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# Behavior of Zinc and Silica in the PWR Primary System: PWR Chemistry Technical Strategy Group Report

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# Behavior of Zinc and Silica in the PWR Primary System: PWR Chemistry Technical Strategy Group Report

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# ABSTRACT

The deposition of silica containing solids on pressurized water reactor (PWR) fuel assemblies is a concern for general fuel assembly fouling. Increased fouling could increase cladding surface temperatures, leading to elevated corrosion, and potentially failure. To that end, PWRs limit the amount of silica in the primary system coolant during operation to minimize the risk of issues associated with the formation of silica containing solids. Maintenance of low silica concentrations in the primary system can be an expensive endeavor for utilities. This can and has included the installation of reverse osmosis (RO) systems to reduce spent fuel pool silica concentrations (the primary source), as other less costly methods are not effective. Furthermore, high silica concentrations can result in core design constraints or zinc injection limitations being imposed by the fuel vendor, which can make operation more costly, both in terms of fuel cost and personnel dose. Recent evaluations of silica solubility data suggest that the solubility of silica in the presence of boric acid is much higher than previously thought. This may be a reason for the differing observations of silicate generation in PWR and boiling water reactor (BWR) fuel crud. The presence of boric acid may ultimately reduce the risk for the formation of silicate materials in PWRs and eventually, potentially through additional experimentation, result in relaxation of silica limits in PWRs. The project evaluates observations of silicon containing solids in PWRs, and the potential for relaxation of control limits associated with silica in the PWR primary system.

**Keywords**
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**PRIMARY AUDIENCE:** PWR primary chemist and fuel cycle designers and plant chemistry managers

**SECONDARY AUDIENCE:** Radiation safety and fuel management staff

### KEY RESEARCH QUESTION

The deposition of silica containing solids on PWR fuel assemblies is a concern for general fuel assembly fouling, and increased fouling could increase cladding surface temperatures, leading to elevated corrosion and potentially failure. To that end PWRs limit the amount of silica in the primary system coolant during operation to minimize the risk of issues associated with the formation of silica containing solids, but these efforts can be costly. Recent evaluations of silica solubility data suggest that the solubility of silica in the presence of boric acid is much higher than previously thought. The presence of boric acid may therefore reduce the risk for the formation of silicate materials in PWRs. This project evaluates observations of silicate formation under PWR primary coolant conditions, and the applicability of control limits associated with silica in the PWR primary system.

### RESEARCH OVERVIEW

The objective of this project was to evaluate available data on the likelihood of zinc silicate precipitation on PWR fuel cladding surfaces and its effect on deposit thermal resistance. To that end, the project evaluated the predictions of two advanced models for the solubility of silica containing species in PWR primary coolant, as well as reviews of available plant and laboratory observations applicable to silicate formation in the PWR primary. The plant data included that information for PWRs, and a noteworthy BWR example where zinc silicate formation led to significant issues. Finally, mass balance analysis of zinc and silica during the cycle was completed to estimate the magnitude of silica bearing compounds that could deposit on the fuel during a PWR fuel cycle.

### KEY FINDINGS

- Reviews of MULTEQ and OLI solution chemistry modeling results at PWR chemistries indicate that differences in the predicted tendencies for zinc silicate precipitation can be significant. While prior versions of MULTEQ predicted zinc silicate formation at relatively low primary coolant to deposit solution concentration factors, the current version predicts zinc oxide is formed before zinc silicate in solutions with silica concentrations less than 5 ppm and a zinc concentration of 10 ppb. Although the solution chemistry modeling results differ in detail between MULTEQ and OLI, formation of a zinc silicate precipitate in PWR fuel deposits is not predicted by current versions of either code as zinc oxide is preferentially formed.
- Zinc silicate formation is predicted to occur at BWR chemistries with MULTEQ at relatively low concentration factors, consistent with the River Bend BWR EOC 11 deposit observations.

- Extrapolation of BWR fuel deposit observations to predictions of PWR deposit chemistry cannot be supported based on the major differences in BWR and PWR chemistries, the impact of these differences on deposit solution chemistry, and the differences in deposit composition, magnitude, and structure.
- Loop studies completed to understand PWR fuel crud formation also do not support concerns associated with zinc silicate formation and its effects on fuel deposit thermal resistance.
- A zinc mass balance to determine the total amount of zinc silicate that could deposit on PWR fuel based on zinc retained in the system could not be used to eliminate the concern of the effect of zinc compound deposition on the deposit thermal resistance.
- The use of a silica mass balance does appear to further reduce concerns regarding zinc silicate precipitation, although more detailed consideration of possible silica sources will be required.

## WHY THIS MATTERS

Relaxation of PWR primary chemistry limits associated with silica could significantly reduce costs associated with silica purification, reduce startup holds associated with high silica, and expand the use of PWR zinc application, which can reduce plant radiation fields.

## HOW TO APPLY RESULTS

The results of this project can be used to inform future revisions of the EPRI *PWR Primary Water Chemistry Guidelines*, but it should be noted that most limits associated with silica are supplied by the fuel suppliers rather than the EPRI Water Chemistry Guidelines. While this project included engagement with two fuel vendors, Framatome and Westinghouse, further engagement with fuel suppliers will be required to fully realize all of the potential benefits. Utilities can use this work to support discussions with their fuel suppliers related to silica limits.

## LEARNING AND ENGAGEMENT OPPORTUNITIES

- Revision 7 of the EPRI PWR Primary Water Chemistry Guidelines, published in 2014, is currently in the industry review process. Review meetings were held in 2017 and 2019 and the Committee did not recommend revision of the document. The next review meetings will be held in 2021 to discuss the status of PWR primary chemistry control. EPRI member utilities are encouraged to engage in the review and revision process.
- The PWR Chemistry Technical Strategy Group (TSG) was the primary funder of this work. In addition to collaborative R&D, the TSG also holds an annual meeting to discuss topics such as this and operating experience. Member utilities are encouraged to attend the meeting and engage in other TSG activities.
- This work was completed collaboratively with the Materials Aging Institute and results will be used to inform future work in the CHEOPS project.

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# 1
# INTRODUCTION

Deposition of compounds such as zinc silicate and calcium, magnesium, and aluminum zeolites (known to have very low thermal conductivities) can increase the thermal resistance between the fuel and the coolant, potentially increasing PWR fuel cladding surface temperatures leading to increased cladding corrosion rates and possibly failures [1]. As a result, PWR fuel vendors have established silica concentration limits for the primary coolant, makeup water, boric acid storage tank and refueling water storage tank [2, 3]. For example, Westinghouse requirements for primary coolant silica concentrations at low and high boiling duty plants prior to and during zinc injection are summarized in Table 1-1 [2].

Revision 7 of the EPRI *PWR Primary Water Chemistry Guidelines* [1] lists primary coolant silica as a diagnostic parameter during power operation but notes that silica limits may be imposed by the fuel vendor. Makeup water silica is listed as a diagnostic parameter with an expected value of <100 ppb. The Guidelines note that operating with primary coolant silica concentrations of 1 to 3 ppm has not resulted in any significant fuel corrosion issues when makeup water aluminum, calcium, and magnesium concentrations are well controlled, i.e., <80, <40 and <40 ppb, respectively. Westinghouse notes that "High silica concentrations in conjunction with coolant zinc have not been associated with CIPS or other crud related problems" [2]. In addition, "zinc silicate deposits have not been detected in fuel deposits" [2]. However, these observations are limited to situations where silica has been controlled within Westinghouse fuel warranty limits.

As indicated in Table 1-1, the primary coolant silica concentration limit is reduced significantly when a plant adopts zinc chemistry to reduce the risk of formation of zinc-silicates on cladding surfaces. Since primary coolant silica concentrations routinely exceed 1 ppm at the beginning of the cycle, particularly when Boraflex is employed in the spent fuel pool, the lower limit extends the time before plants can achieve the full radiation field benefits of zinc injection. In addition, water management can become an issue, and operating costs can increase. Reverse osmosis (RO) systems have been installed at several plants to reduce spent fuel pool silica concentrations even though capital costs are high.

The objective of this project was to evaluate available data on the likelihood of zinc silicate precipitation on PWR fuel cladding surfaces and its effect on deposit thermal resistance. The following issues were addressed during the evaluation:

- Zinc silicate precipitation was predicted to occur in PWR fuel cladding deposits at relatively low deposit solution to primary coolant concentration factors by MULTEQ with Database Version 8 [4]. However, when borate-silicate ion pairs were considered based on solubility data of silicates in boric acid solution [5], zinc precipitation was not predicted until concentration factors were much higher, and the precipitate was zinc oxide not zinc silicate.

- Although there was no evidence of a significant effect of zinc silicate deposition on PWR fuel cladding corrosion, fuel deposit analyses at the River Bend BWR by Framatome (formerly AREVA) at EOC 11 identified zinc silicate crystals at fuel failure locations (see Section 3.1). Pore blocking by the precipitate was identified as a possible cause of the failures [10, 11, 12].
- The likelihood of precipitate formation increases as the coolant silica and zinc concentrations increase and fuel boiling duty increases, and plant data were not available for periods of operation when the silica concentration exceeded 1 ppm and zinc injection was being performed.

To address these issues, the project was divided into several tasks:

- In Section 2, predictions of zinc silicate solubility in PWR fuel cladding deposits based on MULTEQ employing Database Versions 8 and 9 and predictions developed by Framatome [3] using the OLI code are considered.
- Section 3 is an assessment of the applicability to PWRs of the River Bend EOC 11 deposit analyses developed by Framatome.
- WALT loop tests on the effect of silica and zinc concentrations on zinc silicate deposition and its effect on thermal resistance of simulated fuel deposits are considered in Section 4.
- In Section 5, possible application of primary coolant zinc mass balances for estimating zinc compound deposition is assessed. Such balances allow real time assessments of zinc retention in the primary system. In addition, the maximum amount of zinc incorporation into fuel deposits can be estimated.
- Silica mass balances for three high duty plants are developed and discussed in Section 6. These balances allow more accurate estimates of the maximum amount of zinc silicate precipitate incorporated into the fuel deposits to be developed. In addition, they provide a tool for estimating maximum deposition rates during the cycle.

Project results are summarized and recommendations for future work are provided in Section 7.

**Table 1-1**
**Summary of Westinghouse RCS Silica Requirements during Power Operation for Zinc Plants [2]**

| Fuel Duty (1) | Silica (ppb) Prior to Active Injection | Silica (ppb) After 60 Days at BOC | Silica (ppb) During Active Injection | Required Monitoring Frequency |
|---|---|---|---|---|
| Low Duty | ≤ 3000 ppb | ≤ 3000 ppb | ≤ 2000 ppb (2) | 1/week |
| High Duty | ≤ 3000 ppb | ≤ 1000 ppb | ≤ 1000 ppb (2) | 1/week |

Note 1: Fuel duty based on Westinghouse mass evaporation rate criteria per VIPRE-W code

Note 2: Operation above silica limit while actively injecting zinc requires that fuel exams be performed to confirm acceptable corrosion performance

# 2

# MULTEQ PREDICTIONS OF ZINC HYDROXIDE AND SILICATE PRECIPITATION

## 2.1 MULTEQ 4.2 Database Version 8 [4]

To provide an initial perspective relative to the tendencies for zinc oxide and zinc silicate precipitation in PWR fuel deposits when subcooled nucleate boiling is occurring, the soluble zinc concentration in the deposit solution at initiation of precipitation was estimated using MULTEQ 4.2 with Database Version 8 [4]. Note Section 2.2 evaluates the updated MULTEQ Version 9 [5] of the Database, which includes an update to the behavior of silica and zinc. This review of Version 8 is provided for comparison as existing understanding and guidance related to silica behavior in the PWR primary is largely based on these thermodynamic models. Calculations were performed for a primary coolant zinc concentration of 20 ppb in the absence of silica and at a silica concentration of 1 ppm. Results are shown in Figure 2-1 as a function of the primary coolant boron concentration at $pH_{300C}$ of 7.2. All MULTEQ calculations were performed with an initial boiling temperature of 310 °C and a maximum solution temperature of 320 °C. Zinc and silica reactions with iron and nickel were not considered.

Zinc oxide solubility in the absence of silica at beginning of cycle (BOC) chemistries was estimated to be approximately 210 ppb as zinc, which corresponds to a concentration factor (CF) in the deposit solution of approximately 11 relative to the primary coolant (see Figure 2-2). The soluble species were $Zn(OH)_2^0$ (~91%), $Zn(OH)_3^{-1}$ (~7%) and $Zn(OH)^{+1}$ (~2%). In the presence of 1 ppm silica, the zinc solubility decreased to approximately 110 ppb, i.e., a CF of approximately 6 relative to the primary coolant. $Zn_2SiO_4$ was the precipitate. Silica was primarily present in solution as $H_4SiO_4^0$ (~99%).

The relation of the primary coolant zinc and silica concentrations to the deposit zinc concentration at the initiation of zinc silicate precipitation is shown in Figure 2-3 and Figure 2-4 for BOC conditions ($pH_{300C}$ = 7.2 and 1200 ppm boron). As expected, the predicted CF in the deposit at initiation of precipitation decreases as the coolant zinc concentration increases at fixed silica or as the coolant silica concentration increases at fixed zinc (see Figure 2-5).

Note that the concentration factor required for precipitation does not vary linearly with the silica concentration at a fixed coolant zinc concentration, e.g., the allowable CF before precipitation only decreases a factor of 1.8 as the silica concentration varies from 1 to 5 ppm at a zinc concentration of 10 ppb. This result is encouraging relative to relaxing the current silica limit of 1 ppm, i.e., if precipitation does not occur at 1 ppm silica at a zinc concentration of 10 ppb in a deposit with a maximum CF of 11, it also would not occur at a silica concentration of 2 ppm if the zinc concentration was reduced to 8 ppb. The variation in the allowable zinc concentration as a function of silica concentration prior to zinc silicate deposition at a deposit solution CF of 11 is shown in Figure 2-6.

## 2.2 MULTEQ 4.2 Database 9 [5]

A second set of calculations was performed using MULTEQ Database Version 9, which includes consideration of silicate-borate ion pairs. The basis for the consideration of such ion pairs was recently reviewed by Dickinson [6]. Predictions based on Database Version 9 are summarized in Figure 2-7 and Figure 2-8. Results of comparable calculations using Database Version 8 are shown in the same format in Figure 2-9. As shown, Database Version 9 results are markedly different than those with Database Version 8. Much higher deposit concentration factors are necessary before zinc silicate precipitation occurs when the silicate-borate ion pairs are considered. As a result, ZnO precipitation initially occurs, and $Zn_2SiO_4$ precipitation does not occur unless ZnO precipitation is suppressed.

The predicted tendencies for zinc silicate precipitate formation based on Database Version 9 can be summarized as follows:

- At concentrations of 1 to 3 ppm $SiO_2$ and 10 ppb zinc, $Zn_2SiO_4$ precipitation is not predicted at a concentration factor less than 100 as a result of preferential ZnO precipitation and the formation of silicate-borate ion pairs (Figure 2-7). Approximately 80% of the zinc is precipitated as ZnO at a CF of 100. (As shown above, $Zn_2SiO_4$ precipitation is predicted to occur at concentration factors of less than 10 based on Database Version 8.)
- At 5 ppm silica and 10 ppb zinc, $Zn_2SiO_4$ is formed at a CF of 12, but this precipitate dissolves at higher concentration factors, and ZnO becomes the primary precipitate.
- If ZnO precipitation is mathematically suppressed, $Zn_2SiO_4$ precipitation is predicted to occur at concentration factors of approximately 48, 28, 20 and 12 at a zinc concentration of 10 ppb and silica concentrations of 1, 2, 3 and 5 ppm, respectively.

## 2.3 FRAMATOME Calculations [3]

Framatome employed the OLI Analyzer code to evaluate the tendencies for $Zn_2SiO_4$ precipitation for the chemistries summarized in Table 2-1 [3]. Since ZnO precipitation was predicted to occur at very low concentration factors, ZnO and $Zn(OH)_2$ precipitation was suppressed to evaluate the potential for $Zn_2SiO_4$ precipitation. In this case, results indicated that $Zn_2SiO_4$ precipitation would not occur at concentration factors up to 500 at 20 ppb zinc and 1.5 ppm silica. At 3 ppm silica and 20 ppb zinc, $Zn_2SiO_4$ precipitation was still not predicted to occur, but the $Zn_2SiO_4$ solubility limit was being approached.

These results differ significantly from those developed using MULTEQ with Database Versions 8 and 9, although Database Version 9 predictions are more similar to OLI predictions.

## 2.4 Implications

Review of MULTEQ and OLI solution chemistry modeling results at PWR chemistries indicates that differences in the predicted tendencies for zinc silicate precipitation are significant. As a result, such predictions should be viewed with caution. Zinc silicate precipitation is predicted with MULTEQ (Database Version 8) at relatively low primary coolant to deposit solution concentration factors. However, MULTEQ results with Database Version 9, which considers silicate-borate ion pairs, indicate zinc oxide is formed before zinc silicate at silica concentrations less than 5 ppm and a zinc concentration of 10 ppb. OLI code results developed by Framatome also indicate zinc oxide will be formed before zinc silicate. Although the solution chemistry modeling results differ in detail, formation of a zinc silicate precipitate in PWR fuel deposits is not predicted by current versions of either code as a result of preferential zinc oxide formation.

**Table 2-1**
**Solution Chemistry for OLI Zinc Silicate Solubility Calculations [3]**

| Parameter | Concentration |
|---|---|
| Boron | 1200 / 600 / 50 ppm |
| Lithium | 3.5 / 1.75 / 0.5 ppm |
| Hydrogen | 40 cc/kg |
| Silica ($SiO_2$) | 1.5 / 3 / 6 ppm |
| Zinc | 10 / 20 ppb |

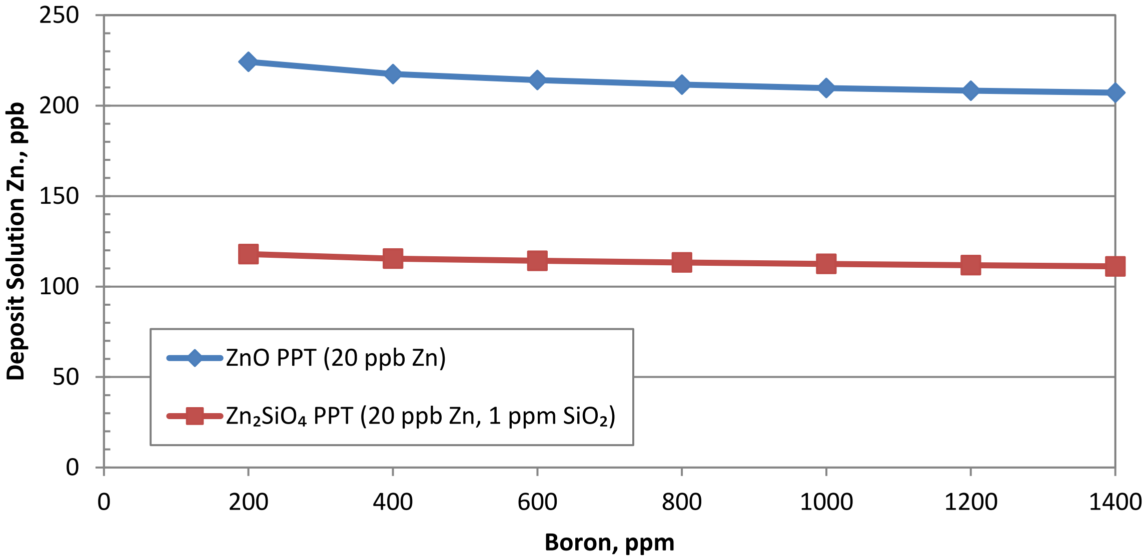

**Figure 2-1**
**Deposit Solution Zinc Concentration at Initiation of Precipitation (Coolant $pH_T$=7.2 at 300 °C) (MULTEQ 4.2 Database Version 8)**

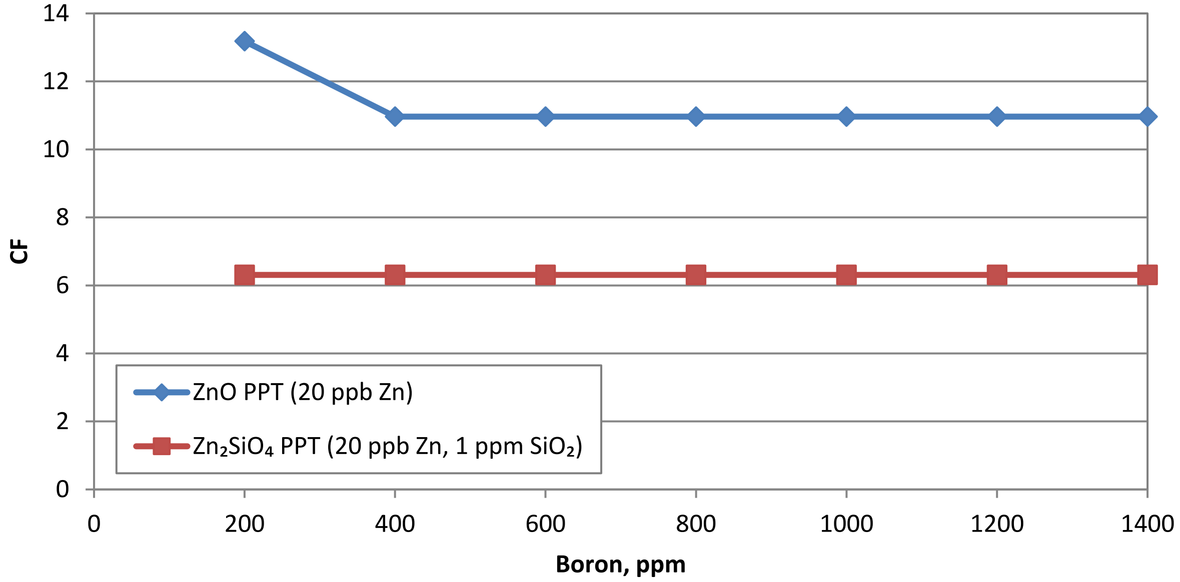

**Figure 2-2**
**Concentration Factor at Initiation of Zinc Oxide and Silicate Precipitation in the Fuel Deposit (Coolant $pH_T$=7.2 at 300 °C) (MULTEQ 4.2 Database Version 8)**

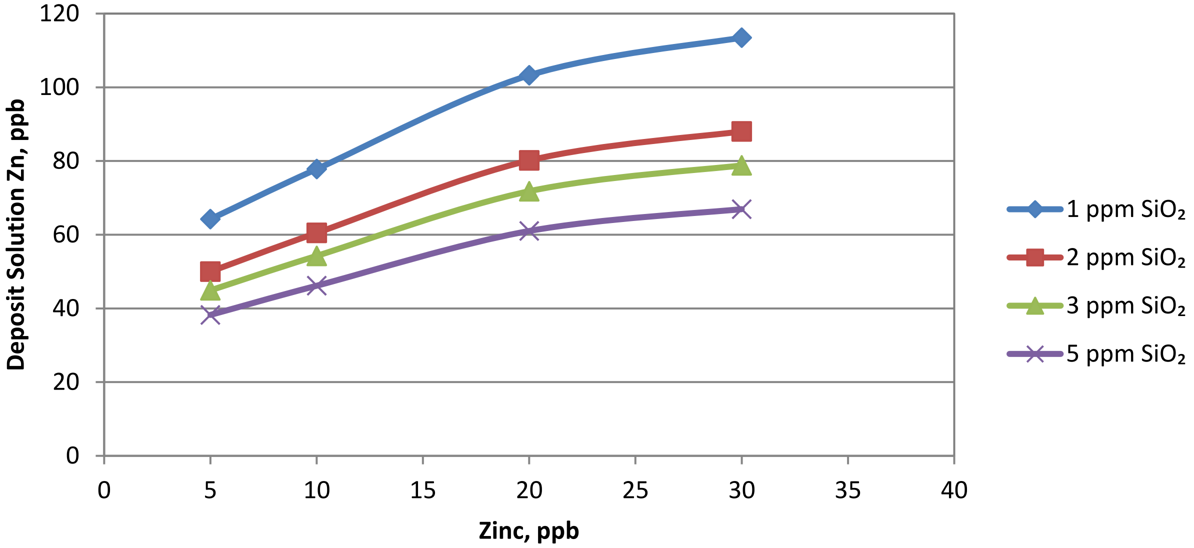

**Figure 2-3**
**Effect of Primary Coolant Zinc Concentrations on Solution Zinc Concentration at Initiation of Precipitation in the Fuel Deposit ($pH_{300C}$ = 7.2, Li = 4.14 ppm, B = 1200 ppm) (MULTEQ 4.2 Database Version 8)**

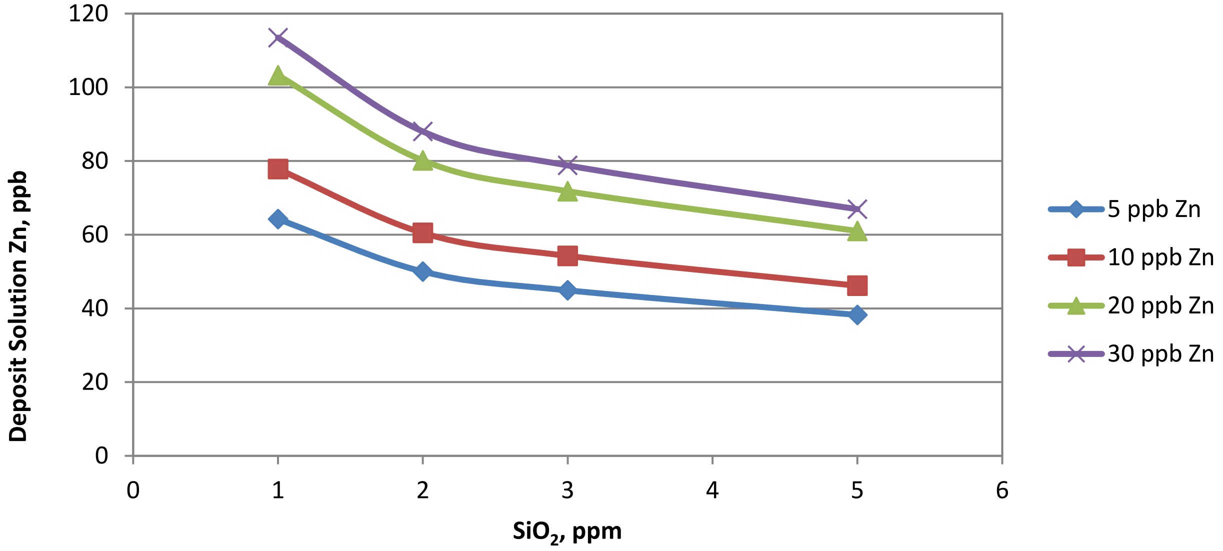

**Figure 2-4**
**Effect of Primary Coolant Silica Concentrations on Deposit Solution Zinc Concentration at Initiation of Precipitation in the Fuel Deposit ($pH_{300C}$ = 7.2, Li = 4.14 ppm, B = 1200 ppm) (MULTEQ 4.2 Database Version 8)**

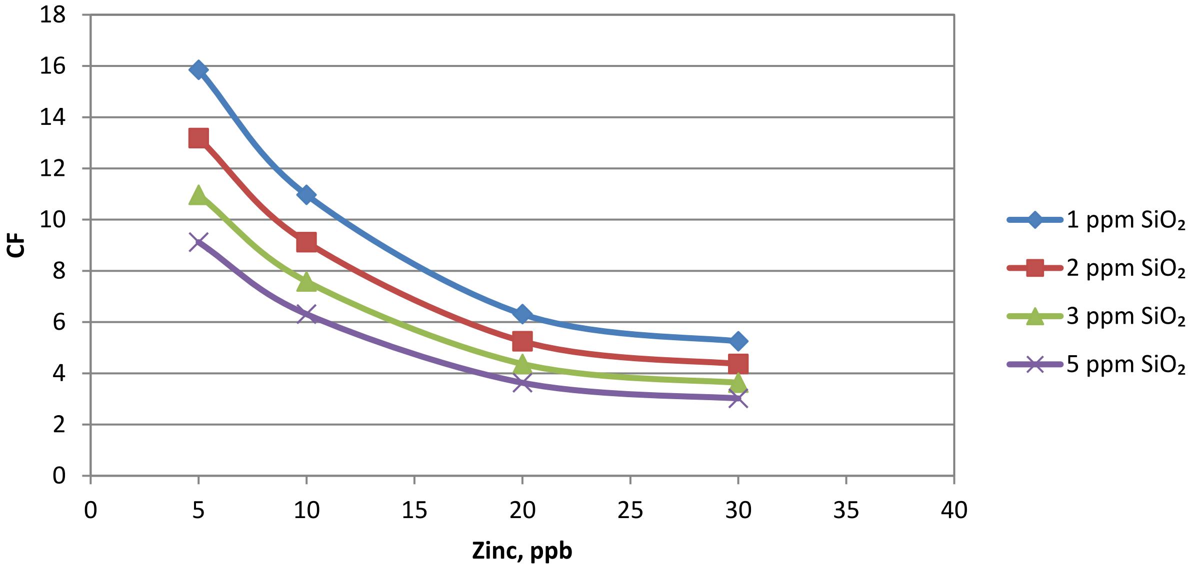

**Figure 2-5**
**Concentration Factor at Initiation of Precipitation in the Fuel Deposit ($pH_{300C}$ = 7.2, Li = 4.14 ppm, B = 1200 ppm) (MULTEQ 4.2 Database Version 8)**

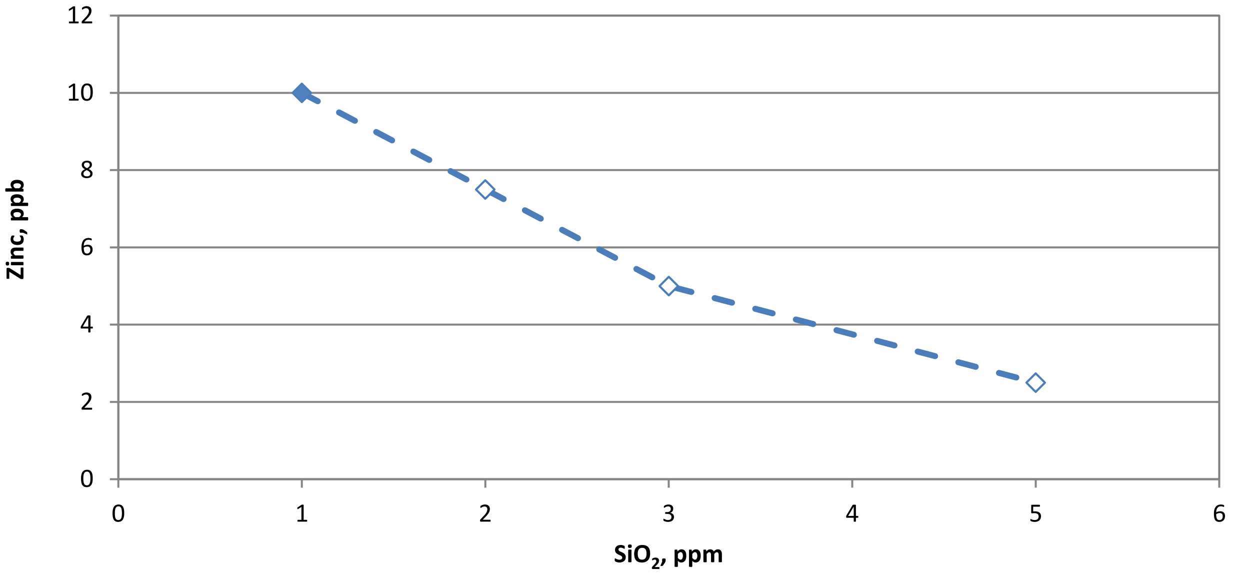

**Figure 2-6**
**Allowable Primary Coolant Zinc Concentration prior to Zinc Silicate Precipitation at a Deposit Solution Concentration Factor of 11 ($pH_{300C}$ = 7.2, Li = 4.14 ppm, B = 1200 ppm) (MULTEQ 4.2 Database Version 8)**

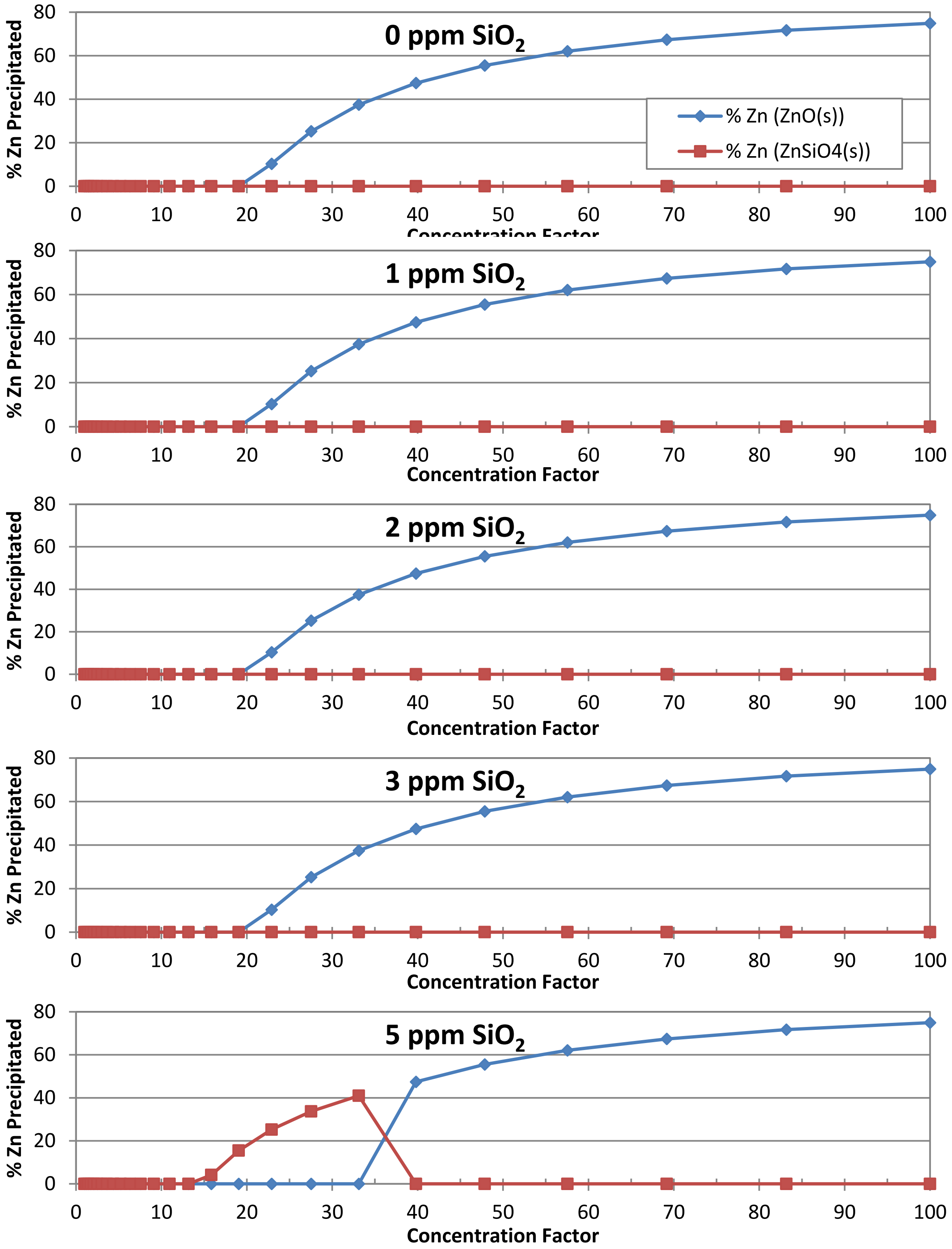

**Figure 2-7**
**Effect of Silica Concentration on Zinc Compound Precipitation (MULTEQ 4.2 Database Version 9: 10 ppb Zn, $pH_{300C}$ = 7.2, (B = 1200 ppm, Li = 4.14 ppm))**

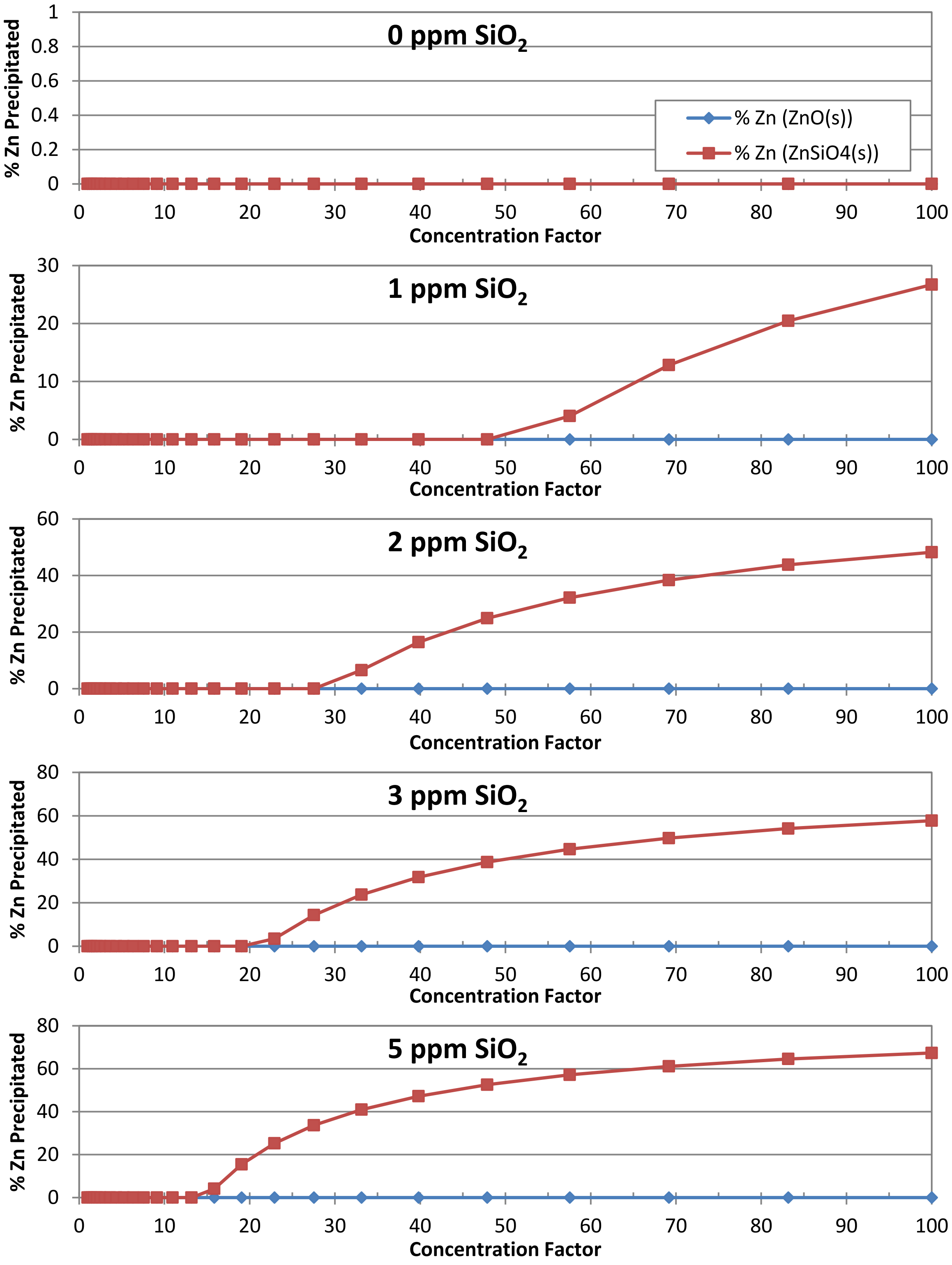

**Figure 2-8**
**Effect of Silica Concentration on Zinc Compound Precipitation (MULTEQ 4.2 Database Version 9 with ZnO Suppressed: 10 ppb Zn, $pH_{300C}$ = 7.2, (B = 1200 ppm, Li = 4.14 ppm))**

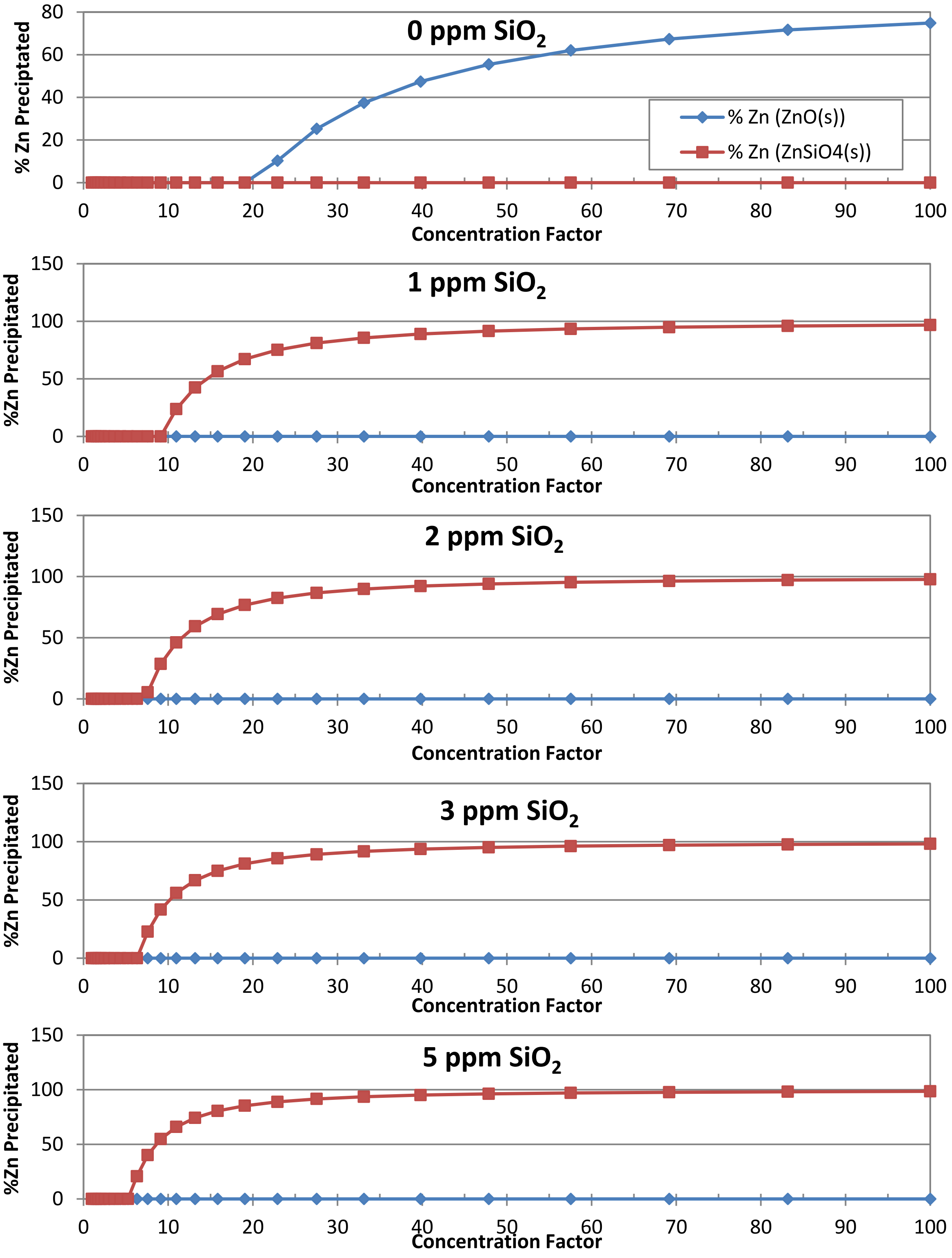

**Figure 2-9**
**Effect of Silica Concentration on Zinc Compound Precipitation (MULTEQ 4.2 Database Version 8: 10 ppb Zn, $pH_{300C}$ = 7.2, (B = 1200 ppm, Li = 4.14 ppm))**

# 3

# CORROSION PRODUCT DEPOSITION ON FUEL

As noted above, deposition of compounds such as zinc silicate and calcium, magnesium, and aluminum zeolites on fuel cladding surfaces can potentially increase cladding surface temperatures leading to increased cladding corrosion rates and possibly failures [1]. Numerous PWR fuel cladding deposit (crud) evaluations have been completed by Westinghouse and Framatome [e.g., 7, 8, 9], and while deposits containing silica have been found, concentrations are generally very low. The silica source has generally been contamination of the reactor coolant by spent fuel pool water during refueling. To date, the presence of silica in PWR fuel deposits has not been identified as a fuel reliability issue.

In a recent summary of crud analyses by Framatome [3], they noted that silicon, aluminum, calcium, magnesium and zinc have been observed in fuel crud. Although the percentages of these elements have normally been low (<1% by weight), high percentages of zinc have been observed. In addition, silica and silicates have been major constituents (>20% by weight) in some samples, but the crud in these cases was very thin (<5 μm) and did not represent a corrosion risk.

A review by Westinghouse for possible connections between zinc/silica and crud induced power shift (CIPS) and crud induced localized corrosion (CILC) was completed for this project [2]. It was concluded that high silica concentrations in conjunction with coolant zinc have not been associated with CIPS or other crud related problems. However, they noted that while zinc silicate deposits have not been detected in fuel deposits, zinc silicate has been found in secondary side steam generator deposits. It is usually found comingled with ZnO deposits, suggesting that the solubilities of the two compounds are similar under steam generator conditions.

In contrast to the PWR fuel deposit observations, zinc silicate crystals have been observed in BWR fuel deposits and have been identified as a possible contributor to fuel failures at River Bend during Cycle 11 as discussed below.

## 3.1 River Bend Cycle 11 Fuel Deposit Observations [10, 11, 12]

In BWRs, deposition of particulate iron is the primary mechanism of deposit formation. Most iron transported to the reactor vessel by the feedwater deposits on the fuel. A significant fraction of the feedwater zinc transport also deposits. Zinc (as well as copper) is enriched in the deposit adjacent to the cladding surface where precipitates of these species develop. Deposition generally peaks at 30 to 60 inches from the core inlet.

Zinc addition, depleted zinc oxide (DZO), was initiated at River Bend in Cycle 7 with Cycle 8 being the first full zinc cycle. Zinc was not applied in Cycle 9 due to fuel failure experience in Cycle 8, but was resumed in Cycle 10 and continued in Cycle 11. Prior cycles were operated under normal water chemistry, NWC, but Cycle 11 was the first cycle operated with moderate hydrogen water chemistry, HWC-M. During Cycle 11, River Bend was operating with full flow deep bed condensate demineralizers without prefilters. This resulted in elevated feedwater iron concentrations, i.e., a cycle average of ~3.1 ppb [13]. The cycle average feedwater zinc and copper concentrations were ~0.5 and ~0.2 ppb, respectively. As shown in Figure 3-1 [10, 11], significant deposition was observed in lower regions of the core. Crud deposition patterns during Cycle 11, when several fuel failures occurred, were consistent with those expected at a BWR.

SEM/EDS analyses of 17 deposit flake samples obtained from River Bend Cycle 11 fuel were performed by Framatome (formerly AREVA). Failures were in 7 rods from 6 Atrium 10 bundles on the F1, G1, A6 and A7 positions, always on the blade side. No interior rods failed. Emphasis was on two flakes (A and C) from a failed rod from bundle KAN036, and one flake (D) from a failed rod and one flake (B) from an adjacent unfailed rod of bundle KAN031. All flakes were brushed and rinsed with acetone to remove loose deposit before analysis. This approach would be expected to preferentially remove iron deposits, which are loose and flocculent at the reactor water/deposit interface.

The following results were reported in EPRI 1009733 [11] and 1012910 [12]:

- Deposit structures at all locations were very complex.
- Enrichment of zinc and silicon was observed in all flakes in the crud layers closest to the fuel pin surface.
- Zinc, silica and copper were the main contributors to increasing crud density in the fuel pin failure region. Zinc silicate crystals were identified in the Flake A deposit at the rod interface.
- In Flake A, large zinc silicate crystals interwoven with copper species covered the walls of the fuel side crud crevice, "apparently closing a number of wick boiling chimneys." None of the other flakes obtained from span 2 of failed pins had such striking crystalline features. The deposit adjacent to the cladding had 61.5% zinc and 11% Si. The exterior of the deposit had 40% Fe, 34% Zn and 3 to 4% Si. The deposit was very dense in the failure region at the fuel rod surface (4.21 g/cm$^3$).
- Flake B had 36% Zn, 29% Fe and 10% Si. Chimney density was 30,000 to 70,000/mm$^2$. The average porosity was ~47 %. The thickness was 2 to 4 mils. Flake A average porosity was 32%.
- The deposit was different at failed and unfailed locations. No crystals were observed at the unfailed locations.
- The authors concluded that the plugging of the exit of capillaries toward the fuel side crud crevices by cementacious agents such as copper, silicate, zinc and aluminum was demonstrated. The perspective of the EPRI Project Manager on this issue differed: "Although no definitive evidence was found with respect to the blockage of the pores and/or capillaries, which will result in reduction in the heat transfer capability of the crud, it is speculated that local deposition of CuO or others may play such a role."

To provide a basis for considering the implications of the River Bend results relative to the tendencies for zinc silicate precipitation in a PWR fuel deposit, deposit formation in BWRs is briefly reviewed below.

## 3.2 Applicability of BWR Observations to a PWR

### 3.2.1 General Considerations

To reduce shutdown dose rates at BWRs, zinc is routinely injected into the feedwater to increase reactor water zinc concentrations. As a result of the elevated zinc concentration, stainless steel corrosion rates, reactor water Co-60 concentrations, and the incorporation rate of Co-60 into out of core deposits are reduced. In the *BWR Water Chemistry Guidelines* [13], the feedwater zinc concentration is limited to a cycle average of 0.4 ppb and a quarterly average of 0.5 ppb to minimize concerns of fuel deposit spalling. In some cases, the feedwater concentration limit has been relaxed after a review of the deposit spalling risk by the fuel vendor.

The effect of zinc on BWR fuel deposits is expected to differ markedly from that in PWRs for several reasons:

- The amount of zinc injected and deposited on the fuel is much greater at a BWR than at a PWR. For example, approximately 36 kg is injected at an 1100 $MW_e$ BWR over an 18-month cycle at a feedwater concentration of 0.4 ppb. The amount injected over a 24-month cycle at a PWR after several cycles of operation with zinc is generally in the range of 3 to 5 kg (see Section 5).
- Sixty to 90% of the injected zinc is deposited on the fuel at a BWR. After 3 to 4 cycles of operation with zinc at a PWR, 20 to 40% of the amount injected is retained in the system based on the difference in the amount injected and that removed by the CVCS. Based on modeling results using the BOA Risk Assessment Tool [14], more than 80% of the retained zinc is incorporated into out of core surfaces by diffusion. Approximately 20% is deposited on the fuel. On this basis, the mass of zinc incorporated into BWR fuel deposits is on the order of 50 to 100 times greater than that incorporated into PWR deposits during a fuel cycle.
- BWR reactor water silica concentrations generally vary from 50 to 300 ppb during a cycle with a fleet median cycle average of ~100 ppb. PWR primary coolant silica concentrations generally are near 1 ppm at the beginning of zinc injection, but are generally higher at the beginning of the cycle. Concentrations gradually decrease with operating time at PWRs to below 100 ppb at the end of the cycle (see Section 6).
- BWRs operate at neutral chemistry ($pH_T$ = ~5.6) whereas PWR $pH_T$ is normally controlled at 7.1 to 7.4 with a minimum $pH_T$ of 6.9.
- BWR reactor water temperature is approximately 288 °C compared to ~320 °C in boiling regions of the PWR core.
- Boiling occurs over most of the BWR fuel surface with deposition peaking markedly at 30 to 60 inches from the bottom of the core. Boiling in the PWR is generally limited to upper regions of the bundle, i.e., generally spans 5 to 6 of Westinghouse cores [15], and the heat transfer mode is subcooled nucleate boiling compared to bulk boiling in a BWR.

### 3.2.2 Deposition on River Bend Fuel during Cycle 11

Feedwater and reactor water zinc and iron concentrations during River Bend Cycle 11 are shown in Figure 3-3 and Figure 3-4, respectively. Zinc and iron mass balances are shown in Figure 3-5. Transport rates to the reactor coolant system were calculated from the feedwater flowrate and iron and zinc concentrations. The amount removed by the reactor water cleanup system (RWCU) was estimated from the RWCU flowrate, reactor water concentrations, and assuming 100% RWCU removal efficiency.

During Cycle 11, the total iron input to the core via the feedwater was 225 kg (495 lb). The zinc input was 30 kg (66 lb). Iron and zinc deposition on the fuel were approximately 92% and 88% of the feedwater inputs, respectively. This results in an average fuel deposit composition of approximately 85% iron and 11% zinc based on the metals. The major phases observed in PWR deposits are nickel iron spinel, nickel oxide, and nickel metal [1], while the major phases in BWR deposits are hematite, $Fe_2O_3$, and magnetite, $Fe_3O_4$.

## 3.3 Zinc Compound Deposition Tendencies based on MULTEQ 4.2 Database Version 9

MULTEQ 4.2 calculations of zinc compound deposition tendencies at a BWR and PWR based on Database Version 9 are compared in Figure 3-6. In the PWR, zinc oxide is predicted to precipitate before zinc silicate with initial precipitation at a deposit solution to bulk water concentration factor of approximately 20. At a BWR, zinc silicate is predicted to precipitate before zinc oxide with initial precipitation at a deposit solution to bulk water concentration factor of approximately 10. The differences appear to result primarily from the formation of silicate-borate ion pairs in the PWR case.

## 3.4 Summary

Based on the major differences in BWR and PWR chemistry, deposit compositions, magnitudes and structures, and the predicted difference in the tendency for zinc silicate formation in BWR and PWR deposits, extrapolation of corrosion product observations made at a BWR to a PWR cannot be supported.

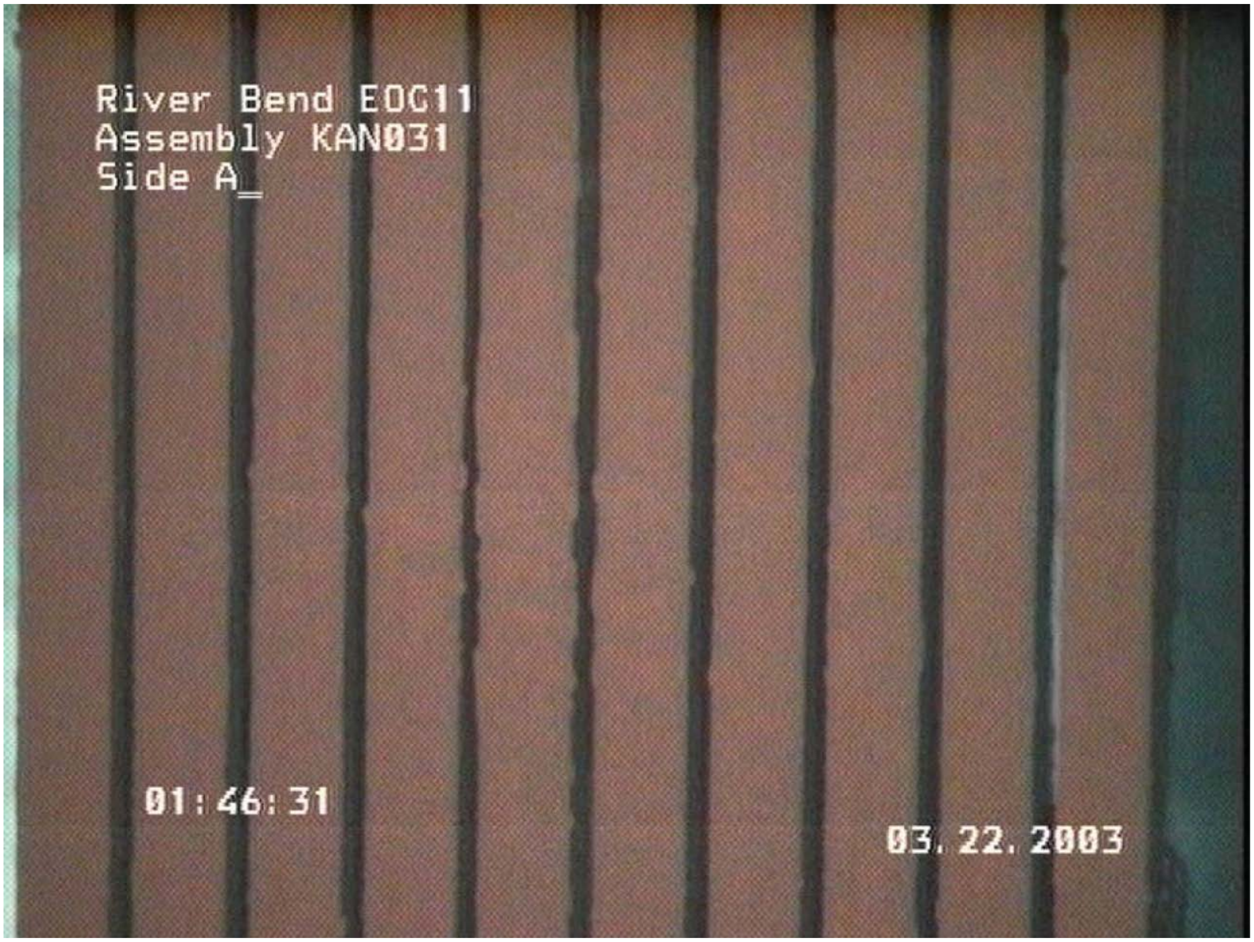

**Figure 3-1**
**Example of Heavy Crud on Span 2 of River Bend Fuel at EOC 11 [11]**

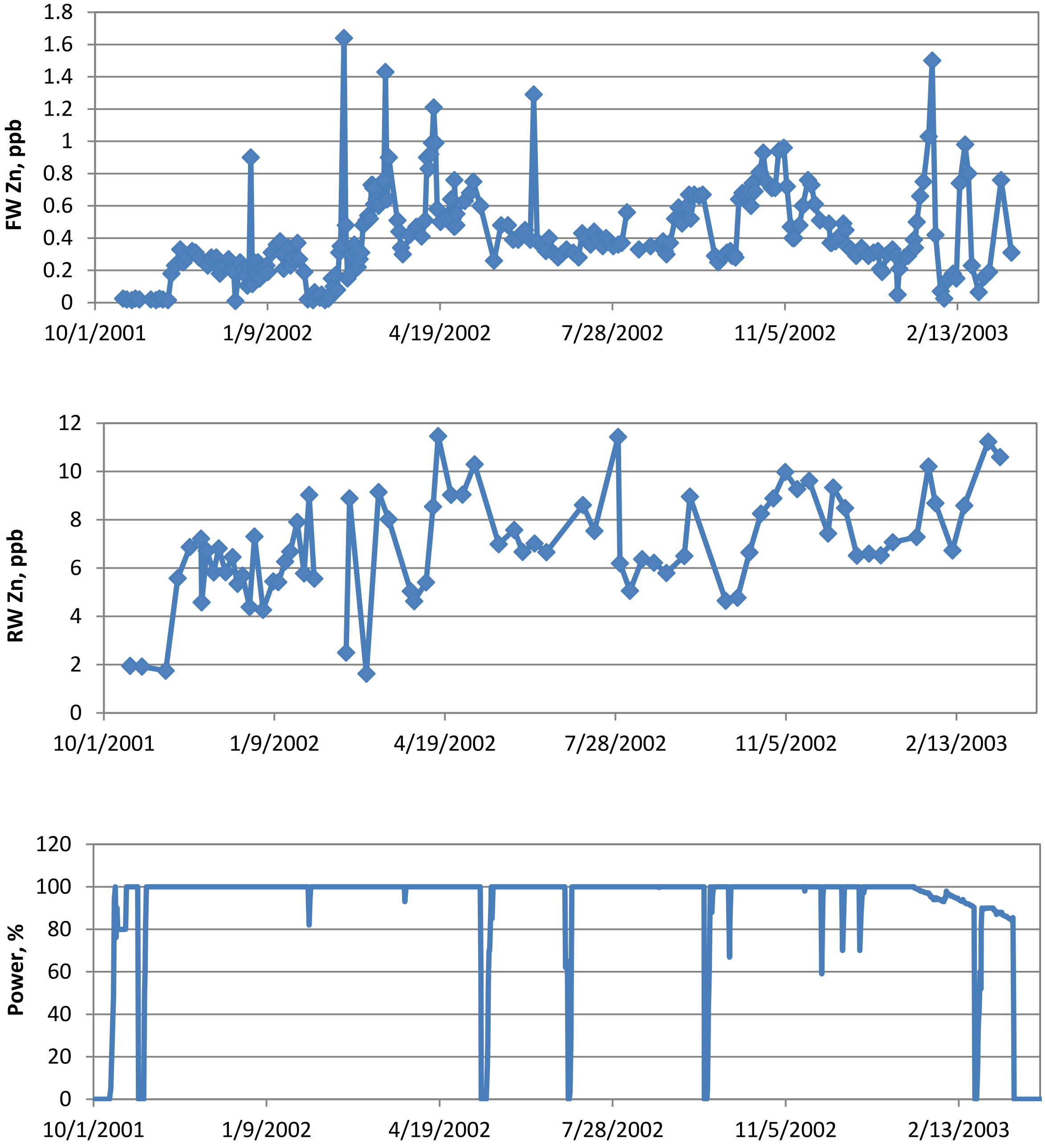

**Figure 3-2**
**River Bend Cycle 11 Zinc Concentrations**

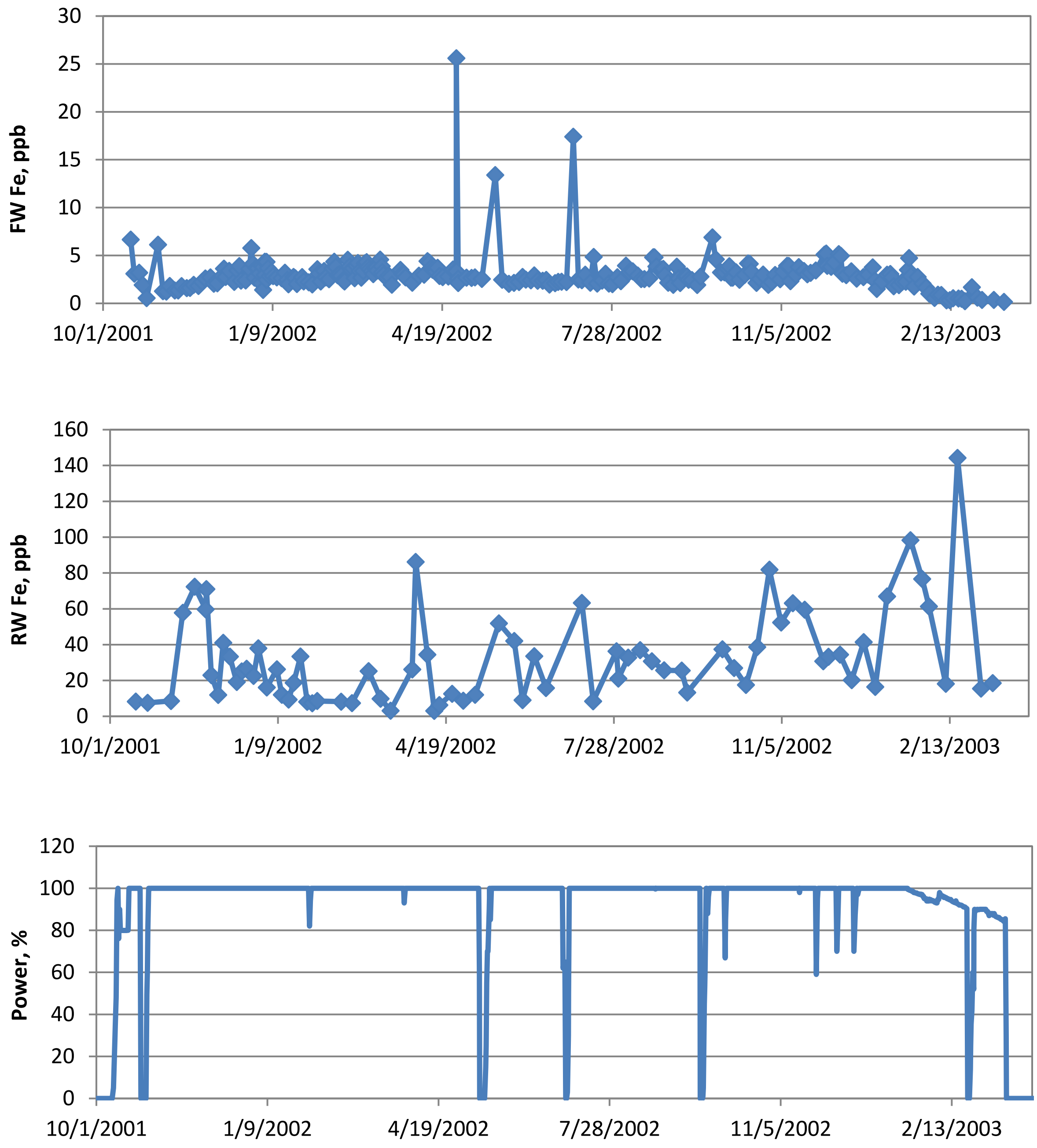

**Figure 3-3**
**River Bend Cycle 11 Iron Concentrations**

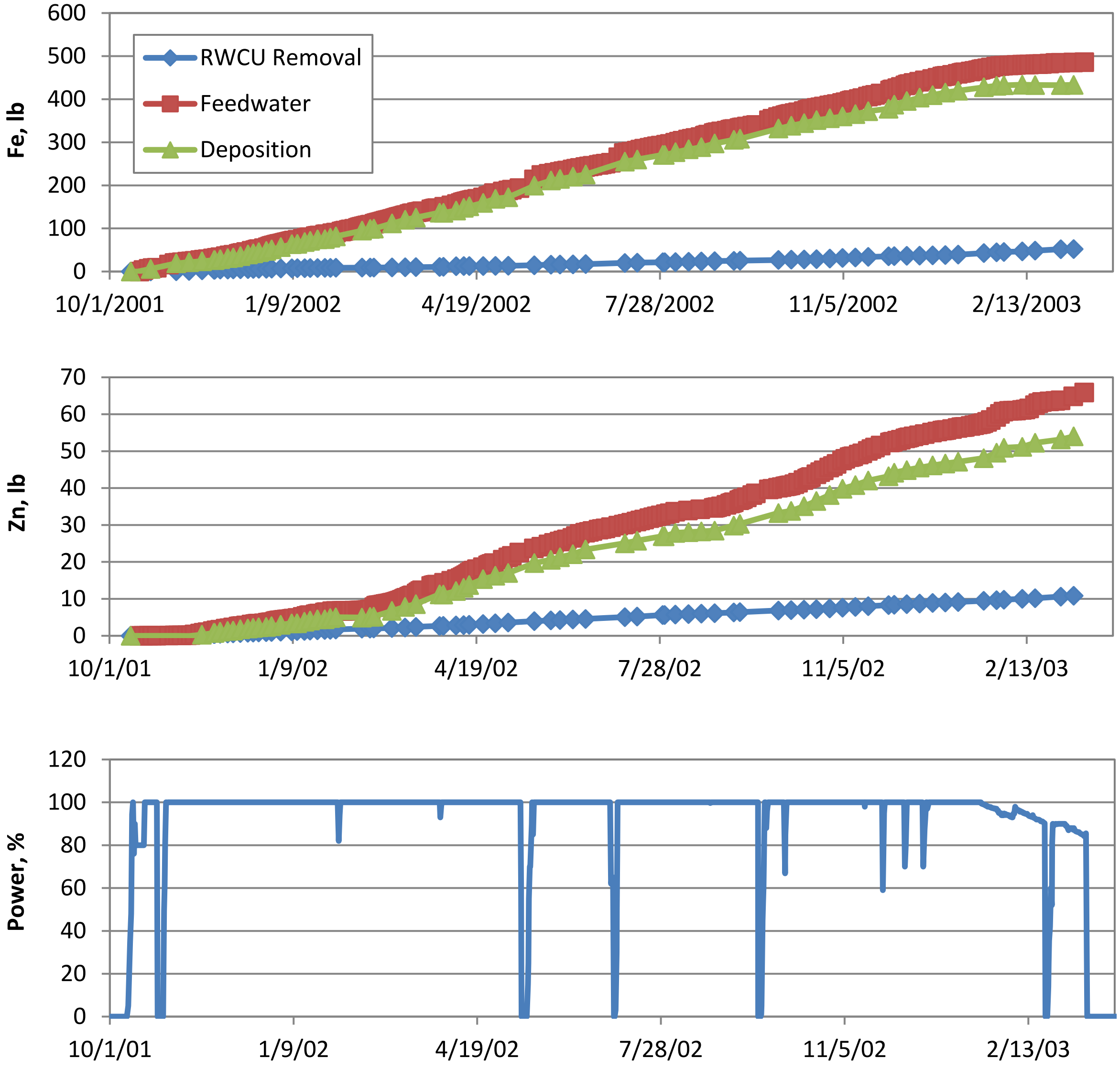

**Figure 3-4**
**River Bend Cumulative Deposit Formation during Cycle 11**

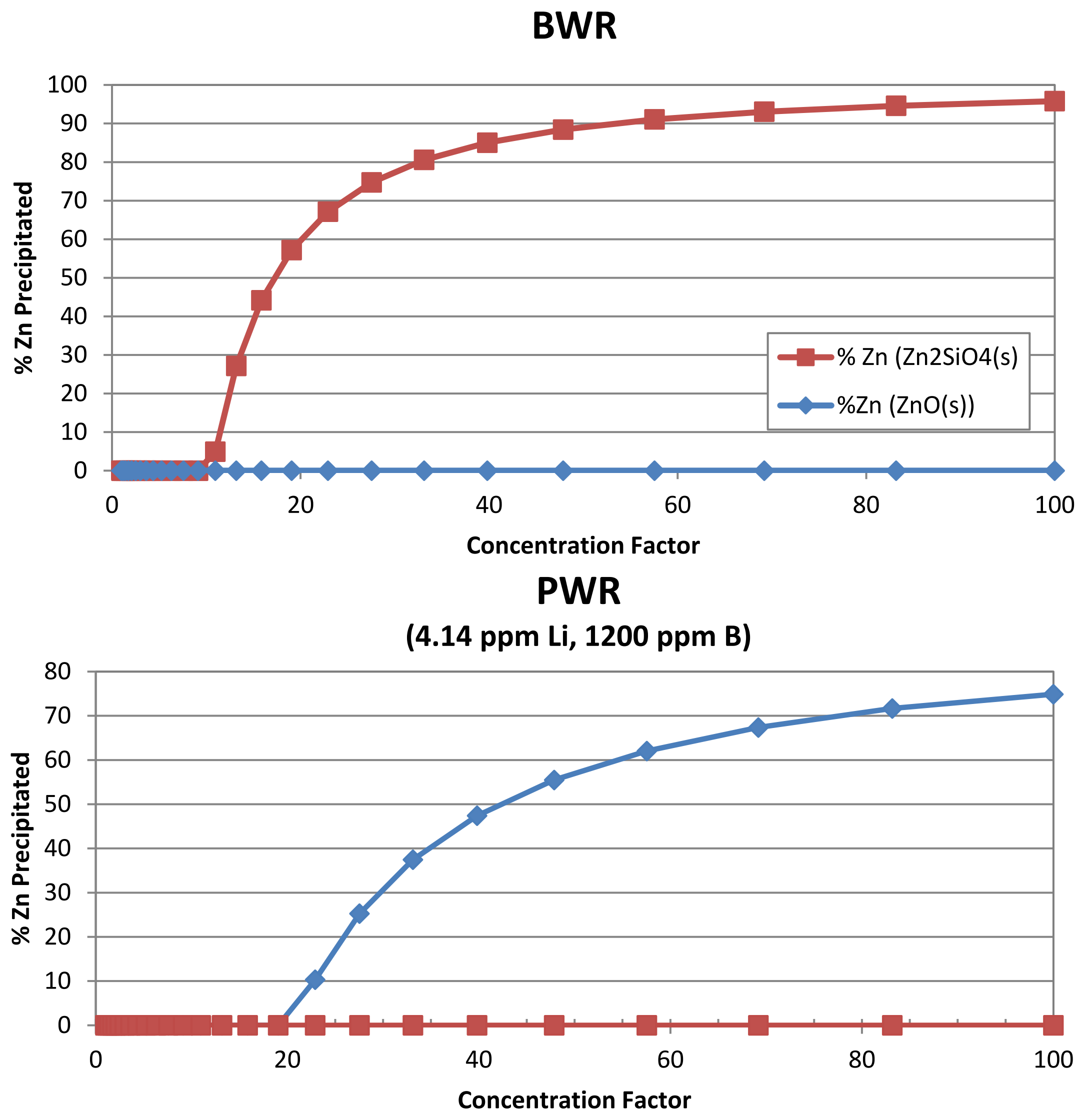

**Figure 3-5**
**Zinc Compound Precipitation Tendencies at BWR and PWR Chemistries (MULTEQ 4.2, Database Version 9; 1 ppm Silica and 10 ppb zinc)**

# 4

# TENDENCIES FOR ZINC COMPOUND PRECIPITATION ON PWR FUEL SURFACES: WALT LOOP TEST RESULTS [16, 17]

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Numerous WALT loop tests have been performed by Westinghouse to evaluate the impact of the precipitation and incorporation of zinc compounds and zeolites on the thermal resistance of simulated PWR corrosion product deposits [e.g., 16, 17]. Deposits simulating those observed on PWR fuel can be developed in the WALT facility on electrically heated Zircaloy tubing. Tests to assess the impact of zinc silicate precipitation on the crud thermal resistance were performed with crud thicknesses of 50 to 75 μm. Zinc silicate precipitation was not observed even in a highly-crudded environment. Although precipitation of zeolite forming compounds significantly increased the cladding temperature, zinc did not co-precipitate within the crud with the zeolite compounds. Precipitation of zinc oxide did lead to an increase in deposit thermal resistance during one test with 60 ppb zinc. However, a similar effect was not observed at a 60 ppb zinc concentration when silica was present.

Results of 29 WALT loop tests were reported in EPRI 3002002891 [16]. Nine tests were performed with zinc addition without calcium, magnesium or aluminum addition. Three of these tests were without silica addition, and 6 were with silica addition. Tests were performed with 1000 ppm boron and 2.2 ppm lithium. Comprehensive analyses of the deposits were performed after each test. All deposits were grown prior to the addition of zinc. Results of tests performed to evaluate the effects of zinc compound precipitation are summarized below and in Table 4-1:

- 20 ppb zinc, no $SiO_2$ (Test 36): Temperature increase was approximately 0.2 °F (0.1 °C) after 112 hours of zinc addition. 0.5 Wt% Zn was present in the deposit. Deposit thickness was 41 to 45 μm.
- 40 ppb zinc, no $SiO_2$ (Test 38): Temperature increase was approximately 2.3 °F (1.3 °C) after 70 hours of zinc addition. 1.5 to 2.5 Wt% Zn in deposit. Deposit thickness was 46 to 48 μm.
- 60 ppb zinc, no $SiO_2$ (Test 39): Temperature increase was approximately 16 °F (9 °C) after 80 hours of zinc addition. Temperature increased shortly after Zn injection. Following a brief power trip at 80 hours, the temperature continued to increase. Deposit thickness was 33 to 34 μm. Chimney density was 2.5E10 to 2.3E11/m$^2$. Chimney density in plant deposits is generally near 1E10/m$^2$. The Zn concentration in the deposit averaged 18 Wt% but was as high as 54% in pores. Cu was present at 8 to 12 Wt%. ZnO was identified by XRD. Minimal Ca, Al and Si were observed in deposit. Average zinc concentration in deposit was 11 to 15 Wt%; Cu was 2.7 to 2.8 Wt%. Al concentration was 9 Wt% in one EDS sample.
- 60 ppb Zn, 7.5 ppm $SiO_2$ (Test 43): Temperature increased approximately 10 °F (5.6 °C) ~20 hours after Zn addition. It then decreased to approximately 6 °F (3.3 °C). Deposit thickness

was 36 to 74 µm. Zn concentration was 0 to 0.3 Wt% in deposit; Si averaged 1.4 Wt%. Per the authors, "if any zinc silicate was present, it was at a very low concentration" [16]. Al and Ca concentrations were 0 to 1.2 Wt%. Cu was 4 to 6 Wt%.

- 40 ppb Zn, 5 ppm $SiO_2$ (Test 44): Temperature increase of 6 °F (3.3 °C) appeared to be continuation following deposit formation. Deposit thickness was 46 µm. Zinc in deposit was 0 to 0.4 Wt%. Average Si was 0.3 Wt%. Per the authors, "if any zinc silicate was present, it was at a very low concentration" [16]. Cu concentration in deposit was 8.7 to 11.7 Wt%.
- 40 ppb Zn, 10 ppm $SiO_2$ (Test 46): No significant temperature increase observed. Deposit thickness was 54 to 57 µm. Zinc concentration in deposit was 0.4 to 0.5 Wt%. Average Si was 2.4 Wt%. Per the authors, "if any zinc silicate was present, it was at a very low concentration" [16]. Deposit Cu concentration was 10 to 11 Wt%.
- 40 ppb Zn, 7.5 ppm $SiO_2$ (Test 71): Temperature decreased significantly after addition. 50 hours of addition. Per the authors, "Zn and Si silicon were not detected by EDS" [16]. Deposit thickness was 47 to 57 µm.
- 60 ppb zinc, 7.5 ppm $SiO_2$ (Test 77): Repeat of Test 43. Multiple transients occurred during first part of test. Temperature increased by 3.9 °F (2.2 °C) over 94 hours of injection. Deposit thickness was 40 to 57 µm. Per the authors, "Zn and Si were not detected by EDS" [16].
- 40 ppb zinc, 5 ppm $SiO_2$ (Test 148): Zinc was added for ~40 hours. Temperature decreased. Silica was then added. Temperature decreased for approximately 20 hours and then increased by approximately 5 °F (2.8 °C) over next 40 hours. Deposit had 0 to 0.4 Wt% Zn, 1.3 to 3.5 Wt% Si. Cu content was 0.3 to 1.1 Wt%. Aluminum (not added deliberately) was generally 6 to 13 Wt%. Aluminum silicate was seen within pores. Per the authors, "zinc was not detected within the deposit so it is not likely that it had any influence on the precipitation of the pore filling phases" [16]. Deposit thickness was 53 to 64 µm.

The observation of a significant temperature increase during Test 39 in the absence of silica addition appears to be an anomaly since later tests with 60 ppb zinc and $SiO_2$ (Tests 43 and 77) did not exhibit a significant temperature increase or significant zinc precipitation. The average zinc concentration in the deposit at the end of Test 39 was 11 to 15 Wt%. Silica concentrations were minimal. In seven of the other tests with zinc injection, the zinc concentration in the deposit was less than 0.5%. In one test, the zinc concentration in the deposit was 1.5 to 2.5 Wt%. Note that the deposit at the end of Test 39 was thinner, and the pore density was 3 to 30 times higher than during the other tests.

The authors succinctly summarized the WALT results relative to zinc and silica interactions:

> "There appeared to be no interaction between zinc and silica, and zinc silicate was not detected in deposits. This was true even in an experiment where the zinc concentration was 40 ppb and the silica concentration was 10 ppm" [2].

In contrast, the WALT loop tests clearly show that precipitation of Al, Ca and Mg zeolites and their incorporation into the deposit structure can significantly increase the deposit thermal resistance. This is consistent with the very low solubilities of such compounds at operating conditions and justifies efforts to minimize concentrations of these species in makeup water, boric acid storage tanks, etc.

**Table 4-1**
**WALT Facility Test Summary**

| Test No. | Zn, ppb | $SiO_2$, ppm | Deposit Thickness, µm | Delta T, °F (°C) | % Zn | % Si | Deposit Chemistry |
|---|---|---|---|---|---|---|---|
| 36 | 20 | 0 | 41-45 | 0.2 (0.1) | 0.5 | NA | |
| 38 | 40 | 0 | 46-48 | 2.3 (1.2) | 1.5-2.5 | NA | |
| 39 | 60 | 0 | 33-34 | 16 (8.9) | 11-15 | NA | Cu 8-12%, Zn 54% max; ZnO identified; Pore volume significantly greater than reported for plant deposits and other WALT Loop tests. Test 39 results difficult to explain. |
| 43 | 60 | 7.5 | 36-74 | 3 (1.7) | 0-0.3 | 1.74 | No zinc silicate detected. |
| 44 | 40 | 5 | 46 | 2 (1.1) | 0-0.4 | 0.3 | No zinc silicate detected. |
| 46 | 40 | 10 | 54-57 | 0 (0) | 0.4-0.5 | 2.4 | Cu 10-11%; No zinc silicate detected. |
| 71 | 40 | 7.5 | 47-57 | Decrease | 0 | 0 | No zinc or silica detected. |
| 77 | 60 | 7.5 | 40-57 | 3.9 (2.2) | 0 | 0 | No zinc or silica detected |
| 148 | 40 | 5 | 53-64 | Variable: -, -/+ 5<br>(-/+ 1.7) | 0-0.4 | 1.3-3.5 | Sequential zinc then silica; no zinc silicate detected. |

# 5
# ZINC TRANSPORT IN THE PWR PRIMARY SYSTEMS

## 5.1 Introduction [18]

To minimize activity buildup on out of core surfaces as a result of Co-58 and Co-60 incorporation into surface oxides, zinc is added to the primary system at most U.S. PWRs and many PWRs worldwide at a rate sufficient to establish a primary coolant concentration, generally in the range of 5 to 10 ppb. The zinc injection rate varies from approximately 3 to 10 grams per day or 2 to 7 kg per cycle. Higher concentrations and injection rates have been employed at several plants in the past.

The total amount of zinc retained in the system can be calculated from the amount injected minus the amount removed by the Chemical and Volume Control System (CVCS) demineralizers. Based on the current BOA model, zinc is retained primarily as a result of incorporation (diffusion) into steam generator tubing and stainless steel surface oxides [14]. However, a fraction of the retained zinc is incorporated into the fuel deposits. EPRI has been developing and attempting to benchmark a model of zinc transport in the primary system to quantify the relative importance of these processes for several years [20, 21, 22].

## 5.2 Zinc Mass Balance

### *5.2.1 Fleet Observations*

Zinc mass balance data for individual cycles were available for numerous PWRs [18]. A summary developed primarily from Reference 18 is given in Appendix A. Note that the results are weighted heavily for early cycles of zinc operation. Retained amounts in terms of kilograms per cycle as a function of the average primary coolant zinc concentration during injection are shown in Figure 5-1. The mass retained per cycle is shown in Figure 5-2 as a function of the ppb-months of zinc exposure during each cycle. No clear correlation of these two parameters to zinc retention is apparent.

In Figure 5-3, cumulative zinc retention is shown as a function of cumulative zinc addition. Variations at individual plants are shown in Figure 5-4 and Figure 5-5. Although the total retention increases as the exposure to zinc increases, the rates of retention vary significantly between plants and at individual plants from cycle to cycle. Note that consideration was not given to the amount removed during outages by coolant purification or refueling operations in estimating total retention.

Since the primary mechanism for zinc retention is diffusion into out of core surface oxides, not deposition on the fuel [14], the amount of retention per cycle should be dependent on the zinc exposure during the cycle and the diffusion rate into the surface oxides. In this case:

- The retention rate at a fixed zinc concentration should decrease as the total zinc exposure increases due to the decrease in the rate of diffusion into the oxide as the surface oxide zinc burden increases
- The amount retained divided by the zinc exposure during each cycle would be expected to be a function of the cumulative exposure (ppb-months) during preceding cycles.

Retention results for the fleet based on this qualitative model are shown in Figure 5-6. A reasonable correlation is present although there are significant variations.

Since detailed mass balance results for McGuire 1 and 2 [23] and STP 1 and 2 [24] were available from the initiation of zinc injection, these retention observations were considered separately. As shown in Figure 5-7, there is a significant improvement in the correlation when individual plants are considered. The rate of zinc retention clearly decreases as exposure to zinc increases, consistent with modeling results indicating retention is primarily a result of diffusion into out-of-core oxides. If retention was primarily a result of deposition on the fuel, it would have been expected to increase with time since core boiling duties have generally increased. However, it is also possible that the reduction in corrosion product release rates and fuel crud loadings resulting from zinc injection could have led to a reduction in zinc deposition on the fuel.

## *5.2.2 Implications of Zinc Retention Results*

### 5.2.2.1 McGuire 1 [23]

Mass balance results for McGuire 1 for Cycles 22 to 25 are shown in Figure 5-8. The amount of zinc injected per cycle varied from approximately 3.3 to 3.7 kg. The amount retained varied from approximately 740 to 800 grams per cycle (20 to 24% of that injected). If it is assumed that the amount retained was a result of zinc silicate deposition on the fuel, 1.25 to 1.35 kg of $Zn_2SiO_4$ deposited. This is approximately 13% of the total amount of nickel iron ferrite, nickel metal, and nickel oxide expected to deposit on the core during a cycle, i.e., approximately 10 kg per cycle [25]. Since the maximum amount of zinc silicate precipitate formation is significant with respect to the total expected amount of deposit formation by nickel and iron compounds, the McGuire 1 mass balance results cannot be used to eliminate the concerns of a negative effect of zinc silicate precipitation on deposit thermal resistance. If BOA modeling results [14] are accepted, i.e., only approximately 20% of the retained zinc incorporates into the fuel deposits, the maximum amount of zinc silicate deposition would be approximately 0.26 kg per cycle.

### 5.2.2.2 South Texas 1 [24]

Mass balance results for STP 1 for Cycles 19 and 20 are shown in Figure 5-9. The amount of zinc injected during these cycles was approximately 5.8 and 4.6 kg, respectively. The amounts retained were approximately 1.94 and 1.05 kg or 34 and 23% of that injected. If it is assumed that the amount retained was a result of zinc silicate deposition on the fuel, 3.28 and 1.77 kg of $Zn_2SiO_4$ deposited during Cycles 19 and 20, respectively. This is approximately 18 to 33 percent of the total amount of nickel and iron compound predicted to deposit on the core during a cycle. As at McGuire 1, the zinc mass balance results cannot be used to eliminate the concerns of a negative effect of zinc silicate precipitation on deposit thermal resistance. If BOA modeling results are accepted, the maximum amount of zinc silicate deposition would be 0.35 to 0.65 kg per cycle.

### 5.2.2.3 South Texas 2 [24]

Mass balance results for STP 2 for Cycles 18 and 19 are shown in Figure 5-10. The amount of zinc injected was approximately 4.8 and 5.6 kg, respectively. The amounts retained were approximately 1.14 and 1.90 kg or 24 and 34% of that injected. If it is assumed that the amount retained was a result of zinc silicate deposition on the fuel, 1.92 and 3.21 kg of $Zn_2SiO_4$ deposited on the fuel during Cycles 18 and 19, respectively. This is approximately 19 and 32% of the total expected amount of nickel and iron compound deposition on the core during a cycle. As at McGuire 1 and STP 1, the zinc mass balance results cannot be used to eliminate the concerns of a negative effect of zinc silicate precipitation on deposit thermal resistance. If BOA modeling results are accepted, the maximum amount of zinc silicate deposition would be 0.38 and 0.64 kg per cycle.

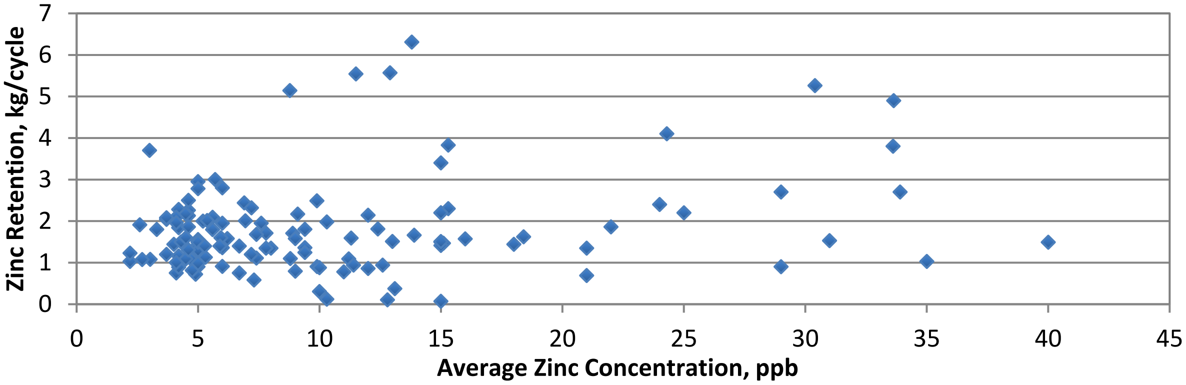


**Figure 5-1**
**Zinc Retention as a Function of Cycle Average Zinc Concentration**

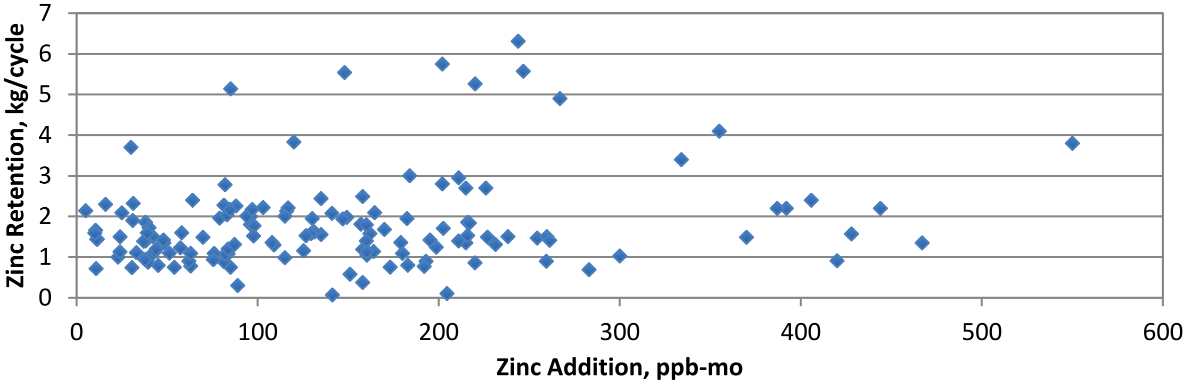


**Figure 5-2**
**Zinc Retention as a Function of Cycle Zinc Exposure (ppb-months)**

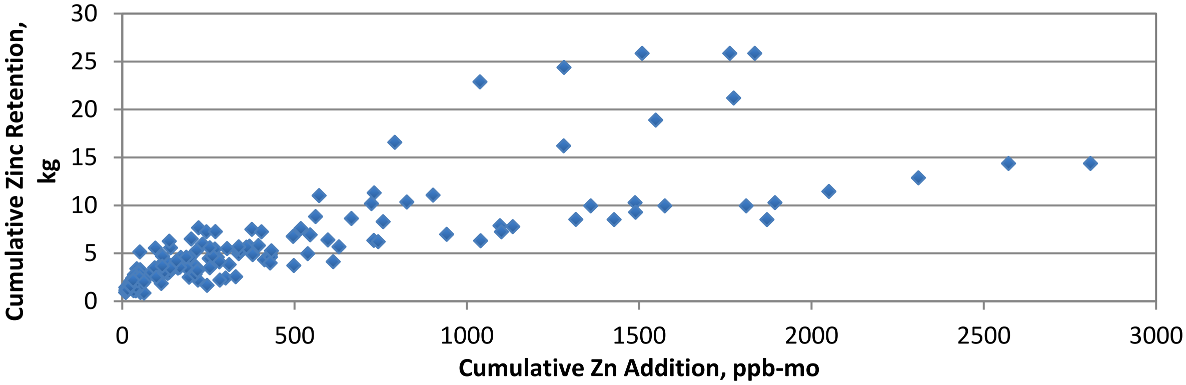


**Figure 5-3**
**Cumulative Zinc Retention as a Function of Cumulative Zinc Exposure (ppb-months)**

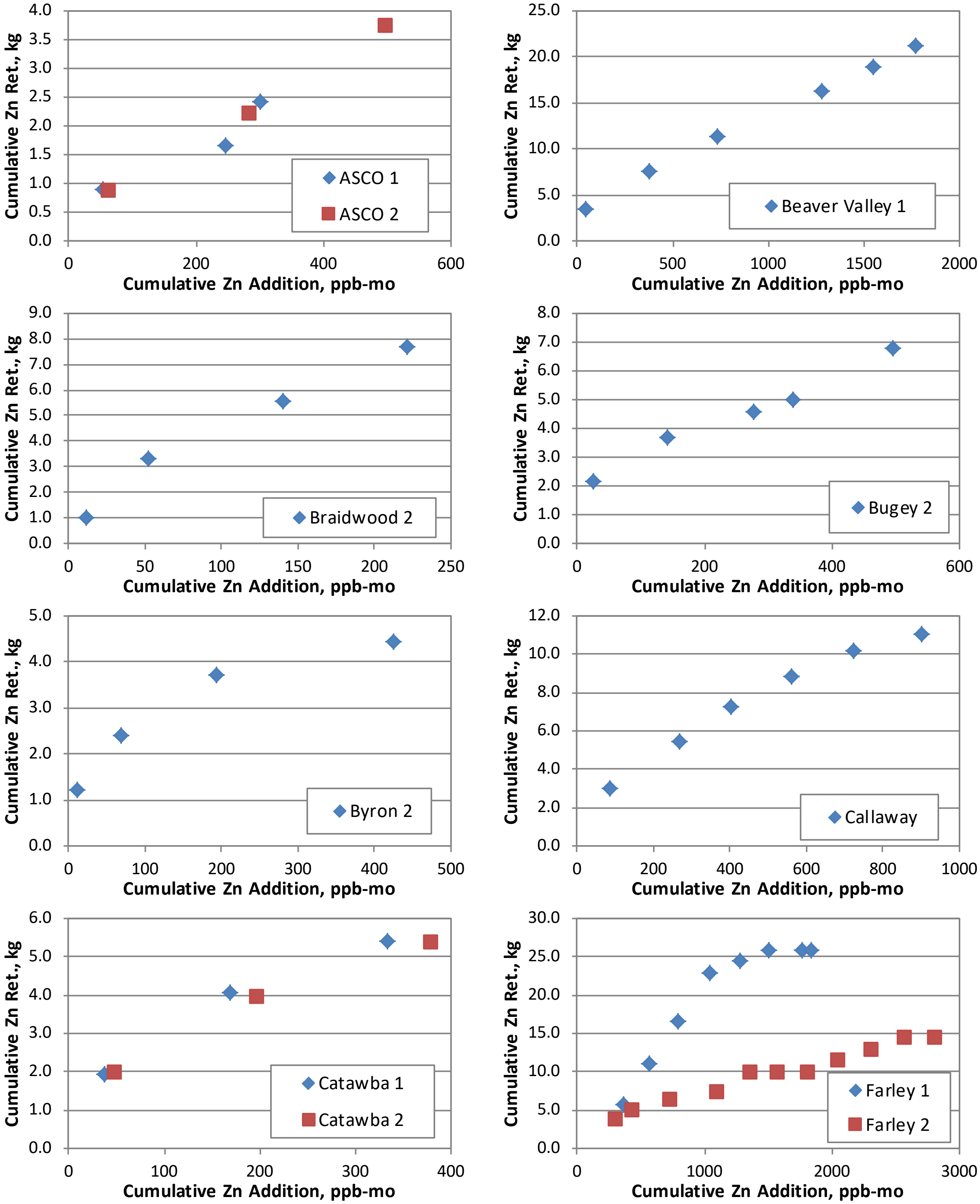


**Figure 5-4**
**Cumulative Zinc Retention for Group 1 PWRs as a Function of Cumulative Zinc Exposure**

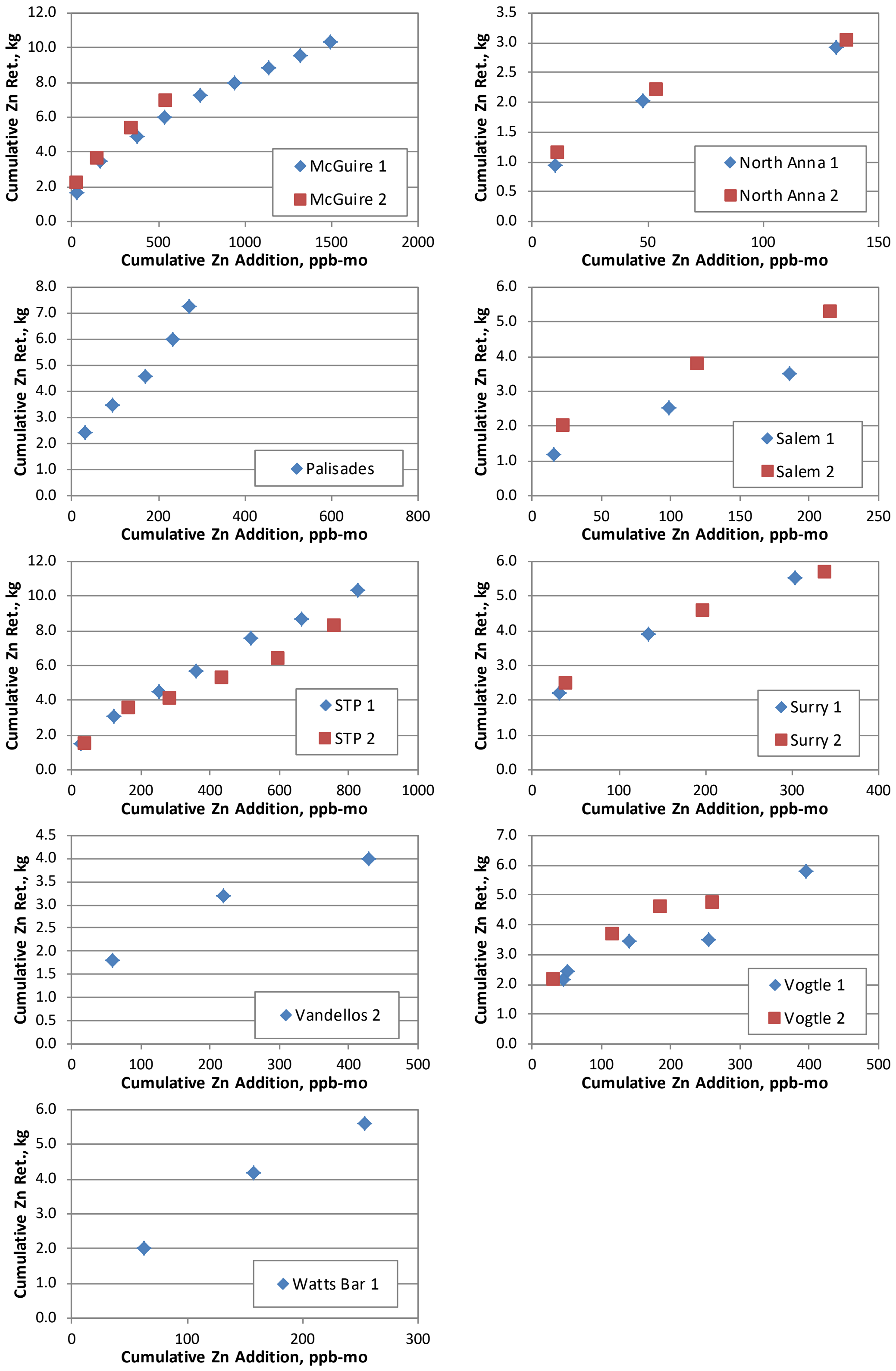


**Figure 5-5**
**Cumulative Zinc Retention for Group 2 PWRs as a Function of Cumulative Zinc Exposure**

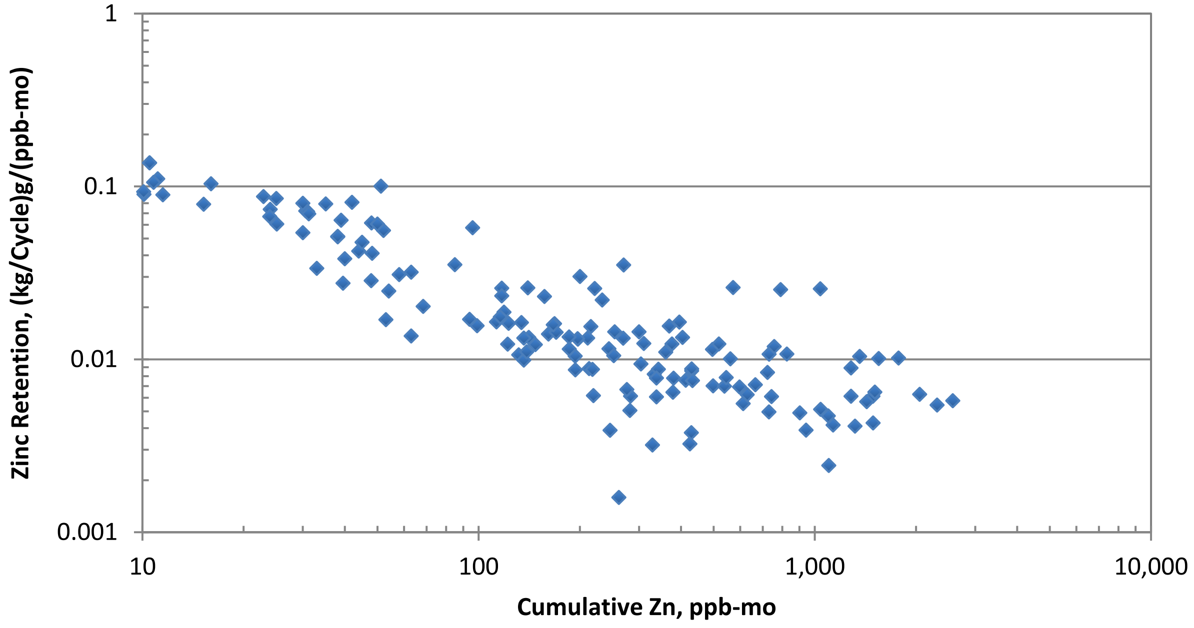


**Figure 5-6**
**Correlation of Fleet Zinc Retention Observations**

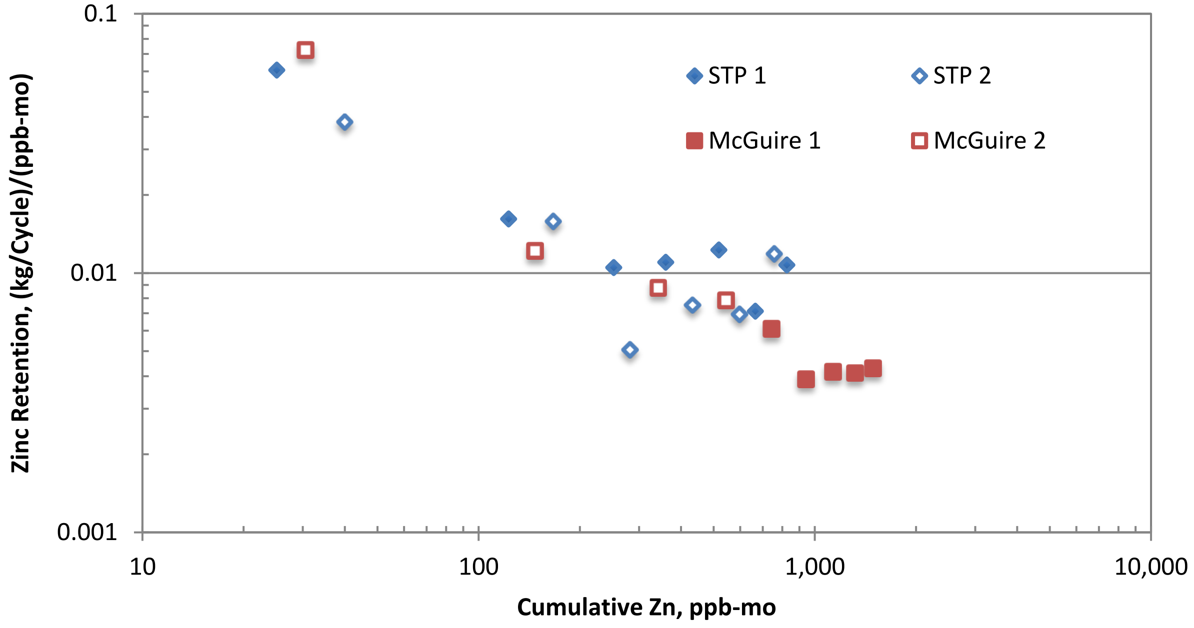


**Figure 5-7**
**Correlation of STP and McGuire Zinc Retention Observations**

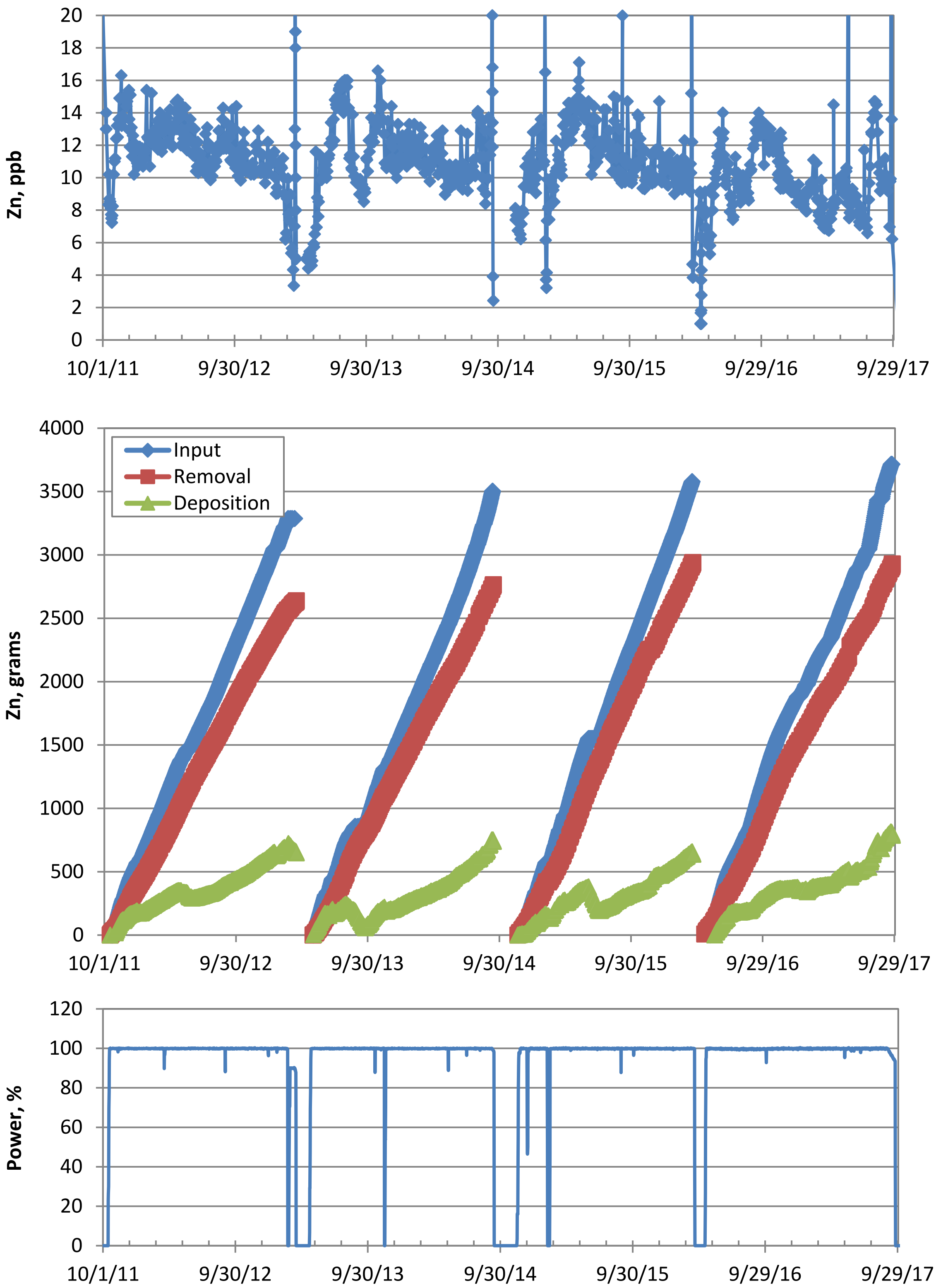


**Figure 5-8**
**McGuire 1 Zinc Mass Balances during Cycles 22 Through 25**

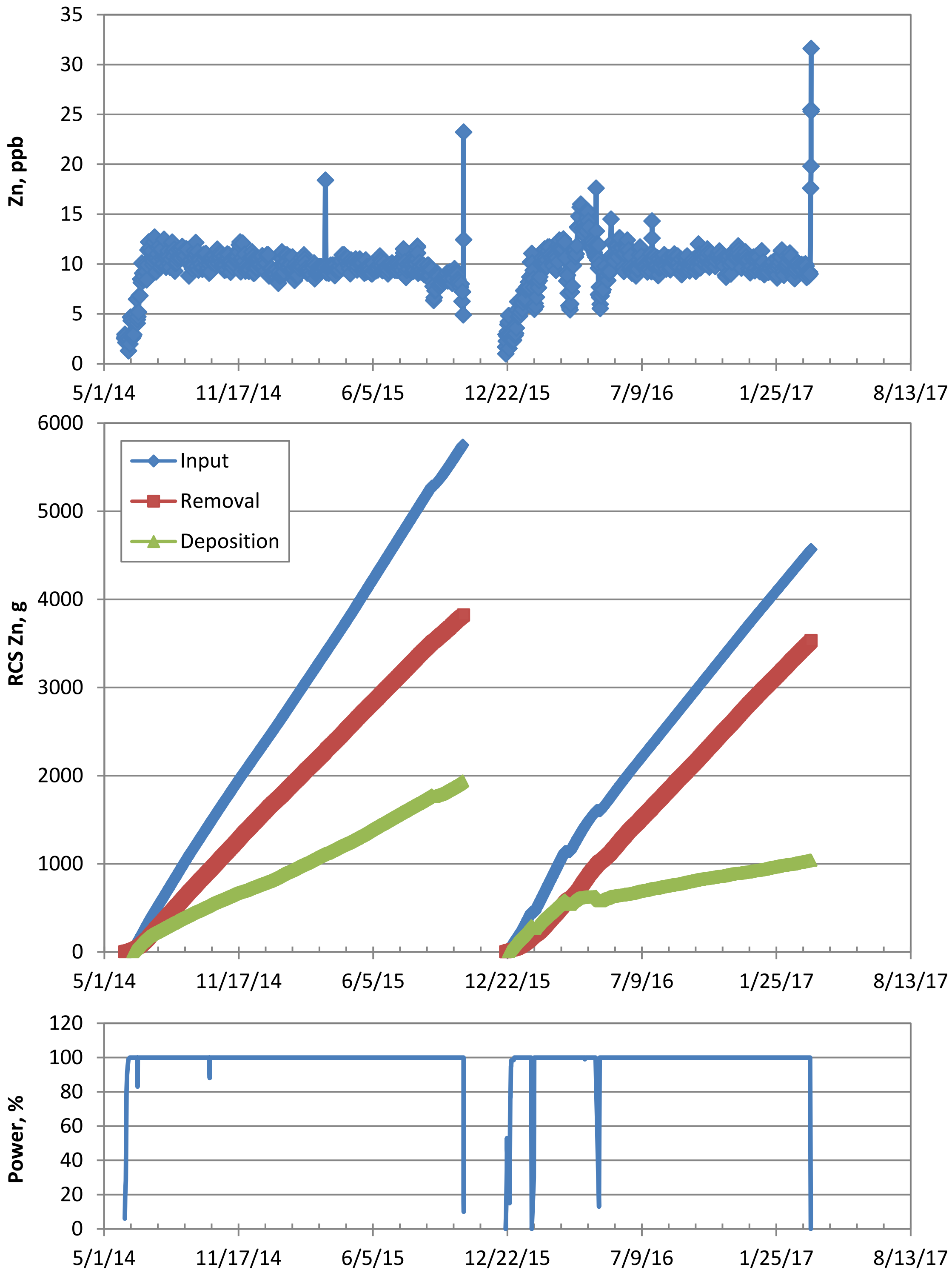


**Figure 5-9**
**STP 1 Zinc Mass Balances during Cycles 19 and 20**

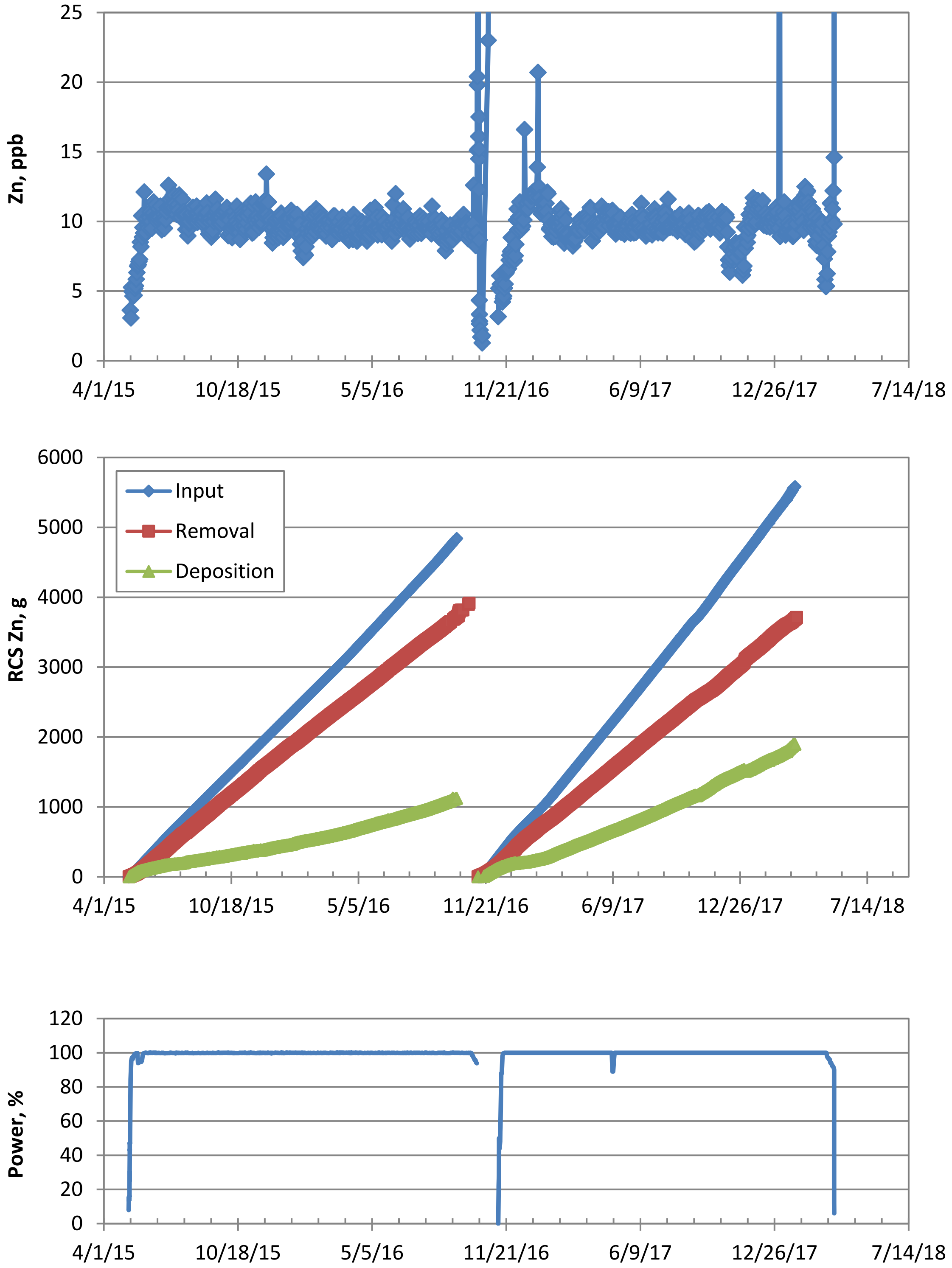


**Figure 5-10**
**STP 2 Zinc Mass Balances during Cycles 18 and 19**

# 6

# SILICA TRANSPORT IN THE PWR PRIMARY SYSTEM

## 6.1 Introduction

Since the possibility of a detrimental effect of zinc silicate deposition on the thermal resistance of the fuel deposit could not be eliminated based on the zinc mass balance approach, an alternate approach to estimate the maximum amount of zinc silicate deposition that could occur based on a silica mass balance was pursued. Although a balance for the entire cycle will eventually require consideration of silica source terms such as makeup water, boric acid addition, startup refueling water, stainless steel and steam generator tubing corrosion, and release from CVCS demineralizers and filters, and removal terms such as bleed flow and CVCS demineralizer removal, a simplified approach was taken to illustrate the process. Specifically, estimates of the maximum amount of zinc silicate formation were developed for the period of continuous power operation following the boron peak at the beginning of the cycle and the time when the CVCS system anion resin beds began to be employed to remove boron for reactivity control.

## 6.2 Silica Mass Balance

### 6.2.1 Fundamentals

Following shutdown and floodup, primary water silica concentrations approach those in the fuel pool. At plants where Boraflex is employed in the fuel storage racks, silica concentrations greater than 20 ppm have been observed. Concentrations at plants without Boraflex racks are much lower but still can be in the range of several ppm. During startup from a refueling outage, the silica concentration is reduced approximately a factor of two as a result of the dilution required to establish the BOC boron operating value. Feed and bleed techniques continue to be used as needed to reduce concentrations to several ppm during startup. After the period when the boron concentration is gradually increased to offset the effects of burnable poison, the boron concentration is gradually decreased by bleed flow and dilution to compensate for the core reactivity loss. During this period, the silica concentration gradually decreases with time as the boron concentration decreases. (Boron and silica concentration variations for selected plant cycles are shown in Appendix B.) This silica decrease theoretically could result from an increase in the letdown demineralizer anion resin silica capacity as the boron concentration decreases, dilution of the coolant to decrease boron for reactivity control, or silica compound deposition on the fuel. Note that during the periods of operation that were considered, the input of silica to the primary system by makeup water was relatively low due to the low bleed flow rates, i.e., at a makeup water silica concentration of approximately 10 ppb, i.e., approximately 5 grams would be added to the system over a 12-month period at an average makeup water flow rate of 0.25 gpm.

### 6.2.2 Letdown Demineralizer Silica Capacity

Although demineralization of the fuel pool water and primary coolant are routinely employed to minimize ionic impurity concentrations, demineralization is not an effective approach for removing silica from water containing even modest concentrations of boric acid for several reasons:

- The anion resin selectivity coefficient for silica is very low.
- Borate anions have much higher anion resin selectivity coefficients than silica.
- Silicic acid is only slightly ionized at ambient temperature.
- Boric acid is present at much higher concentrations than silica throughout the cycle.

At ambient temperatures, silica is present in near neutral solutions primarily as $H_4SiO_4$, which ionizes to a very limited extent to $(H_3SiO_4)^-$. For example, the following species are present in the solution at 25 °C at primary coolant concentrations of 2.5 ppm lithium, 3 ppm silica (5E-5 eq/kg) and 1000 ppm boron, based on MULTEQ Database Version 8, run in ChemWorks Tools Version 4.2:

- 3.053E-8 eq/kg $H_3SiO_4^-$,
- 4.99E-5 eq/kg $H_4SiO_4$ and
- 4.03E-8 eq/kg $OH^{-1}$
- 8.69E-5 eq/kg $B_2O(OH)_5^-$
- 5.38E-5 eq/kg $B_3(OH)_{10}^-$
- 2.217E-4 eq/k $B(OH)_4^-$

To determine the strong base anion resin capacity for silica at equilibrium in the primary coolant, the anion resin was assumed to be at equilibrium with respect to the exchange reactions of $H_3SiO_4$, the boron anionic monomer ($B(OH)_4$), the boron anionic dimer ($B_2O(OH)_5$), the boron anionic trimer ($B_3O_3(OH)_4$) and hydroxide. The selectivity coefficients for the exchange reactions can be written as follows:

1. Boron Monomer Exchange

$$ROH + B(OH)_4^- = RB(OH)_4 + OH^-$$

$$K_{OH}^{B(OH)_4} = \frac{RB(OH)_4 \times [OH^-]}{[ROH] \times [B(OH)_4^-]} = 1.65$$

2. Boron Dimer Exchange

$$ROH + \mathrm{B_2O(OH)_5^-} = R\mathrm{B_2O(OH)_5} + OH^-$$

$$K_{OH}^{\mathrm{B_2O(OH)_5}} = \frac{[R\mathrm{B_2O(OH)_5}] \times [OH^-]}{[ROH] \times [\mathrm{B_2O(OH)_5^-}]} = 6.22$$

3. Boron Trimer Exchange (B3O3(OH)4 )

$$ROH + B_3(OH)_{10}^- = RB_3(OH)_{10} + OH^-$$

$$K_{OH}^{B_3(OH)_{10}} = \frac{[RB_3(OH)_{10}] \times [OH^-]}{[ROH] \times [B_3(OH)_{10}^-]} = 10.8$$

4. $H_3SiO_4^-$ Exchange

$$ROH + H_3SiO_4^- = RH_3SiO_4 + OH^-$$

$$K_{OH}^{H_3SiO_4} = \frac{[RH_3SiO_4] \times [OH^-]}{[ROH] \times [H_3SiO_4^-]} = 1.0$$

Based on these equations, the fraction of the resin capacity exhausted to each monovalent anionic species can be shown to be given by:

$$\text{Resin Fraction} = C_xK_x/(C_aK_a + C_bK_b + C_cK_c + C_dK_d + C_eK_e)$$

Where:

K = Selectivity coefficient relative to hydroxide
C = Anion concentration, molal
ROH = Hydroxide form anion resin
$RB(OH)_4$ = Boron monomer form anion resin
$RB_2O(OH)_5$ = Boron dimer form anion resin
$RB_3(OH)_{10}$ = Boron trimer form anion resin
$RH_3SiO_4$ = Silica form anion resin
Subscripts:
a = OH
b = Anionic boron monomer
c = Anionic boron dimer
d = Anionic boron trimer
e = Anionic silica species, $H_3SiO_4$
x = Selected anionic species, (a, b, c, d or e)

Anion selectivity coefficients of 1 for hydroxide, 1.65 for the boron monomer, 6.22 for the boron dimer, 10.8 for the boron trimer and 1 for $H_3SiO_4^-$ were used in the calculations. The value for the boron dimer was arbitrarily assumed to be the average of that for the monomer and trimer.

The fraction of the anion resin exhausted to silica at a coolant silica concentration of 1 ppm is shown in Figure 6-1 as a function of the coolant boron concentration for the case of $pH_{300C} = 7.2$. As shown, the fraction of the resin in the silica form is less than 0.1% until the coolant boron concentration falls below 50 ppm. For example, it is ~0.03% at 200 ppm boron and 0.002% at 1,000 ppm boron.

For a total anion resin volume of 10 $ft^3$ in a mixed bed letdown demineralizer, the total anion resin capacity for silica assuming total exhaustion to silica is approximately 311 gram equivalents or approximately 19,000 grams of $SiO_2$ as a monovalent anion. However, in the presence of boric acid, the estimated silica capacities are much lower, i.e., 36, 4.5 and 0.36 grams, respectively at boron concentrations of 50, 200 and 1,000 ppm boron.

The mass of silica in the primary coolant at a concentration of 1 ppm is approximately 270 grams. Thus, the letdown demineralizer anion resin silica inventory throughout most of the cycle (until the boron is in the range of 100 ppm) is minimal compared to the amount present in the coolant. This is also true for boron, i.e., the variation in the anion resin boron loading is minimal compared to the primary coolant inventory until the end of the cycle. Thus, the silica concentration decrease normally observed during the cycle must be due to removal by the bleed flow employed for boron removal for reactivity control or deposition on the fuel. Note that although silica is known to adsorb on and desorb from steam generator tubing surfaces on the secondary side of the system, the effect of adsorption/desorption from the primary side surfaces of the steam generators can be neglected based on engineering judgment since results of secondary side hideout return studies indicate adsorption is minimal, i.e., values in the range of 3 grams per steam generator are generally observed.

### 6.2.3 Mass Balance Development

At most plants, the boron concentration is increased during the first several months of the cycle to offset burnable poison depletion. To develop a silica mass balance during this period, detailed concentrated boric acid and makeup water addition rate and primary system bleed rate data would be needed. Thus, a mass balance for this period was not pursued, and the evaluation focused on the period when the primary coolant boron concentration was being gradually decreased by dilution. During this period, the mass balance for silica and boron should be similar, i.e., there should be no boron additions from the BAST, makeup water additions should be minimal, and makeup water flow rates will equal bleed flow rates.

During the period of gradual boron reduction due to bleed flow (e.g., primary coolant boron concentration of approximately 1200 to 200 ppm), the rates of change of the mass of boron and silica in the primary coolant can be equated to the rates of input via the makeup water minus the rate of deposition on the fuel and the rate of removal by dilution or bleed flow, i.e.:

$$M_{RCS}\, dC_{Si}/dt = W_{MU}C_{MUSi} - \text{Silica Compound Deposition Rate} - W_{Bl}\, C_{Si} \qquad \textbf{(Eq. 6-1)}$$

$$M_{RCS}\, dC_B/dt = W_{MU}C_{MUB} - W_{Bl}\, C_B \qquad \textbf{(Eq. 6-2)}$$

where:

$M_{RCS}$ = Primary coolant mass
$W_{Bl}$ = Primary coolant bleed flow
$C_{Si}$ = Primary coolant silica concentration
$C_B$ = Primary coolant boron concentration
$W_{MU}$ = Makeup Water Flow rate
$C_{MU}$ = Makeup water silica concentration

The following assumptions were made to develop these relations:

- The effect of release from or removal of boron and silica by the letdown demineralizers during normal power operation during most of the cycle (B >200 ppm) can be neglected.

Note that the mass of silica on the letdown system demineralizer anion resin is negligible compared to the mass in the primary coolant during this period. In addition, the anion resin boron inventory change is minimal compared to the primary coolant boron inventory until very late in the cycle when boron concentration is less than approximately 100 ppm.

- Boron additions to the primary system are not being made from the boric acid storage tank.
- Adsorption on and desorption of silica from primary system surfaces can be neglected. Note that silica returns of 2 to 10 grams per steam generator are routinely observed during secondary side hideout return studies and are believed to be due to desorption from surface oxides. Thus, consideration of desorption effects will be necessary in the future.
- No boron deposition is occurring on the fuel.
- Silica is not being released to the primary coolant as a corrosion product from the primary system materials. As discussed below, corrosion release will have to be considered in the future.
- Silica is not being released to the primary coolant from the CVCS filters.
- The effect of $^{10}$B burnout on the boron concentration is negligible.

Assuming the primary system makeup water silica concentration is well below the EPRI PWR Primary Water Chemistry Guideline limit of 100 ppb [1], i.e., generally <10 ppb, and the makeup water boron concentration is negligible, the above equations can be further simplified:

$$M_{RCS}\, dC_{Si}/dt = -\text{Silica Deposition Rate} - W_{Bl}\, C_{Si} \qquad \textbf{(Eq. 6-3)}$$

$$M_{RCS}\, dC_B/dt = -W_{Bl}\, C_B \qquad \textbf{(Eq. 6-4)}$$

Based on these relations, $(dC_B/dt)/C_B$ and $(dC_{Si}/dt)/C_{Si}$ should be equal to $(-W_{Bl}/M_{RCS})$ if deposition of a silica bearing species is not occurring. When deposition is occurring, the deposition rate can be calculated as follows based on these relations:

$$\text{Silica Deposition Rate} = M_{RCS}\, C_{Si}\, [(dC_B/dt)/C_B - (dC_{Si}/dt)/C_{Si}] \qquad \textbf{(Eq. 6-5)}$$

### *6.2.4 Mass Balance Application*

#### 6.2.4.1 South Texas Project

To illustrate the silica mass balance approach for estimating the maximum amount of zinc silicate deposition on the fuel, South Texas Project Unit 1 Cycles 18 and 19 boron and silica concentration data were considered. Due to the variations in the number of days between silica concentration measurements, an integration interval of 14 days was selected. In Figure 6-2, boron and silica concentrations and their percentage rates of change are compared. As shown, the rates are very similar indicating that removal by bleed flow controls the rates of decrease of both species. Scatter in the silica rates is greater than those for boron due to the differences in the analytical accuracy for these two species.

Subtracting the amount of silica removal by bleed flow based on the bleed flow rate calculated from the boron removal rate allows the maximum amount of silica that could be depositing on the fuel during each time interval to be estimated. Maximum cumulative deposition estimates for zinc silicate based on this approach are shown in Figure 6-3 for the period of decreasing boron concentration and steady power operation at a boron concentration >200 ppm. For both Cycles 19 and 20, negative values result from this approach, and the values become more negative as the integration time increases. The negative values and their trend indicate that a source of silica was not considered in the silica mass balance.

Silica mass balance results for STP 2 Cycles 18 and 19 are shown in Figure 6-4 and Figure 6-5. Results are very similar to those at STP 1 with negative values of maximum zinc silicate deposition again calculated.

#### 6.2.4.2 McGuire 1

Silica mass balance results for McGuire 1 for Cycles 24 and 25 are shown in Figure 6-6 and Figure 6-7. Results are very similar to those for STP 1 and STP 2, i.e., negative values of maximum zinc silicate deposition are calculated, and the values become more negative with time.

### 6.3 Mass Balance Interpretation

As summarized in Table 6-1, the estimated maximum zinc silicate deposit mass was consistently negative indicating that there was a silica source that was not considered during the six periods of operation that were evaluated. Maximum zinc silicate deposition values at STP 1 and 2 and McGuire 1 during the periods of boron dilution by bleed flow varied from -9 to -147 grams. The maximum average deposition rate varied from -0.7 to -11 grams per month with an average of -6.1 grams per month.

Assuming minimal deposition of any silica bearing species, the error in the silica source term, i.e., the source of silica that was not considered during the evaluations, varied from 0.2 to 3.1 grams per month. Although silica input via the makeup water generally was low, estimates are based solely on reactive, not total silica. Another known but difficult to quantify source of silica is release from stainless steel and Alloy 600 or 690 as a result of corrosion. Other silica sources also may be present at some plants, e.g., EDF has identified CVCS fiberglass filter media as a significant silica source in French PWRs [26]. Desorption of silica from system surfaces also may be occurring.

Although the list of possible source terms is extensive, development of reasonable estimates of the magnitude of each source appears possible. For example, silicon release due to Alloy 690 steam generator tube corrosion was estimated to be <43 grams over an 18-month cycle at a nickel release rate of 0.10 $mg/dm^2$-month [27] and a steam generator tube surface area of 3E5 $ft^2$ (2.787E4 $m^2$) assuming release rates are proportional to alloy composition (58% Ni and <0.5% Si). This would lead to the formation of <98 grams of silica in the primary coolant during an 18-month cycle or <5.1 grams per month.

In summary, the silica mass balance approach offers significant promise with respect to providing reasonable estimates of the maximum amount of zinc silicate and silicate bearing compounds depositing on the fuel. In addition to allowing maximum values to be estimated for the cycle, the mass balance also should allow estimation of maximum deposition rates of silica compounds, thereby providing a basis for possible correlation of deposition rates to primary coolant chemistry and fuel duty. Accuracy of such estimates will depend on the frequency and accuracy of primary coolant silica analyses.

**Table 6-1**
**Summary of Silica Mass Balance Results**

| Plant | Cycle | Mass Balance Period, mo | Predicted Maximum $ZnSiO_4$ Deposition, grams | Average $ZnSiO_4$ Deposition Rate, g/mo | Unidentified $SiO_2$ Source, g/mo |
|---|---|---|---|---|---|
| **McGuire 1** | 24 | 11.5 | -9.3 | -0.7 | 0.2 |
| | 25 | 12.9 | -77.5 | -7.7 | 2.1 |
| **STP 1** | 19 | 13.3 | -66.5 | -5.8 | 1.6 |
| | 20 | 10.1 | -147.2 | -11.4 | 3.1 |
| **STP 2** | 18 | 12.4 | -99.2 | -8.0 | 2.2 |
| | 19 | 13.3 | -42.3 | -3.2 | 0.9 |

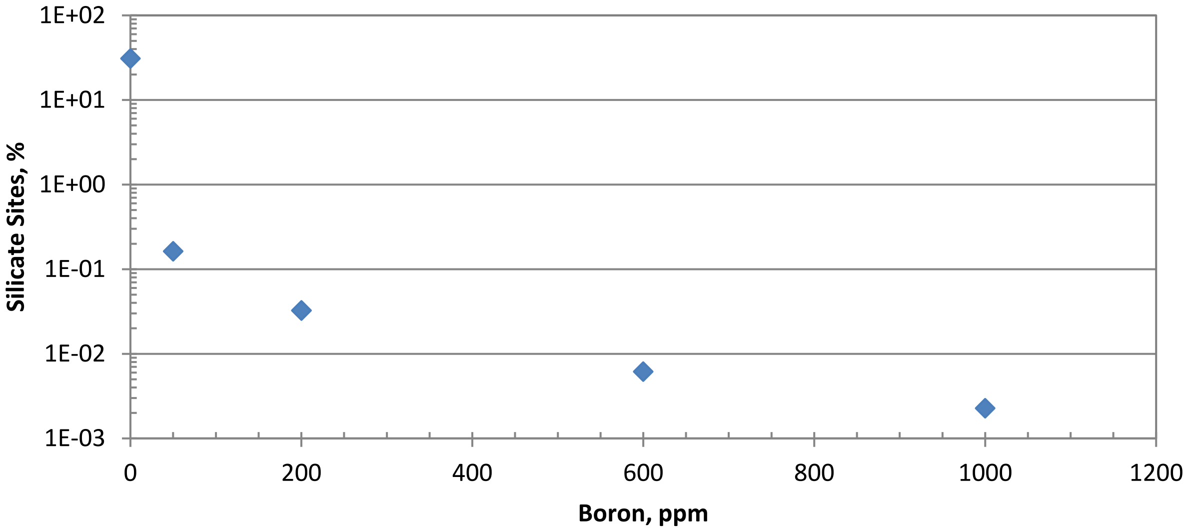


**Figure 6-1**
**Anion Resin Silicate Site Percentage at 25 °C ($pH_{300\,°C}$ 7.2; 1 ppm Silica)**

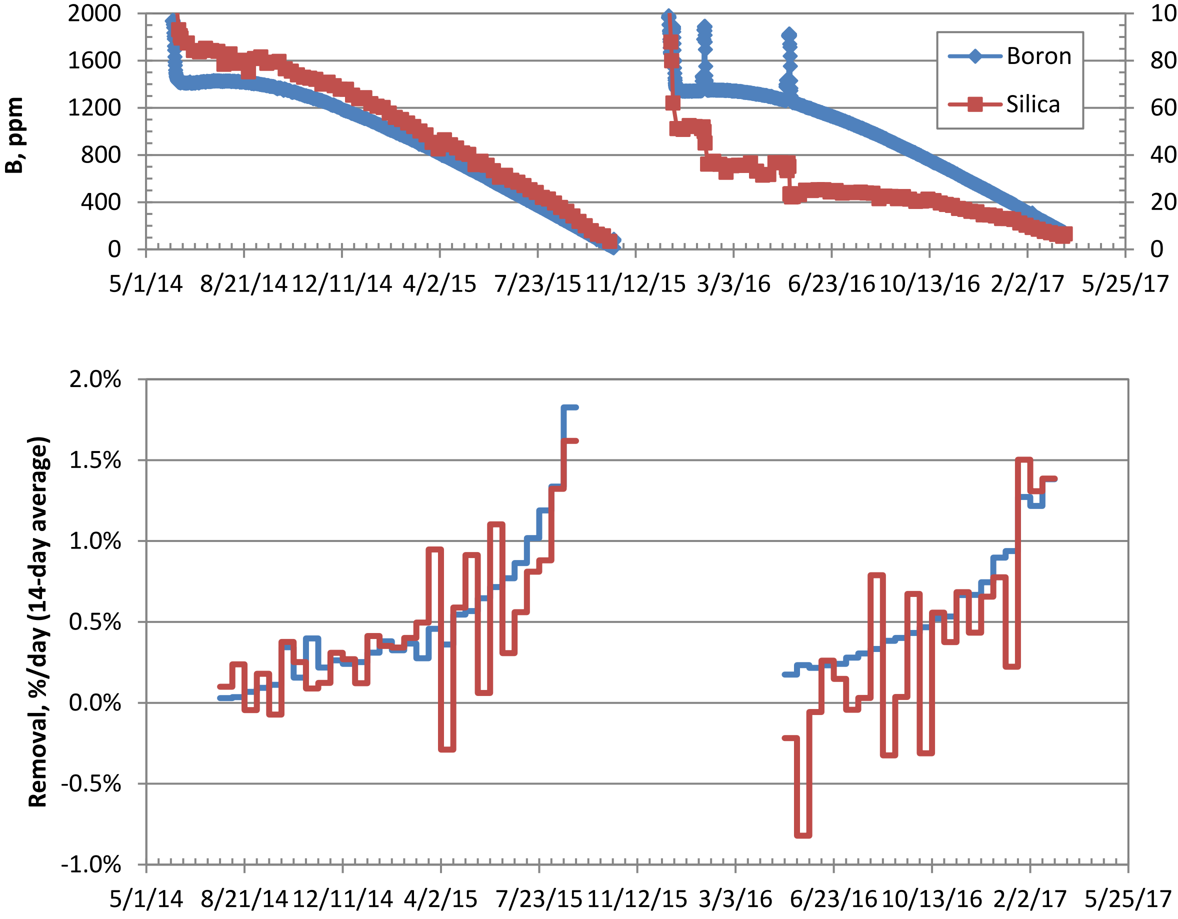


**Figure 6-2**
**Boron and Silica Removal Rates at STP 1 during Cycles 19 and 20**

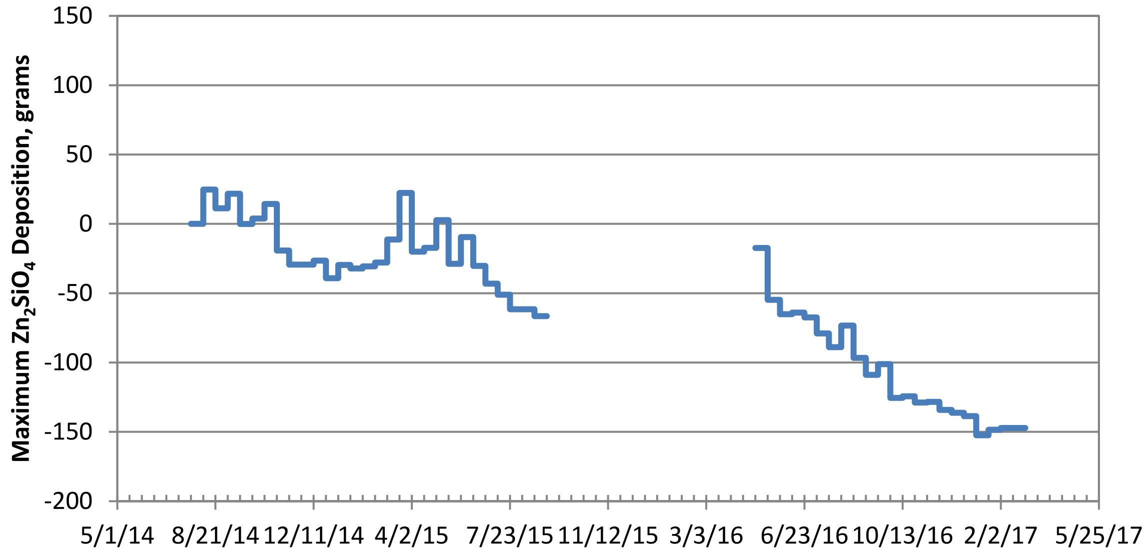


**Figure 6-3**
**Maximum Zinc Silicate Deposition at STP 1 during Cycles 19 and 20**

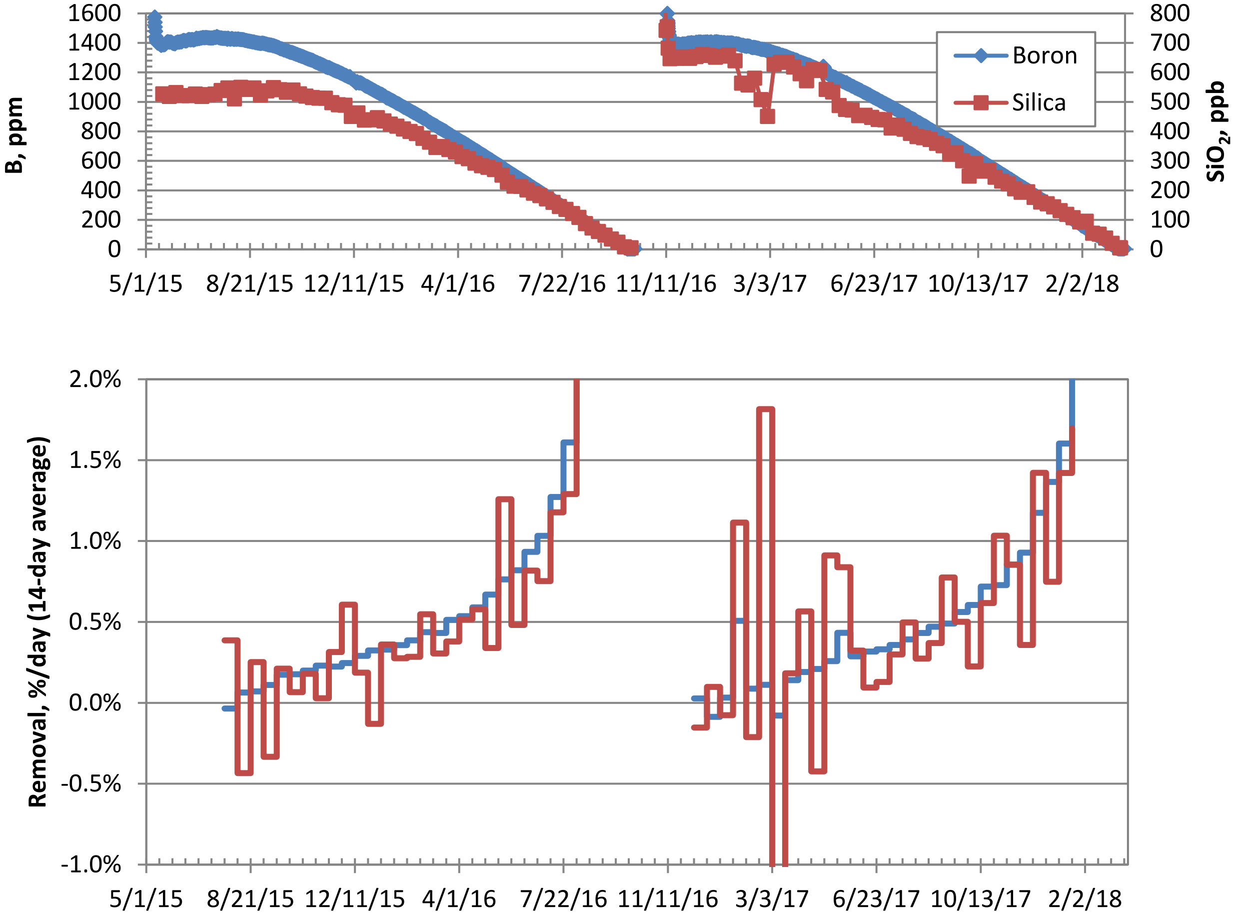


**Figure 6-4**
**Boron and Silica Removal Rates at STP 2 during Cycles 18 and 19**

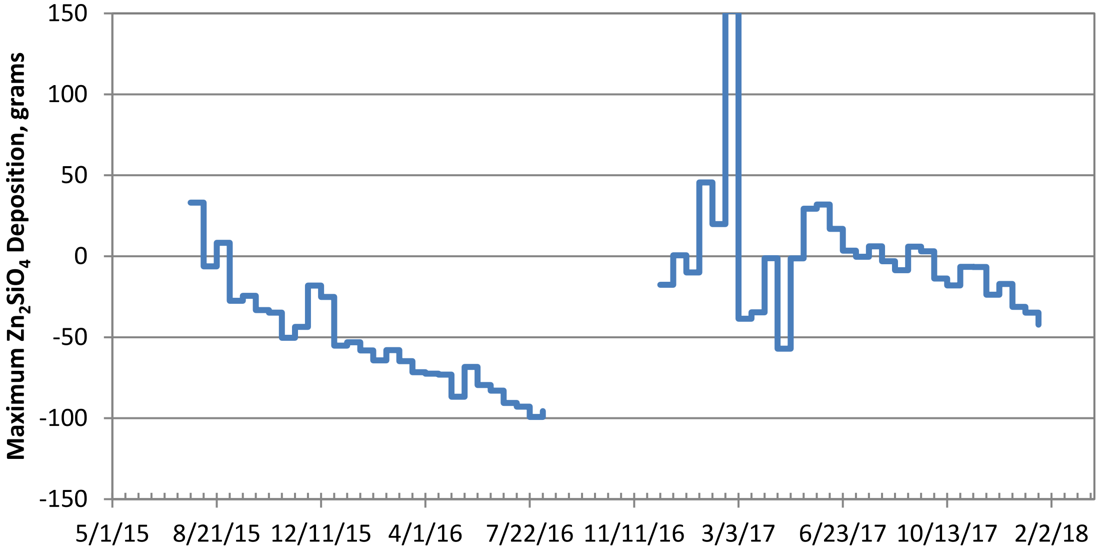
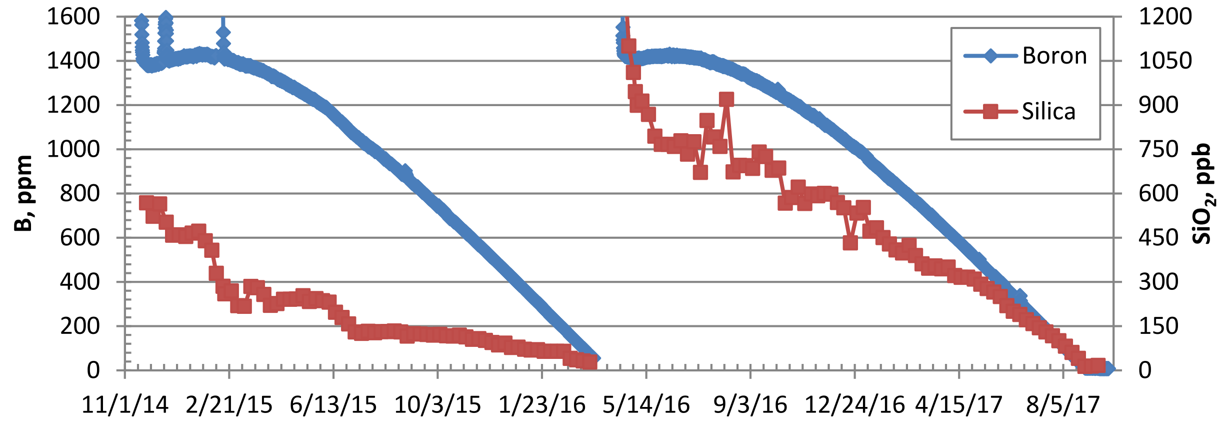


**Figure 6-5**
**Maximum Zinc Silicate Deposition at STP 2 during Cycles 18 and 19**



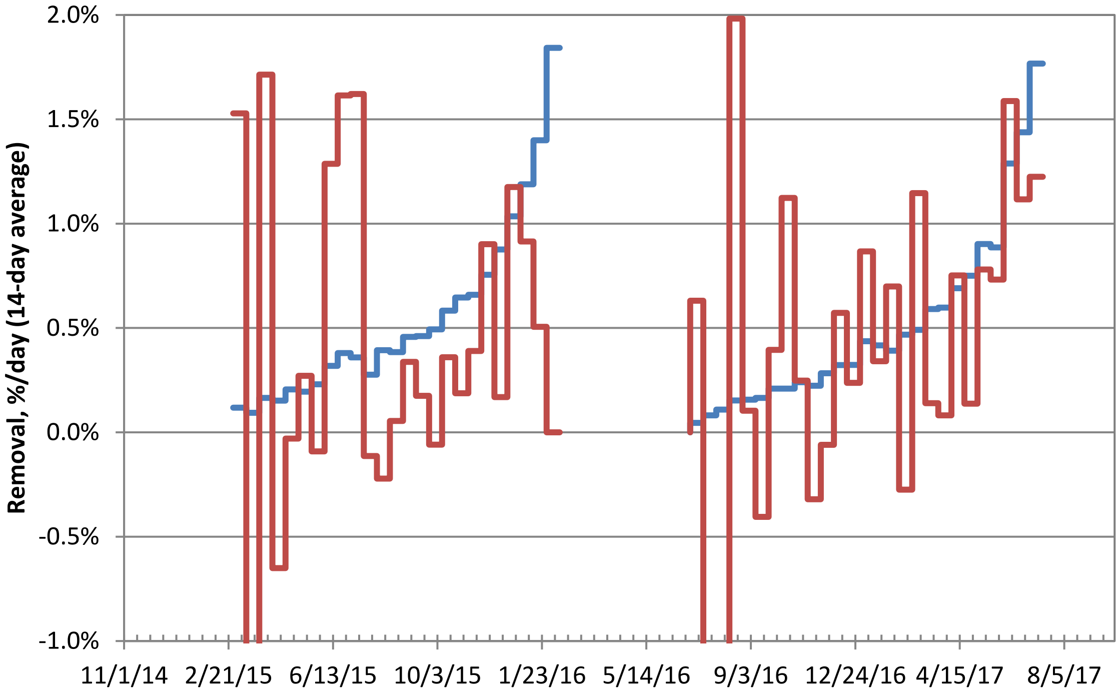


**Figure 6-6**
**Boron and Silica Removal Rates at McGuire 1 during Cycles 24 and 25**

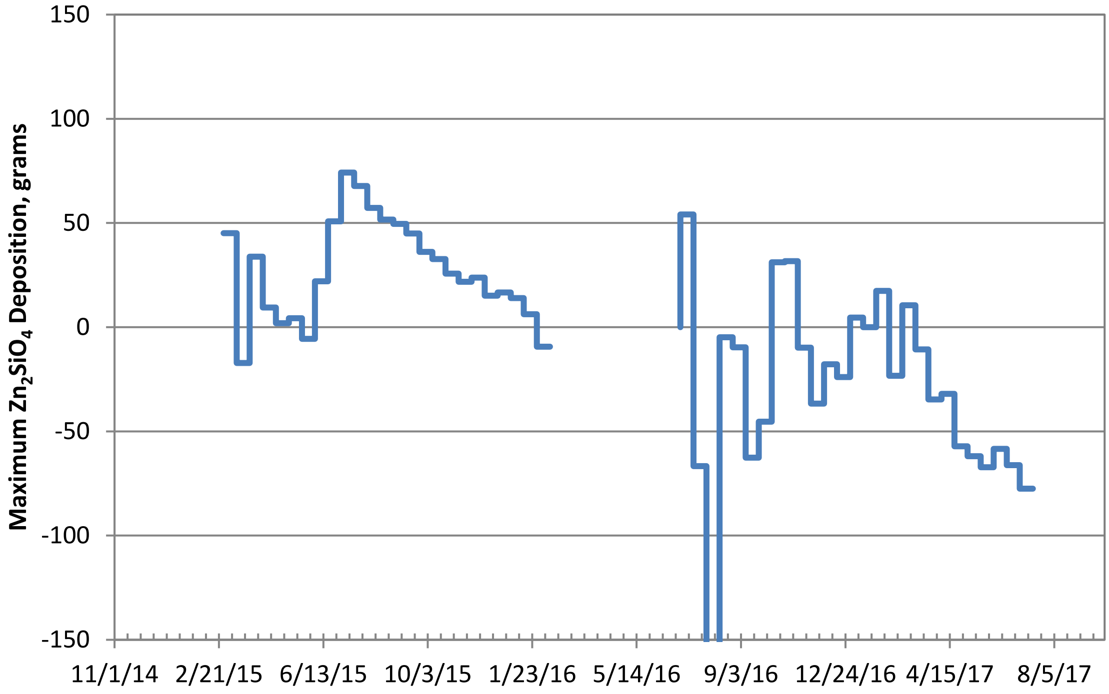


**Figure 6-7**
**Maximum Zinc Silicate Deposition at McGuire 1 during Cycles 24 and 25**

# 7
# SUMMARY

Deposition of compounds such as zinc silicate and calcium, magnesium and aluminum zeolites can increase PWR fuel cladding surface temperatures leading to increased cladding corrosion rates and possibly failures [1]. As a result, PWR fuel vendors have established silica concentration limits for the primary coolant, makeup water, boric acid storage tank and refueling water storage tank [2, 3]. Although Westinghouse notes that “High silica concentrations in conjunction with coolant zinc have not been associated with CIPS or other crud related problems” and “zinc silicate deposits have not been detected in fuel deposits” [2], these observations are limited to situations where silica has been controlled within current Westinghouse fuel warranty limits. Previous work evaluating operation at higher silica concentrations was complicated by issues with the accuracy of the fuel crud data, therefore they are not discussed here in detail [30], but these results were included in the fuel vendor evaluations included in this project.

In this project, the bases for establishing current silica limits were considered. These concerns were based both on solution chemistry modeling results and plant observations, e.g.:

- Zinc silicate precipitation was predicted to occur in PWR fuel cladding deposits at relatively low deposit solution to primary coolant concentration factors by MULTEQ with Database Version 8 [4], which does not consider the effect of borate-silicate ion pairs.
- Fuel deposit analyses at the River Bend BWR by Framatome (formerly AREVA) at EOC 11 identified zinc silicate crystals at fuel failure locations. Pore blocking by the precipitate was identified as a possible cause of the failures [10, 11, 12]
- Operating plant data were not available for periods of operation when the silica concentration exceeded 1 ppm and zinc injection was being performed, although there is beginning of cycle experience where silica is >1 ppm and residual zinc is present in the system from previous cycles of operation with zinc.

Results of the review and the bases for concerns regarding zinc silicate formation in PWR fuel deposits and its impact on PWR primary zinc application program optimization can be summarized as follows:

- Review of MULTEQ and OLI solution chemistry modeling results at PWR chemistries indicates that differences in the predicted tendencies for zinc silicate precipitation can be significant. Zinc silicate precipitation is predicted with MULTEQ (Database Version 8) at relatively low primary coolant to deposit solution concentration factors. However, MULTEQ results with the updated Database Version 9, which considers borate-silicate ion pairs, indicate zinc oxide is formed before zinc silicate in solutions with silica concentrations less than 5 ppm and a zinc concentration of 10 ppb. OLI code results developed by Framatome also indicate zinc oxide will be formed before zinc silicate. Note that borate-silicate ion pairs are not considered in the OLI code, but the activity model used in the code does not require explicit modeling of ion pair interactions. Although the solution chemistry modeling results differ in detail, formation of a zinc silicate precipitate in PWR fuel deposits is not predicted by current versions of either code as zinc oxide is preferentially formed.

- Zinc silicate formation is predicted to occur at BWR chemistries with MULTEQ at relatively low concentration factors both with Database Version 8 and Database Version 9, consistent with the River Bend BWR EOC 11 deposit observations.
- Extrapolation of BWR fuel deposit observations to prediction of PWR deposit chemistry cannot be supported based on the major differences in BWR and PWR chemistries, the impact of these differences on deposit solution chemistry, and the differences in deposit composition, magnitude and structure.

The concerns of zinc silicate formation and its effects on fuel deposit thermal resistance also are not supported by the WALT loop test data, i.e., Westinghouse succinctly summarized the WALT results relative to zinc and silica interactions:

> *"There appeared to be no interaction between zinc and silica, and zinc silicate was not detected in deposits. This was true even in an experiment where the zinc concentration was 40 ppb and the silica concentration was 10 ppm" [2].*

To support the modeling results and the WALT loop test observations, PWR primary coolant zinc and silica concentration variations during power operation were considered. The initial focus was on a zinc mass balance, i.e., the amount of zinc retained in the system during periods of injection was estimated from zinc injection rates and removal rates by the letdown system demineralizers. The maximum amount of zinc silicate deposition on the fuel was calculated from the amount of retained zinc. (Note that current BOA predictions indicate that only approximately 20% of the retained zinc deposits on the fuel with the remainder diffusing into out-of-core surface oxides [14].) Although it could be shown that the amount of retained zinc decreased with exposure to zinc (ppb-months), and the amount could be correlated to this parameter, the amount retained was 10 to 50% of the predicted amount of iron and nickel compound deposit formed during normal operation. Thus, the zinc mass balance could not be used to eliminate the concern of the effect of zinc compound deposition on the deposit thermal resistance. Note that the ability to correlate the zinc retention to the zinc exposure was consistent with expectations based on retention primarily being a result of diffusion into out of core oxides. This type of correlation would not be expected if retention was primarily a result of deposition of a zinc compound on the fuel.

In contrast, it does appear possible to further reduce the concerns regarding zinc silicate precipitation based on a silica mass balance during plant operation, although more detailed consideration of possible silica sources will be required. Silica balances, which were performed at three relatively high boiling duty plants over 10 to 13 month periods, yielded negative values for the maximum amount of zinc silicate deposition on the fuel, indicating a silica source term of 0.2 to 3.1 grams per month had not been considered. The magnitude of each of the identified but non-quantified silica source terms appear to be in the range of several grams per month. Once a reasonable estimate of the magnitude of each source is developed, the maximum rate of zinc silicate deposition can be more accurately estimated. The silica mass balance approach should significantly improve the ability to assess zinc silicate deposition tendencies during the cycle and the dependence of the deposition rate on primary chemistry and core boiling duty. Such assessments are recommended for consideration at high boiling duty plants. To estimate rates, during the period of operation preceding the gradual reduction in boron concentration by dilution, detailed data on concentrated boric acid and makeup water flow rates, and silica concentrations will be needed.

In summary, plant observations, modeling results, and fuel deposit loop testing results appear sufficient to justify fuel vendor consideration of relaxation of the current primary coolant silica limits prior to zinc injection. For higher boiling duty plants, assessments of the maximum zinc compound and zinc silicate deposition rates are considered prudent, particularly during initial periods of operation at elevated silica concentrations. Additional studies will be needed to estimate allowable deposition rates of zinc compounds based on their effects on deposit thermal resistance.

# 8
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# A

# ZINC INPUT, REMOVAL, RETENTION AND EXPOSURE AT PWRS

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**Table A-1**
**Zinc Input, Removal, Retention and Exposure at PWRs**

| Plant | Cycle | No. Cycles with Zinc | Zinc Added (kg) | Zinc Removed by Ion Exchange (kg) | Zinc on Plant Surfaces (kg) | Avg. Zinc Conc. (ppb) | Reference | ppb months |
|---|---|---|---|---|---|---|---|---|
| Angra 1 | | | | | | | [18] | |
| Angra 2 | | | | | | | [18] | |
| Asco1 | 19 | 1 | 1.73 | 0.83 | 0.9 | 6.7 | [18] | |
| Asco 1 | 20 | 2 | 3.68 | 2.93 | 0.75 | 11 | [18] | |
| Asco 1 | 21 | 3 | 1.65 | 0.87 | 0.78 | 12 | [18] | |
| Asco 2 | 17 | | 1.77 | 0.91 | 0.86 | 8 | [18] | |
| Asco 2 | 18 | | 4.79 | 3.44 | 1.35 | 13 | [18] | |
| Asco 2 | 19 | | 4.74 | 3.23 | 1.51 | 15 | [18] | |
| ANO 1 | 19 | 1 | | | | 5 | [18] | |
| ANO 1 | 20 | 2 | | | | 5.32 | [18] | |
| ANO 1 | 21 | 3 | | | | 5.2 | [18] | |
| ANO 1 | 22 | 4 | | | | 5 | [18] | |
| Beaver Valley | 15 | 1 | 4 | 0.6 | 3.4 | 24.3 | [18] | |
| Beaver Valley | 16 | 2 | 16.5 | 12.4 | 4.1 | 33.61 | [18] | |
| Beaver Valley | 17 | 3 | 17.6 | 13.8 | 3.8 | 33.64 | [18] | |
| Beaver Valley | 18 | 4 | 26.5 | 21.6 | 4.9 | 33.9 | [18] | |
| Beaver Valley | 19 | 5 | 12.9 | 10.2 | 2.7 | 15.3 | [18] | |
| Beaver Valley | 20 | 6 | 10.9 | 8.6 | 2.3 | 13.9 | [18] | |
| Braidwood 1 | 15 | 1 | 1.6 | 0.13 | 1.44 | 2.2 | [18] | |
| Braidwood 2 | 12 | 1 | 1.24 | 0.21 | 1.03 | 4.6 | [18] | |
| Braidwood 2 | 13 | 2 | 3.08 | 0.82 | 2.26 | 4.2 | [18] | |
| Braidwood 2 | 14 | 3 | 3.85 | 1.57 | 2.28 | 5.6 | [18] | |
| Braidwood 2 | 15 | 4 | 3.75 | 1.66 | 2.09 | 4.6 | [18] | |
| Bugey 2 | 22 | 1 | 2.5 | 0.383 | 2.132 | 5 | [18] | |
| Bugey 2 | 23 | 2 | 4.02 | 2.465 | 1.555 | 9.9 | [18] | |
| Bugey 2 | 24 | 3 | 1.966 | 1.062 | 0.904 | 13.1 | [18] | |
| Bugey 2 | 25 | 4 | 1.405 | 1.029 | 0.376 | 9.4 | [18] | |

| Plant | Cycle | No. Cycles with Zinc | Zinc Added (kg) | Zinc Removed by Ion Exchange (kg) | Zinc on Plant Sur-faces (kg) | Avg. Zinc Conc. (ppb) | Reference | ppb months |
|---|---|---|---|---|---|---|---|---|
| Bugey 2 | 26 | 5 | 3.434 | 1.63 | 1.804 | 11.5 | [18] | |
| Bugey 4 | 23 | 1 | 6.779 | 1.239 | 5.54 | 8.9 | [18] | |
| Bugey 4 | 24 | 2 | 3.034 | 1.329 | 1.705 | 12.2 | [18] | |
| Bugey 4 | 25 | 3 | | | | 18 | [18] | |
| Byron 1 | 17 | 1 | 1.56 | 0.125 | 1.44 | 2.2 | [18] | |
| Byron 2 | 12 | 1 | 1.49 | 0.26 | 1.23 | 4.2 | [18] | |
| Byron 2 | 13 | 2 | 2.03 | 0.87 | 1.16 | 4.8 | [18] | |
| Byron 2 | 14 | 3 | 2.6 | 1.29 | 1.31 | 4.1 | [18] | |
| Byron 2 | 15 | 4 | 2.68 | 1.93 | 0.75 | 5.7 | [18] | |
| Callaway | 13 | 1 | 4.4 | 1.4 | 3 | 6.9 | [18] | |
| Callaway | 14 | 2 | 5.84 | 3.4 | 2.44 | 12.4 | [18] | |
| Callaway | 15 | 3 | 4.42 | 2.61 | 1.81 | 9 | [18] | |
| Callaway | 16 | 4 | 4.66 | 3.08 | 1.58 | 9.4 | [18] | |
| Callaway | 17 | 5 | 4.48 | 3.12 | 1.36 | 10 | [18] | |
| Callaway | 18 | 6 | 3.68 | 2.81 | 0.877 | 11.2 | [18] | |
| Calvert Cliffs 1 | 18 | 1 | 1.4 | 0.36 | 1.09 | 5 | [18] | |
| Calvert Cliffs 1 | 19 | 2 | 3 | 1.12 | 1.11 | 7.4 | [18] | |
| Calvert Cliffs 2 | 17 | 1 | 1.52 | 0.33 | 1.11 | 5 | [18] | |
| Calvert Cliffs 2 | 18 | 2 | 11.5 | 1.3 | 1.4 | 7.6 | [18] | 33 |
| Catawba 1 | 17 | 1 | 2.365 | 0.418 | 1.95 | 4.1 | [18] | 161 |
| Catawba 1 | 18 | 2 | 3.866 | 1.773 | 2.093 | 7.8 | [18] | |
| Catawba 1 | 19 | 3 | 3.524 | 2.174 | 1.35 | 10.3 | [18] | |
| Catawba 2 | 15 | 1 | 2.641 | 0.66 | 1.98 | 6 | [18] | |
| Catawba 2 | 16 | 2 | 4.12 | 2.17 | 1.95 | | [18] | |
| Catawba 2 | 17 | 3 | 3.887 | 2.48 | 1.42 | 5 | [18] | |
| Crystal River 3 | 16 | 1 | 3.49 | 0.54 | 2.95 | 6 | [18] | |
| Diablo Canyon 1 | 9 | 1 | 2.8 | 3.05 | 2.8 | 31 | [18] | |
| Diablo Canyon 1 | 10 | 2 | 1.53 | 2.55 | 1.53 | 21 | [18] | |
| Diablo Canyon 1 | 11 | 3 | 1.35 | 2.69 | 1.35 | 15 | [18] | |
| Diablo Canyon 1 | 12 | 4 | 2.2 | 5.8 | 2.2 | 24 | [18] | |
| Diablo Canyon 1 | 13 | 5 | 2.4 | 6.2 | 2.4 | 25 | [18] | |
| Diablo Canyon 1 | 16 | 8 | 7.13 | 5.52 | | 22 | [18] | |
| Diablo Canyon 2 | 9 | 1 | 1.86 | 1.62 | 1.86 | 21 | [18] | |
| Diablo Canyon 2 | 10 | 2 | 0.69 | 2.87 | 0.69 | 16 | [18] | |
| Diablo Canyon 2 | 11 | 3 | 1.57 | 3.34 | 1.57 | 15 | [18] | |
| Diablo Canyon 2 | 12 | 4 | 2.2 | 5.8 | 2.2 | 25 | [18] | |

| Plant | Cycle | No. Cycles with Zinc | Zinc Added (kg) | Zinc Removed by Ion Exchange (kg) | Zinc on Plant Sur-faces (kg) | Avg. Zinc Conc. (ppb) | Reference | ppb months |
|---|---|---|---|---|---|---|---|---|
| Diablo Canyon 2 | 13 | 5 | 2.2 | 5.8 | 2.2 | 25 | [18] | |
| Diablo Canyon 2 | 16 | 8 | 6.29 | 4.95 | | 25 | [18] | |
| Doel 3 | 29 | 1 | | | | | [18] | |
| Farley 1 | 16 | 1 | 12.87 | 7.12 | 5.75 | 30.4 | [18] | |
| Farley 1 | 16 | 1 | 12.95 | 7.63 | 5.32 | 29.8 | [29] | |
| Farley 1 | 17 | 2 | 8.4 | 3.14 | 5.26 | 12.9 | [18] | |
| Farley 1 | 17 | 2 | | | | 13.1 | [29] | |
| Farley 1 | 18 | 3 | 8.3 | 2.73 | 5.57 | 13.8 | [18] | |
| Farley 1 | 19 | 4 | 8.8 | 2.49 | 6.31 | 15 | [18] | |
| Farley 1 | 20 | 5 | 6.786 | 5.293 | 1.493 | 15.1 | [18] | |
| Farley 1 | 21 | 6 | 6.622 | 5.154 | 1.468 | 14.8 | [18] | |
| Farley 1 | 22 | 7 | | | | 15.1 | [18] | |
| Farley 1 | 23 | 8 | | | | 15.3 | [18] | |
| Farley 2 | 10 | 1 | 10.89 | 7.06 | 3.83 | 35 | [18] | |
| Farley 2 | 12 | 1 | 4.06 | 3.03 | 1.03 | 40 | [18] | |
| Farley 2 | 13 | 2 | 8.1 | 6.61 | 1.49 | 29 | [18] | |
| Farley 2 | 13 | 2 | 5.8 | 5.06 | 0.74 | 30.2 | [29] | |
| Farley 2 | 14 | 3 | 10.58 | 9.68 | 0.9 | 29 | [18] | |
| Farley 2 | 14 | 3 | 10.05 | 7.57 | 2.48 | 29.2 | [29] | |
| Farley 2 | 15 | 4 | 8.1 | | | 14 | [18] | |
| Farley 2 | 15 | 4 | 7.27 | 4.57 | 2.7 | 14.2 | [29] | |
| Farley 2 | 16 | 5 | 8.4 | | | 15 | [18] | |
| Farley 2 | 17 | 6 | 6.84 | 5.335 | 1.505 | 15 | [18] | |
| Farley 2 | 18 | 7 | 6.45 | 5.037 | 1.413 | 15 | [18] | |
| Farley 2 | 19 | 8 | 6.49 | 5.091 | 1.505 | 15 | [18] | |
| Farley 2 | 20 | 9 | | | | 14.9 | [18] | |
| Fort Calhoun | 21 | 1 | 2.27 | | | 2.3 | [18] | |
| Fort Calhoun | 22 | 2 | 2.16 | | | 5.1 | [18] | |
| Fort Calhoun | 23 | 3 | | | | 4.5 | [18] | |
| Fort Calhoun | 24 | 4 | | | | 5.5 | [18] | |
| Fort Calhoun | 25 | 5 | | | | 6 | [18] | |
| Fort Calhoun | 26 | 6 | 0.878 | | | 6 | [18] | |
| Indian Point 2 | 18 | 1 | 1.31 | 0.14 | 0.91 | 3 | [18] | |
| Indian Point 2 | 19 | 2 | 8.81 | 5.2 | 3.7 | 18.4 | [18] | |
| McGuire 1 | 18 | 1 | 2.04 | 0.43 | 1.62 | 4.2 | [18] | |
| McGuire 1 | 19 | 2 | 3.38 | 1.54 | 1.84 | 6.7 | [18] | |

| Plant | Cycle | No. Cycles with Zinc | Zinc Added (kg) | Zinc Removed by Ion Exchange (kg) | Zinc on Plant Sur-faces (kg) | Avg. Zinc Conc. (ppb) | Reference | ppb months |
|---|---|---|---|---|---|---|---|---|
| McGuire 1 | 20 | 3 | 4.36 | 2.96 | 1.4 | 12.8 | [18] | |
| McGuire 1 | 21 | 4 | 4.246 | 3 | 1.246 | | [23] | |
| McGuire 1 | 22 | 5 | 3.287 | 2.512 | 0.774 | | [23] | |
| McGuire 1 | 23 | 6 | 3.473 | 2.673 | 0.8 | | [23] | |
| McGuire 1 | 24 | 7 | 3.57 | 2.818 | 0.752 | | [23] | |
| McGuire 1 | 25 | 8 | 3.699 | 2.957 | 0.743 | | [23] | |
| McGuire 2 | 17 | 1 | 2.688 | 0.48 | 2.21 | | [18] | |
| McGuire 2 | 18 | 2 | 2.8 | 1.39 | 1.42 | 7.8 | [18] | |
| McGuire 2 | 19 | 3 | 4.18 | 2.47 | 1.71 | 11.3 | [18] | |
| McGuire 2 | 20 | 4 | 4.52 | 2.93 | 1.59 | 12.6 | [18] | |
| North Anna 1 | 23 | 1 | 1.08 | 0.14 | 0.94 | 3.03 | [28] | 10.08 |
| North Anna 1 | 24 | 2 | 1.62 | 0.54 | 1.08 | 4.2 | [28] | 37.83 |
| North Anna 1 | 25 | 3 | 2.082 | 1.19 | 0.889 | 4.9 | [28] | 83.69 |
| North Anna 1 | 26 | 4 | 1.88 | 1.16 | 0.72 | 4.9 | [28] | 81.4 |
| North Anna 2 | 23 | 1 | 1.28 | 0.14 | 1.14 | 2.7 | [28] | 10.79 |
| North Anna 2 | 24 | 2 | 1.633 | 0.56 | 1.075 | 4.76 | [28] | 43.26 |
| North Anna 2 | 25 | 3 | 1.877 | 1.06 | 0.813 | 4.84 | [28] | 82.19 |
| Oconee 3 | 29 | | | | | | [23] | |
| Palisades | 14 | 1 | 2.87 | 0.47 | 2.4 | 4.7 | [18] | |
| Palisades | 15 | 2 | 1.49 | 0.4 | 1.09 | 4.5 | [18] | |
| Palisades | 16 | 3 | 1.43 | 0.34 | 1.09 | 5 | [18] | |
| Palisades | 17 | 4 | 2.3 | 0.91 | 1.39 | 5 | [18] | |
| Palisades | 18 | 5 | 2.16 | 0.86 | 1.3 | 5.8 | [18] | |
| Palisades | 19 | 6 | 2.85 | | | 7.13 | [18] | |
| Palisades | 20 | 7 | 2.1 | | | 7.18 | [18] | |
| Palisades | 21 | 8 | 1.9 | | | 7.19 | [18] | |
| Salem 1 | 18 | 1 | 2.3 | 1.1 | 1.2 | 4.6 | [18] | |
| Salem 1 | 19 | 2 | 1.5 | 0.19 | 1.31 | 4.1 | [18] | |
| Salem 1 | 20 | 3 | 2.2 | 1.2 | 1 | 5.2 | [18] | |
| Salem 2 | 16 | 1 | 2.3 | 0.3 | 2 | 3.3 | [18] | |
| Salem 2 | 17 | 2 | 2.8 | 1 | 1.8 | 4.3 | [18] | |
| Salem 2 | 18 | 3 | 2.8 | 1.3 | 1.5 | | [18] | |
| San Onofre 2 | 15 | 1 | 1.92 | 0.15 | 1.77 | 3.7 | [18] | |
| San Onofre 2 | 16 | 2 | 4.6 | 0.4 | 1.2 | 4.6 | [18] | |
| San Onofre 3 | 15 | 1 | 2.15 | 0.28 | 1.86 | 4.1 | [18] | |
| Sequoyah 1 | 12 | 1 | 2.4 | 0.44 | 1.96 | 3.7 | [18] | |

| **Plant** | **Cycle** | **No. Cycles with Zinc** | **Zinc Added (kg)** | **Zinc Removed by Ion Exchange (kg)** | **Zinc on Plant Surfaces (kg)** | **Avg. Zinc Conc. (ppb)** | **Reference** | **ppb months** |
|---|---|---|---|---|---|---|---|---|
| Sequoyah 1 | 13 | 2 | 2.89 | 0.85 | 2.04 | 4.6 | [18] | |
| Sequoyah 1 | 14 | 3 | 3.4 | 0.9 | 2.5 | 4.8 | [18] | |
| Sequoyah 1 | 15 | 4 | | | | 4.8 | [18] | |
| Sequoyah 1 | 16 | 5 | | | | 4.6 | [18] | |
| Sequoyah 1 | 17 | 6 | | | | 5 | [18] | |
| Sequoyah 2 | 12 | 1 | 3.24 | 0.46 | 2.78 | 2.6 | [18] | |
| Sequoyah 2 | 13 | 2 | 2.73 | 0.83 | 1.91 | 4.8 | [18] | |
| Sequoyah 2 | 14 | 3 | | | | 5 | [18] | |
| Sequoyah 2 | 15 | 4 | | | | 6 | [18] | |
| Sequoyah 2 | 16 | 5 | | | | 4.9 | [18] | |
| Sequoyah 2 | 17 | 6 | | | | 5 | [18] | |
| STP 1 | 15 | 1 | 2.074 | 0.552 | 1.522 | 6.2 | [18] | |
| STP 1 | 15 | 1 | 2.074 | 0.552 | 1.522 | | [24] | 25.1 |
| STP 1 | 16 | 2 | 5.316 | 2.21 | | 6 | [18] | |
| STP 1 | 16 | 2 | 3.789 | 2.21 | 1.579 | | [24] | 97.7 |
| STP 1 | 17 | 3 | 4.297 | 2.938 | 1.359 | | [24] | 129.4 |
| STP 1 | 18 | 4 | 3.74 | 2.552 | 1.188 | | [24] | 108 |
| STP 1 | 19 | 5 | 5.751 | 3.811 | 1.94 | | [24] | 158 |
| STP 1 | 20 | 6 | 4.568 | 3.519 | 1.048 | | [24] | 147 |
| STP 1 | 21 | 7 | 5.634 | 3.91 | 1.723 | | [24] | 160.4 |
| STP 2 | 14 | 1 | 2.431 | 0.9 | 1.512 | 6.95 | [18] | |
| STP 2 | 14 | 1 | 2.431 | 0.903 | 1.528 | | [24] | 40 |
| STP 2 | 15 | 2 | 4.84 | 2.83 | | 7.3 | [18] | |
| STP 2 | 15 | 2 | 4.829 | 2.823 | 2.006 | | [24] | 126.7 |
| STP 2 | 16 | 3 | 2.59 | 2.008 | 0.582 | | [24] | 115 |
| STP 2 | 17 | 4 | 4.55 | 3.413 | 1.137 | | [24] | 151 |
| STP 2 | 18 | 5 | 4.841 | 3.706 | 1.136 | | [24] | 164 |
| STP 2 | 19 | 6 | 5.584 | 3.682 | 1.903 | | [25] | 160 |
| Surry 1 | 22 | 1 | 2.74 | 0.52 | 2.22 | 7.4 | [18] | |
| Surry 1 | 23 | 2 | 3.53 | 1.85 | 1.68 | 5.94 | [18] | |
| Surry 1 | 24 | 3 | 4.42 | 2.82 | 1.6 | 9.89 | [18] | |
| Surry 2 | 21 | 1 | 3.13 | 0.64 | 2.49 | 3.7 | [18] | |
| Surry 2 | 22 | 2 | 4.91 | 2.83 | 2.08 | 8.8 | [18] | |
| Surry 2 | 23 | 3 | 3.59 | 2.49 | 1.1 | 8.78 | [18] | |
| TMI 1 | 16 | 1 | 5.63 | 0.49 | 5.14 | 5.3 | [18] | |
| TMI 1 | 17 | 2 | 2.31 | 1.18 | 1.13 | 4.5 | [18] | |

| Plant | Cycle | No. Cycles with Zinc | Zinc Added (kg) | Zinc Removed by Ion Exchange (kg) | Zinc on Plant Sur-faces (kg) | Avg. Zinc Conc. (ppb) | Reference | ppb months |
|---|---|---|---|---|---|---|---|---|
| Ulchin 1 | 17 | 1 | 1.83 | 0.23 | 1.6 | 5.6 | [18] | |
| Vandellos II | 15 | | 2.4 | 0.53 | 1.795 | 5.9 | [18] | |
| Vandellos II | 16 | | 3.67 | 1.9 | 1.4 | 9 | [18] | |
| Vandellos II | 17 | | 3.525 | 1.97 | 0.795 | 12 | [18] | |
| Vogtle 1 | 12 | 1 | 2.75 | 0.61 | 2.14 | 10 | [18] | |
| Vogtle 1 | 13 | 2 | 0.38 | 0.07 | 0.303 | 5 | [18] | |
| Vogtle 1 | 14 | 3 | 3.02 | 1.27 | 0.984 | 15 | [18] | |
| Vogtle 1 | 15 | 4 | 1.99 | 1.96 | 0.07 | 7.2 | [18] | |
| Vogtle 1 | 16 | 5 | 4.2 | 1.88 | 2.32 | 9.1 | [18] | |
| Vogtle 2 | 11 | 1 | 2.63 | 0.46 | 2.17 | 5 | [18] | |
| Vogtle 2 | 12 | 2 | 3.17 | 1.68 | 1.49 | 11.4 | [18] | |
| Vogtle 2 | 13 | 3 | 2.51 | 1.57 | 0.94 | 10.3 | [18] | |
| Vogtle 2 | 14 | 4 | 1.55 | 1.43 | 0.12 | 5 | [18] | |
| Waterford 3 | 17 | 1 | 1.5489 | 0.2889 | | 5.37 | [18] | |
| Watts Bar 1 | 8 | 1 | 2.9 | 0.932 | 2.013 | 4.49 | [18] | |
| Watts Bar 1 | 9 | 2 | 3.3 | 1.182 | 2.173 | 5.27 | [18] | |
| Watts Bar 1 | 10 | 3 | 2.6 | 1.198 | 1.4 | 6.08 | [18] | |

# B

# VARIATIONS IN PRIMARY COOLANT BORON AND SILICA CONCENTRATIONS

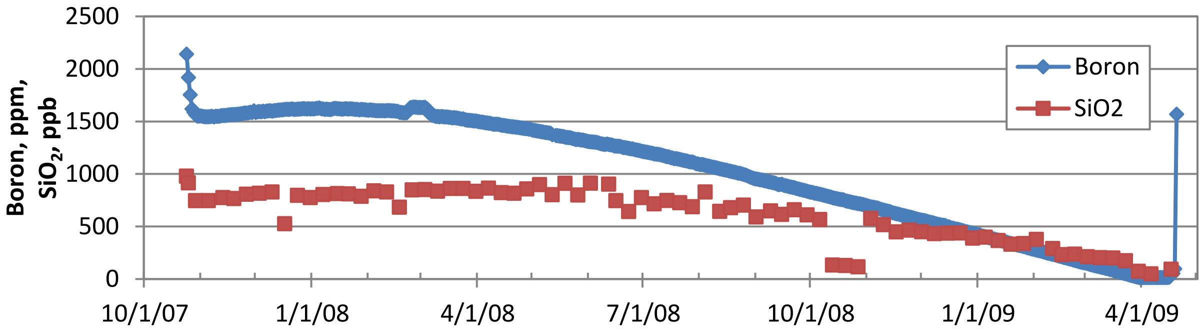

**Figure B-1**
**Boron and Silica Concentration Variations at Beaver Valley 1**

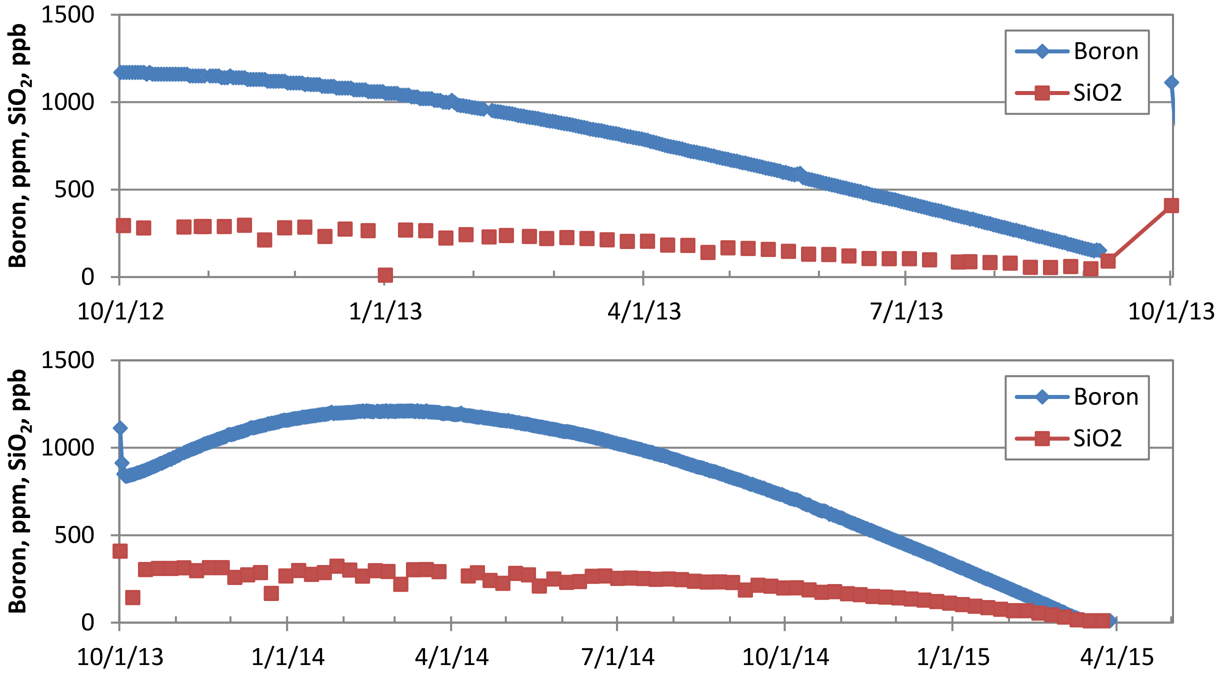

**Figure B-2**
**Boron and Silica Concentration Variations at Braidwood 1**

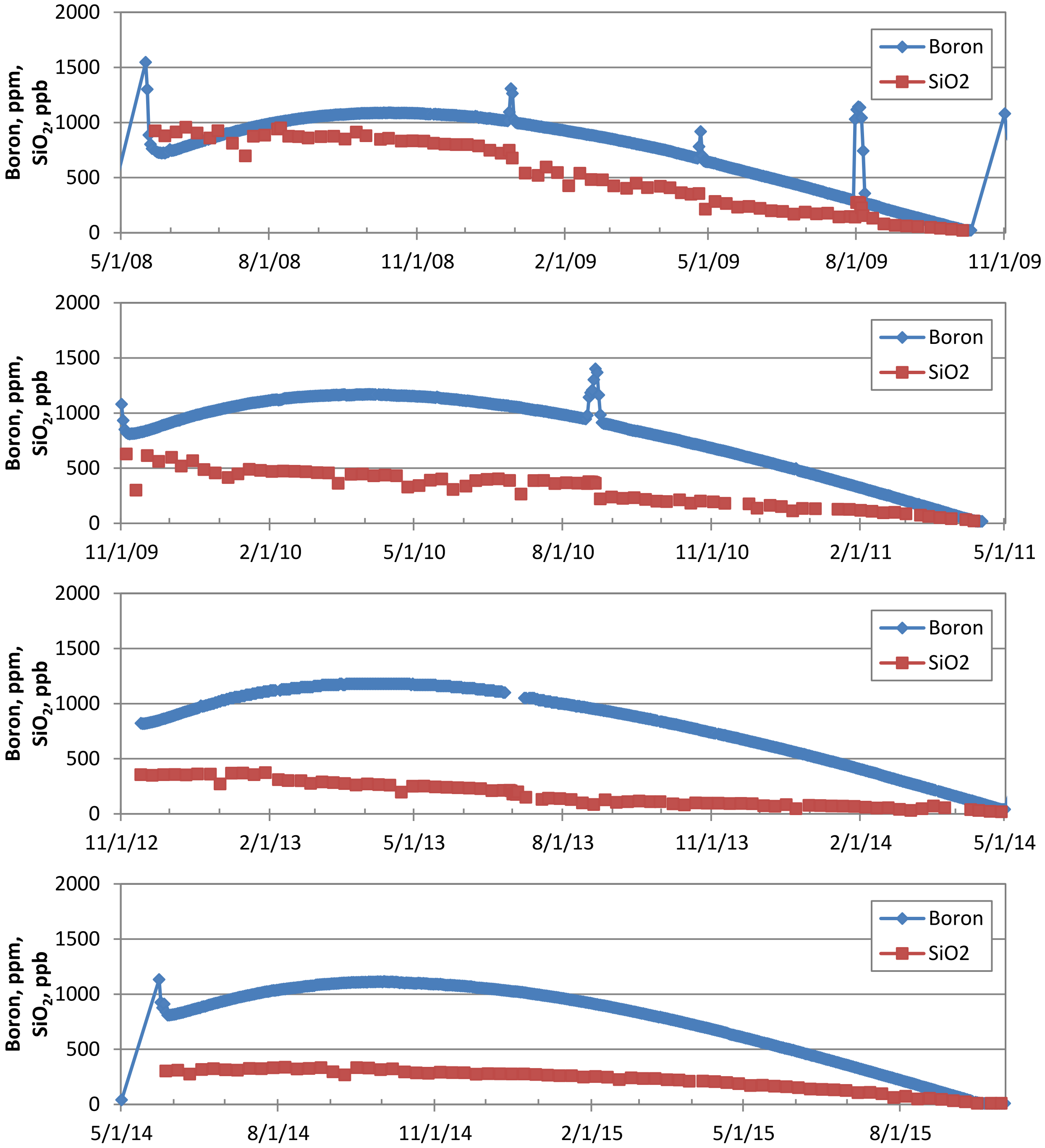

**Figure B-3**
**Boron and Silica Concentration Variations at Braidwood 2**

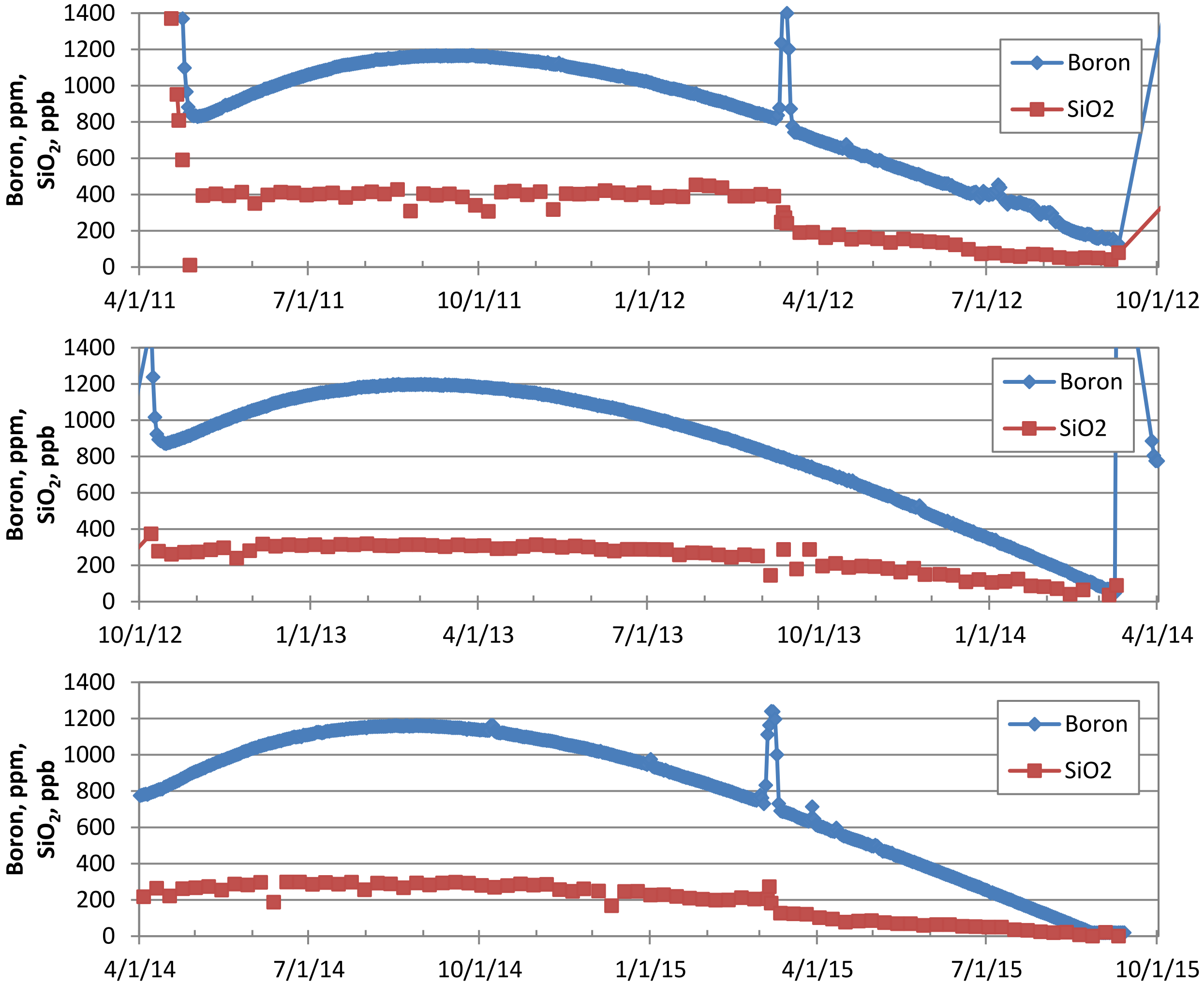

**Figure B-4**
**Boron and Silica Concentration Variations at Byron 1**

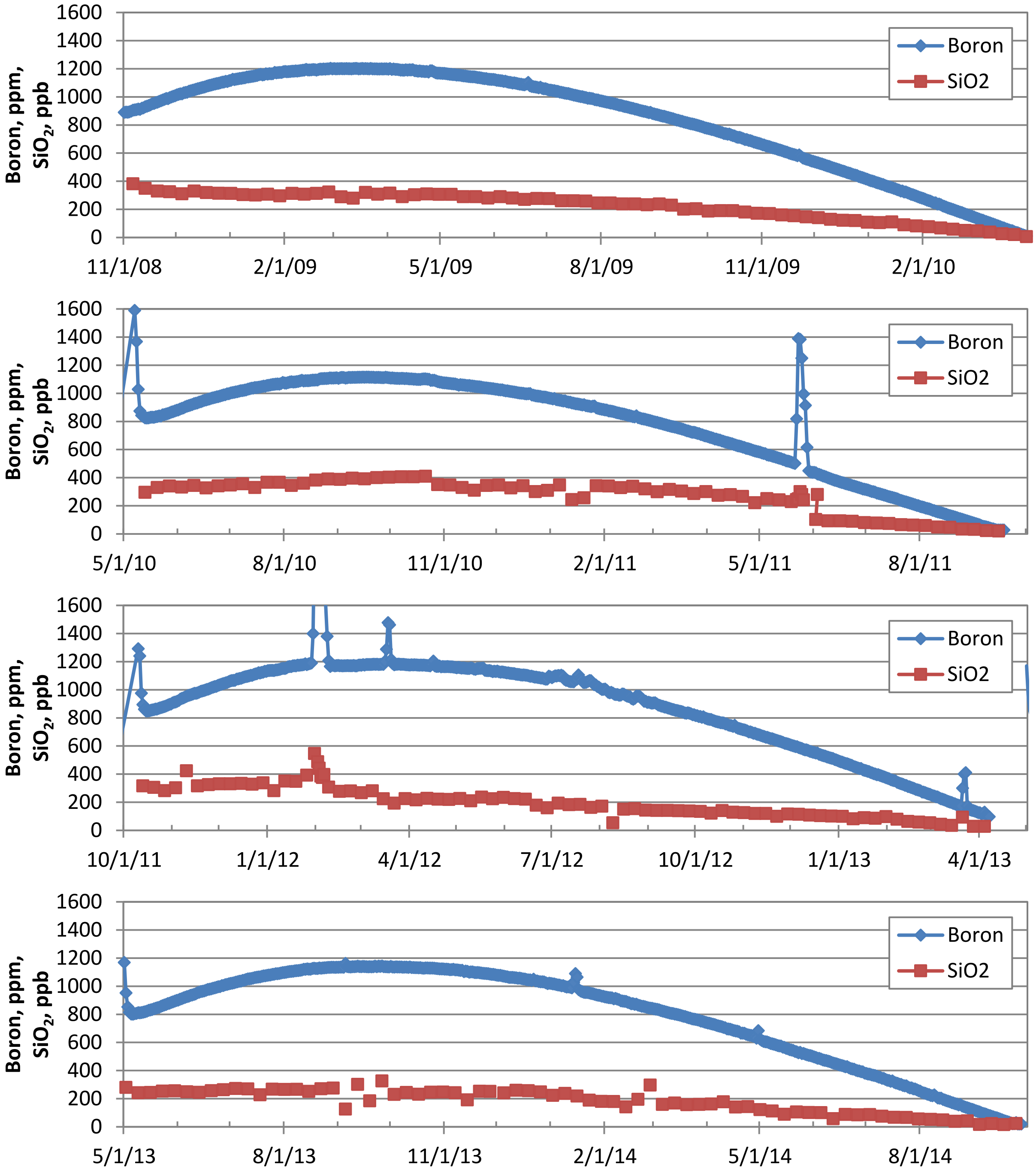

**Figure B-5**
**Boron and Silica Concentration Variations at Byron 2**

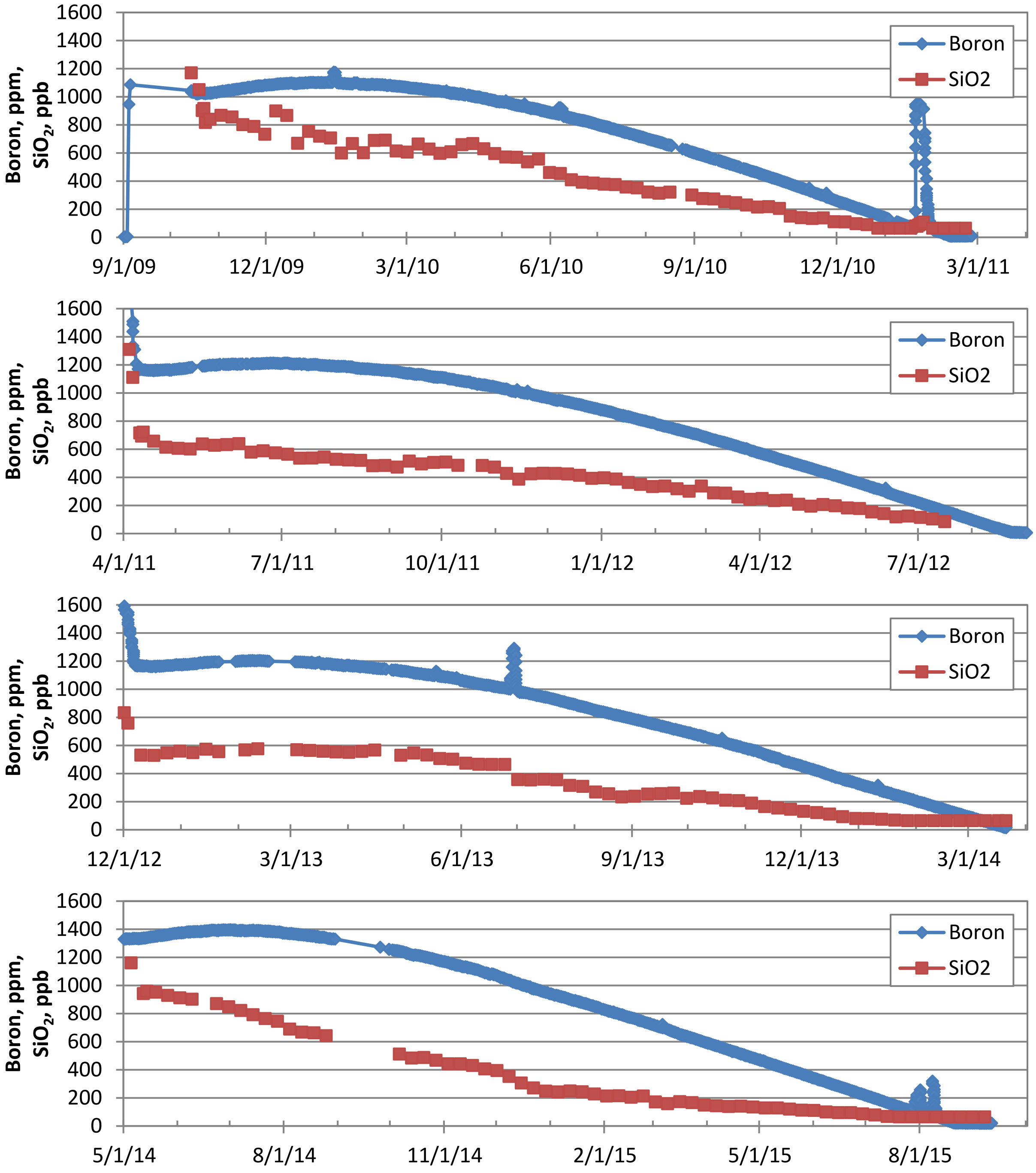

**Figure B-6**
**Boron and Silica Concentration Variations at McGuire 2**

# C

# TRANSLATED TABLE OF CONTENTS

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# Comportement du zinc et de la silice dans le système primaire d’un REP (réacteur à eau sous pression) : Rapport du groupe Stratégie technique et chimique des REP

**3002015884**

Rapport final, août 2019

Responsable de projet EPRI
D. Wells

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# RESUME

Le dépôt de particules contenant de la silice sur les assemblages à combustible d'un réacteur à eau sous pression (REP) est source d'inquiétude en raison de l'encrassement de l'ensemble des assemblages à combustible. Un encrassement accru pourrait mener à l'augmentation des températures des surfaces des revêtements, entraînant une corrosion élevée et des défaillances potentielles. À cette fin, les REP limitent la quantité de silice présente dans l'eau de refroidissement du circuit primaire durant le service afin de réduire le risque de problèmes associés à la formation de particules contenant de la silice. Le maintien de faibles concentrations de silice dans le circuit primaire peut s'avérer un effort coûteux pour l'opérateur. Ceci peut comprendre, et a d'ores et déjà compris, l'installation de systèmes à osmose inverse (RO en anglais) afin de réduire les concentrations en silice dans la piscine de stockage du combustible usé (la source primaire), étant donné que d'autres méthodes moins onéreuses ne sont pas efficaces. En outre, des concentrations élevées en silice peuvent entraîner l'imposition de contraintes pour la conception du cœur ou des limites dans l'injection de zinc, imposées par le fournisseur de combustible, ce qui peut rendre l'exploitation plus onéreuse, tant en termes de coût du combustible que de doses pour le personnel. De récentes évaluations des données de solubilité de la silice suggèrent que la solubilité de la silice en présence d'acide borique est bien plus élevée que l'on ne le pensait jusqu'alors. Ceci peut être une des raisons expliquant les observations divergentes en matière de génération de silice dans les impuretés de combustible des REP et des réacteurs à eau bouillante (REB). La présence d'acide borique peut, à terme, réduire le risque de formation de matériaux silicatés dans les REP et finalement, potentiellement via d'autres expérimentations, entraîner l'assouplissement des limites de silice imposées pour les REP. Le projet évalue des observations de particules contenant du silicium dans les REP, et le potentiel d'assouplissement des limites de contrôle de la silice imposées dans le circuit primaire des REP.

### Mots-clés

Composition chimique du circuit primaire des REP
Impuretés de combustible des REP
silice
zinc

# TABLE DES MATIERES

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# LISTE DES FIGURES

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# LISTE DES TABLEAUX

# PWR 一次系での亜鉛およびシリカの挙動：PWR 化学技術戦略グループレポート

**3002015884**

最終報告 2019 年 8 月

EPRI プロジェクトマネージャ
D. Wells

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# 概要

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加圧水型原子炉(PWR)の燃料集合体上に堆積する、固体を含むシリカは、一般的な燃料集合体の付着物に関する懸念のひとつです。付着物が増すにつれ、クラッディング表面の温度も上昇し、腐食が進み、破損の可能性が高くなります。そのような結果を考慮し、固体を含むシリカの形成に関連した問題のリスクを最小にするため、PWR では、運転中の一次系冷却水内のシリカの量を制限しています。電力会社は一次系でのシリカの濃度を低く保つよう努力していますが、それには費用がかかります。これには、使用済み核燃料プール(これが主要なソース)のシリカ濃度を下げるために逆浸透(RO)システムを設置することや、それほど高額ではないものの効果も劣る他の手段が含まれます。さらに、シリカの濃度が高いと、燃料ベンダーが炉心の設計や亜鉛注入において制限を求める場合があり、その結果、燃料の費用と人員の線量の両方の点で運転コストが高くなることになります。シリカの溶解度データに関する最近の評価は、ホウ酸が存在する場合のシリカの溶解度が、以前考えられていたよりもずっと高いことを示唆しています。観察されている、PWR と沸騰水型原子炉(BWR)の燃料沈殿物内でのシリカ生成の違いは、これが原因かもしれません。ホウ酸の存在は、究極的には PWR 内でのケイ酸塩の生成リスクを低くし、(付加的な実験が必要ですが)やがては PWR でのシリカの制限を緩和することにつながるかもしれません。プロジェクトでは、PWR 内での固体を含むケイ素の観察結果と、PWR 一次系でのシリカに関連した管理限界緩和の可能性を評価します。

**キーワード**
PWR 一次水水質
PWR の燃料付着物
シリカ
亜鉛

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# 図の一覧

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# 아연 및 실리카의 PWR 일차 계통 내 거동: PWR 화학 기술 전략 그룹 보고서

3002015884

최종 보고서, 2019년 8월

EPRI 프로젝트 매니저
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# 초록

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가압 경수로(PWR) 연료 어셈블리에 고형물을 함유한 실리카가 침적되는 것은 일반적인 연료 어셈블리 파울링과 관련한 우려 사항입니다.  파울링이 증가하면 피복재 표면 온도가 상승하여 부식이 증가하고, 잠재적 고장의 가능성이 발생합니다. 이를 해결하기 위해 PWR은 작동 중에 일차 계통 냉각재 실리카의 양을 제한하여 고형물을 함유한 실리카의 형성과 관련된 문제의 위험을 최소화합니다. 일차 계통에서 낮은 실리카 농도를 유지하려면 시설은 많은 비용을 지불해야 합니다. 여기에는 사용 후 연료 풀 실리카 농도(일차 원천)를 줄이기 위한 역삼투압(RO) 시스템의 설치가 포함되는데, 그 이유는 비용이 저렴한 여타의 방법이 효과적이지 않기 때문입니다. 또한 높은 실리카 농도는 코어 설계 제약 또는 아연 주입 제한(연료 공급업체에 의한)을 초래할 수 있으며, 이는 연료 비용과 개인 선량 측면에서 운영비를 높일 수 있습니다. 실리카 용해도 데이터에 관한 최근 평가에 따르면 붕산 존재 시 실리카의 용해도는 생각보다 훨씬 높습니다. 이는 PWR과 비등수형 원자로(BWR) 연료 크러드에서 규산염 생성이 상이하게 관찰되는 이유일 수 있습니다. 붕산의 존재는 PWR에서 규산염 물질의 형성 위험을 궁극적으로 감소시킬 수 있으며, 결국 잠재적으로 추가 실험을 통해 PWR에서 실리카 한도를 완화할 수 있습니다. 이 프로젝트는 PWR에서 고형물을 함유한 실리콘의 관찰과 PWR 일차 계통에서 실리카와 관련된 제어 한도의 완화 가능성을 평가합니다.

**키워드**

PWR 일차 화학
PWR 연료 크러드
실리카
아연

# 목차

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# 그림 목록

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# 표 목록

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