

Modeling and Analysis of Pressurized Water Reactor (PWR) Primary Coolant Zinc Transients

2009 Zinc User Group Product

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REPORT SUMMARY

Background

Analysis of plant responses to transients in power production and zinc injection rates has the potential to reveal additional information about how, where, and at what rate zinc is deposited and incorporated into the films on primary system surfaces. Although the process of zinc transport and incorporation is complicated by the numerous mechanisms and surfaces available for incorporation, a control theory type analysis (linear systems analysis) could be useful for the analysis of transients, including initial injection of zinc, normal plant transients (such as shifts in core boiling or coastdowns at end of cycle), and off-normal plant transients (such as responses to unplanned shutdowns).

Objectives

- To document the development of a potential model based on linear systems analysis to aid in the evaluation of zinc concentration measurements during plant transients
- To provide guidance regarding data collection needs for enhancing the understanding of zinc behavior in primary circuits

Approach

In order to develop a model that could be used to describe transient zinc distributions in a typical pressurized water reactor (PWR) reactor coolant system (RCS) and chemical and volume control system (CVCS or letdown system), individual model components were developed and then combined into a system model.

In general, the model elements were derived from specific locations in or components of the RCS. The following model elements were explicitly considered:

- Fuel cladding surfaces
- Steam generator surfaces
- Letdown heat exchanger surfaces (hot and cold side considered separately)
- Injection into the CVCS
- Purification in the CVCS
- Reactor coolant (that is, the water volume)

Results

The model elements described above combine to form a highly complex description of the behavior of zinc in the primary system. Unfortunately, the complexity of the model makes it impractical for several reasons, including the following:

- The model introduces too many unknown parameters and variables. For appropriate benchmarking evaluations of these parameters, numerous sets of plant data would need to be analyzed. Such an extensive evaluation is outside the scope of the current project.
- Even if an extensive benchmarking were to be performed, the large number of unknown parameters would make separation of plant-specific, cycle-specific, and event-specific phenomena very difficult.
- Determination of many of the parameters requires data that are not generally available.

Because of these difficulties, the model elements developed were evaluated to develop insights into the behavior of zinc without actually solving the model. This evaluation included application to specific plant experiences.

The most important result of this modeling effort is the elimination of boiling precipitation as a likely mode of zinc deposition on the fuel surfaces. Evaluation of the diffusion of zinc out of deposits where it has been concentrated by boiling indicates that concentrations at the fuel surface will generally not reach saturation. The model developed to demonstrate this lack of precipitation was benchmarked against laboratory testing with good results, giving a high level of confidence to the computed limits on precipitation. An evaluation of the zinc concentrations and boiling duty for several U.S. units indicated that none of the plants were operating under conditions where zinc precipitation was a significant risk.

EPRI Perspective

This report provides a summary of the results to date of on-going zinc transient modeling efforts. Benchmarking through the use of plant data is ongoing and will be documented in the future. These results and all further assessments will be considered for application to the next revision of the *PWR Primary Water Zinc Application Guidelines*.

Keywords

Pressurized water reactor Primary water chemistry Primary water zinc application guidelines Zinc addition

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1 INTRODUCTION AND OVERVIEW

Analysis of plant responses to transients in power production and zinc injection rates has the potential to reveal additional information about how, where, and at what rate zinc is deposited and incorporated into the films on primary system surfaces. Although the process of zinc transport and incorporation is complicated by the numerous mechanisms and surfaces available for incorporation, a control theory type analysis (linear systems analysis) could be useful for analysis of transients, including initial injection of zinc, normal plant transients (such as shifts in core boiling or coastdowns at end of cycle), and off-normal plant transients (such as responses to unplanned shutdowns).

The analyses performed for this project were performed in order to provide further insight into questions such as the following:

- When system temperatures are lowered and there is a zinc return, where is the zinc coming from? This could be a significant issue because there should be less concern about high zinc concentrations affecting fuel integrity if the zinc is coming from the fuel, i.e., if zinc is dissolving off the fuel, it is not likely to be simultaneously depositing there in a significant way, nor will subsequent re-deposition increase the mass of zinc on the fuel.
- Where does excess zinc get deposited if, following a transient such as a downpower, there are high levels of zinc in the coolant at the time that higher power is resumed? This type of situation appears to be relatively common and has not caused problems to date, but could be a concern for plants with higher duty cores.
- How does the extent of boiling affect the location of zinc deposition? It is possible that during periods of extensive core boiling, reduced amounts of zinc are deposited on ex-core surfaces while increased amounts are deposited in the core. This could lead to significant return later in the cycle as boiling duty decreases and deposited zinc is released from the core. Alternatively, zinc deposited by boiling might be permanently isolated from the system and never be incorporated into ex-core surfaces (providing no dose rate or PWSCC benefit). This issue may become increasingly important as more plants with higher boiling duties consider zinc injection.
- What are the relevant time scales for zinc incorporation? The type of analysis described above could provide information on how long the primary system requires to respond to various transients. For example, daily adjustments of zinc injection rates may not be appropriate if the system responds to changes over the course of weeks. Although most plants do not control zinc injection rates through integrated controllers, the same principles of controller tuning apply to the development of a manual control procedure. For example, attempts to adjust zinc injection rates on frequencies that are too high could lead to instability in the concentration.

Introduction and Overview

• Does an extended period without zinc addition "reset" the plant to a pre-addition condition? How long must a no-addition interval be in order to effectively remove zinc from the system? Such issues are of particular significance in plants which intend to add zinc only in the later portions of a cycle when AOA risks are presumed to have passed.

At the time of the formulation of the EPRI Zinc Application Guidelines, no formal analysis of zinc/plant transients had been completed, although a similar methodology has been considered at EDF. This project was initiated to provide answers to the questions listed above and to provide guidance regarding data collection needs for enhancing the understanding of zinc behavior in primary circuits.

The remainder of this report is structured as follows:

- CHAPTER 2 gives the main conclusions of this report, specifically focusing on the answers to the questions posed above. This chapter also provides recommendations for further data acquisition/analysis.
- CHAPTER 3 describes the model used to evaluate zinc behavior in the primary circuit.
- CHAPTER 4 gives the detailed results of the modeling.
- CHAPTER 5 gives detailed recommendations for additional analyses.
- CHAPTER 6 provides the references used in writing this report.

2 CONCLUSIONS AND RECOMMENDATIONS

As discussed in Chapter 1, this project attempted to address five specific questions. The conclusions reached regarding these questions are addressed in Sections 2.1 through 2.5. Recommendations for further analyses are summarized in Section 2.6. More details regarding the conclusions arising from the modeling are given in Chapter 4. Details regarding recommendations for further analysis are given in Chapter 5.

2.1 Zinc Return on Temperature Reduction

The solubility of zinc under RCS conditions is generally much higher than the concentrations that are present. Therefore, any zinc return upon temperature reduction is not likely to be due to the inverse solubility of zinc oxide. Instead, increases in zinc concentration are more likely to arise from desorption of reversibly adsorbed zinc on RCS surfaces. The total mass of zinc available for desorption is likely to be less than would produce a 25 ppb concentration increase in the RCS. A moderate temperature change (such as transitioning from full power operation to zero power hot standby) would result in a concentration increase on the order of 5 ppb (from 10 ppb to 15 ppb, for example).

Adsorbed zinc is distributed in comparable masses between the fuel surfaces and the steam generators. For example, in a four-loop plant with a RCS zinc concentration of 10 ppb, approximately 2 g are adsorbed on SG surfaces, while 1 g is adsorbed on the fuel (with another 2.6 g dissolved in the coolant). Note that this division between the steam generators and the fuel (2:1) is somewhat different than the relative areas (4:1) due to the higher degree of saturation on the fuel relative to the steam generators due to the higher temperature.

The main implication of these findings is that zinc returns due to temperature changes are likely to be small. The total mass which could be released (\sim 3 g) is less than what would be incorporated into system surfaces during the course of a single day under normal operation.

2.2 Deposition of Zinc Returns

As indicated in the previous section, zinc returns due to temperature changes involve a very small mass of zinc. This implies that readsorption of zinc after a transient will not significantly alter the uptake rates on any given surface.

2.3 Significance of Boiling

The most important result of this modeling effort is the elimination of boiling precipitation as a likely mode of zinc deposition on the fuel surfaces. Evaluation of diffusion of zinc out of deposits where it has been concentrated by boiling indicates that concentrations at the fuel surface will generally not reach saturation. The model developed to demonstrate this lack of precipitation was benchmarked against laboratory testing with good results, giving high confidence to the computed limits on precipitation. An evaluation of the zinc concentrations and boiling duty for several US units indicated that none of the plants were operating under conditions where zinc precipitation was a significant risk.

2.4 Time Scales of Zinc Incorporation

Evaluation of the mass transport kinetics, bulk uptake rates observed in plants, and laboratory data from the literature, indicate that adsorption of zinc from the coolant onto RCS surfaces is essentially instantaneous. Comparison of laboratory data and plant experience provides good agreement that the general incorporation rate of zinc into RCS surfaces (after adsorption) is on the order of 2-4 g/day (for a four loop plant). This implies, roughly, that the entire RCS inventory of zinc is incorporated within a day at steady state conditions. This would imply that responses to transients are likely to be relatively rapid.

2.5 Return to "Non-Zinc" Conditions

Due to modeling assumptions, no information regarding the extent to which a plant returns to a "non-zinc" condition after cessation of injection was developed.

2.6 Recommendations

Recommendations for future analysis are given in Chapter 5. The chief recommendation is for a change in the framework of assessing risks at high duty plants to one that addresses zinc bulk concentration as well as local boiling rates. In Chapter 5, a precipitation threshold is predicted to be a function of local boiling duty and bulk zinc concentration. Figure 5-1 (repeated below as Figure 2-1) shows the precipitation threshold as a curve in a concentration versus boiling duty plot. (The location of the curve depends upon a third parameter, the crud thickness.) Above the curve precipitation is predicted. Below, no precipitation is predicted. This analysis shows that it is not boiling duty and zinc concentration. The derivation of this correlation and its validation by experimental data from the literature are discussed further in Chapter 5.



Figure 2-1 US Zinc Experience Relative to the Risk of Zinc Deposition by Boiling Precipitation

In addition to changing the assessment of zinc limits, the following additional data collection efforts are recommended:

- It is recommended that utilities collect more frequent measurements of RCS zinc concentrations during transients.
- It is recommended that utilities measure RCS zinc concentrations during shutdown.
- It is recommended that EPRI collect additional information regarding zinc injection rates.

While these additional data are not considered necessary to maintaining an active zinc injection program, it is anticipated that analyses of these data would enhance the industry understanding of zinc deposition and lower the technical barriers to zinc addition for higher duty plants, which are to some extent currently based on conservatism in the absence of a detailed understanding of the potential effects of zinc on fuel integrity.

3 FUNDAMENTAL MODEL ELEMENTS

This chapter discusses a model which could be used to describe transient zinc distributions in a typical pressurized water reactor (PWR) reactor coolant system (RCS) and chemical and volume control system (CVCS or letdown system). In the first subsection, the individual modeling components are discussed. The second section describes how the model components are combined into the system model. The third section provides typical values for the many input parameters needed in the model.

3.1 Model Elements

In general, the model elements are derived from specific locations in or components of the RCS. The following model elements are explicitly considered:

- Fuel cladding surfaces
- Steam generator surfaces
- Letdown heat exchanger surfaces (hot and cold side considered separately)
- Injection into the CVCS
- Purification in the CVCS
- Reactor coolant (i.e., the water volume)

Each of these is discussed separately in the following sections. In these discussions, parameters are treated abstractly. Typical values for the parameters are discussed in Section 3.3.

3.1.1 Fuel Clad Surface

It is assumed that the fuel clad surface is coated in corrosion product deposits (crud) and that zinc is incorporated into the crud in a homogeneous manner, i.e., there are no separate zinc phases. This assumption is generally supported by crud scrape analyses.[1] However, it should be noted that these analyses have all been performed on fuel crud that has been exposed to shutdown chemistry maneuvers that most likely remove all of the crud surface. Additionally, there are obvious limits in spatial resolution that limit the extent to which the existence of very small heterogeneities can be assessed.

It is assumed that the zinc may be incorporated into the crud in the following two manners:

• Initial surface incorporation, which is reversible and has a rate that is dependent on the difference between the local RCS zinc concentration and the theoretical saturation

Fundamental Model Elements

concentration associated with the crud. It is further assumed that this incorporation takes place through two parallel processes, boiling and non-boiling.

• Subsequent incorporation into the bulk deposit, which is permanent (or at least has a very slow reaction rate for release) and has a rate that is dependent on the mass on the deposit surface.

A schematic of these processes and their interaction with the three relevant zinc masses is shown in Figure 3-1.



Figure 3-1 Schematic Fuel Deposit Zinc Model

The following differential equation summarizes the model element discussed above:

$$\frac{d}{dt}m_{fuel \ deposit \ surface} = r_{non-boiling} + r_{boiling} - r_{release} - r_{bulk \ incorporation}$$
Eq. 3-1

In Equation [3-1] $m_{fuel deposit surface}$ is the mass of zinc reversibly deposited on the corrosion product deposit surface in the core. For convenience, Equation [3-1] is applied to the entire core. Assumed models for each of the reaction rates given in Equation [3-1] are discussed in the sections below.

3.1.1.1 Non-Boiling Deposition

As discussed above, it is assumed that the rate of non-boiling, reversible deposition on the crud surface is dependent on the difference between the RCS concentration and the concentration that would be in equilibrium with the crud. However, the concentration of zinc in the RCS is expected to change across the core as the fuel crud takes up or releases zinc. Therefore, a log-mean difference in concentration is used to quantify the driving concentration difference. Specifically, the log-mean concentration difference is defined as follows:

$$\Delta C_{lm, core} = \frac{\left(\Delta C_{core inlet} - \Delta C_{core outlet}\right)}{\ln\left(\frac{\Delta C_{core inlet}}{\Delta C_{core outlet}}\right)} = \frac{\left(\left[C_{RCS, core inlet} - C_{crud, core inlet}\right] - \left[C_{RCS, core outlet} - C_{crud, core outlet}\right]\right)}{\ln\left(\frac{C_{RCS, core inlet} - C_{crud, core inlet}}{C_{RCS, core outlet} - C_{crud, core outlet}}\right)}$$
Eq. 3-2

The concentrations in the RCS (C_{RCS}) are different at the inlet and outlet of the core due to deposition or release from the crud. The equilibrium concentrations (C_{crud}) are different at the inlet and outlet due to the differences in the core temperatures. (As discussed in Section 3.2, the various concentrations, except for the measured concentration, are variables for which the model is solved.)

The assumption that the surface incorporation rate is dependent on the concentration difference is expressed in the following equation:

$$r_{non-boiling} = k_{non-boiling} \rho A_{fuel} \Delta C_{lm, core}$$
 Eq. 3-3

where ρ is the density of water, used to convert the mass based concentration to a volume based concentration. The proportionality constant, $k_{non-boiling}$, is assumed to be identical to the mass transfer coefficient, i.e., the incorporation reaction is assumed to be very fast compared to the rate at which zinc is transported to the crud surface. Mass transfer coefficients ($h_{non-boiling}$) can be easily derived from empirical correlations. Thus Equation [3-3] is more tractable in the following form:

$$r_{non-boiling} = h_{non-boiling} \rho A_{fuel} \Delta C_{lm, core}$$
 Eq. 3-4

Note that Equation [3-4] holds only when $\Delta C_{im, core}$ is positive. When the RCS concentration is less than the equilibrium concentration, zero incorporation is assumed. In reality, there is always a dynamic equilibrium. The model discussed in this section addresses release and incorporation separately. Although there would be some modeling simplification if the incorporation and release reactions were modeled as a single reaction that could progress in either direction, it is assumed that these reactions will have different rate limiting steps. Specifically, incorporation is expected to have relatively low activation energy barriers so that incorporation (a phase change from soluble to solid) occurs at the same rate as mass transfer. However, the release reaction (a phase change from solid to dissolved) is expected to involve higher activation energies and be limited by solid state reaction rates.

The mass transfer coefficient $(h_{non-boiling})$ can be determined from the mass transfer analog [2] of the modified Dittus-Boelter Equation, as follows [3]:

$$Sh_D = \psi 0.023 Re_D^{0.8} Sc^{0.4}$$
 Eq. 3-5

where the non-dimensional parameters are defined as follows:

$$Sh_D = \frac{h_{non-boiling} d_{hydraulic}}{D_{Zn-H_2O}}$$
 Eq. 3-6

$$\psi = 0.9217 + 0.1478 \frac{p_{clad}}{d_{clad}} - 0.1130e^{-7\left(\frac{p_{clad}}{d_{clad}} - 1\right)}$$
 Eq. 3-7

$$Re_{D} = \frac{V_{core}d_{hydraulic}}{V}$$
Eq. 3-8
$$Sc = \frac{V}{D_{Zn-H_{2}O}}$$
Eq. 3-9

Values of ψ , the bundle correction factor per Equation [3-7], are given in Table 3-1 for typical PWR fuel assembly dimensions. [4, 5] Since these values differ very little for most assembly designs, a single value of 1.1 is used in this analysis.

The hydraulic diameter, $d_{hydraulic}$ in Equations [3-6] and [3-8], is defined as follows:

$$d_{hydraulic} = \frac{4A_{cell}}{P_{cell}} = \frac{4\left(p_{clad}^2 - \pi \frac{d_{clad}^2}{4}\right)}{\pi d_{clad}}$$
Eq. 3-10

Values of the hydraulic diameter for various fuel assembly geometries are given in Table 3-1.

Pitch*	Diameter*	ψ	Hydraulic Diameter
p_{clad} (cm)	d_{clad} (cm)	_	$d_{hydraulic}$ (cm)
1.25984	0.94996	1.11	1.18
1.25984	0.9144	1.12	1.30
1.27	0.95	1.11	1.21
1.28525	0.97028	1.11	1.20
1.397	1.06172	1.10	1.28
1.41	1.072	1.10	1.29
1.43	1.075	1.11	1.35
1.43002	1.07188	1.11	1.36
1.4732	1.1176	1.10	1.35

 Table 3-1

 Geometric Parameters for Typical PWR Assembly Geometries

*significant figures as reported in references

3.1.1.2 Boiling Deposition

Boiling increases the local concentration of zinc near the boiling surface. It is likely that the concentrations achieved are significantly greater than the concentrations in equilibrium with the crud. In this case, incorporation of zinc due to boiling will be a function only of the boiling rate and the RCS zinc concentration. It is assumed that the arithmetic average of the RCS inlet and

outlet concentrations is the concentration value upon which boiling driven incorporation is related. It is also assumed that all of the zinc in the boiled water mass is incorporated. These assumptions lead to the following mathematical expression for the rate of incorporation due to boiling:

$$r_{boiling} = \dot{M}_{boiling} \frac{C_{RCS, core inlet} + C_{RCS, core outlet}}{2}$$
 Eq. 3-11

where \dot{M}_{holling} is the boiling rate for the entire core (e.g., lb/hr).

Note that $\dot{M}_{boiling}$ changes during an operating cycle so that it should be possible to determine the effect of incorporation driven by boiling on the distribution of zinc by observing differences in system zinc consumption as the cycle progresses.

The model described above was used for initial consideration of boiling deposition. However, analysis using this model yielded results contradicted by field data. In reality, at zinc concentrations and boiling rates currently in typical plant applications, zinc deposition through boiling is negligible. This issue is discussed in depth in Section 0.

3.1.1.3 Release from the Fuel Crud to the RCS

The release of zinc from the crud surface is assumed to follow a relationship similar to that in Equation [3-3] as follows:

$$r_{release} = k_{release} \rho A_{fuel} \Delta C_{lm, core}$$
 Eq. 3-12

It is assumed that the rate controlling step in the release of zinc is the release from the solid phase, i.e., there is an activation energy such that the release rate is controlled not by transfer in the liquid phase but by reaction in the solid phase, thereby distinguishing it from the incorporation reaction which is assumed to have very low activation energies. Thus, the release rate constant $k_{release}$ is not the mass transfer coefficient as was the case for incorporation. (Note that Equations [3-4] and [3-12] differ only in nomenclature, i.e., the distinction between a mass transfer coefficient and a reaction rate. This difference is useful since mass transfer rates can be predicted from standard correlations, while reaction rates cannot.)

Note that Equation [3-12] holds only when $\Delta C_{ln, core}$ is negative. When the RCS concentration is more than the equilibrium concentration, zero release is assumed. In reality, it is expected that there is always a dynamic equilibrium, with some release and some incorporation. However, only the net transfer is modeled.

3.1.1.4 Permanent Incorporation into the Fuel Crud

As discussed above, it is assumed that zinc that is deposited in or on the surface of the fuel crud is eventually incorporated into the bulk of the deposit, isolating it from the RCS. This process is

Fundamental Model Elements

assumed to be proportional to the total mass of zinc in or on the fuel crud surface. This assumption is expressed in the following equation:

 $r_{bulk\ incorporation} = k_{bulk\ incorporation} m_{fuel\ deposit\ surface}$ Eq. 3-13

Thus, the bulk incorporation reaction is assumed to be a ripening reaction, which is dependent only on the time that the mass is present in the crud. There is no assumption that crud closer to the cladding is more prone to permanent incorporation (i.e., this reaction does not depend on a concentration gradient within the crud).

3.1.1.5 Equilibrium Zinc Concentrations

As discussed above, it is assumed that zinc is incorporated in a reversible manner on fuel crud surfaces. The non-boiling incorporation rate and the release rate (discussed in Sections 3.1.1.1 and 3.1.1.3, respectively) depend on the concentration that would be in equilibrium with the zinc in the solid phase. It is generally assumed that the zinc is incorporated homogeneously such that there is no distinct zinc phase.

Despite the assumption that zinc is incorporated into the crud homogeneously, there are very few data on equilibria associated with zinc substituted precipitates. In the absence of reliable data on mixed species, the equilibrium properties of zinc oxide [6] were considered for use in this model. However, plants injecting zinc operate at concentrations well below that needed to precipitate solid zinc phases. Therefore, an alternate approach was pursued.

One model of zinc incorporation into oxide films and other primary system surfaces postulates adsorption as the first step.[7] For an iron oxide substrate, this adsorption is described by the following chemical reaction [8]:

$$2S - FeOH + Zn^{2+} \rightleftharpoons S - Fe_2O_3 + S - ZnOH_2^+ + H^+ + H_2O$$
 Eq. 3-14

The adsorption of zinc on a substrate is governed by an equilibrium coefficient that relates the concentration of various surface conditions to the concentration of zinc, as follows:

$$k_{adsorption} = \frac{\left[S - Fe_2O_3\right]\left[S - ZnOH_2^+\right]\left[H_2O\right]\left[H^+\right]}{\left[S - FeOH\right]^2\left[Zn^{2+}\right]}$$
Eq. 3-15

Assuming that zinc is the only significant metal in solution (which is most likely true, at least at high zinc concentrations), Equation [3-14] can be used to show that the concentration of substrate sites adsorbing zinc is the same as the number of sites in the oxide state, so that the following relationship holds:

$$\left[S - Fe_2 O_3\right] = \left[S - ZnOH_2^+\right]$$
 Eq. 3-16

Substituting Equation [3-16] into Equation [3-15] yields the following:

$$k_{adsorption} = \frac{\left[S - ZnOH_2^+\right]^2 \left[H_2O\right] \left[H^+\right]}{\left[S - FeOH\right]^2 \left[Zn^{2+}\right]}$$
 Eq. 3-17

This can also be expressed in terms of the fraction of surface sites in a given condition (σ), as follows:

$$k_{adsorption} = \frac{\sigma_{S-ZnOH_2^+}^2 [H_2 O] [H^+]}{\sigma_{S-FeOH}^2 [Zn^{2+}]}$$
 Eq. 3-18

Equation [3-18] can be used to relate the concentration of zinc on a surface to the bulk concentration that would be in equilibrium with that concentration. For example, in Equation [3-2], the concentration $C_{crud,inlet}$ is the concentration in equilibrium with the concentration on the crud surface at the core inlet ($\sigma_{s-ZnOH_{*}^{+},inlet}$) and is given by the following equation:

$$C_{crud, core inlet} = \frac{\sigma_{S-ZnOH_{2}^{+}, inlet}^{2} \left[H_{2}O\right] \left[H^{+}\right]}{\sigma_{S-FeOH, inlet}^{2} k_{adsorption}} MW_{Zn}$$
 Eq. 3-19

Values of $k_{adsorption}$ are discussed further in Section 3.3.3.4.

Because the σ terms in Equation [3-19] are fractions of the total concentrations of surface sites, one of the terms may be eliminated, as follows:

$$C_{crud, core inlet} = \frac{\sigma_{S-ZnOH_{2}^{+}, inlet}^{2} \left[H_{2}O\right] \left[H^{+}\right]}{\left(1 - 2\sigma_{S-ZnOH_{2}^{+}, inlet}\right)^{2} k_{adsorption}} MW_{Zn}$$
 Eq. 3-20

Equation [3-20] may be put on a zinc-mass basis by introducing a total site density parameter m_{total} , which is twice the total mass per area of zinc that could be adsorbed (the factor of two is present because a single zinc ion requires two sites). Equation [3-20] then becomes:

$$C_{crud, core inlet} = \frac{\left(\frac{m_{zinc, inlet}}{m_{total}}\right)^{2} [H_{2}O] [H^{+}]}{\left(1 - 2\left(\frac{m_{zinc, inlet}}{m_{total}}\right)\right)^{2} k_{adsorption, inlet}} MW_{Zn}$$
Eq. 3-21

Fundamental Model Elements

For simplicity, the crud is modeled as a single unit with a constant zinc concentration (with the equilibrium bulk concentration varying along the core due to the temperature dependence of $k_{adsorption}$). The equilibrium concentration is then given as follows:

$$C_{crud, core inlet} = \frac{\left(\frac{m_{zinc,crud}}{m_{total}}\right)^2 [H_2 O] [H^+]}{\left(1 - 2\left(\frac{m_{zinc,crud}}{m_{total}}\right)\right)^2 k_{adsorption,inlet}} MW_{Zn}$$
Eq. 3-22

where $m_{zinc,crud}$ is the total mass of zinc adsorbed on the crud surface and m_{total} is the total mass that could be adsorbed on the crud surface. Substituting the symbols defined in Equation [3-1], Equation [3-22] becomes:

$$C_{crud, core inlet} = \frac{\left(\frac{m_{fuel \ deposit \ surface}}{m_{total}}\right)^{2} [H_{2}O][H^{+}]}{\left(1 - 2\left(\frac{m_{fuel \ deposit \ surface}}{m_{total}}\right)\right)^{2} k_{adsorption, inlet}} MW_{Zn}$$
Eq. 3-23

3.1.1.6 Overall Fuel Crud Incorporation Model

Substituting the various results of the previous sections into Equation [3-1] yields the following results:

$$\frac{d}{dt}m_{fuel \ deposit \ surface} = h_{non-boiling} \Delta C_{lm,core} A_{fuel} + \dot{M}_{boiling} \frac{C_{RCS,core \ inlet} - C_{RCS,core \ outlet}}{2} A_{fuel} - k_{release} \Delta C_{lm,core} A_{fuel} - k_{bulk \ incorporation} m_{fuel \ deposit \ surface}$$
Eq. 3-24

where $\Delta C_{lm,core}$ is given by the following expression:



3.1.2 Steam Generator Surfaces

On the primary side of the steam generators similar exchanges of zinc occur as shown in Figure 3-2. Note the absence of boiling.



Figure 3-2 Schematic SG Zinc Model

The analogous equations are as follows:

$$\frac{d}{dt}m_{SG \text{ oxide surface}} = r_{SG, \text{ surface}} - r_{SG, \text{ release}} - r_{SG, \text{bulk incorporation}}$$
Eq. 3-26

Fundamental Model Elements

$$\Delta C_{lm,SG} = \frac{\left(\Delta C_{SG \text{ inlet}} - \Delta C_{SG \text{ outlet}}\right)}{\ln\left(\frac{\Delta C_{SG \text{ outlet}}}{\Delta C_{SG \text{ outlet}}}\right)}$$

$$= \frac{\left(\left[C_{RCS,SG \text{ outlet}} - C_{crud,SG \text{ inlet}}\right] - \left[C_{RCS,SG \text{ outlet}} - C_{crud,SG \text{ outlet}}\right]\right)}{\ln\left(\frac{C_{RCS,SG \text{ outlet}} - C_{crud,SG \text{ outlet}}}{C_{RCS,SG \text{ outlet}} - C_{crud,SG \text{ outlet}}}\right)}$$

$$r_{SG,surface} = h_{SG}\rho A_{SG}\Delta C_{lm,SG}$$

$$Eq. 3-28$$

$$r_{SG,release} = k_{SG,release}\rho A_{SG}\Delta C_{lm,SG}$$

$$Eq. 3-29$$

$$r_{SG,bulk \text{ incorporation}} = k_{SG,bulk \text{ incorporation}}m_{SG \text{ oxide surface}}$$

$$Eq. 3-30$$

3.1.3 Letdown Heat Exchanger Surfaces

Coolant entering the RCS from the CVCS passes through a regenerative heat exchanger (RGHX) and receives heat from letdown flow from the RCS. The concentration of zinc may be changed on either side of the heat exchanger. (Note that this discussion focuses on a typical Westinghouse-design CVCS. Specific designs vary significantly, especially between NSSS designs, i.e., B&W, CE, Westinghouse.)

3.1.3.1 RGHX Cold Side

The processes which would promote deposition on fuel (except boiling) might also be expected to promote deposition on the cold side of the regenerative letdown heat exchanger. These processes are shown schematically in Figure 3-3.



Figure 3-3 Schematic RGHX Cold Side Zinc Model

The relevant equations describing the interaction of zinc on the cold side of the letdown heat exchanger are as follows:

$$\frac{d}{dt}m_{RGHX \ cold \ side \ deposit \ surface} = r_{RGHX \ cold \ side, \ surface} - r_{RGHX \ cold \ side, \ release} - r_{RGHX \ cold \ side, \ bulk \ incorporation} \qquad \mathbf{Eq. 3-31}$$

$$\Delta C_{lm, \ RGHX \ cold \ side} = \frac{\left(\Delta C_{RGHX \ cold \ side \ inlet} - \Delta C_{RGHX \ cold \ side \ outlet}\right)}{\ln\left(\frac{\Delta C_{RGHX \ cold \ side \ inlet}}{\Delta C_{RGHX \ cold \ side \ outlet}}\right)}$$

$$= \frac{\left(\left[C_{RCS, \ RGHX \ cold \ side \ inlet} - C_{crud, \ RGHX \ cold \ side \ outlet}\right]}{\ln\left(\frac{C_{RCS, \ RGHX \ cold \ side \ inlet}}{C_{RCS, \ RGHX \ cold \ side \ outlet}}\right)}$$

$$= \frac{\left(\left[C_{RCS, \ RGHX \ cold \ side \ inlet} - C_{crud, \ RGHX \ cold \ side \ outlet}\right]}{\ln\left(\frac{C_{RCS, \ RGHX \ cold \ side \ outlet}}{C_{RCS, \ RGHX \ cold \ side \ outlet}}\right)}$$

$$= \frac{r_{RGHX \ cold \ side, \ surface}}{R_{RGHX \ cold \ side \ cold \ side \ outlet}} - C_{crud, \ RGHX \ cold \ side \ outlet}}}{\ln\left(\frac{C_{RCS, \ RGHX \ cold \ side \ outlet}}{C_{RCS, \ RGHX \ cold \ side \ outlet}}\right)}$$

$$= \frac{r_{RGHX \ cold \ side, \ surface}}{R_{RGHX \ cold \ side, \ release}} - r_{RGHX \ cold \ side \ cold \ side \ outlet}}}{\ln\left(\frac{C_{RCS, \ RGHX \ cold \ side \ outlet}}{C_{RCS, \ RGHX \ cold \ side \ outlet}}\right)}$$

$$= \frac{r_{RGHX \ cold \ side, \ surface}}{R_{RGHX \ cold \ side \ cold \ side \ cold \ side \ cold \ side \ outlet}}}{\ln\left(\frac{C_{RCS, \ RGHX \ cold \ side \ cold \ s$$

3.1.3.2 HX Hot Side

Deposition may also occur on the hot side of the heat exchangers. In general, this will not affect concentrations of zinc in the RCS because it is expected that essentially all zinc will be removed from the letdown flow by the letdown demineralizers. However, changes due to passing through the regenerative heat exchanger may affect the concentration of zinc in samples drawn from the letdown line. For simplicity, the non-regenerative heat exchanger is incorporated into the same model element as the hot side of the regenerative heat exchanger. Figure 3-4 shows a schematic hot side model for the heat exchanger.



Figure 3-4 Schematic HX Hot Side Zinc Model

Fundamental Model Elements

The relevant equations describing the interaction of zinc on the hot side of the letdown heat exchangers (both regenerative and non-regenerative) are as follows:

$$\frac{d}{dt}m_{HX \text{ hot side deposit surface}} = r_{HX \text{ hot side, surface}} - r_{HX \text{ hot side, release}} - r_{HX \text{ hot side, bulk incorporation}}$$
Eq. 3-36

$$\Delta C_{lm, HX hot side} = \frac{\left(\Delta C_{HX hot side inlet} - \Delta C_{HX hot side outlet}\right)}{\ln\left(\frac{\Delta C_{HX hot side inlet}}{\Delta C_{HX hot side outlet}}\right)}$$

$$= \frac{\left(\left[C_{RCS, HX hot side inlet} - C_{crud, HX hot side inlet}\right] - \left[C_{RCS, HX hot side outlet} - C_{crud, HX hot side outlet}\right]\right)}{\ln\left(\frac{C_{RCS, HX hot side inlet} - C_{crud, HX hot side inlet}}{C_{RCS, HX hot side outlet} - C_{crud, HX hot side outlet}}\right)}$$
Eq. 3-37

$$r_{HX hot side, surface} = h_{HX hot side} \rho A_{HX hot side} \Delta C_{lm, HX hot side}$$
 Eq. 3-38

$$r_{HX hot side, release} = k_{HX hot side, release} \rho A_{HX hot side} \Delta C_{lm, HX hot side}$$
 Eq. 3-39

Eq. 3-40 $r_{HX hot side, bulk incorporation} = k_{HX hot side, bulk incorporation} m_{HX hot side deposit surface}$

3.1.4 Injection into the CVCS

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Injection into the CVCS is assumed to result in the injected mass being entirely mixed with the charging flow upstream of the regenerative heat exchanger.

3.1.5 Purification in the CVCS

The letdown flow is assumed to be completely purified by the combined action of the hot side of the letdown heat exchangers, the letdown demineralizers, and the letdown filters.

3.1.6 Reactor Coolant

The reactor coolant model is divided into the following segments, which are assumed to be homogenous:

- Cold leg coolant (downstream of the SGs, upstream of the charging inlet) •
- Cold leg coolant with charging (downstream of charging inlet, upstream of RPV) ٠
- Hot leg coolant (downstream of the core, upstream of the SGs) •
- Charging coolant (downstream of the regenerative heat exchanger, upstream of the cold leg) •

- CVCS coolant (downstream of zinc injection, upstream of the regenerative heat exchanger)
- Letdown coolant (downstream of the letdown heat exchangers, upstream of the letdown demineralizers)

Figure 3-5 gives a schematic of a four-loop plant. Note that the reactor coolant segments listed above are assumed to have no zinc sources or sinks except bulk flow.



Figure 3-5 Schematic of Major RCS Components



Figure 3-6 Schematic of Significant CVCS Components

3.2 Combination of Model Elements

The model elements are combined by assuming that for the RCS segments there are no sources or sinks for zinc except bulk flows. With this assumption, mass balances on each of the RCS segments link the model elements together.

For the RCS cold leg segment, the following mass balance applies:

$$\frac{d}{dt}m_{cold \ leg} = 0 = \dot{M}_{RCP}\left(C_{SG,outlet} - C_{core, \ inlet}\right) + \dot{M}_{charging}\left(C_{RGHX, \ outlet} - C_{SG, \ outlet}\right)$$
 Eq. 3-41

For the RCS hot leg segment, the mass balance yields an equivalence between the core outlet and the SG inlet, as follows:

$$C_{core, outlet} = C_{SG, inlet}$$
 Eq. 3-42
For the CVCS segment, the concentration is equivalent to the SG outlet, as follows:

$$C_{CVCS} = C_{SG, outlet}$$
 Eq. 3-43

For the charging flow, the inlet to the regenerative heat exchanger is, per the assumptions discussed in Section 3.1.4, equal to the mass injection rate divided by the charging flow rate, as follows:

$$C_{charging} = \frac{m_{injection}}{\dot{M}_{charging}}$$
 Eq. 3-44

3.3 Typical Values for Model Parameters

3.3.1 Geometric Parameters

Various geometric parameters (physical dimensions of system components) are used in the model. Typical values are discussed in the following sections.

3.3.1.1 Fuel Dimensions

The following are typical fuel dimensions:

- Clad diameter (d_{clad}) : Typical values of $d_{hydraulic}$ are given in Table 3-1.
- Clad pitch (p_{clad}) : Typical values of $d_{hydraulic}$ are given in Table 3-1.

3.3.1.2 Fuel Area

A typical fuel area can be calculated as follows (with inputs from Reference [9]¹):

$$A_{fuel} = n_{assemblies} n_{rods} \pi d_{clad} L = (193)(264) \pi (0.95 \ cm)(3.658 \ m) = 5,562 \ m^2$$
 Eq. 3-45

3.3.1.3 Steam Generator Area

The steam generator area is taken from Reference [10] as $55,000 \text{ ft}^2/\text{SG}$ or $20,400 \text{ m}^2$ for four steam generators. Note that this area does not include the tube surface area within the tubesheet. However, this discrepancy is not expected to be significant relative to the total areas under consideration.

¹ Note that the fuel area is calculated using the number of fuel rods, e.g., excluding control rods.

3.3.1.4 Regenerative Heat Exchanger Cold Side Area

The nominal heat transfer area of a typical regenerative heat exchanger is 520 ft² or 48 m².[11]

3.3.1.5 Letdown Heat Exchangers Hot Side Area

The non-regenerative heat exchanger surface area is 780 ft² or 72 m².[12]

3.3.2 Water Properties

The following paragraphs describe the properties of water used in the model.

Diffusion of zinc in water (D_{Zn-H20}) : The diffusion coefficient of zinc ions in water at 25°C is 0.72 x 10⁻⁵ cm²/s.[13] For temperatures other than 25°C, the Stokes-Einstein relationship [14] is used to adjust this value, according to the following equation:

$$D_{Zn-H_2O}(T) = D_{Zn-H_2O}(25^{\circ}C) \frac{T}{298.15} \frac{\mu_{25^{\circ}C}}{\mu_T}$$
 Eq. 3-46

where T is the absolute temperature and μ is the viscosity (with the subscript indicating the applicable temperature). Values of the diffusion coefficient calculated at various temperatures are given in Table 3-2.

Water viscosity (μ): Values for the viscosity of water at various temperatures were taken from Reference [15]. These values were fit to a three parameter equation using a least squares method, with the following results:

$$\mu_T = e^{\left(\frac{314348.4}{T^2} + \frac{-178.94}{T} - 9.92984\right)}$$
 Eq. 3-47

where T is the absolute temperature in K and the viscosity is given in kg/m-s. Values of the viscosity calculated at various temperatures are given in Table 3-2.

Water density (ρ): Values for the density of water at various temperatures were taken from Reference [15]. These values were fit to a three parameter equation using a least squares method, with the following results:

$$\rho_T = -0.00281T^2 - 1.41515T + 824.0641$$
 Eq. 3-48

where T is the absolute temperature in K and the density is given in kg/m³. Values of the density calculated at various temperatures are given in Table 3-2.

Water kinematic viscosity (ν): The values of the kinematic viscosity used are calculated from the density and the viscosity per the following definition of the kinematic viscosity:

$$v = \frac{\mu}{\rho}$$

Eq. :	3-49
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Table 3-2
Properties of Water

<i>T</i> (°C)	<i>T</i> (°F)	μ (kg/m-s)	ρ (kg/m³)	ν (m²/s)	D _{Zn-H2O} (m ² /s)
25	77	9.18E-04	996	9.21E-07	7.20E-10
50	122	5.68E-04	988	5.75E-07	1.26E-09
75	167	3.90E-04	976	3.99E-07	1.98E-09
100	212	2.88E-04	961	3.00E-07	2.87E-09
125	257	2.26E-04	942	2.40E-07	3.91E-09
150	302	1.85E-04	919	2.01E-07	5.08E-09
175	347	1.56E-04	893	1.75E-07	6.35E-09
200	392	1.36E-04	864	1.57E-07	7.72E-09
225	437	1.21E-04	831	1.45E-07	9.15E-09
250	482	1.09E-04	795	1.37E-07	1.06E-08
275	527	1.00E-04	755	1.33E-07	1.21E-08
300	572	9.28E-05	711	1.30E-07	1.37E-08
325	617	8.69E-05	664	1.31E-07	1.52E-08
343	649.4	8.34E-05	628	1.33E-07	1.64E-08

3.3.3 Flow Rates

In order to calculate the Reynolds Numbers for each component, the flow velocity must be known (see Equation [3-8]). The sections below demonstrate the calculation of typical values.

3.3.3.1 Velocity along the Fuel

A volumetric flow rate per fuel rod (Q_{rod}) may be approximated by dividing the total volumetric flow rate (Q_{core}) by the number of assemblies $(n_{assemblies})$ and the number of fuel rods per assembly (n_{rods}) . A velocity may be approximated by dividing the flow rate per fuel rod by the flow area, as given in Equation [3-10]. These calculations are shown in Equation [3-50].

$$V_{core} = \frac{Q_{rod}}{\left(p_{clad}^2 - \pi \frac{d_{clad}^2}{4}\right)} = \frac{\frac{Q_{core}}{n_{assemblies}n_{rods}}}{\left(p_{clad}^2 - \pi \frac{d_{clad}^2}{4}\right)}$$

Eq. 3-50

Typical values for use in Equation [3-50] are as follows [4, 9]:

- $Q_{core} = 25 \text{ m}^3/\text{s}$
- $n_{assemblies} = 193$
- $n_{rods} = 17 \text{ x } 17 = 289^2$
- $p_{clad} = 1.26 \text{ cm}$
- $d_{clad} = 0.95 \text{ cm}$

These values combine to give a prototypical velocity of 5 m/s. Note that there is some approximation in this value due to neglecting edge effects and bypass flow. However, as a typical value, the accuracy of this approximation is acceptable. (Also note that the number of rods is slightly different than that used to determine the fuel area since only the heat producing rods were considered in calculating the area.)

3.3.3.2 Velocity through the Steam Generator Tubes

The velocity through the steam generators can be calculated from the total core flow (Q_{core}), the number of tubes (n_{uubes}), and the tube ID (ID_{uube}), per the following equation:

$$V_{SG} = \frac{Q_{core}}{n_{SG}n_{tubes} \left(\pi \frac{ID_{tube}^2}{4}\right)} = \frac{25\frac{m^3}{s}}{(4)(5626) \left(\pi \frac{(0.648 in)^2}{4} \left(\frac{0.0254 m}{in}\right)^2\right)} = 5\frac{m}{s}$$
 Eq. 3-51

with the values of n_{SG} , n_{tubes} , and ID_{tube} from Reference [10] and the value of Q_{core} from Reference [9].

3.3.3.3 Regenerative Letdown Heat Exchanger Cold Side Velocity

Calculation of the velocity on the cold (tube) side of the regenerative heat exchanger requires the following inputs:

• Total flow rate $Q_{RGHX-Cold}$ 27,300 lb/hr (0.00344 m³/s) Reference [16]

 $^{^{2}}$ Note that these sample calculations use 289 rods when estimating hydraulic parameters (like the velocity) but 264 rods when estimating the heat transfer area. This reflects the presence of non-fuel rods, e.g., control rods.

- Number of parallel tubes $n_{RGHX-tubes}$ 54 Reference [11]
- Tube Internal Diameter $ID_{tube, RGHX}$ ¹/2"-14 gauge (0.0085 m) Reference [11]

From these inputs, the velocity in the tubes is calculated as follows:

$$V_{RGHX-Cold} = \frac{Q_{RGHX-Cold}}{n_{RGHX-tubes}\pi \frac{ID_{tube-RGHX}^2}{4}} = \frac{0.00344 \frac{m^3}{s}}{(54)\pi \frac{(0.0085 m)^2}{4}} = 1.1 \frac{m}{s}$$
 Eq. 3-52

3.3.3.4 Non-Regenerative Letdown Heat Exchanger Hot Side Velocity

Calculation of the velocity on the hot (tube) side of the non-regenerative heat exchanger requires the following inputs:

- Total flow rate $Q_{LDHX-Hot}$ 55 gpm (0.00347 m³/s)Reference [16]• Number of parallel tubes $n_{IDHX-nubes}$ 142Reference [12]
- Tube Internal Diameter $ID_{ube, RGHX}$ 3/4"-18 gauge (0.0166 m) Reference [12]

From these inputs, the velocity in the tubes is calculated as follows:

$$V_{LDHX-Hot} = \frac{Q_{LDHX-Hot}}{n_{LDHX-tubes}\pi \frac{ID_{tube-LDHX}^2}{4}} = \frac{0.00347 \frac{m^3}{s}}{(142)\pi \frac{(0.0166 m)^2}{4}} = 0.113 \frac{m}{s}$$
 Eq. 3-53

3.3.4 Adsorption Parameters

Adsorption parameters are based on the following set of chemical reaction equations:

$$2 S - FeOH + Zn^{2+} \rightleftharpoons S - Fe_2O_3 + S - ZnOH_2^+ + H^+ + H_2O$$
 Eq. 3-54

$$Zn^{2+} + H_2O \rightleftharpoons Zn(OH)^+ + H^+$$
 Eq. 3-55

$$Zn^{2+} + 2H_2O \rightleftharpoons Zn(OH)_2 + 2H^+$$
 Eq. 3-56

$$Zn^{2+} + 3H_2O \rightleftharpoons Zn(OH)_3^- + 3H^+$$
 Eq. 3-57

These chemical reactions are governed by the following equilibrium coefficients:

$$k_{adsorption} = \frac{\left[S - Fe_2O_3\right]\left[S - ZnOH_2^+\right]\left[H_2O\right]\left[H^+\right]}{\left[S - FeOH\right]^2\left[Zn^{2+}\right]}$$
Eq. 3-58

$$k_{S1} = \frac{\left[Zn(OH)^{+}\right]\left[H^{+}\right]}{\left[Zn^{2+}\right]\left[H_{2}O\right]}$$
 Eq. 3-59

$$k_{S2} = \frac{\left[Zn(OH)_{2}\right]\left[H^{+}\right]^{2}}{\left[Zn^{2+}\right]\left[H_{2}O\right]^{2}}$$
 Eq. 3-60

$$k_{S3} = \frac{\left[Zn(OH)_{3}^{-}\right]\left[H^{+}\right]^{3}}{\left[Zn^{2+}\right]\left[H_{2}O\right]^{3}}$$
 Eq. 3-61

$$k_{S4} = \frac{\left[Zn(OH)_{4}^{2^{-}}\right]\left[H^{+}\right]^{4}}{\left[Zn^{2^{+}}\right]\left[H_{2}O\right]^{4}}$$
 Eq. 3-62

These descriptive equations are related to the total concentration of zinc by the following definition:

$$\left[Zn_{total}\right] = \left[Zn^{2+}\right] + \left[Zn\left(OH\right)^{+}\right] + \left[Zn\left(OH\right)_{2}\right] + \left[Zn\left(OH\right)^{-}_{3}\right] + \left[Zn\left(OH\right)^{2-}_{4}\right]$$
 Eq. 3-63

Substituting Equations [3-59] through [3-62] into Equation [3-63] yields the following relationship between the total zinc concentration and the concentration of the non-hydrolyzed zinc cation:

$$\begin{bmatrix} Zn^{2+} \end{bmatrix} = \begin{bmatrix} Zn_{total} \end{bmatrix} - \frac{k_{s1} \begin{bmatrix} Zn^{2+} \end{bmatrix} \begin{bmatrix} H_2O \end{bmatrix}}{\begin{bmatrix} H^+ \end{bmatrix}} - \frac{k_{s2} \begin{bmatrix} Zn^{2+} \end{bmatrix} \begin{bmatrix} H_2O \end{bmatrix}^2}{\begin{bmatrix} H^+ \end{bmatrix}^2} - \frac{k_{s3} \begin{bmatrix} Zn^{2+} \end{bmatrix} \begin{bmatrix} H_2O \end{bmatrix}^3}{\begin{bmatrix} H^+ \end{bmatrix}^3} - \frac{k_{s4} \begin{bmatrix} Zn^{2+} \end{bmatrix} \begin{bmatrix} H_2O \end{bmatrix}^4}{\begin{bmatrix} H^+ \end{bmatrix}^4}$$

$$\begin{bmatrix} Zn^{2+} \end{bmatrix} = \frac{\begin{bmatrix} Zn_{total} \end{bmatrix}}{1 + \frac{k_{s1} \begin{bmatrix} H_2O \end{bmatrix}}{\begin{bmatrix} H^+ \end{bmatrix}} + \frac{k_{s2} \begin{bmatrix} H_2O \end{bmatrix}^2}{\begin{bmatrix} H^+ \end{bmatrix}^2} + \frac{k_{s3} \begin{bmatrix} H_2O \end{bmatrix}^3}{\begin{bmatrix} H^+ \end{bmatrix}^3} + \frac{k_{s4} \begin{bmatrix} H_2O \end{bmatrix}^4}{\begin{bmatrix} H^+ \end{bmatrix}^4}$$

Substituting Equation [3-64] into Equation [3-58] yields the following:

$$k_{adsorption} = \frac{\left[S - Fe_2O_3\right]\left[S - ZnOH_2^+\right]\left[H_2O\right]\left[H^+\right]}{\left[S - FeOH\right]^2 \frac{\left[Zn_{total}\right]}{1 + \frac{k_{s1}\left[H_2O\right]}{\left[H^+\right]} + \frac{k_{s2}\left[H_2O\right]^2}{\left[H^+\right]^2} + \frac{k_{s3}\left[H_2O\right]^3}{\left[H^+\right]^3} + \frac{k_{s4}\left[H_2O\right]^4}{\left[H^+\right]^4}}$$
Eq. 3-65

Equation [3-65] can be simplified by defining k^{T} as follows:

$$k^{T} = 1 + \frac{k_{s1} [H_{2}O]}{[H^{+}]} + \frac{k_{s2} [H_{2}O]^{2}}{[H^{+}]^{2}} + \frac{k_{s3} [H_{2}O]^{3}}{[H^{+}]^{3}} + \frac{k_{s4} [H_{2}O]^{4}}{[H^{+}]^{4}}$$
Eq. 3-66

such that $k_{adsorption}$ is given by the following equation:

$$k_{adsorption} = \frac{\left[S - Fe_2O_3\right]\left[S - ZnOH_2^+\right]\left[H_2O\right]\left[H^+\right]}{\left[S - FeOH\right]^2\left[Zn_{total}\right]}k^T$$
Eq. 3-67

The equilibrium coefficients k_{SI} , k_{S2} , k_{S3} , and k_{S4} are available as functions of temperature from Reference [6]. Likewise, the hydrogen ion concentration is a function of temperature and the concentrations of lithium and boron. Table 3-3 gives the values of the ratio of k_T at various temperatures (assuming lithium and boron concentrations of 1.9 ppm and 600 ppm, respectively, for a pH_{300°C} of 7.15). The value of $k_{adsorption}$ is 0.0025 mol/kg at 234°C [8]. Based on Equation [3-67], the following approximation is used for the adsorption constant at different temperatures:

$$k_{adsorption}(T) = k_{adsorption}(234^{\circ}C)\frac{k^{T}}{k_{234^{\circ}C}^{T}}$$
 Eq. 3-68

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Fundamental Model Elements

Values for $k_{adsorption}$ at various temperatures using this approximation are also given in Table 3-3.

T (°C)	k [⊺] (Unitless)	k _{adsorption} (mol/kg)
25	1.41E+11	5.24E-10
40	5.39E+11	2.01E-09
50	1.29E+12	4.79E-09
100	7.95E+13	2.96E-07
120	3.66E+14	1.36E-06
234	6.72E+17	2.50E-03
250	2.07E+18	7.71E-03
285	4.18E+19	1.56E-01
300	2.17E+20	8.07E-01
315	1.51E+21	5.64E+00
325	6.78E+21	2.52E+01
335	3.65E+22	1.36E+02
343	1.63E+23	6.08E+02

Table 3-3 Values of k_{τ} and $k_{adsorption}$ at Various Temperatures

Typical RCS pH_{T} values are about 7. This implies the following hydronium ion concentration:

$$\left[H^{+}\right] = 10^{-pH_{T}} = 10^{-7} \frac{mol}{kg}$$
 Eq. 3-69

The concentration of water is given approximately as:

$$[H_2O] = \frac{1}{MW} = \frac{1}{0.018 \frac{kg}{mol}} = 55.56 \frac{mol}{kg}$$
 Eq. 3-70

Substituting these values and the value of $k_{adsorption}$ into Equation [3-23] gives the following (assuming that the core inlet is at 300°C):

$$C_{crud, core inlet} = \frac{\left(\frac{m_{fuel \ deposit \ surface}}{m_{total}}\right)^2 \left(55.56 \frac{mol}{kg}\right) \left(10^{-7} \frac{mol}{kg}\right)}{\left(1-2\left(\frac{m_{fuel \ deposit \ surface}}{m_{total}}\right)\right)^2 \left(0.807 \frac{mol}{kg}\right)} \left(0.06539 \frac{kg}{mol}\right) \left(10^9 \frac{ppb}{kg \ kg}\right)$$

$$= \frac{\left(\frac{m_{fuel \ deposit \ surface}}{m_{total}}\right)^2}{\left(1-2\left(\frac{m_{fuel \ deposit \ surface}}{m_{total}}\right)\right)^2} \left(450 \ ppb\right)$$

From this equation, concentrations can be calculated based on the fraction of adsorption sites filled. Bulk concentrations are given in Figure 3-7 as a function of the fraction of sites filled at three different temperatures. Note that because adsorption of a single zinc atom is assumed to consume two active sites (see Equation [3-54]), surface saturation (and hence an infinite concentration) is associated with a value of 0.5 for $m_{deposit surface}/m_{total}$.



Figure 3-7 Equilibrium Bulk Concentrations as a Function of the Fraction of Adsorption Sites Filled

3.3.5 Mass Transfer Coefficients

As discussed in Section 3.1.1.1, the mass transfer coefficient can be calculated from the Reynolds Number and the Schmidt Number. Typical values for the Reynolds Number, the Schmidt Number, the Sherwood Number, and the mass transfer coefficient are given in the following sections. Sections 3.3.5.1 through 3.3.5.4 demonstrate the calculation of these parameters for flow through the core. Mass transfer coefficients for the steam generators, the regenerative heat exchanger cold side, and the heat exchanger hot sides are given in Sections 3.3.5.5, 3.3.5.6, 3.3.5.7, and 3.3.5.8. An overall summary of the relative magnitudes of the mass transfer coefficients is given in Section 3.3.5.9.

3.3.5.1 Reynolds Number

The Reynolds Number is based on the velocity, diameter, and kinematic viscosity. Typical values for these inputs are as follows:

- V_{core} 5 m/s (see Section 3.3.3.1)
- $d_{hydraulic}$ 1.2 cm (see Table 3-1)
- v 1.31 x 10⁻⁷ m²/s (see Table 3-2 for 325°C)

From these values, a Reynolds Number can be calculated as follows:

$$Re_{D} = \frac{V_{core}d_{hydraulic}}{V} = \frac{\left(5\frac{m}{s}\right)(0.012\ m)}{1.31\ \text{x}\ 10^{-7}\ \frac{m^{2}}{s}} = 458,000$$
 Eq. 3-72

3.3.5.2 Schmidt Number

The Schmidt Number is based on the kinematic viscosity and the diffusion coefficient. Typical values for these inputs are as follows:

- v 1.31 x 10⁻⁷ m²/s (see Table 3-2 for 325°C)
- D_{Z_n-H20} 1.53 x 10⁻⁸ m²/s (see Table 3-2 for 325°C)

From these values, a Schmidt Number can be calculated as follows:

$$Sc = \frac{v}{D_{Zn-H_2O}} = \frac{1.31 \times 10^{-7} \frac{m^2}{s}}{1.53 \times 10^{-8} \frac{m^2}{s}} = 8.56$$
 Eq. 3-73

3.3.5.3 Sherwood Number

The Sherwood Number is based on the following three non-dimensional inputs:

- Re_{D} 458,000 (see Section 3.3.5.1)
- *Sc* 8.56 (see Section 3.3.5.2)
- ψ 1.1 (see Table 3-1)

From these values, a Sherwood Number can be calculated as follows:

$$Sh_D = \psi 0.023Re_D^{0.8}Sc^{0.4} = (1.1)(0.023)(458,000)^{0.8}(8.56)^{0.4} = 2,000$$
 Eq. 3-74

3.3.5.4 Mass Transfer Coefficient, Core

The mass transfer coefficient can be calculated from the definition of the Sherwood Number using the following inputs:

- $d_{hydraulic}$ 1.2 cm (see Table 3-1)
- D_{Zn-H20} 1.53 x 10⁻⁸ m²/s (see Table 3-2 for 325°C)

From these values and the value of the Sherwood Number a typical mass transfer coefficient can be calculated as follows:

$$h_{non-boiling} = \frac{Sh_D D_{Zn-H_2O}}{d_{hvdraulic}} = \frac{\left(2,000\right) \left(1.53 \ge 10^{-8} \frac{m^2}{s}\right)}{0.012 m} = 0.00255 \frac{m}{s}$$
 Eq. 3-75

3.3.5.5 Mass Transfer Coefficient, Steam Generator

In determining the mass transfer coefficient in the steam generators, the following input parameters are different than for the core:

• ID_{tube} 0.016 m (see Reference [10]) • Ψ unity (see Reference [3])

This leads to a different Reynolds Number as follows:

$$Re_{SG} = \frac{V_{SG}ID_{tube}}{v} = \frac{\left(5\frac{m}{s}\right)(0.016\ m)}{1.31\ \text{x}\ 10^{-7}\ \frac{m^2}{s}} = 610,000$$
 Eq. 3-76

The Sherwood Number is then given by:

$$Sh_{SG} = 0.023Re_{SG}^{0.8}Sc^{0.4} = (0.023)(610,000)^{0.8}(8.56)^{0.4} = 2,300$$
 Eq. 3-77

The mass transfer coefficient for the steam generator is then:

$$h_{SG} = \frac{Sh_{SG}D_{Zn-H_2O}}{ID_{tube}} = \frac{(2,300)\left(1.53 \times 10^{-8} \frac{m^2}{s}\right)}{0.016 m} = 0.0022 \frac{m}{s}$$
 Eq. 3-78

3.3.5.6 Mass Transfer Coefficient, Regenerative Heat Exchanger Cold Side

In determining the mass transfer coefficient on the cold side of the regenerative letdown heat exchanger, the following input parameters are different than for the core:

•	$ID_{tube, RGHX}$	0.0085 m	(¹ / ₂ "-14 gauge, per Reference [11])
•	Ψ	unity	(see Reference [3])
•	$V_{\scriptscriptstyle RGHX\text{-}cold}$	1.1 m/s	(see Section 3.3.3.3)
•	V	$2.01 \text{ x } 10^{-7} \text{ m}^2/\text{s}$	(see Table 3-2 for 150°C)
•	D_{Zn-H2O}	5.09 x 10 ⁻⁹ m ² /s	(see Table 3-2 for 150°C)

This leads to a different Reynolds Number as follows:

$$Re_{RGHX-tube} = \frac{V_{RGHX-cold}ID_{tube,RGHX}}{V} = \frac{\left(1.1\frac{m}{s}\right)(0.0085\,m)}{2.01\,\mathrm{x}\,10^{-7}\,\frac{m^2}{s}} = 46,500$$
 Eq. 3-79

The Schmidt Number is given by:

$$Sc = \frac{V}{D_{Zn-H_2O}} = \frac{2.01 \text{ x } 10^{-7} \frac{m^2}{s}}{5.09 \text{ x } 10^{-9} \frac{m^2}{s}} = 39.5$$
 Eq. 3-80

The Sherwood Number is then given by:

$$Sh_{RGHX-tube} = 0.023 Re_{RGHX-tube}^{0.8} Sc^{0.4} = (0.023)(46,500)^{0.8} (39.5)^{0.4} = 540$$
 Eq. 3-81

The mass transfer coefficient on the cold side of the regenerative letdown heat exchanger is then:

$$h_{RGHX-tube} = \frac{Sh_{RGHX-tube}D_{Zn-H_2O}}{ID_{tube,RGHX}} = \frac{(540)\left(5.09 \times 10^{-9} \frac{m^2}{s}\right)}{0.0085 m} = 3.2 \times 10^{-4} \frac{m}{s}$$
 Eq. 3-82

3.3.5.7 Mass Transfer Coefficient, Regenerative Heat Exchanger Hot Side

Because the regenerative heat exchanger (RGHX) is a shell and tube heat exchanger with a convoluted shell-side flow path, the methodology used to determine the core mass transfer coefficient is not suitable for the shell-side of the RGHX. To estimate the mass transfer coefficient, the analogy to the heat transfer coefficient was used. Specifically, the non-dimensional heat transfer correlation was combined with the mass transfer analog to yield a relationship between the Nusselt Number and the Sherwood Number, as follows:

$$Nu_{crossflow} = 1.13 C Re^{m} Pr^{\overline{3}}$$

$$Sh_{crossflow} = 1.13 C Re^{m} Sc^{\frac{1}{3}}$$

$$\frac{Nu}{Sh} = \left(\frac{Pr}{Sc}\right)^{\frac{1}{3}} = Le^{-\frac{1}{3}}$$

$$Sh = Nu Le^{-\frac{1}{3}}$$
Eq. 3-83

where the Nusselt Number correlation is for cylinders in crossflow.[2]

1

The Nusselt Number can be determined from the overall heat transfer coefficient. The following inputs are required for this analysis:

•	Temperature, $T_{shell-hot}$	560°F (290°C)	Reference [16]
•	Temperature, $T_{shell-cold}$	290°F (143°C)	Reference [16]
•	Temperature, $T_{tube-hot}$	518°F (270°C)	Reference [16]
•	Temperature, $T_{tube-cold}$	130°F (54°C)	Reference [16]
•	Total flow rate, $Q_{LDHX-Hot}$	55 gpm (3.47 kg/s)	Reference [16]
•	Heat Exchanger Area, A_{RGHX}	$520 \text{ ft}^2 (48 \text{ m}^2)$	Reference [11]
•	Heat Capacity of Water, C_p	4.59 kJ/kg-K (216°C)	Reference [14]
•	Prandtl Number, Pr	0.87 (216°C)	Reference [14]

•	Conductivity of Water, k_{water}	0.651 W/m-K (216°C)	Reference [14]
•	Density of Water, ρ	864 kg/m ³ (200°C)	Table 3-2
•	Diffusion Coefficient, D_{Zn-H2O}	6.36 x 10 ⁻⁴ m ² /s (225°C)	Table 3-2
•	Tube ID, <i>ID</i> _{tube, RGHX}	¹ /2"-14 gauge (0.0085 m)	Reference [11]
•	Tube OD, <i>OD</i> _{tube, RGHX}	¹ ⁄2" (0.0127 m)	Reference [11]
•	Thermal Conductivity, k_{tube}	17 W/m-K	Reference [15]

From these inputs, the total heat transfer can be determined as follows:

$$q = Q_{LDHX-hot} \left(T_{shell-hot} - T_{shell-cold} \right) C_p = \left(3.47 \frac{kg}{s} \right) (290^{\circ}C - 143^{\circ}C) \left(4.59 \frac{kJ}{kg - K} \right) = 2340 \frac{kJ}{s} \quad \text{Eq. 3-84}$$

The log mean temperature difference is as follows:

$$\Delta T_{lm} = \frac{\Delta T_{shell} - \Delta T_{tube}}{\ln\left(\frac{\Delta T_{shell}}{\Delta T_{tube}}\right)} = \frac{(290 - 143) - (270 - 54)}{\ln\left(\frac{290 - 143}{270 - 54}\right)} = 179^{\circ}C$$
 Eq. 3-85

From the total heat flux and the log mean temperature difference, an overall heat transfer coefficient can be calculated as follows:

$$UA = \frac{q}{\Delta T_{lm}} = \frac{\left(2340\frac{kJ}{s}\right)}{179^{\circ}C} = 13\frac{kJ}{s - {}^{\circ}C}$$
 Eq. 3-86

The tube side heat transfer coefficient can be calculated from the Dittus-Boelter Correlation [2] as follows:

$$Nu_{RGHX-tube} = 0.023Re_{RGHX-tube}^{0.8} Pr^{0.4} = (0.023)(46,500)^{0.8} (0.87)^{0.4} = 118$$
Eq. 3-87
$$h_{heat-tube} = \frac{Nu_{heat}k_{water}}{ID_{Tube-RGHX}} = \frac{(118)\left(0.651\frac{W}{m-K}\right)}{0.0085 m} = 9040\frac{W}{m^2 - K}$$

The overall heat transfer coefficient can also be calculated from the series of resistances as follows:

$$\frac{1}{UA} = \frac{1}{h_{heat-shell}A} + \frac{\ln\left(\frac{OD_{tube-RGHX}}{ID_{tube-RGHX}}\right)}{2\pi k \frac{A_{RGHX}}{\pi OD_{tube-RGHX}}} + \frac{1}{h_{heat-tube}A}$$
Eq. 3-88

which can be rearranged to determine the shell-side heat transfer coefficient as follows:

$$h_{heat-shell} = \frac{1}{A_{RGHX} \left(\frac{1}{UA} - \frac{\ln\left(\frac{OD_{tube-RGHX}}{ID_{tube-RGHX}}\right)}{2k_{tube} \frac{A_{RGHX}}{OD_{tube-RGHX}}} - \frac{1}{h_{heat-tube} A_{RGHX}} \right)}$$

$$= \frac{1}{\left(48 \ m^2\right) \left(\frac{1}{13 \frac{kJ}{s - {}^{\circ}C}} - \frac{\ln\left(\frac{0.0127 \ m}{0.0085 \ m}\right)}{2\left(17 \frac{W}{m - K}\right) \frac{48 \ m^2}{0.0127 \ m}} - \frac{1}{\left(9040 \frac{W}{m^2 - K}\right) (48 \ m^2)}\right)}$$

4

$$=\frac{1}{\left(48\ m^2\right)\left(0.077\ \frac{K}{kW}-0.00312\ \frac{K}{kW}-0.0023\ \frac{K}{kW}\right)}=291\ \frac{W}{m^2-K}$$
 Eq. 3-89

From the shell-side heat transfer coefficient, the shell-side Nusselt Number can be calculated as follows:

$$Nu_{shell} = \frac{h_{heat-shell}OD_{tube-RGHX}}{k_{water}} = \frac{\left(291\frac{W}{m^2 - K}\right)(0.0127 m)}{0.651\frac{W}{m - K}} = 5.68$$
 Eq. 3-90

Fundamental Model Elements

The Lewis Number is given as follows:

$$Le = \frac{k_{water}}{\rho C_p D_{Zn-H_2O}} = \frac{0.651 \frac{W}{m-K}}{\left(864 \frac{kg}{m^3}\right) \left(4590 \frac{J}{kg-K}\right) \left(5.09 \times 10^{-9} \frac{m^2}{s}\right)} = 32.3$$
 Eq. 3-91

The shell-side mass transfer coefficient is calculated via the Sherwood Number as follows:

$$Sh = Nu_{shell} Le^{-\frac{1}{3}} = (5.68)(32.3)^{-\frac{1}{3}} = 1.8$$
Eq. 3-92
$$h_{shell} = \frac{ShD_{Zn-H_2O}}{OD_{tube-RGHX}} = \frac{(1.8)\left(5.09 \times 10^{-9} \frac{m^2}{s}\right)}{0.0127 m} = 7.21 \times 10^{-7} \frac{m}{s}$$

3.3.5.8 Mass Transfer Coefficient, Non-Regenerative Heat Exchanger

In determining the mass transfer coefficient on the hot (tube) side of the non-regenerative letdown heat exchanger, the following input parameters are different than for the core:

 • $ID_{tube, LDHX}$ 0.0166 m
 (3/4"-18 gauge, per Reference [12])

 • Ψ unity
 (see Reference [3])

 • $V_{LDHX-hot}$ 0.154 m/s
 (see Section 3.3.3.4)

 • v 3.99 x 10⁻⁷ m²/s
 (see Table 3-2 for 75°C)

 • D_{zn-H20} 1.98 x 10⁻⁹ m²/s
 (see Table 3-2 for 75°C)

This leads to a different Reynolds Number as follows:

$$Re_{LDHX-tube} = \frac{V_{LDHX-hot}ID_{tube,LDHX}}{\nu} = \frac{\left(0.154\frac{m}{s}\right)(0.0166m)}{3.99 \times 10^{-7}\frac{m^2}{s}} = 6,400$$
 Eq. 3-93

The Schmidt Number is given by:

$$Sc = \frac{v}{D_{Zn-H_2O}} = \frac{3.99 \text{ x } 10^{-7} \frac{m^2}{s}}{1.98 \text{ x } 10^{-9} \frac{m^2}{s}} = 200$$
 Eq. 3-94

The Sherwood Number is then given by:

$$Sh_{LDHX-tube} = 0.023 Re_{LDHX-tube}^{0.8} Sc^{0.3} = (0.023)(6,400)^{0.8} (200)^{0.3} = 125$$
 Eq. 3-95

The mass transfer coefficient on the cold side of the regenerative letdown heat exchanger is then:

$$h_{LDHX-tube} = \frac{Sh_{LDHX-tube}D_{Zn-H_2O}}{ID_{tube,LDHX}} = \frac{(125)\left(1.98 \times 10^{-9} \frac{m^2}{s}\right)}{0.0166 m} = 1.5 \times 10^{-5} \frac{m}{s}$$
 Eq. 3-96

3.3.5.9 Comparison of Mass Transfer Coefficient Magnitudes

In the previous sections, the mass transfer coefficients shown in Table 3-4 were derived. The large disparity in mass transfer coefficients is principally due to the significant changes in the diffusion coefficient with temperature (see Table 3-2). Also shown are the relevant surface areas derived in the previous sections. Total mass transfer is governed by the following equation:

$$r = hA\Delta C$$
 Eq. 3-97

In general, because RCS surfaces are continuously being renewed due to release and deposition of corrosion products, the surfaces are never expected to be completely saturated. This places a limit on the variation in ΔC . For comparable concentration gradients, the difference in deposition in the core (the lesser of the major components) and the RGHX hot side (the greatest of the minor components) is a factor of 5000. In order for the RGHX surfaces to affect the overall zinc movement in the RCS, the core would need to approach 99.98% saturation in zinc. This is considered highly unlikely, given that significant masses of nickel and iron are being continuously deposited in the core at rates that are at most one or two orders of magnitude below the rate of zinc deposition (based on typical concentrations).

Surface	Mass Transfer Coefficient (m/s)	Area (m ²)	hA (m³/s)
Core	0.0026	5562	14.4612
Steam Generators	0.0022	20400	44.88
RGHX Cold Side	3.20E-04	48	0.02
RGHX Hot Side	7.21E-07	48	0.00003
LDHX Hot Side	1.50E-05	72	0.0011

Table 3-4Mass Transfer Coefficients for Various Surfaces

The comparisons shown in Table 3-4 support the simplifying assumption that the only surfaces which affect zinc transport are the core (fuel) and the steam generators.

3.3.6 Boiling Rate

The rate of steam production (boiling rate) in the core is highly plant specific and may vary from cycle to cycle as core designs are changed. The boiling rate also changes with time as the cycle progresses. A significant complication is that the boiling rate is not typically measured, but must be calculated, for example using EPRI's Boron-Induced Offset Anomaly Risk Assessment Tool (BOA) [17].

Because core boiling rates vary from unit to unit and cycle to cycle, a *typical* value cannot be given. Figure 3-8 shows example values for four different cycles at a Westinghouse 4-loop unit. An alternative example would be a unit which had no sub-nucleate boiling, i.e., in which the core boiling was zero for the entire cycle.



Figure 3-8 Total Core Boiling as a Function of Time for Four Cycles at a Westinghouse 4-Loop Unit

3.3.7 Parameters Not Known A Priori

A number of parameters necessary for complete modeling of zinc transients are not known. These include the following:

- Release rate of adsorbed zinc, $k_{release}$
- Rate of non-reversible incorporation into deposits, $k_{bulk incorporation}$
- Total mass of zinc which could be adsorbed, m_{total}

Initial estimates for each of these parameters are discussed in the sections below.

3.3.7.1 Zinc Release Rate

An order of magnitude estimate of the release rate may be obtained from a dimensional analysis. Specifically, it is likely that the release rate is proportional to the system volume and inversely proportional to the system area and a characteristic time, as follows:

$$k_{release} = \frac{V_{system}}{A_{system}\tau}$$
 Eq. 3-98

Fundamental Model Elements

A representative value for the system volume is the RCS volume, for example, 12,000 ft³ or 340 m³.[10] A representative value for the system area is the fuel area, for example, 5,562 m², per Equation [3-45]. Characteristic times as a function of temperature may be calculated using an Arrhenius relationship as follows:

$$\tau = a e^{\frac{E_{act}}{RT}}$$
 Eq. 3-99

A typical energy of activation (E_{act}) for a chemical adsorption/desorption reaction is 65,000 J/mol.[18] The pre-exponential factor *a* may be determined from a room temperature value for τ . For example, a typical characteristic time for a room temperature desorption would be that for lead from aluminum oxide, which is about half an hour or 1,800 s.[19] This yields a value for a as follows:

$$a = \tau \frac{1}{e^{\frac{E_{act}}{RT}}} = (1,800 \text{ s}) \frac{1}{\frac{65,000 \frac{J}{mol}}{\frac{65,000 \frac{J}{mol}}{\frac{65}{mol}}}} = 7.3 \text{ x } 10^{-9} \text{ s}$$
Eq. 3-100

Calculated values for the characteristic time and the release rate constant for various temperatures are given in Table 3-5.

Table 3-5Release Rate Constant for Various Temperatures

T (°C)	τ (S)	k _{release} (m/s)
25	1.80E+03	3.40E-05
50	2.36E+02	2.59E-04
75	4.15E+01	1.47E-03
100	9.21E+00	6.63E-03
125	2.47E+00	2.48E-02
150	7.73E-01	7.90E-02
175	2.76E-01	2.22E-01
200	1.10E-01	5.58E-01
225	4.78E-02	1.28E+00
250	2.26E-02	2.71E+00
275	1.14E-02	5.36E+00
300	6.13E-03	9.98E+00
325	3.46E-03	1.77E+01

3.3.7.2 Zinc Saturation

In order to estimate the total mass of zinc that could be adsorbed on system surfaces, the following properties of hydrous ferric oxide were used [20]:

- Specific Surface Area, s_{HFO} 600 m²/g
- Molecular weight, MW_{HFO} 89 g/mol_{Fe}
- Capacity, r_{site} 0.2 mol_{2n}/mol_{Fe}

These inputs were used to compute a maximum zinc surface density as follows:

$$\rho_{surface, zinc} = \frac{r_{site} M W_{Zn}}{s_{HFO} M W_{HFO}} = \frac{\left(0.2 \frac{mol_{Zn}}{mol_{Fe}}\right) \left(0.065 \frac{kg_{Zn}}{mol_{Zn}}\right)}{\left(600 \frac{m^2}{g}\right) \left(89 \frac{g}{mol_{Fe}}\right)} = 2.4 \times 10^{-7} \frac{kg_{Zn}}{m^2}$$
 Eq. 3-101

From the surface density, total masses can be computed using the component surface areas. The results of such calculations are given in Table 3-6. Note that, consistent with the treatment in Sections 3.1.1.1 and 3.3.4, m_{total} is the mass equivalent of the number of sites and only half the sites can be occupied by zinc. Therefore, the saturation mass is $\frac{1}{2}$ of m_{total} , as m_{total} is defined here.

Surface	Area (m ²)	1/2 m _{total} (g)
Core	5562	1.33488
Steam Generators	20400	4.896
RGHX Cold Side	48	0.01
RGHX Hot Side	48	0.01
LDHX Hot Side	72	0.0173

Table 3-6Saturation Masses on Component Surfaces

3.3.7.3 Bulk Incorporation Rate

Figure 3-9 shows the zinc oxide mass incorporated into an oxide film on Alloy 600 as a function of time at 260°C, $pH_T = 6.7$ and 45 cc/kg hydrogen.[21] These data are considered reasonably representative of the rate at which zinc might be incorporated into primary surface films when the surface is saturated in adsorbed zinc. These data indicate an incorporation rate of 8.23 x 10⁻¹³ kg/m²-s. This rate can be combined with the saturation surface density from Equation [3-101] and the definition of the incorporation rate constant given in Equation [3-13] to allow the derivation of a value for the incorporation rate constant, as follows:

$$k_{bulk \text{ incorporation}} = \frac{r_{bulk \text{ incorporation}}}{m_{fuel \text{ deposit surface}}} = \frac{\overline{r}_{bulk \text{ incorporation}}}{\overline{m}_{fuel \text{ deposit surface}}} = \frac{8.23 \times 10^{-13} \frac{kg}{m^2 - s}}{2.4 \times 10^{-7} \frac{kg}{m^2}} = 3.4 \times 10^{-6} \frac{1}{s}$$
 Eq. 3-102

where the overbars are used in indicate values normalized to surface area.



Figure 3-9 Incorporation of Zinc into Oxide Film on Alloy 600

4 CONCLUSIONS FROM THE MODEL

The model elements derived in the previous chapter combine to form a highly complex description of the behavior of zinc in the primary system. Unfortunately, the complexity of the model makes it impractical for several reasons, including the following:

- The model introduces too many unknown parameters. For appropriate benchmarking evaluations of these parameters numerous sets of plant data would need to be analyzed. Such an extensive evaluation is outside the scope of the current project.
- Even if an extensive benchmarking were to be performed, the large number of unknown parameters would make separation of plant-specific, cycle-specific, and event-specific phenomena very difficult.
- Determination of many of the parameters requires data that are not generally available.

Because of these difficulties, the model elements developed in the previous chapter were evaluated to develop insights into the behavior of zinc without actually solving the model. This evaluation included application to specific plant experiences. Various insights are discussed in the sections below.

4.1 Relative Importance of Various Components

One important conclusion from the development of the model discussed in Chapter 3 is that the steam generator tubes and the fuel cladding are the most important surfaces with respect to zinc. This is confirmation of expectations based purely on surface area. Table 4-1 gives the surface areas of components in a Westinghouse 4-loop primary system.[22] Although the specific values differ slightly from those used in Chapter 3, it is evident that the majority of the surface area is due to the steam generator tubes and the fuel.

Table 4-1Primary System Component Wetter Surface Areas

Component	Area (m ²)	% of Total
SG Tubesheet Cladding	23.78	0.1
SG Partition Plate	31.96	0.1
SG Tubes	17873.59	68.9
SG Channel Head	69.11	0.3
Reactor Vessel Cladding	167.21	0.6
Reactor Vessel Nozzle	24.86	0.1
Reactor Vessel Thermal Sleeves	21.52	0.1
Reactor Coolant Piping	205.69	0.8
Pressurizer	125.69	0.5
Letdown Heat Exchanger - Charging	32.94	0.1
Letdown Heat Exchanger - Letdown	49.70	0.2
Letdown Heat Exchanger	40.23	0.2
Seal Water Heat Exchanger	25.85	0.1
Fuel	7233.96	27.9
Total	25926.09	100.0
Totals Less Fuel and SG	818.54	3.2
Total Not Included in Model	695.67	2.7

Bold indicates inclusion in Model

Although the saturation capacity of the surfaces is expected to be directly proportional to the available surface area, the analyses in Chapter 3 provide additional insight, as follows:

- The rate of deposition on the various components (as given in Table 3-4) indicates that the fuel and steam generator tubes are at least an order of magnitude higher relative to the letdown heat exchangers on an area basis. That is, less zinc is transferred to the letdown heat exchangers than would be predicted based solely on available area. This is because the mass transfer coefficients for the letdown heat exchangers are substantially less than for the steam generators or the fuel due to the lower temperature (this is mostly a viscosity effect).
- The difference in the total rate of deposition between the fuel and the steam generators is somewhat less than would be predicted based solely on surface areas. For the values used in

Chapter 3, the deposition on the steam generator tube surfaces is about three times the deposition on the fuel, while the area in the steam generators is approximately three-and-a-half times that of the fuel. This difference in deposition rates is due to the mass transfer coefficients. Mass transfer at the fuel surface is somewhat faster due to the higher temperature (and the resultant lower viscosity).

4.2 Mass Adsorbed on Various Components

The analyses in Chapter 3 indicate that mass of zinc deposited on RCS surfaces through reversible adsorption is on the order of 6 g. This is the mass of zinc calculated (see Section 3.3.7.2 and Table 3-6) to saturate the fuel and steam generator adsorption sites. This mass of zinc is very small compared to the estimated deposition during the course of a cycle, which, based strictly on injection rates and letdown purification removal, is typically on the order of 1-5 kg.[22]

The discrepancy between the mass adsorbed and the mass deposited implies that one of the following is true:

- The assumptions used to calculate the mass absorbed are grossly inaccurate.
- The deposition of zinc is dominated by mechanisms other than adsorption (e.g., boiling deposition or particulate deposition).
- The adsorbed zinc is very rapidly incorporated into the deposits continuously providing new adsorption sites.

In order to evaluate which or what combination of these explanations might be valid, it is useful to compare the relative rates of deposition and incorporation. As indicated above, about 1-5 kg of zinc may be deposited each cycle. If a value of 2 kg per cycle is used, this corresponds to a daily deposition rate given in the following equation:

$$R_{typical} = 2 \frac{kg}{cycle} \frac{cycle}{550 \, days} \frac{1000 \, g}{kg} = 3.6 \frac{g}{day}$$
 Eq. 4-1

Based on the evaluation given in Section 3.3.7.3, a typical incorporation rate (using only the fuel and SG areas) is given as follows:

$$R_{incorporation} = \left(8.23 \ x \ 10^{-13} \ \frac{kg}{m^2 s}\right) \left(5562 \ m^2 + 20400 \ m^2\right) \frac{1000 \ g}{kg} \frac{3600 \ s}{hr} \frac{24 \ hr}{day} = 1.8 \frac{g}{day} \qquad \text{Eq. 4-2}$$

Note that the value given in Equation [4-1] is based on plant experience and is completely independent of the value given in Equation [4-2] which is based on laboratory testing. Given that the laboratory testing was conducted at different conditions (30 ppb zinc and $pH_T=6.70$ at 260°C) and the wide variation in actual plant deposition rates, these two values are quite close. This implies that the incorporation is dominated by adsorption which is reasonably well modeled in the analyses above. Therefore, it is concluded that nearly all of the zinc adsorbed on fuel surfaces is rapidly incorporated into the bulk deposits.

Conclusions from the Model

Using these masses given in Table 3-6, it is possible to calculate the magnitude of concentration transients which might rise from desorption of zinc from the wetted surfaces. The following equation gives a bound on such concentrations by assuming that all of the surface sites are filled:

$$\Delta C_{RCS} = \frac{\rho_{surface, zinc} A}{\rho_{water} V_{RCS}} = \frac{\left(2.4 \times 10^{-7} \frac{kg_{Zn}}{m^2}\right) (5563 \, m^2 + 20400 \, m^2)}{\left(711 \frac{kg}{m^3}\right) (372m^3)} = 23.6 \, ppb \qquad \text{Eq. 4-3}$$

where the density is taken at 300°C (see Table 3-2) and the volume is taken from Reference [23]. The concentration change indicated by Equation [4-3] implies that, although the mass that is available for desorption is small, it is quite possible that such a release could cause a significant concentration excursion.

4.3 Surface Equilibration/Saturation

As discussed in Chapter 3, the deposition of zinc is assumed to occur in a two-step process beginning with reversible adsorption on the wetted surface and proceeding through a relatively irreversible incorporation into the bulk deposit.

Based on the mass transfer coefficients and areas given in Table 3-4 and assuming a zinc concentration of 10 ppb, the following expression for the adsorption rate can be derived:

$$R_{adsorption} = hAC\rho = \left(14.5\frac{m^{3}}{s} + 44.9\frac{m^{3}}{s}\right) \left(10 \ x \ 10^{-9} \frac{kg}{kg}\right)$$

$$\left(1000\frac{kg}{m^{3}}\right) \left(3600\frac{s}{hr}\right) \left(24\frac{hr}{day}\right) = 51,300\frac{g}{day}$$
Eq. 4-4

This rate far exceeds the range of deposition rates calculated from actual plants (see Equation [4-1]), implying that adsorption is very rapid and is limited by equilibration between adsorbed zinc and dissolved zinc, not by kinetic factors.

4.4 Relevance of Boiling Deposition

As discussed in Section 3.3.6, boiling rates in PWR cores can be on the order of 50 kg/s. Assuming a RCS concentration of 10 ppb, this boiling rate can be used to calculate a total zinc deposition rate as follows:

$$R_{boiling} = \left(50 \frac{kg_{water}}{s}\right) \left(10 \ge 10^{-9} \frac{kg_{zinc}}{kg_{water}}\right) \left(\frac{1000 \ g}{kg}\right) \left(\frac{3600 \ s}{hr}\right) \left(\frac{24 \ hr}{day}\right) = 43 \frac{g}{day} \quad \text{Eq. 4-5}$$

This deposition rate far exceeds the typical rates inferred from plant data, which are on the order of 1-5 g/day (see Equation [4-1]). This implies that deposition due to boiling is not as simple as initially modeled, i.e., not all of the zinc in the boiled mass of water is deposited.

Zinc in the mass of water boiled might avoid being deposited through one of the following mechanisms:

- Precipitation in the bulk water
- Diffusion away from the surface

1

The relevance of these mechanisms depends on the geometry of the boiling process.

For relatively clean surfaces, bubble formation is thought to occur at nucleation sites. As the initial vapor phase grows in size, it forms a bubble, which eventually detaches, leaving a vapor phase nucleus behind to grow into a new bubble. This process is shown schematically in Figure 4-1. Note that when bubbles grow by this process, evaporation (boiling) is occurring at the bubble/bulk interface, such that any high concentrations of dissolved species are created in the bulk fluid. Therefore, boiling occurring on clean surfaces is expected to deposit very little zinc on the fuel surface. Zinc precipitated in the bulk would be quickly redissolved, since concentrations would only approach saturation at the bubble interface.

An alternative model of boiling that is likely to be more relevant is wick boiling in which a porous deposit results in small channels bringing liquid nearer the hot surface and large channels, referred to as chimneys, allowing steam to escape. A schematic of the deposit structure associated with this model is shown in Figure 4-2. In this model of boiling, zinc can escape deposition only if the diffusional flux away from the surface is greater than the convective flux toward the surface. The diffusional flux can be estimated as follows:

$$n_{diffusion} = \frac{D(C_{sat} - C_{RCS})\rho_{water}}{x_{deposit thickness}}$$

$$= \frac{\left(1.64 \ x \ 10^{-8} \ \frac{m^2}{s}\right) \left(250 \ x \ 10^{-9} \ \frac{kg_{zinc}}{kg_{water}} - 10 \ x \ 10^{-9} \ \frac{kg_{zinc}}{kg_{water}}\right) \left(628 \ \frac{kg}{m^3}\right)}{100 \ x \ 10^{-6} m}$$
Eq. 4-6

The concentration at the fuel surface is taken as 250 ppb, the approximate solubility of zinc under these conditions.[24] The thickness of the deposit layer is taken as 100 μ m, a high but reasonable value for deposits derived from crud scrapes of relatively high duty cores.[1]

Conclusions from the Model



Figure 4-1 Bubble Formation on a Clean Surface



Figure 4-2 Bubble Formation on a Fouled Surface

The convective flux may be approximated as follows:

$$n_{convection} = \dot{m}_{e} C_{RCS} = \left(500 \frac{lb_{water}}{ft^{2}hr}\right) \left(10 \ge 10^{-9} \frac{kg_{zinc}}{kg_{water}}\right) \left(\frac{454 \ g}{lb_{water}}\right) \left(\frac{ft}{0.3048 \ m}\right)^{2} \left(\frac{hr}{3600 \ s}\right)$$

$$= 6.8 \ge 10^{-6} \frac{g}{m^{2} s}$$
Eq. 4-7

where \dot{m}_{e} is the local boiling rate, taken here as 500 lb/ft²hr, a high but reasonable rate for a core with significant boiling. Comparing Equation [4-6] and Equation [4-7] shows that the diffusional flux is approximately double the convective flux, indicating that the concentration will not reach the postulated value of 250 ppb.

Conclusions from the Model

The calculations shown in Equation [4-6] and Equation [4-7] can be combined to derive a relationship between the local boiling rate and the bulk concentration required to precipitate zinc oxide. Specifically, setting the two fluxes equal to each other defines the point of incipient precipitation. The combined equation can then be rearranged to find either the bulk concentration for a given boiling rate or the boiling rate for a given concentration, as shown in the following equations, respectively:

It is possible to validate the analyses given above by comparison to laboratory data generated in a Westinghouse study performed for EPRI. Reference [25] describes a heated rod test in which zinc solutions were boiled in the pores of a deposit on a heated rod. The relevant test parameters are as follows:

- $x_{deposit thickness} = 50-75 \ \mu m \ (taken as 60 \ \mu m)$
- $\dot{m_e} = 460 \text{ lb/ft}^2\text{hr}$
- $T = 625^{\circ} F (329^{\circ} C)$

At this temperature, Equations [3-46] and [3-47] yield a diffusion coefficient of 1.55 x 10^{-8} m²/s. Equation [3-48] indicates that ρ_{water} is 656 kg/m³. Substituting these values into Equation [4-9] yields the following:

$$C_{RCS} \ge \frac{\left(1.55 \ge 10^{-8} \frac{m^2}{s}\right) \left(250 \ge 10^{-9} \frac{kg_{zinc}}{kg_{water}}\right) \left(656 \frac{kg_{water}}{m^3}\right)}{\left(60 \ge 10^{-6} m\right)}$$

$$C_{RCS} \ge \frac{\left(460 \frac{lb_{water}}{ft^2 hr}\right) \left(\frac{0.454 kg_{water}}{lb_{water}}\right) \left(\frac{ft}{0.3048 m}\right)^2 \left(\frac{hr}{3600 s}\right) + \frac{\left(1.55 \ge 10^{-8} \frac{m^2}{s}\right) \left(656 \frac{kg_{water}}{m^3}\right)}{\left(60 \ge 10^{-6} m\right)}}$$
Eq. 4-10
$$\ge 53 \ge 10^{-9} \frac{kg_{zinc}}{kg_{water}} = 53 \ ppb$$

This evaluation indicates that, for the conditions tested by Westinghouse [25], a bulk concentration of 53 ppb is necessary to precipitate zinc. The actual tests under these conditions resulted in precipitation at 60 ppb and no precipitation at 40 ppb, in agreement with the predicted results.

The increase in zinc concentration in the boiling area, although not enough to precipitate zinc on the fuel surface, does lead to an increase in the extent of adsorption site saturation. However, as shown in Figure 3-7, at typical fuel surface temperatures (~343°C) increases in concentration (above, for example, approximately 10 ppb) result in only small increases in the surface saturation. Therefore, changes in the extent and location of boiling during a cycle are not expected to lead to significant zinc transients.

Note that in this regard the behavior of nickel, which is known to deposit heavily in boiling region of PWR cores, is expected to be substantially different from that of zinc. Specifically, the solubility of nickel under primary chemistry conditions is thought to be on the order of 0.02 ppb.[26] The ~4 orders of magnitude higher solubility of zinc allows concentrations to form in the deposit layer which are sufficient to drive significant diffusion fluxes countering the convective flux due to boiling. Concentration gradients of this size are not possible with nickel because of its low solubility. The behavior of iron is somewhat intermediate, with solubilities from nickel ferrite on the order of 5 ppb.[27]

4.5 Release Due to Power/Temperature Reduction

It has been observed in several plants that reduction in the RCS temperature leads to the release of deposited zinc. Previously, this has been attributed to the retrograde solubility of zinc.[24, 28] However, zinc concentrations in the RCS are typically well below solubility limits of zinc oxide. A more plausible explanation for releases upon temperature reduction is the desorption of reversibly adsorbed zinc.

The relationship between the extent of surface saturation and the RCS zinc concentration is shown in Figure 4-3. In this figure, calculated values (per Section 0) are shown for the following representative temperatures:

- 300°C (572°F) is used as a typical hot standby temperature (i.e., essentially zero power production, but no cooldown)
- 315°C (599°F) is used as an average steam generator temperature (i.e., midway between hot leg and cold leg temperatures)
- 335°C (635°F) is used as the average fuel surface temperature (i.e., midway between hot leg and pressurizer temperatures; the pressurizer temperature is assumed to be the approximate temperature at which sub-cooled nucleate boiling occurs on the fuel surface)

With the relationship between concentration, surface saturation, and temperature given, the effect on zinc concentration of a reduction in temperature can be determined.

Conclusions from the Model





Calculation of the RCS zinc concentration after a temperature change is based on the assumption that the adsorption/release of reversibly adsorbed zinc is rapid relative to other time scales, for example, the cleanup half-life (see Sections 3.3.7.1 and 4.3). This assumption leads to the following mass balance for zinc in the RCS:

$$M_{zinc} = \left(M_{RCS}C_{RCS} + m_{fuel \ surface} + m_{steam \ generator \ surface}\right)_{condition 1}$$

$$= \left(M_{RCS}C_{RCS} + m_{fuel \ surface} + m_{steam \ generator \ surface}\right)_{condition 2}$$
Eq. 4-11

For example, if the average fuel temperature is 335°C, the average steam generator temperature is 315°C, and the initial RCS concentration is 10 ppb, the mass in the RCS is as follows:

 $M_{zinc} = M_{RCS}C_{RCS} + m_{fuel \ surface} + m_{steam \ generator \ surface}$

$$= \rho V_{RCS} C_{RCS} + 2 \frac{m}{m_{total}} \bigg|_{10 \text{ ppb}, 335^{\circ}C} \left(\frac{1}{2} m_{total, fuel}\right) + 2 \frac{m}{m_{total}} \bigg|_{10 \text{ ppb}, 315^{\circ}C} \left(\frac{1}{2} m_{total, steam generator}\right)$$
Eq. 4-12
$$= \left(711 \frac{kg_{water}}{m^3}\right) (372 \ m^3) 10^{-8} \frac{kg_{zinc}}{kg_{water}} + 2(0.4)(1.3 \ g) + 2(0.2)(4.9 \ g)$$

$$= 2.64 \ g + 1.04 \ g + 1.96 \ g = 5.64 \ g$$

Although the relationship between temperature, concentration, and adsorption are non-linear, it can be shown that a mass of 5.64 g distributed between the RCS coolant, the fuel surface, and the steam generator surface, all at 300°C, results in a coolant concentration of approximately 15 ppb. The distribution of zinc mass would then be as follows:

$$m_{RCS} = \rho V_{RCS} C_{RCS} = \left(711 \frac{kg_{water}}{m^3}\right) (372 \ m^3) 15 \ x \ 10^{-9} \ \frac{kg_{zinc}}{kg_{water}} = 3.97 \ g$$
$$m_{fuel \ surface} = 2 \frac{m}{m_{total}} \bigg|_{15 \ ppb, \ 300^{\circ}C} \left(\frac{1}{2} m_{total, \ fuel}\right) = 2(0.13)(1.3 \ g) = 0.34 \ g$$
Eq. 4-13
$$m_{steam \ generator \ surface} = 2 \frac{m}{m_{total}} \bigg|_{15 \ ppb, \ 300^{\circ}C} \left(\frac{1}{2} m_{total, \ steam \ generator}\right) = 2(0.13)(4.9 \ g) = 1.27 \ g$$

with slight differences due to rounding errors.

This analysis indicates that the zinc concentration increase experienced during a power decrease (a reduction to zero power hot standby in the example above) is due to desorption from RCS surfaces and that the zinc entering the coolant comes in roughly equal portions from the fuel and the steam generators, with a higher release per area from the fuel compensated by the lower surface area, relative to the steam generators.

It is also of note that the increase in zinc concentration due to a downpower without substantial cooling is relatively small (e.g., from 10 ppb to 15 ppb). This is generally consistent with plant observations. However, zinc concentration data from plant maneuvers such as this are not abundant.

4.6 Readsorption Following after Power/Temperature Reduction

After a power or temperature reduction, the coolant zinc concentration can increase, as discussed in Section 4.5. In the absence of other phenomena, adsorption will return the zinc distribution to its original status during the subsequent return to full power operating conditions. That is, the mass of zinc from the coolant that will return to the fuel will be equal to the mass which desorbed during the temperature/power reduction. Other phenomena which could result in a hysteresis effect (distributions at the end of the excursion which differ from those at the beginning) include the following:

- Continued injection of additional zinc during the transient
- Incorporation of adsorbed zinc into permanent deposits
- Deposition by boiling

Of the above phenomena, deposition by boiling is not expected to be significant (see Section 4.4). However, the first two are of comparable magnitude and would be expected to significantly affect RCS zinc concentrations.

4.7 Resetting to a Non-Zinc Program Condition

Plants are occasionally required to halt zinc injection. In some cases, suspending zinc injection during the early portion of a cycle when corrosion product accumulation on the fuel is expected to be high may be a desirable mode of operation. Therefore, it is useful to determine the extent to which such suspensions can "reset" the plant to a pre-zinc condition. Based on adsorption, the equilibration of system surfaces to the absence of zinc is expected to be quite rapid (see Section 4.3) such that reductions in adsorbed zinc are likely to differ imperceptibly from reductions in dissolved zinc. However, the model used in this report assumes that adsorption is followed by a permanent incorporation into the system surfaces. Therefore, the conclusion that the plant never fully resets is merely an artifact of the model assumptions. Nevertheless, the model is relatively consistent with plant experience, indicating that it is not unreasonable to assume that the plant does not "reset" until the corrosion product deposits are removed in bulk, i.e., only through decontamination of surfaces or replacement of components.

5 RECOMMENDATIONS FOR ADDITIONAL ASSESSMENTS

5.1 Evaluation of Zinc Concentration Limits

Much of the model developed for this project was premised on the assumption that zinc deposited on the fuel cladding due to boiling. In general, the concern over boiling deposition has been a major consideration in the use of zinc injection at high duty plants. As discussed in Section 4.4, deposition by boiling is not expected to be relevant in most zinc applications. The following equations give bulk concentration and local boiling duty requirements for boiling deposition:

Evaluation of available experimental data support the validity of the models used to generate Equations [5-1] and [5-2]. This analysis suggests that the vulnerability to zinc deposition on fuel surfaces during a cycle should be assessed not just as a function of duty (steaming rate) but also as a function of concentration. Figure 5-1 shows a simplified plot of a sampling of US cycles with zinc giving the local boiling rate and the average zinc concentration (for the time during which a zinc residual was present).[24] Equation [5-1] (or equivalently, Equation [5-2]) is also plotted in Figure 5-1. The results of the Westinghouse WALT loop tests are also shown and are consistent with the model predictions.[25]





It should be noted that the presentation of data in Figure 5-1 is somewhat simplistic. For example, Equations [5-1] and [5-2] contain terms that are dependent on temperature (the density and viscosity of water). The model equation in Figure 5-1 is given at 329°C (for comparison to the Westinghouse WALT data), but temperature will vary from unit to unit. As indicated by the curve for 300°C in Figure 5-1, the temperature effect is not particularly large.

Another simplification in Figure 5-1 is the use of a single deposit thickness (again, the selected value, 60 μ m, was chosen for comparison to the WALT data, which was generated on a surface with a 60 μ m deposit layer). As can be seen from the 100 μ m curve, reasonable variations in deposit thickness could have a significant effect on the thresholds for zinc deposition. (Note that this is the local deposit thickness in the region of peak boiling.) Eliminating this simplification would require analyses outside the scope of this project. Possible means of addressing this issue would be inclusion of deposit thicknesses for individual cycles (either from crud scrapes or from deposit thickness and boiling duty which would allow redrawing the model curve to implicitly incorporate a predicted thickness. This would likely result in a somewhat steeper slope.

One interesting observation from Figure 5-1 is that the Byron 2 cycles, which have been considered to bound most of the US fleet in terms of zinc injection programs, were actually at less risk of zinc deposition than the early Farley 2 cycle. While the incorporation of deposit
thickness variations into the model is likely to reduce the apparent margin that existed during the Byron cycles, it is unlikely that the apparent margin would be eliminated by a more refined calculation.

Pursuit of additional data to refine this interpretation of current zinc experience is recommended. Specifically, the following data should be assessed:

- Data for additional cycles
- Hot leg temperatures for the cycles under consideration
- Crud thicknesses for zinc cycles, both calculated and measured
- Data to determine a correlation between local steaming rates and deposit thickness (which could be based on data from cycles without zinc in addition to those with zinc)

5.2 Additional Measurements for Additional Analyses

5.2.1 Refined Measurements of Zinc Transients

At present, EPRI has only collected daily average zinc measurements. It is recommended that EPRI and member utilities pursue a program of obtaining more frequent data during plant transients. Additionally, it has been practice at some utilities to cease zinc concentration measurements if injection is suspended. It is recommended that all utilities continue to monitor zinc concentrations during suspension of injection.

5.2.2 Evaluation of Zinc Injection Rates

In general, the only data reported to EPRI on zinc programs have been daily average measurements of RCS zinc concentration. It is recommended that EPRI collect data on the rate of zinc injection into the RCS. As with many mass transport related processes, the incorporation of zinc into RCS surfaces is dependent on rates, including the net rate of incorporation. This rate cannot be determined solely from concentration.

5.2.3 Zinc Concentrations during Shutdown

At some utilities, zinc concentrations are not measured during shutdown (i.e., during the crud burst). Because the efficacy of zinc is expected to be proportional to the mass of zinc incorporated into surface films on the RCS boundaries, it is important to determine the mass of zinc which actually remains in the RCS system. Zinc removal during shutdown is a non-negligible factor in determining the mass of zinc in the RCS system.

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