at around 150-200°C, as previously noted.

Figure 5.4. Bulk conductivity for NWC (A) and HWC (B) 0.5 ppm H_2 operation.

Figure 5.5. CGR values for NWC (A) and HWC (B) 0.5 ppm H₂ operation.

The predicted CGR in the coolant circuit components during NWC and HWC operation of the BWR is shown in Figure 5.5. The data presented in Figures 5.3 and 5.5 reveals a close correlation between the predicted ECP and CGR, no doubt recognizing the latter is a quasi exponential function of the former. The calculation results of 10 reactor cycles in Figure 5.11 in the Extended Operation shows the obvious exponential trend. Accordingly, it is expected the core internal components at high ECP values have high CGR values, and vice versa.

FOCUS predicts the accumulated damage (crack length) in components in the reactor primary coolant circuit under any given set of operating conditions. In this way, it is possible to compare the accumulated damage (crack depth) between NWC and HWC operating conditions over identical corrosion evolutionary paths (operating histories). In doing so, it is important to note the damage is considered to develop from initial, 0.1 cm long cracks. This approach, of course, ignores the initiation process which, in this case, is the time for the crack to nucleate and grow to a 0.1 cm length. Figure 5.6 and 5.12 display the accumulated damage is similar in both NWC and HWC operations, because the crack growth rate in the fuel channels is virtually the same for both NWC and HWC (0.5 ppm H₂ in the feedwater). On the other hand, the accumulated crack growth in the core bypass for the one year of NWC operation is 0.21 cm, but is only 0.04 cm for the one year HWC operation. The accumulated damage (crack length) is distinctly lower as the result of HWC operation compared with NWC operation, at least for out-of-core components. Furthermore, because the ECP is much lower under HWC than under NWC in all components except those in the core and upper plenum, and assuming that passivity breakdown followed by micro pit growth is the precursor to IGSCC, DFA [2] predicts the initiation time will be considerably longer under HWC conditions than under NWC conditions [3]. Accordingly, it is likely that FOCUS significantly underestimates the benefits of HWC, but only in those regions where the ECP is greatly reduced.

Figure 5.6. Crack depth versus operating time for NWC (A) and HWC (B) 0.5 ppm H_2 operation of a BWR.

Focusing now on crack growth only, the calculated damage at various points around the primary coolant circuit under both NWC and HWC conditions is summarized in bar-graph form in Figure 5.7. This data again indicates the CGR values in the BWR internals are closely related to the ECP values during both NWC and HWC operations. In particular, they indicate only marginal benefit of HWC over NWC for cracks in the upper plenum (UP), the mixing plenum (MP), and the jet pumps, where “marginal” is taken to be a diminution in CGR of no more than 50%. The calculations also demonstrate the facility offered by FOCUS for estimating accumulated damage at many locations within the coolant circuit simultaneously, while the plant traverses a complicated Corrosion Evolutionary Path (CEP). Clearly, the inclusion of a viable crack initiation model is an important future development.

Figure 5.7. Comparison of the accumulated damage of the Rx. internals after 14 month NWC and HWC operation.

Extended Operation

Figure 5.8. Reactor operation scenario over 10 Rx. cycles (140 months)

Figure 5.9. ECP of NWC (A) and HWC (B) 0.5 ppm H_2 operation (10 Rx. operation cycles).

Figure 5.10. Bulk conductivity of NWC (A) and HWC (B) 0.5 ppm H₂ operation (10 Rx. operation cycles).

Figure 5.11. CGR of NWC (A) and HWC (B) 0.5 ppm H₂ (10 Rx. operation cycles).

Figure 5.12. Crack depth versus operating time for NWC (A) and HWC (B) 0.5 ppm H₂ operation of a BWR (10 Rx. operation cycles).

5.1.4 Comparison of the calculated and measured ECP data

An important point that needs to be emphasized is the maximum contribution that any given radiolytic species can make to the ECP is roughly proportional to its concentration. The accuracy of the mixed potential model and Radio-chemistry model incorporated in the FOCUS code has been evaluated by comparing calculated ECP values for Type 304 SS against measured BWR plant data. Two sets of data have been employed, as shown in Tables 5.3 and 5.4. ECP_{calc} values in the Table 5.3 and 5.4 are calculated by FOCUS code using the same operational conditions with the experimental conditions.

The first set of ECP data (Table 5.3) was measured by Indig et al. [4] in an autoclave attached to the recirculation piping of the Dresden-2 BWR. The measured data and calculated data show some differences in the ECP values. The uncertainty in the calculated ECP is principally due to uncertainties in the kinetic parameters and input data (e.g., flow velocity and hydrodynamic diameter, etc.). FOCUS code uses electrochemical kinetic parameters of Type 304 SS. It is expected the measured ECP data and the actual (real) ECP values will be different because of the different configurations and flow conditions.

Table 5.3. Calculated vs. measured ECP data for Dresden-2 BWR

Test No.	[H ₂] (mg/kg)	[O ₂] (mg/kg)	ECP _{meas.} /V _{she}	ECP _{calc.} /V _{she}
1	0.01	0.270	-0.040	-0.046
2	0.08	0.040	-0.185	-0.078
3	0.15	0.020	-0.235	-0.111

4	0.135	0.005 to 0.020	-0.255	-0.106 to -0.104
5	0.135	0.005 to 0.023	-0.240	-0.106 to -0.103
6	0.135	0.003 to 0.030	-0.250	-0.106 to -0.103
7	0.135	0.007 to 0.019	-0.255	-0.105 to -0.104
8	0.135	0.012 to 0.020	-0.265	-0.103 to -0.104

Flow velocity = 5 cm/s. Hydrodynamic diameter = 10 cm. T = 288 °C.

The second case, we employ measurement data shown in Table 5.4 obtained during a Hydrogen Water Chemistry (HWC) mini-test at the Leibstadt BWR in Switzerland. The ECP_{calc} values are also calculated by the FOCUS code using the input data which are the same as the experimental conditions. Excellent agreement is obtained in both measured and calculated ECP values agreeing within the combined uncertainty levels.

Table 5.4. Calculated vs. measured ECP data for the Leibstadt BWR

Feed water [H ₂] (mg/kg)	Recirc. [H ₂] (mg/kg)	Recirc. [O ₂] (mg/kg)	ECP_{meas} / V_{she}	$ECP_{calc.}$ / V_{she}
0	0.005	0.200	0.125	-0.031
0.5	0.070	0.004	-0.15	-0.321
0.8	0.200	0.002	-0.320	-0.322
1.2	0.400	0.002	-0.338	-0.323
1.5	0.450	0.002	-0.340	-0.324
2.0	0.700	0.002	-0.380	-0.324

Flow velocity = 50 cm/s.

Hydrodynamic diameter = 2.54 cm.

T = 279 °C.

5.1.5 Summary and Conclusions

From the simulation results for Normal Water Chemistry (NWC) operation, the highest ECP values occur in the fuel channels and lay around 270 mV_{SHE}. This value is very high when compared to the critical potential for Intergranular Stress Corrosion Cracking (IGSCC) in sensitized Type 304 SS, EIGSCC, of about -230 mV_{SHE} at the BWR operating temperature of 288°C. While the ECP is lower than the core channel value in the balance of the primary coolant circuit, it is predicted to exceed (be more positive than) E_{IGSCC} for all sections under NWC conditions. On the other hand, except for the core channels, in which hydrogen is removed by boiling, the ECP values during the HWC operation are considerably lower than during the NWC operation (by as much as 800mV). Under HWC operation, it is concluded the injected hydrogen suppresses the radiolytic production of the oxygen and hydrogen peroxide and provides an additional oxidation reaction (the oxidation of molecular hydrogen) at very negative potentials, thereby shifting the ECP in the negative direction with the value that prevails being a delicate balance between the concentrations of hydrogen and hydrogen peroxide. The decomposition of hydrogen peroxide and its reaction with hydrogen, particularly in the downcomer, where a sufficiently high γ dose rate exists to facilitate the recombination

process, is postulated to be the most important factor in controlling the ECP in BWR primary coolant circuits.

5.2 Code Performance Evaluation for Pressurized Water Reactors

5.2.1 Simulation of Plant Operation

The PWR_ECP code can compute some electrochemical parameters for PWRs, such as ECP, and the concentrations of reduction and oxidation species. This code takes into account the effectiveness of the water-chemistry of PWRs. The water chemistry contains water radiolysis, chemical reactions, and convection of the injected chemicals, like H₂ injection, boron and lithium (to maintain the proper pH). The combination of these source terms, along with mass transport and conservation is evaluated at each time and distance in the primary reactor loop to calculate the spatial-temporal concentration variation of 14 chemical species and ECP values.

In order to illustrate the performance of the PWR_ECP code, we have carried out simulations on the typical PWR power plant shown schematically in Figure 5.13. The reactor operates as a normal power (3400MWth) and normal pressure (15.5 MPa). Normally, PWR water chemistry is accomplished by the chemical volume control system (CVCS), where hydrogen is injected to maintain around 25 cc/kg (correspond to 5 ppm). For the purpose of the code evaluation in this chapter, we carried out the calculation of the ECP values through the reactor coolant circuit under the Hydrogen Injection and No-hydrogen Injection operations. Note the No-hydrogen Injection operation in the PWR power plants is not a real case, it is just for the comparison of the calculation performance of the PWR_ECP code.

5.2.2 Corrosion Evolutionary Path

Typical PWR nuclear power plants operate at pressure of 15.5 Mpa and the highest and lowest temperatures are approximately 326°C (T_{hot}) and 292°C (T_{cold}), respectively. PWRs use borated water in their primary coolant system to control the reactivity of the nuclear core by absorbing the excess neutrons. Borated water can cause significant primary water stress corrosion cracking (PWSCC) in PWR reactor coolant loops. Boron concentration for initial operation after start up of the NPP is around 2000 ppm of H₃BO₃ and it continuously decreased to below 100 ppm at the end of the core life in one cycle operation as the uranium burned up. Currently, the uranium enrichment level is being increased to extend the one cycle operation period, as a result, the capacity factor also increases. One cycle operation period was 12 months a decade ago, but now it has been extended to 18 months. With the increase in the uranium enrichment level, more borate concentration is needed to control reactivity. In addition to the extension of the fuel burn up, most of the utilities are trying to increase the electrical power of the NPP. This power up rate needs higher coolant temperature and higher thermal outputs. The corrosive impact of these factors is significant in most situations, and may be critical in other cases.

Figure 5.13. Typical equipment and coolant flow in the PWR primary system.

5.2.3 Simulation Results and Discussion

Figure 5.14 displays the predicted ECP vs. distance from the bottom of the core for full power, both HWC and NWC operations. The ECP values under HWC operation are slightly more negative than the No-hydrogen Injection operation. Considering the harsh environment in the nuclear core where oxidants such as O_2 and H_2O_2 produced from the radiolytic decomposition of the coolant water, the hydrogen effect to suppress the ECP value to the more negative will be limited. The ECP values lie between $-280 \text{ mV}_{\text{SHE}}$ and $-427 \text{ mV}_{\text{SHE}}$ in the No-hydrogen Injection case and -283 to $430 \text{ mV}_{\text{SHE}}$ in the Hydrogen Injection case. The Figure 5.15 through 5.20 show the predicted ECP vs. distance plots in the reactor coolant loops for the both HWC and NWC operations in PWRs.

Figure 5.14. ECP vs. distance for the fuel channels in a PWR under Hydrogen Injection and No-hydrogen Injection operation conditions

Figure 5.15. ECP vs. distance for the Hot Leg in a PWR under Hydrogen Injection and No-hydrogen Injection operation conditions

Figure 5.16. ECP vs. distance for the Upper Plenum in a PWR under Hydrogen Injection and No-hydrogen Injection operation conditions

Figure 5.17. ECP vs. distance for the Steam Generator in a PWR under Hydrogen Injection and No-hydrogen Injection operation conditions

Figure 5.18. ECP vs. distance for the Cold Leg in a PWR under Hydrogen Injection and No-hydrogen Injection operation conditions

Figure 5.19. ECP vs. distance for the Spray Line in a PWR under Hydrogen Injection and No-hydrogen Injection operation conditions

Figure 5.20. ECP vs. distance for the Pressurizer in a PWR under Hydrogen Injection and No-hydrogen Injection operation conditions

5.2.4 Summary and Conclusions

From the simulation results for No-hydrogen Injection Water Chemistry operation, the highest ECP values occur in the fuel channels and lay around $-270 \text{ mV}_{\text{SHE}}$ and the lowest ECP values in the spray line about $-0.734 \text{ mV}_{\text{SHE}}$. In the case of hydrogen injection operation, the highest ECP values occur also in the fuel channels around $-270 \text{ mV}_{\text{SHE}}$ and the lowest ECP values $-0.735 \text{ mV}_{\text{SHE}}$. The predicted ECP values in the pressurizer under both Hydrogen injection and No-hydrogen Injection operations are essentially identical, because H_2 is removed from the liquid (water) phase in the core by boiling transfer to the steam phase. We can see the abrupt change of the ECP values in the pressurizer, because of the phase difference between liquid (bottom side, normally 60% of the pressurizer level) and steam phase (upper 40% of the pressurize level).

5.3 References

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Task 6. Technology Demonstration and Transfer

Objectives

Once developed, the codes will be demonstrated by calculating the operating envelope for hypothetical plants within which MT, AT and AOA are prevented or maintained at acceptable levels. The result of these calculations will be circulated to reactor operators for critique and comment. Shortcomings of the models and codes identified by industry personnel will be noted and modifications will be made accordingly. Finally, once completed, the code will be offered to reactor operators for beta testing in a plant environment.

Task Status

This task “Technology Demonstration and Transfer” was performed in Task 5.

Issues and Concerns: None

III. STATUS SUMMARY OF TASKS

Activity	Months After Start				
	0	12	24	36	48
Task 1. Modification of the Boiling Crevice Model
Task 2. Development of Link to consolidated code
Task 3. Further Development of the BWR_ECP and PWR_ECP Code.
Task 4: Model Integration and Development of BWR and PWR Primary Water Chemistry codes
Task 5: Code Performance Evaluation.
Task 6: Technology Demonstration and Transfer.
Reports: A= Annual, F= Final, M=Milestone	A	A	A	A	F

All tasks were completed as proposed.