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Pressurized Water Reactor Zinc Application: Data Analysis and Evaluation of Primary Chemistry Responses

Data Analysis and Evaluation of Primary Chemistry Responses

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REPORT SUMMARY

Background

The Electric Power Research Institute (EPRI) Pressurized Water Reactor Zinc Application Users Group (PWR ZUG) facilitates and improves the use of zinc injection in PWR primary coolant systems by assisting in the evaluation of zinc injection performance; documentation of lessons learned; communication of information on zinc injection qualification, monitoring, and operating experience; and review of zinc application effectiveness regarding primary water stress corrosion cracking (PWSCC) and radiation field reduction. Since the establishment of this group in 2005, the PWR ZUG has funded various research activities related to PWR zinc addition, including the collection of plant data for cycles in which zinc injection was performed. This report presents results of the latest EPRI industry benchmarking assessments for reactor coolant system (RCS) zinc addition using available plant data.

Objective

- To evaluate the available plant data and determine whether plant responses to both near- and long-term stages of a zinc injection program can be predicted

Approach

The PWR ZUG identified several areas for further research related to RCS zinc addition that were desired to support both the implementation of RCS zinc injection and long-term program strategy. Several plant response factors were identified for assessment. These include an evaluation of system responses to zinc injection and identification of any relationship between corrosion product release and zinc injection. Development of generic predictions for a zinc injection cycle and prediction for system responses to plant transients during a zinc injection cycle were also evaluated. Based on the results of the assessment, a performance indicator for zinc injection program performance was also evaluated. EPRI has been collecting primary chemistry and Standard Radiation Monitoring Program (SRMP) data from PWRs for many years. A statistical assessment of the available data will be performed to determine whether the relationship and predictions mentioned previously can be developed.

Results

Evaluation of plant responses to initial cycles of zinc injection yielded mixed results related to both primary coolant radiocobalt activity and nickel concentrations. For both parameters, there were statistically significant increases for some plants and a statistically significant lack of response for other plants. There was no statistically significant increase in the mass of nickel released during shutdown following the initial cycle of zinc injection.

Attempts to quantify long-term trends resulting from zinc injection identified the following: initiation of PWSCC continues to slow, the fraction of zinc retained by system surfaces decreases over time, and ex-core dose rates decrease with additional cycles of zinc injection at rates greater than the rates of decrease without zinc addition.

Evaluation of plant data collected during plant transients yielded varying results. In general, RCS zinc concentration is relatively unaffected by power transient and associated minimal temperature changes.

None of the performance indicators considered for these assessments (short-term dose rate reduction, PWSCC mitigation, axial offset anomaly/crud induced power shift susceptibility minimization, and program compliance) was deemed a good candidate for single-cycle performance. However, there is sufficient industry experience for benchmarking long-term trends in dose rate reductions.

EPRI Perspective

This report documents the results of industry benchmarking for PWR RCS zinc addition using plant data. These results and all further assessments will be considered for future EPRI Zinc Users Group research activities and application to the next revision of the PWR Primary Water Zinc Application Guidelines. It is anticipated that evaluations will be periodically updated as additional industry data are collected.

Keywords

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

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1
INTRODUCTION AND OVERVIEW

As of June 2009, fifty-seven pressurized water reactor (PWR) units were adding zinc to their primary coolant systems. This represents about 22% of the world's PWR units. Zinc injection is used in at least six different countries and in essentially all major Nuclear Steam Supply System, NSSS, designs. Plant-specific strategies for zinc injection are now tailored with respect to concentrations, injection location, injection timing, and monitoring protocols. At least fourteen additional plants are expected to begin injection of zinc within in the next two years and many more plants are investigating options for zinc injection [1].

In 2006, EPRI published the *Pressurized Water Reactor Primary Water Zinc Application Guidelines* [2] to provide utilities with a comprehensive reference on zinc injection at PWRs. Publication of the *EPRI Zinc Guidelines* marked the transition of zinc injection from a developing technology requiring detailed case-by-case analyses before implementation to a developed application with standard practices for application and monitoring. However, at the time of the preparation of the *EPRI Zinc Guidelines* there had been no systematic industry-wide primary coolant data collection effort which focused on the effects of zinc injection on primary chemistry. The *EPRI Zinc Guidelines* therefore established standards for such data collection.

In the years since the publication of the *EPRI Zinc Guidelines*, EPRI received operating chemistry data from numerous plants. The purpose of this report is to provide an initial assessment of this data.

It is anticipated that in the future the *EPRI Zinc Guidelines* will be revised to include lessons learned from continued use of zinc. One of the factors that will be considered in such revisions will be chemistry responses such as those discussed herein.

While the benefits of zinc have largely been well established, there are some side-effects and uncertainties that are of interest to utilities. These include:

- *Fuel Performance Issues*: Although fuel performance at plants injecting zinc has been satisfactory, there remains concern that zinc injection could lead to increased buildup of corrosion products (or zinc itself) on the fuel, which could lead to increased risk of axial offset anomaly (AOA, also known as crud induced power shift, CIPS).
- *Ex-core Surfaces*: The means by which zinc incorporates into ex-core surfaces has been studied, but is not sufficiently understood in enough detail to allow utilities to tailor a zinc program over time. For example, it is suspected that, over time, zinc will become incorporated into the oxide films on system surfaces and that these films will become thinner and more protective. Accordingly, less zinc might be required over time to achieve the desired beneficial outcome.

- *Overall Zinc Injection Evaluation*: Currently, utilities do not have a reliable performance indicator with which to assess the success of their zinc program. Zinc injection is expected to reduce ex-core dose rates and to mitigate primary water stress corrosion cracking (PWSCC). However, there is no definitive measure of how much these benefits have been realized at a specific unit.
- *Zinc and Plant Transients*: The extent to which plant transients change the efficacy of a zinc program are not well understood. For example, the duration of zinc suspension that would result in a loss of the benefits of injection is not known.

The review of the chemistry data discussed in this report is expected to contribute to the resolution of these issues.

The remainder of this report is organized as follows:

- Chapter 2 summarizes the conclusions from the analyses documented in other chapters of the report.
- Chapter 3 discusses system responses to initial zinc injection. The principal focus of this chapter is the release of corrosion products upon initiation of zinc injection, which may have implications for fuel reliability.
- Chapter 4 addresses how plant-specific (or cycle-specific) factors are expected to affect the plants response to zinc injection.
- Chapter 5 assesses data from plant transients and discusses the implications for attempts to predict responses to future transients.
- Chapter 6 discusses expectations regarding how a unit’s response to zinc will change with long-term use of zinc injection.
- Chapter 7 addresses the definition of performance indicators.

The references which are cited in this report are given in Chapter 8. An appendix is provided to summarize the mathematics of some of the statistical analyses used in this evaluation.

Two other points should be noted. First, the reader should be aware that the techniques used herein to evaluate plant chemistry responses to zinc injection are based on quantitative, standard statistical tests. Therefore, the ability to discuss trends or effects depends not only on the amount or quality of the data, but also the confidence level chosen to distinguish the effect from random variation. That is, some engineering judgment is required to assess the significance of an effect, even though quantitative statistical techniques are used. Second, the ability to measure chemical changes that could be significant is potentially challenged by the measurement accuracy. More specifically, the lower level of detectability of nickel may be higher than the concentration at which a significant effect could occur. Finally, the models of zinc and nickel behavior discussed in this report are based on first principals such as solubilities and may not encompass all of the physical and chemical phenomena that affect the primary chemistry response to zinc injection.

2
CONCLUSIONS AND RECOMMENDATIONS

This chapter summarizes some of the more important observations and conclusions presented in the remainder of this report and discusses some of the possible implications of these conclusions.

2.1 Plant Response to Initial Injection

A principal concern regarding the plant response to initial injection is that the presence of zinc will interact with ex-core oxide films in a manner that causes a release of nickel to the RCS system. It is possible that nickel so released could deposit in the core and result in fuel performance problems. Section 2.1.1 summarizes the previous understanding of this phenomenon (e.g., as discussed in previous EPRI reports). Section 2.1.2 briefly summarizes the findings of this study, which are given in much greater detail in Chapter 3. Section 2.1.3 discusses the context in which these findings can be interpreted. The implications of these findings are discussed in Section 2.1.4.

2.1.1 Previous Understanding

Whether or not the addition of zinc to a PWR RCS results in the displacement or release of species such as nickel from the ex-core surfaces is a subject of uncertainty and debate. For example, the *EPRI Zinc Guidelines* [2] describe a mechanism in which zinc injection results in the release of nickel and radiocobalts from ex-core surfaces. This mechanism involves the displacement of divalent cations (Ni^{2+} and Co^{2+}) from a non-stoichiometric spinel matrix caused by the incorporation of zinc. To account for this mechanism, one fuel vendor uses a 1:1 molar estimate for nickel accumulation on the core. That is, for every mole of zinc initially retained in the system a mole of nickel is deposited in the core [3]. (As discussed extensively in Chapter 5, the zinc initially retained is the mass injected less the mass removed by letdown purification. Some of the initially retained zinc is released during shutdown.) A similar calculation is included in EPRI's BOA code [4].

On the other hand, these models appear to be based on limited plant data (as is indicated in Reference [3]) and possibly on some experimental work [5]. Other reviews of these experimental results [6] indicates that the displacement of nickel and cobalt by zinc is not likely to be significant. The *EPRI Zinc Guidelines* [2] acknowledge this fact and cite other research that indicates that displacement of nickel and cobalt by zinc addition is minimal.

Some of the basis for assuming nickel release is also based on the behavior of zinc in boiling water reactors (BWRs) and analysis of primary system surface oxides, which show changes in nickel concentration after zinc injection. As discussed in Chapter 1, these issues have not been addressed in this report, which is generally limited to a statistical assessment of the available plant chemistry data.

2.1.2 Findings

The following conclusions are supported by the data analyses discussed in this chapter:

- There is strong evidence that at some units there has been a statistically significant increase in primary coolant radiocobalt activity upon initiation of zinc injection. However, there have been some units for which the data clearly indicate that there has been no statistically significant response.
- While there have been statistically significant responses at some units, a corresponding statistically significant increase in coolant nickel concentration was not found upon initial zinc injection. However, the statistical evaluation of data from several units evaluated were inconclusive in this regard, i.e., there could have been a nickel response at some low level but it could not be validated with the statistical tests used herein.
- There was no statistically significant increase in the mass of nickel released during shutdown chemistry maneuvers following the initial injection of zinc.
- For some units (with Alloy 800NG steam generator tubes) there was a short-term increase in iron concentrations upon initial zinc injection. (Note that this conclusion is based on data published in the literature rather than data made available to EPRI by utilities.)

It is important to note that these results are far from “definitive” given significant challenges with obtaining representative PWR reactor coolant system samples [2, 7].

On the other hand, theoretical considerations indicate that nickel and cobalt may not respond to zinc injection in the same way. Therefore, a radiocobalt release is not necessarily accompanied by a corresponding nickel release.

2.1.3 Context

Analyses discussed in Chapter 5 suggest that approximately 25-50% of zinc injected into the primary system is incorporated into deposit and oxide structures. The remainder is removed by letdown purification. This implies that, if there were a 1:1 molar substitution of zinc for nickel, then the nickel concentration would be expected to increase by about a third of the zinc concentration. On a mass basis, this would correspond to an increase of 0.3 ppb for each ppb of zinc in the coolant. For example, a 5 ppb concentration of zinc would be expected to result in approximately a 1.5 ppb increase in the nickel concentration. A change on this order would most likely be observable. However, it is possible that it might not be evident given the variability observed in the plant nickel data.

A molar substitution mechanism that resulted in 1:1 deposition on the fuel would also be expected to result in an increase of 1-2 kg in the mass of nickel released during shutdown. However, an effect of this magnitude does not occur.

For some plants, an increase in fuel crud loading on the order of 500 g might be considered "significant." This would correspond to operating for about one half of a cycle at 2-3 ppb of zinc (per a typical uptake rate of about 0.1 g/hr, based on the analysis in Chapter 5 or the core loading predictions given in Reference [3]). Such a loading would be expected to correspond with an increase in the RCS nickel concentration of less than 1 ppb, which would not be distinguishable from other variations at most plants. Therefore, a nickel release of significant magnitude with respect to plant operations could occur without being readily apparent in the data analyzed in this report.

2.1.4 Implications

While the variability in the available data makes it impossible to rule out a nickel release due to zinc injection, the data do show that a 1:1 displacement mechanism is highly unlikely. Even in the absence of evidence of any nickel displacement, it might be appropriate to conservatively assume some lesser extent of displacement when making plant operations decisions (e.g., core designs, zinc injection programs, etc.). However, determining the extent of conservatism warranted is beyond the scope of this study.

2.2 Plant-Specific Factors in Zinc Response

Plant-specific factors were considered in Chapter 4. The most important conclusion reached regarding plant-specific factors was as follows:

- Operating experience indicates that plants have not had significant issues with zinc deposition due to boiling. However, theoretical considerations, with limited experimental validation, indicate that both the zinc concentration and the boiling duty should still be carefully considered in assessing the risk of zinc deposition in the core.

2.3 Evaluation of Plant Transients

Data from a number of plant transients were assessed in Chapter 5. Evaluation of plant transients indicated that there were two significantly different responses to transients, as follows:

- In general, the increase in zinc concentration resulting from an increase in the injection rate (whether from resumption of a halted feed or from an increase in the feedrate associated with increasing the zinc concentration) is consistent with an uptake rate that is linearly proportional to the zinc concentration. Furthermore, the proportionality constant relating concentration and the uptake rate remains constant through the transient, allowing a prediction of the zinc concentration.
- In contrast, other types of transients (letdown flow rate changes or decreases in the zinc feed rate) led to unpredictable and inconsistent changes, with some transients leading to no change and others to unexplained step changes.

The cause of this difference in behavior was not identifiable.

2.4 Predictions of Behavior in Future Cycles

Utility personnel are also concerned with long-term trends resulting from zinc injection. Chapter 6 discusses evaluation of cycle-to-cycle trends present in the available plant data. Examination of plant data revealed the following trends:

- PWSCC mitigation continues to increase (i.e., initiation of PWSCC continues to slow) with ongoing zinc application.
- Ex-core dose rates decrease with additional cycles of zinc injection at rates that are significantly greater than the rates of decrease without zinc addition.
- The fraction of zinc injected that is retained by system surfaces decreases with time.

In no case was there a significant effect of zinc concentration noted, although the available data were not necessarily sufficient to distinguish such an effect.

2.5 Performance Indicators

Chapter 7 discusses the potential use of several plant measurements as performance indicators. To date, none of the performance indicators that have been considered is yet a good candidate for short-term (single-cycle). However, the following actions may be feasible:

- Use industry experience for bench-marking long-term trends in dose rate reductions.
- Pursue the evaluation of PWSCC of Alloy 600TT tube ends as an indication of the efficacy of zinc injection in mitigating PWSCC (such an evaluation has not been performed).[1]
- Evaluate data regarding sub-threshold axial offsets. The occurrence of AOA (CIPS) in excess of the current industry reporting threshold is not likely to occur often enough to become a useful performance metric. However, it is possible that sub-threshold offsets might become a useful measure of deposition in the core.

2.6 Recommendations for Additional Analyses and Data Collection

The main recommendation for further work in this area is that plant data continue to be collected. In addition, it is recommended that the industry consider the following actions:

- Evaluate the root cause of nickel concentration variability.
- Collect AOA data for cycles that do not necessarily meet the current reporting threshold.
- Evaluate the effect of zinc injection on trends in Alloy 600TT tube-end PWSCC.

[1] It is not anticipated that there will ever be enough data regarding PWSCC of SG tubes to use this as a performance metric in current steam generators (i.e., tubed with Alloy 600TT or Alloy 690TT).

3
PLANT RESPONSE TO INITIAL INJECTION

3.1 Introduction

A strong technical basis has been established for injecting zinc into the primary coolant of PWRs (i.e., mitigation of primary water stress corrosion cracking (PWSCC) initiation and shutdown doserate reduction). Nevertheless, there is a continuing concern that the changes in ex-core oxide and deposit structures caused by the presence of zinc could lead to side effects, some of which are considered adverse. Specifically, there has been a concern that the initial injection of zinc could lead to the following sequence of events:

- Accelerated release of corrosion products from ex-core surfaces
- More rapid buildup of deposits on fuel cladding
- Increased issues with fuel performance, such as deposit related cladding corrosion or axial offset anomaly (AOA, also known as crud induced power shift, CIPS)

Historically, an accelerated release of corrosion products has been postulated to result from the displacement of nickel or iron from surface oxides by zinc. In parallel, it is thought that radiocobalts could also be displaced in a similar manner. Since cobalt is a minor chemical species in ex-core deposits and oxides, the concerns regarding releases of corrosion products have chiefly focused on nickel release since accumulation of nickel deposits on fuel cladding is associated with axial offset anomaly (AOA or crud induced power shifts, CIPS) and possibly accelerated corrosion of fuel cladding materials. The negative consequences to increased RCS activity are much less severe (e.g., potential increases in the activity of letdown purification resins). If independent of accelerated surface corrosion, release of radiocobalts from ex-core surfaces is generally considered desirable, i.e., this phenomenon, if it occurred, would be an on-line decontamination process that lowered plant dose rates.

In order to assess whether or not releases of nickel or radiocobalt are caused by zinc addition, theoretical considerations (modeling) and plant experience were reviewed. In addition, the release of iron was also reviewed. Sections 3.4, 3.5, and 3.6 discuss plant experience available in the open literature and from EPRI databases with respect to the release of radiocobalts, nickel, and iron, respectively. Theoretical considerations are discussed in Section 3.7. Conclusions based on both theoretical considerations and plant experience are discussed in Section 3.8.

3.2 Caveats Regarding the Use of Plant Data

As with any plant data, there are several caveats on their use in such an analysis. These caveats arise from two concerns: accuracy of the data (i.e., the extent to which they actually represent the conditions which were present in the RCS) and variability introduced through uncontrolled differences. These are discussed qualitatively in the next two sections, which include a discussion of how these issues were dealt with in the analyses presented in this chapter.

3.2.1 Accuracy

Accuracy of the PWR primary system corrosion product data, taken here to mean the extent to which a reported datum is a true representation of the reported conditions in the RCS coolant at the time of sampling, has been a significant issue of concern for plant chemists. Various problems with accuracy are discussed in both the EPRI Primary Water Chemistry Guidelines [7] and the *EPRI Zinc Application Guidelines* [2]. Among the issues that are known are the following:

- Sample line conditioning is required to obtain accurate samples since deposition and release of corrosion products in sample lines can alter the liquid as it flows from the coolant to the sample point. For some plants, continuous sampling is not feasible.
- Different sample locations are known to give different values for coolant concentrations. For example, letdown sampling and hot leg sampling can often give different coolant radiocobalt activities and different concentrations of corrosion products (or zinc). The extent to which some sample locations provide samples that are more representative of the coolant is not well understood.
- Changes in temperature and hydrogen or oxygen concentration can cause dramatic changes in solubility. Very few plants have installed the equipment necessary to filter high temperature samples so that accurate measurements of soluble versus insoluble fractions can be made.

In assessing the data from the EPRI Zinc Database, the following steps have been made to address some of these issues:

- It has been assumed that there have been no substantive changes in analytical accuracy within a single data series. While it is possible that analytical techniques have been changed during the collection of a data series, it is assumed that utility quality assurance procedures have adequately verified that any new technique delivers an accuracy that is at least comparable to that of the previous technique.
- It has been assumed that there are no changes in sample location during a single data series. General practice in the industry would call for the creation of a new data series (i.e., a new plant computer point) if the sampling location has been changed. It is also general practice to maintain a single sampling location for consistency. However, there has not been any consistency across the industry with respect to reporting the sampling location (i.e., most utilities specify *RCS* as the sample location, without additional information).

- When considering corrosion product concentrations, only the total concentration has been considered. No attempt has been made to distinguish between filterable material and non-filterable material.

3.2.2 Uncontrolled Parameters

No two cycles are ever truly the same. Thus from plant data it is never possible to conclude without doubt that an observed difference is due to a single change, i.e., zinc addition. Similarly, during the course of a typical cycle, the dynamics of corrosion product transport in the core are changing as the extent of boiling in local areas changes, deposits age, or plant transients occur (either planned, such as rod testing, or unplanned such as down powers). In general, it was assumed that the only difference between cycles and between times during a cycle was the injection of zinc. This assumption was made for simplification, not because it represents reasonable accuracy. However, the following reasons make the use of this assumption reasonable in the current study:

- As discussed in Chapter 1, this is a preliminary and limited analysis, focusing only on the primary chemistry response to zinc injection. To the extent that normal undocumented changes in other operating parameters can cause larger changes that would mask the effect of zinc, zinc may be considered a minor factor in a particular type of response. That is, the effect of zinc was measured against the normal variability in the plant response. Whether that variability is due to random unknown factors or due to deliberate changes in plant operating conditions is somewhat immaterial to the determination of whether or not an effect of zinc rises to significance relative to normal variability. Therefore, as discussed in Chapter 1, the conclusion, for example, that zinc addition does not significantly affect a particular plant parameter is not a conclusion that there is no effect, but rather that the effect is smaller than the net effect caused by the many other parameters being changed.
- In assessing the statistical significance of responses to zinc injection, comparisons were made both between the first zinc cycle and previous cycles during the same time periods and between the pre-zinc and post-zinc periods of the first zinc cycle. Comparison of the pre-zinc and post-zinc data for the first zinc cycle is the most direct indicator of a zinc effect. If all other parameters were being held constant, a change coinciding with zinc injection would be a direct indicator of a zinc effect. Unfortunately, other parameters are not held constant during the course of the cycle. Of particular relevance with respect to monitoring of corrosion product release is the fact that there are changes in the regions of the core with significant boiling as the cycle progresses. At some units, the initial injection of zinc has been specifically delayed until peak boiling has passed, and as a result, changes within a given cycle can be misleading. Therefore, comparisons have also been made between specific time periods in the first zinc cycle and the two prior cycles. This measurement of the zinc effect is less direct since there can be significant cycle-to-cycle variability in corrosion product concentrations. However, if the cycles are relatively comparable such an analysis eliminates cycle trends. By considering both comparisons, a more reliable determination of whether or not there is a zinc effect can be reached (although in some cases that determination is that the data are not sufficient to make a conclusive assessment).

3.3 General Methodology for Assessing Plant Data

An assessment of the EPRI Zinc Database (see Section 3.3.1 for a definition of this database) was performed to determine if there were significant differences in primary coolant chemistry (corrosion product activities and concentrations) as a result of zinc injection. Separate analyses were conducted for radiocobalts (Co-58 and Co-60), nickel, and iron. These analyses are discussed in Sections 3.4, 3.5, and 3.6, respectively. Each of these sections is composed of the following:

- Unit-specific statistical assessments based on the EPRI Zinc Database
- Supplemental unit-specific information from literature sources
- Summary and conclusions

Each summary and conclusion section discusses the theoretical considerations and modeling issues given in Section 3.7. Theory and modeling are used to assist in understanding the limitations and implications of the conclusions drawn from the plant data, which are the primary focus of this chapter.

The statistical assessments focus on determining the differences between primary chemistry with and without zinc injection. The following sections discuss the basic analysis techniques used in this project. While these techniques represent the standard which was applied to each unit-specific data set (where data were available), they are somewhat limited (due, in part, to limits in the data, as discussed in Section 3.2). Therefore, in all cases, these simplified statistical analyses were supplemented with engineering judgment. Because such judgment is by definition subjective and open to interpretation, all reasonable efforts were made to present the data upon which judgments were made and to fully explain the reasoning used to arrive at a particular assessment.

Details of the statistical techniques used are given in A.

3.3.1 Data Sources

Chemistry and operating data (i.e., zinc concentrations, radiocobalt activities, and power levels) from various units were available in the form of spreadsheets created by utility personnel, spreadsheets created by EPRI, and data available in the Chemistry Monitoring and Assessment (CMA) Database [8]. Note that data obtained from the CMA Database were converted to daily averages when appropriate. Zinc injection data (i.e., injection-start and initial-detection dates) were also obtained from information presented at the 2007, 2008, and 2009 meetings of the Zinc Users' Group (ZUG) [9, 10, 11]. Cycle start and end dates were obtained using chemistry and operating data, information presented at the ZUG meetings, the CMA Database, and the Steam Generator Degradation Database (SGDD) [12]. Together these various data sources are referred to in this report as the *EPRI Zinc Database*. Data from the first cycle of zinc injection (Cycle N) and from the two cycles immediately preceding this cycle (Cycle N-1 and Cycle N-2) were considered in this assessment.

3.3.2 Data Presentation

Using the data obtained from each unit for the cycles discussed above, plots showing the cycle profiles of the following parameters were created:

- Corrosion product (Co-58, Co-60, nickel, or iron)
- Power

The times of the initiation of zinc injection and the first detection of zinc are presented as vertical lines on each plot. Note that specific activity (i.e., the ratio of radiocobalt activity to nickel concentration) trends were also considered, but these trends did not provide any significantly better trending information and were therefore not included in this section. Also note that in several instances, data for one or more of these parameters at a given unit were unavailable, and it was therefore not possible to analyze such parameters at these units.

These plots are presented in the appropriate sections on the unit-specific analyses. Engineering judgments discussed in those sections are generally based on inspection of these plots, in some cases supplemented by additional information which is explicitly stated in each unit-specific discussion.

3.3.3 Time Periods

A typical dataset for zinc concentration during the initial zinc cycle is shown in Figure 3-1. There are two distinct phases following zinc injection initiation that are generally considered to be associated with actual physical phenomena: the *grow-in phase* and the *steady state phase*.

The grow-in phase is characterized by zinc concentrations below the target concentration. During this period, it is generally assumed that the RCS system surfaces (ex-core oxides and fuel deposits) have excess capacity to take up zinc. That is, the RCS surfaces have a near-term deficit of zinc with respect to the reporting limit concentration. The grow-in phase can be divided into periods preceding and following the first detection of zinc. However, it is likely that the actual physical phenomena governing these periods are not significantly different.

During the steady state phase, the injection of zinc is balanced with removal by a combination of purification flow (leakoff or letdown return) and incorporation into surfaces. RCS coolant purity is maintained by bleeding off a side stream (termed leakoff or letdown, depending on the original NSSS vendor), purifying the water by passage through ion exchange beds, and returning the purified water to the system. Purification of this stream is typically close to perfect (>95%) such that the rate of zinc removal by purification is well approximated by multiplying the concentration by the purification flow rate. When the zinc concentration is unchanging, the difference between the injection rate and the purification rate gives the rate of incorporation.

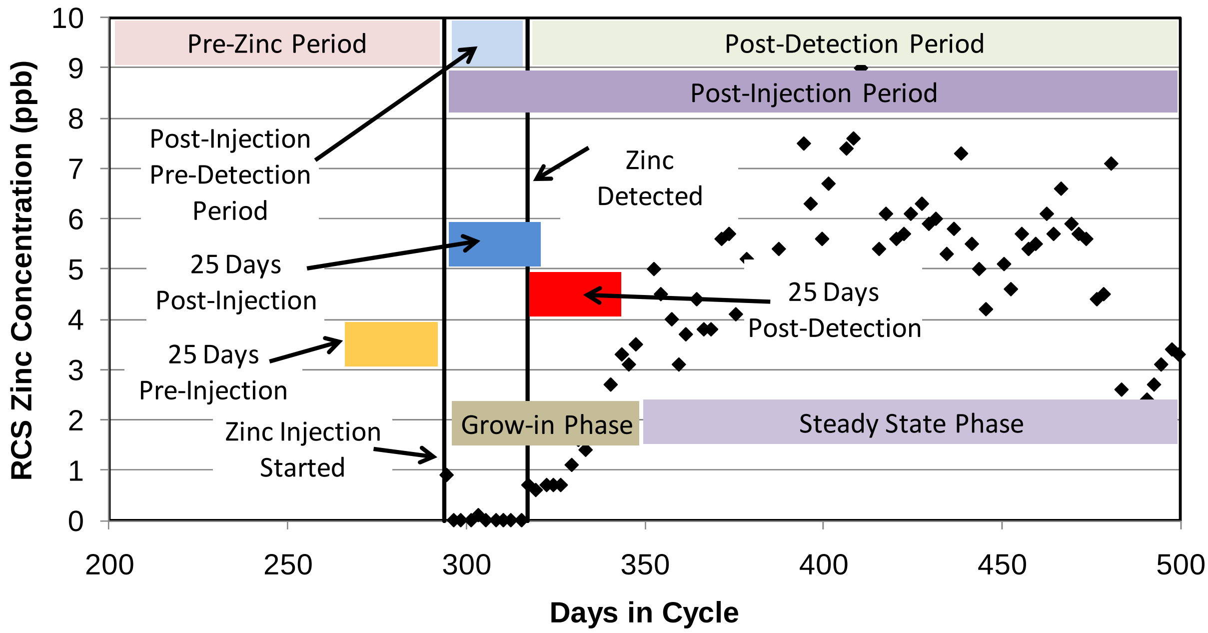

Figure 3-1
Periods and Phases Associated with Zinc Concentrations following Initial Injection (McGuire 1 Cycle 18)

The steady state period as described in the previous paragraph is really a pseudo-steady state, since over long periods of time (cycles) there are changes in the uptake rate as zinc modifies the system surfaces. This is discussed further in Section 6.2.3.

For several reasons, the transition between the grow-in phase and the steady state phase is not easily determined. These reasons include the following:

- The injection rate is often adjusted near or during the transition.
- There remain long-term trends which may mask the transition from grow-in to short-term stability.
- In some data sets, zinc concentrations are not available.

For these reasons, the four time periods that were selected for analysis are only loosely related to the phenomenological phases.

- The four periods selected for analysis are shown in Figure 3-1. They are defined as follows:
- Pre-zinc period: The period before the day zinc injection was started during the first zinc cycle.
- Post-zinc, pre-detection period: The period after the day zinc injection was started during the first zinc cycle to the day zinc was detected during the first zinc cycle.
- Post-zinc period: The period after the day zinc injection was started during the first zinc cycle (concluding at the end of the cycle).

- Post-detection period: The period after the day zinc was first detected during the first zinc cycle (concluding at the end of the cycle).

Note that these periods are defined with respect to the first cycle in which zinc was injected but were used to divide cycles in which zinc was not injected for comparison purposes (see Section 3.3.4.

Three additional periods were also considered, specifically in addressing trends before and after zinc injection. These periods were as follows:

- The 25 days preceding commencement of zinc injection
- The 25 days following commencement of zinc injection
- The 25 days following the first detection of zinc

The length of these periods (25 days) was chosen based on the available data and expectations of usefulness. For specific data sets, other period lengths were considered as part of the engineering judgment assessment.

3.3.4 Comparison Pairs

The main focus of the statistical comparisons performed was the comparison of concentrations or activities for periods with zinc to periods without. The statistical methods used are discussed in Section 7.1.1.1.1A.1. This section defines the various pairs of data sets used for comparison. In general, the following two types of comparisons were made:

- Comparisons for specific time periods between the first zinc cycle and each of the two preceding cycles (comparison of Cycle N average with Cycle N-1 and Cycle N-2):
  - Post-zinc, pre-detection (averages)
  - Post-zinc (averages)
  - Post-detection (averages)
  - 25-day pre-zinc slope
  - 25-day post-zinc slope
  - 25-day post-detection slope
- Comparisons between the time periods within the first zinc cycle:
  - Pre-zinc Cycle N average versus post-zinc Cycle N average
  - Pre-zinc Cycle N average versus post-detection Cycle N average
  - 25-day pre-zinc Cycle N slope versus 25-day post-zinc Cycle N slope
  - 25-day pre-zinc Cycle N slope versus 25-day post-detection Cycle N slope

As discussed in Section 3.2.2, there are often other changes in plant operations that affect corrosion product concentrations and activities. The two types of comparisons listed above attempt to account for these changes in different ways.

Comparisons with previous cycles attempt to eliminate the effects of within-cycle changes. Zinc injection is sometimes delayed until the core boiling duty has passed its peak [2]. This results in zinc injection possibly being coordinated with changes in corrosion product behavior that are independent of zinc. Comparison of the same time periods between two different cycles can be used to reduce the probability that zinc will be incorrectly identified as the cause in a change in corrosion product behavior associated with operating parameter changes independent of zinc. However, such comparisons cannot account, for example, for changes in core design or chemistry (pH) (see Section 3.2.2).

From cycle to cycle there can be core design and chemistry changes that are thought to significantly affect corrosion product behavior. Comparison of periods within a single cycle eliminates the effects of cycle-to-cycle parameter changes. However, such comparisons cannot account for changes in operating parameters that occur coincidentally with zinc injection.

While the comparison types discussed above have significant flaws, they are complementary. Consideration of all of these comparisons in the assessment of the effect of zinc requires engineering judgment but allows consideration of many units on essentially the same basis, which would not be possible if a more detailed analysis of each unit, accounting for all of the within cycle and cycle to cycle changes, were used instead. Collection of the data necessary to perform such a detailed analysis was not in the scope of this project and would not be practical for the number of units considered.

3.4 Radiocobalt Response

As discussed in Section 3.3 plant data of the coolant activity of Co-58 and Co-60 were evaluated by comparing activities before zinc injection with those after zinc injection. Data available in the EPRI Zinc Database are discussed in Section 3.4.1. Additional data available in the literature are discussed in Section 3.4.2. Conclusions based on the unit-specific evaluations in Sections 3.4.1 and 3.4.2 are discussed in Section 3.4.3. While these conclusions are informed by theoretical and modeling considerations discussed in Section 3.7, they are principally based on the plant data.

In the discussions that follow, the inputs for the statistical comparisons are the logarithms of the measured activity. Because of the order of magnitude variability in measurements, this is a convenient method of analysis. As discussed in A, the distribution of activities during periods of relative stability (i.e., when differences in reported activities represent random variability rather than a systematic change) indicates that the data are log-normally distributed, which makes analysis of the logarithms appropriate.

3.4.1 Assessments from EPRI Zinc Database

The sections below discuss the analyses performed for each of the data sets available in the EPRI Zinc Database. Data were available for the first zinc cycle for the following units:

- Angra 1
- Asco I
- Asco II
- Braidwood 2
- Byron 2
- Calvert Cliffs 1
- Crystal River 3
- McGuire 1
- McGuire 2
- Surry 1
- Surry 2
- Three Mile Island 1
- Vandellos II

3.4.1.1 Angra 1

Chemistry and operating data were taken from several spreadsheets prepared by Angra personnel [13]. Zinc injection at Angra 1 began approximately 13 days into the 12th fuel cycle and zinc was detected roughly 90 days later. Note that a zinc concentration of <15 ppb – it is understood that this is the original detection limit of the equipment available at Angra 1 – was reported starting at the 23rd day in cycle up through what is considered to be the true detection of zinc on the 103rd day of the cycle. A reading of 14.4 ppb was reported on the 70th day in cycle and it was noted by Angra personnel that this value may be considered the first detection of zinc in the primary system. It is unlikely that this datum represents the true first detection of zinc in the primary system as a concentration of this magnitude was not again reached until roughly the 171st day in cycle. A concentration of 0.78 ppb was measured using Angra 2 equipment on the 84th day of the cycle, but this information was included as a comment and was not explicitly reported in the Angra 1 data sheet. Therefore, the initial detection of zinc in the primary coolant is assumed to have occurred when the first zinc concentration other than the limit of detection (1.8 ppb) was reported after the 84th day of the cycle. The Cycle 12 average zinc concentration was 9.2 ppb. Prior to replacement in 2009 with Alloy 690TT tubes, the Angra 1 steam generators were tubed with Alloy 600MA.

Angra 1 operated with primary-to-secondary leakage during Cycles 10 (Cycle N-2), Cycle 11 (Cycle N-1) and Cycle 12 (Cycle N). About three quarters of the way through Cycle 10, the power was reduced to 80% in response to this leakage and this power level was maintained through Cycles 11 and 12 [14]. Due to this major difference between Cycle 10 and Cycles 11 and 12, Cycle 10 data were not used in this analysis even though they were available.

Data for Co-58 and plant power are given in Figure 3-2. Data for Co-60 and plant power are given in Figure 3-3. These data were analyzed using the statistical comparisons described in Section 3.3. The results are given in Table 3-1 through Table 3-3 for Co-58 and Table 3-4 through Table 3-6 for Co-60.

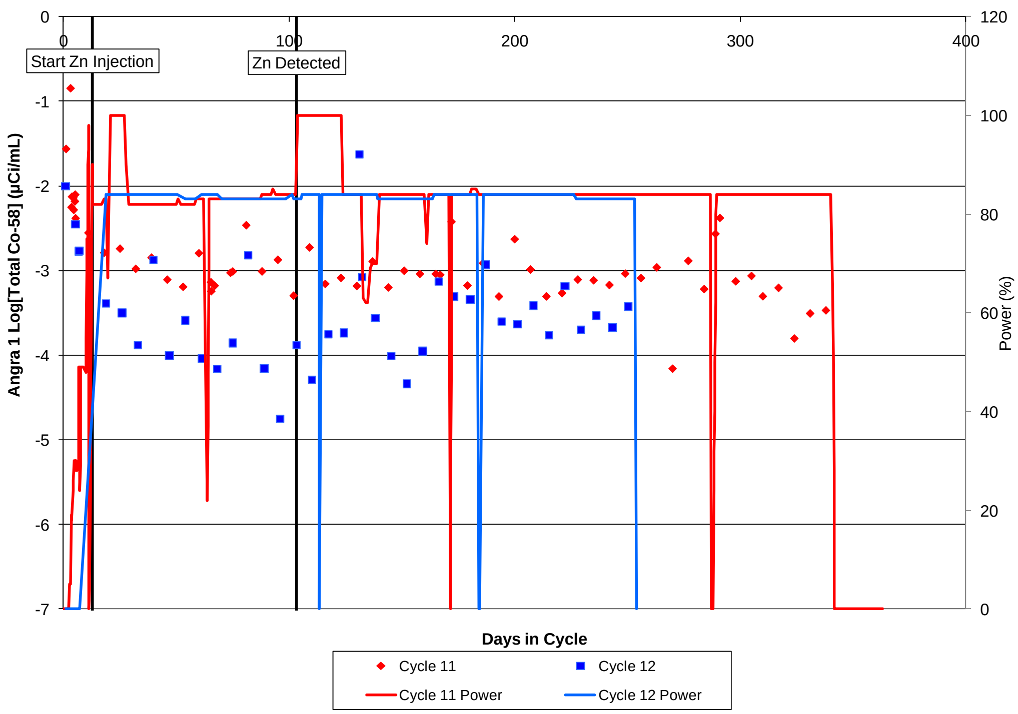

Figure 3-2
Angra 1 Total Co-58 Activity before and during Zinc Injection

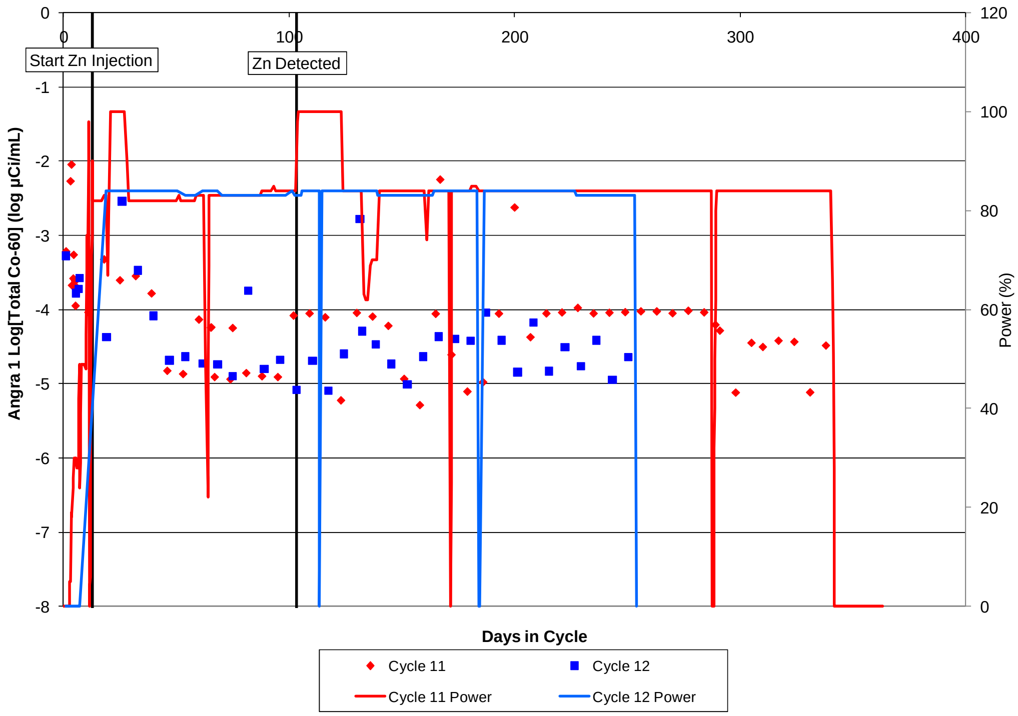

Figure 3-3
Angra 1 Total Co-60 Activity before and during Zinc Injection

Table 3-1
Angra 1 Total Co-58 Activity Multiple Cycle Statistical Analysis Results

Time Period	Change Versus Cycle N-1			
	α=0.01	α=0.05	α=0.2	α=0.5
Pre-Zinc	-1.17	-0.91	-0.67	-0.46
Post-Injection/Pre-Detection	-1.22	-1.07	-0.91	-0.77
Post-Injection	-0.78	-0.70	-0.62	-0.53
Post-Detection	-0.72	-0.63	-0.52	-0.41

Table 3-2
Angra 1 Total Co-58 Activity Same Cycle Statistical Analysis Results

Time Period for Comparison to Pre-Zinc Period	Cycle N				Cycle N-1			
	α=0.01	α=0.05	α=0.2	α=0.5	α=0.01	α=0.05	α=0.2	α=0.5
Post-Injection/Pre-Detection	-1.95	-1.70	-1.47	-1.25	-1.39	-1.23	-1.08	-0.94
Post-Injection	-1.86	-1.53	-1.29	-1.10	-1.47	-1.31	-1.16	-1.02
Post-Detection	-1.74	-1.45	-1.21	-1.01	-1.51	-1.35	-1.20	-1.06

Table 3-3
Angra 1 Total Co-58 Activity Profile Slope Analysis

Period of Analysis	Cycle N		Cycle N-1	
	Slope	R^2	Slope	R^2
Pre-Zinc	-1.28E-01	0.97	-1.15E-01	0.35
25 Days Post-Injection	-3.53E-02	0.91	-1.36E-02	0.57
25 Days Post-Detection	1.38E-02	0.24	-2.58E-02	0.60
Detection through EOC	7.85E-04	0.00	-1.44E-03	0.09
Post-Injection/Pre-Detection	-9.65E-03	0.19	-2.21E-03	0.06

Table 3-4
Angra 1 Total Co-60 Activity Multiple Cycle Statistical Analysis Results

Time Period	Change Versus Cycle N-1			
	α=0.01	α=0.05	α=0.2	α=0.5
Pre-Zinc	-0.90	-0.68	-0.46	-0.25
Post-Injection/Pre-Detection	-0.57	-0.37	-0.15	0.06
Post-Injection	-0.49	-0.40	-0.29	-0.18
Post-Detection	-0.65	-0.55	-0.43	-0.30

Table 3-5
Angra 1 Total Co-60 Activity Same Cycle Statistical Analysis Results

Time Period for Comparison to Pre-Zinc Period	Cycle N				Cycle N-1			
	α=0.01	α=0.05	α=0.2	α=0.5	α=0.01	α=0.05	α=0.2	α=0.5
Post-Injection/Pre-Detection	-1.31	-1.11	-0.90	-0.69	-1.66	-1.45	-1.22	-1.00
Post-Injection	-1.28	-1.13	-0.99	-0.85	-1.53	-1.33	-1.12	-0.92
Post-Detection	-1.37	-1.22	-1.07	-0.94	-1.52	-1.31	-1.09	-0.89

Table 3-6
Angra 1 Total Co-60 Activity Profile Slope Analysis

Period of Analysis	Cycle N		Cycle N-1	
	Slope	R^2	Slope	R^2
25 Days Pre-Zinc	-6.56E-02	0.67	-1.41E-01	0.29
25 Days Post-Injection	6.44E-02	0.24	-1.60E-02	0.57
25 Days Post-Detection	1.47E-02	0.26	-8.40E-02	0.79
Detection through EOC	-6.23E-04	0.00	-8.18E-04	0.01
Post-Injection/Pre-Detection	-1.50E-02	0.29	-1.50E-02	0.43

The statistical comparisons given in Table 3-1 through Table 3-6 generally do not show evidence of a statistically significant zinc affect. Cycle to cycle comparisons (Cycle N versus Cycle N-1) show a decrease in Co-58 and Co-60 activities. This occurred during each of the time periods considered including the pre-zinc period, which indicates that this difference was not caused by zinc addition. Within cycle analyses indicate that the post-zinc periods have lower activity than the pre-zinc period. This was true during the cycle before zinc injection as well. Inspection of the actual data indicates that this is likely an artifact of high activities early in the cycle. The slope analyses indicate a possible difference in the trends following zinc detection. In Cycle 11 (Cycle N-1), Co-58 and Co-60 trended downward in the 25 days corresponding to the 25 days after zinc detection in Cycle 12 (Cycle N). However, the correlations for this time period have significant residual errors ($R^2 = 0.26$ for Cycle 12 and $R^2 = 0.79$ for Cycle 11). Given that both cycles showed no significant trends in activity for the entire post-detection period, the trends in the first 25 days are probably not real.

Inspection of the data for Cycles 11 and 12 support the conclusions that there are no significant effects of zinc injection. Both cycles show the same general trends, starting at about the same value, dropping about two orders of magnitude over the first fifty days of the cycle, and then remaining essentially constant (with significant scatter) for the remainder of the cycle. Because data are available for a prior cycle and for the pre-zinc and post-zinc periods, these conclusions are considered reasonably robust.

3.4.1.2 Asco I

Chemistry and operating data were available in the form of several spreadsheets prepared by Asco personnel.[15] Asco I began injecting zinc 125 days into the 19th fuel cycle, reported a measurable concentration on the 191st day of the cycle, and averaged 9.5 ppb over the course of the cycle. The first day of the cycle was taken to be the day of the first at-power data point. The Asco I steam generators have Alloy 800NG tubing.

Data for Co-58 and plant power are given in Figure 3-4. Data for Co-60 and plant power are given in Figure 3-5. These data were analyzed using the statistical comparisons described in Section 3.3. The results are given in Table 3-7 and Table 3-8 for Co-58 and Table 3-9 and Table 3-10 for Co-60.

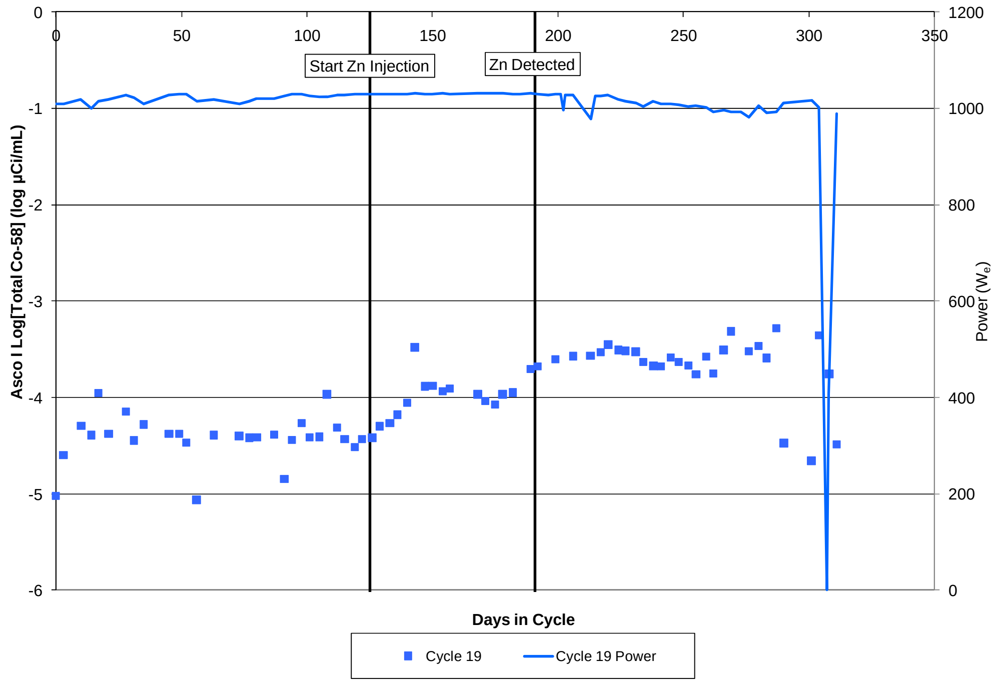

Figure 3-4
Asco I Total Co-58 Activity before and during Zinc Injection

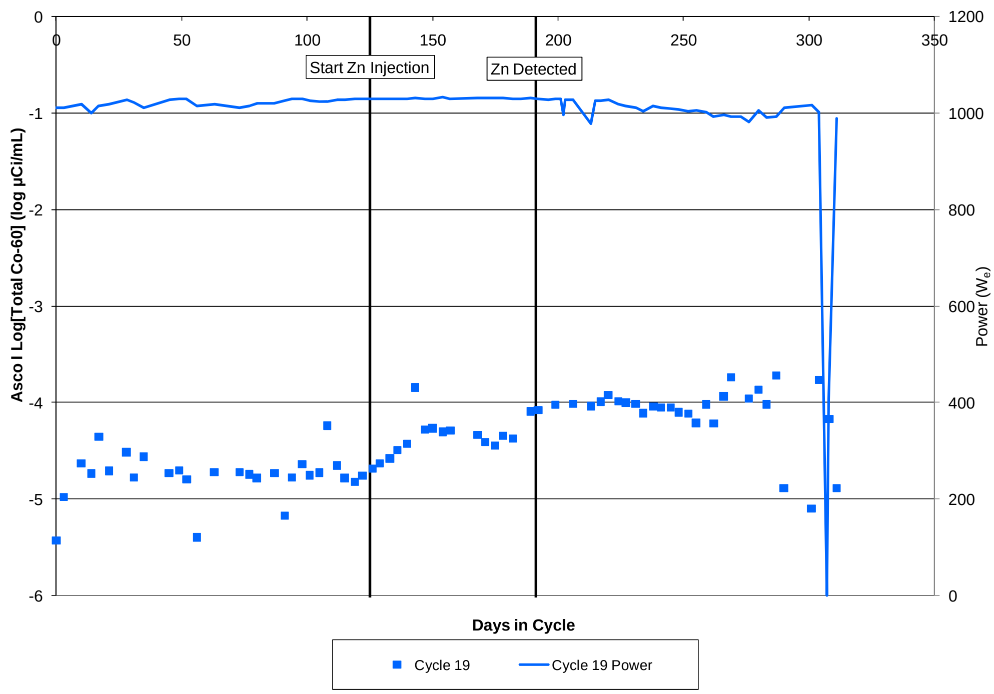

Figure 3-5
Asco I Total Co-60 Activity before and during Zinc Injection

Table 3-7
Asco I Total Co-58 Activity Same Cycle Statistical Assessment Results

Time Period for Comparison to Pre-Zinc Period	Cycle N				Cycle N-1				Cycle N-2			
	α=0.01	α=0.05	α=0.2	α=0.5	α=0.01	α=0.05	α=0.2	α=0.5	α=0.01	α=0.05	α=0.2	α=0.5
Post-Injection/Pre-Detection	0.24	0.30	0.36	0.42	-	-	-	-	-	-	-	-
Post-Injection	0.48	0.52	0.58	0.64	-	-	-	-	-	-	-	-
Post-Detection	0.57	0.63	0.69	0.76	-	-	-	-	-	-	-	-

Table 3-8
Asco I Total Co-58 Activity Profile Slope Analysis

Period of Analysis	Cycle N		Cycle N-1		Cycle N-2	
	Slope	R^2	Slope	R^2	Slope	R^2
25 Days Pre-Zinc	-7.69E-03	0.10	-	-	-	-
25 Days Post-Injection	2.83E-02	0.63	-	-	-	-
25 Days Post-Detection	5.06E-03	0.83	-	-	-	-
Pre-Zinc	5.32E-04	0.01	-	-	-	-

Table 3-9
Asco I Total Co-60 Activity Same Cycle Statistical Assessment Results

Time Period for Comparison to Pre-Zinc Period	Cycle N				Cycle N-1				Cycle N-2			
	α=0.01	α=0.05	α=0.2	α=0.5	α=0.01	α=0.05	α=0.2	α=0.5	α=0.01	α=0.05	α=0.2	α=0.5
Post-Injection/Pre-Detection	0.23	0.28	0.34	0.40	-	-	-	-	-	-	-	-
Post-Injection	0.41	0.46	0.51	0.57	-	-	-	-	-	-	-	-
Post-Detection	0.48	0.53	0.59	0.66	-	-	-	-	-	-	-	-

Table 3-10
Asco I Total Co-60 Activity Profile Slope Analysis

Period of Analysis	Cycle N		Cycle N-1		Cycle N-2	
	Slope	R^2	Slope	R^2	Slope	R^2
25 Days Pre-Zinc	-7.90E-03	0.09	-	-	-	-
25 Days Post-Injection	2.35E-02	0.54	-	-	-	-
25 Days Post-Detection	1.81E-03	0.34	-	-	-	-
Pre-Zinc	8.40E-04	0.02	-	-	-	-

Statistical analyses of the Co-58 and Co-60 data showed that there was a statistically significant increase in activity following the initiation of zinc injection and that the post-detection values were also significantly higher than the pre-injection values. There were reasonably linear increases in the logs of the activities (both Co-58 and Co-60) during the 25 days after injection.

The upward trends in both data sets (1) leveled off and began decreasing immediately when zinc injection was secured (Day 149), (2) began immediately increasing after injection was restarted (Day 173), and (3) essentially leveled off a second time after a measurable concentration of zinc was present in the coolant. The behavior of the radiocobalt activities in response to zinc injection transients further supports that statistical assessment, i.e., zinc did cause an increase in coolant activity.

No prior cycle data were available for this analysis. However, the response of the radiocobalts to the zinc transient makes this data set very robust with respect to the conclusion that zinc caused an increase in radiocobalts.

3.4.1.3 Asco II

Chemistry and operating data were available in the form of several spreadsheets prepared by Asco personnel [15]. Injection of zinc at Asco II was initiated on the 67th day of Cycle 17, the concentration in the RCS was measurable 11 days later, and the calculated average concentration was 9.6 ppb. The first day of the cycle was taken to be the day of the first at-power data point. The Asco II steam generators are tubed with Alloy 800NG.

Data for Co-58 and plant power are given in Figure 3-6. Data for Co-60 and plant power are given in Figure 3-7. These data were analyzed using the statistical comparisons described in Section 3.3. The results are given in Table 3-11 and Table 3-12 for Co-58 and Table 3-13 and Table 3-14 for Co-60.

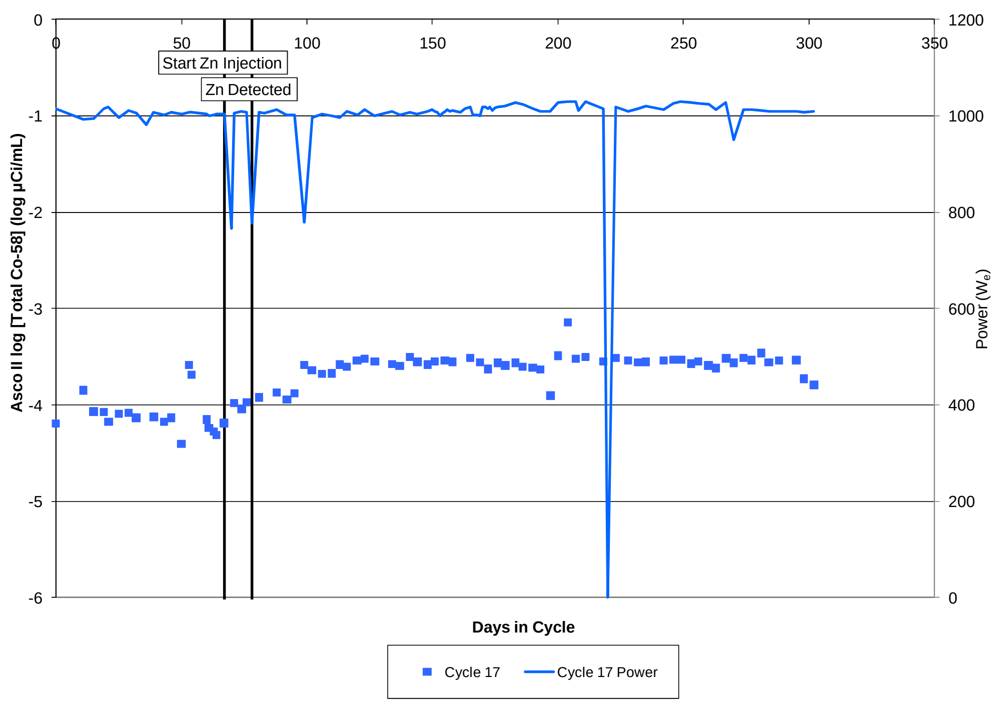

Figure 3-6
Asco II Total Co-58 Activity before and during Zinc Injection

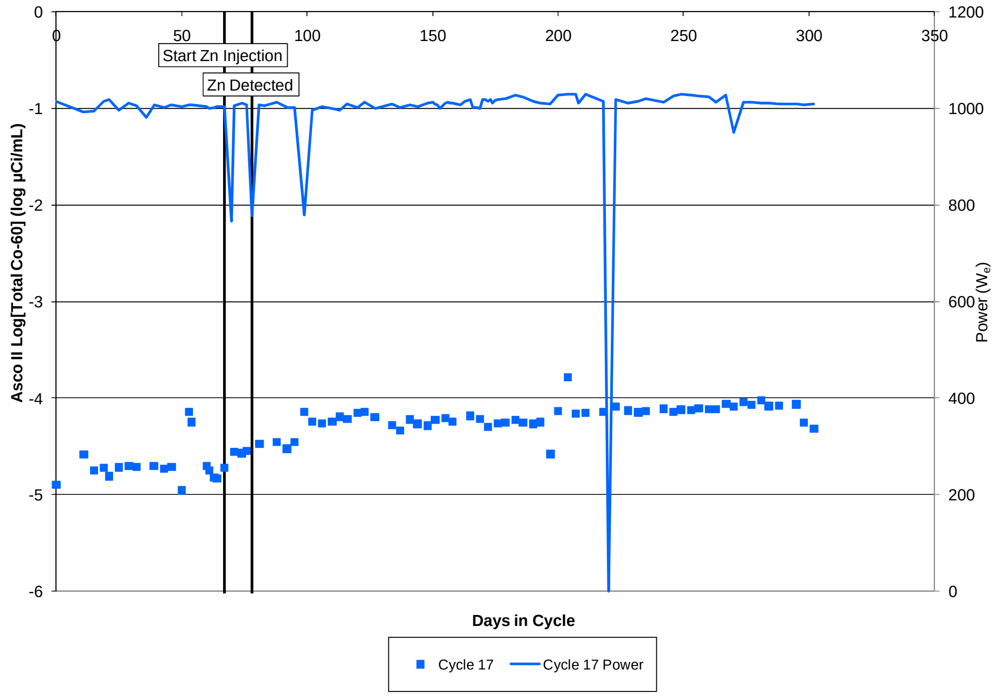

Figure 3-7
Asco II Total Co-60 Activity before and during Zinc Injection

Table 3-11
Asco II Total Co-58 Activity Same Cycle Statistical Assessment Results

Time Period for Comparison to Pre-Zinc Period	Cycle N				Cycle N-1				Cycle N-2			
	α=0.01	α=0.05	α=0.2	α=0.5	α=0.01	α=0.05	α=0.2	α=0.5	α=0.01	α=0.05	α=0.2	α=0.5
Post-Injection/Pre-Detection	-0.14	-0.08	-0.01	0.05	-	-	-	-	-	-	-	-
Post-Injection	0.27	0.31	0.36	0.40	-	-	-	-	-	-	-	-
Post-Detection	0.29	0.33	0.37	0.42	-	-	-	-	-	-	-	-

Table 3-12
Asco II Total Co-58 Activity Profile Slope Analysis

Period of Analysis	Cycle N		Cycle N-1		Cycle N-2	
	Slope	R^2	Slope	R^2	Slope	R^2
25 Days Pre-Zinc	-6.76E-03	0.03	-	-	-	-
25 Days Post-Injection	8.61E-03	0.58	-	-	-	-
25 Days Post-Detection	1.55E-02	0.60	-	-	-	-
Pre-Zinc	1.27E-07	0.00	-	-	-	-
25 Days Post-Detection through EOC	-2.62E-07	0.07	-	-	-	-

Table 3-13
Asco II Total Co-60 Activity Multiple Cycle Statistical Assessment Results

Time Period for Comparison to Pre-Zinc Period	Cycle N				Cycle N-1				Cycle N-2			
	α=0.01	α=0.05	α=0.2	α=0.5	α=0.01	α=0.05	α=0.2	α=0.5	α=0.01	α=0.05	α=0.2	α=0.5
Post-Injection/Pre-Detection	-0.07	-0.02	0.04	0.09	-	-	-	-	-	-	-	-
Post-Injection	0.30	0.34	0.38	0.42	-	-	-	-	-	-	-	-
Post-Detection	0.31	0.35	0.40	0.44	-	-	-	-	-	-	-	-

Table 3-14
Asco II Total Co-60 Activity Profile Slope Analysis

Period of Analysis	Cycle N		Cycle N-1		Cycle N-2	
	Slope	R^2	Slope	R^2	Slope	R^2
25 Days Post-Injection	7.33E-03	0.57	-	-	-	-
25 Days Post-Detection	1.42E-02	0.51	-	-	-	-
Pre-Injection	1.82E-07	0.05	-	-	-	-
25 Days Post-Detection through EOC	-4.73E-08	0.06	-	-	-	-

Relative to the pre-injection data, statistically significant increases in the Co-58 and Co-60 activities were both observed to follow the initiation of zinc injection. Analysis of the slopes indicates that there is a significant increasing trend following detection of zinc.

Qualitative analysis of the data shown in Figure 3-6 and Figure 3-7 indicate that there is about a factor of 2-3 increase in the Co-58 and Co-60 activities due to zinc injection. The activities start to increase upon initiation of injection and reach a new plateau after about 30 days.

Based on the available data, it is reasonable to conclude that zinc addition at Asco II led to an increase in radiocobalt activity. This conclusion would be more robust if prior cycle data were available. This would allow consideration of whether or not the changes observed upon zinc injection would have occurred without zinc, i.e., they were due to a change in some other operating parameter.

3.4.1.4 Braidwood 2

Braidwood 2 chemistry and operating data were available in the CMA Database [8]. Zinc injection at Braidwood 2 was initiated approximately 428 days into the 12th fuel cycle and a measurable concentration was quantified 24 days later [9]. The average zinc concentration in the coolant was 4.6 ppb [10]. The Braidwood 2 steam generators have Alloy 600TT tubing.

Data for Co-58 and plant power are given in Figure 3-8. Data for Co-60 and plant power are given in Figure 3-9. These data were analyzed using the statistical comparisons described in Section 3.3. The results are given in Table 3-15 through Table 3-17 for Co-58 and Table 3-18 through Table 3-20 for Co-60.

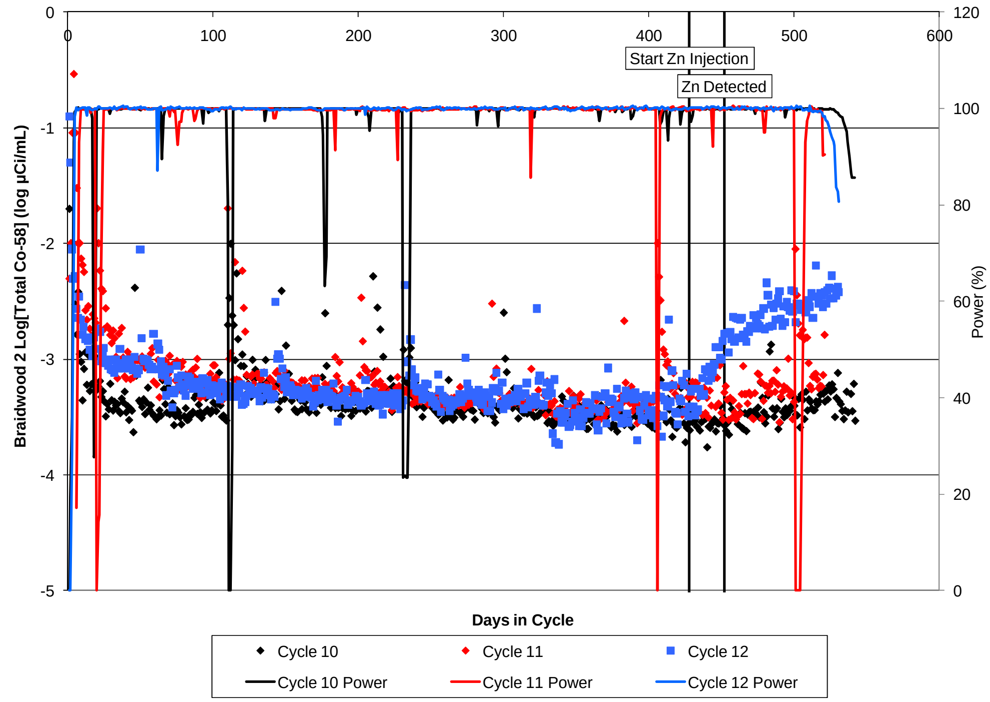

Figure 3-8
Braidwood 2 Total Co-58 Activity before and during Zinc Injection

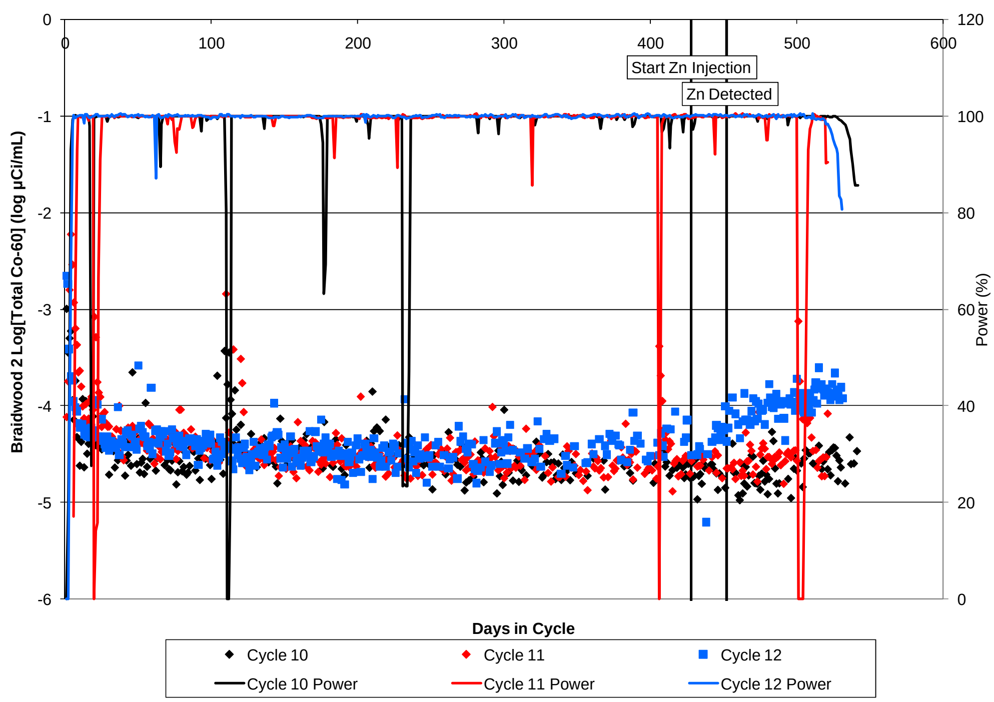

Figure 3-9
Braidwood 2 Total Co-60 Activity before and during Zinc Injection

Table 3-15
Braidwood 2 Total Co-58 Activity Multiple Cycle Statistical Assessment Results

Time Period	Change Versus Cycle N-1				Change Versus Cycle N-2			
	α=0.01	α=0.05	α=0.2	α=0.5	α=0.01	α=0.05	α=0.2	α=0.5
Pre-Zinc	-0.13	-0.11	-0.09	-0.08	0.05	0.06	0.07	0.09
Post-Injection/Pre-Detection	0.02	0.06	0.10	0.14	0.27	0.31	0.34	0.38
Post-Injection	0.42	0.44	0.47	0.51	0.64	0.66	0.69	0.72
Post-Detection	0.53	0.55	0.58	0.61	0.77	0.79	0.80	0.82

Table 3-16
Braidwood 2 Total Co-58 Activity Same Cycle Statistical Assessment Results

Time Period for Comparison to Pre-Zinc Period	Cycle N				Cycle N-1				Cycle N-2			
	α=0.01	α=0.05	α=0.2	α=0.5	α=0.01	α=0.05	α=0.2	α=0.5	α=0.01	α=0.05	α=0.2	α=0.5
Post-Injection/Pre-Detection	-0.03	0.01	0.04	0.08	-0.22	-0.19	-0.17	-0.14	-0.26	-0.24	-0.23	-0.21
Post-Injection	0.45	0.47	0.50	0.52	-0.13	-0.11	-0.09	-0.06	-0.15	-0.13	-0.12	-0.10
Post-Detection	0.61	0.62	0.64	0.66	-0.12	-0.09	-0.06	-0.03	-0.12	-0.11	-0.09	-0.07

Table 3-17
Braidwood 2 Total Co-58 Activity Profile Slope Analysis

Period of Analysis	Cycle N		Cycle N-1		Cycle N-2	
	Slope	R^2	Slope	R^2	Slope	R^2
25 Days Pre-Injection	3.71E-03	0.02	-2.32E-02	0.21	-3.83E-03	0.05
25 Days Post-Injection	2.55E-02	0.84	-1.85E-03	0.01	-1.85E-04	0.00
25 Days Post-Detection	4.99E-03	0.21	1.03E-02	0.18	5.95E-03	0.24
25 Days Pre-Zinc	4.20E-03	0.03	-1.76E-02	0.13	-2.56E-03	0.02
Detection through EOC	5.05E-03	0.62	6.26E-03	0.22	2.00E-03	0.16

Table 3-18
Braidwood 2 Total Co-60 Activity Multiple Cycle Statistical Assessment Results

Time Period	Change Versus Cycle N-1				Change Versus Cycle N-2			
	α=0.01	α=0.05	α=0.2	α=0.5	α=0.01	α=0.05	α=0.2	α=0.5
Pre-Zinc	-0.03	-0.02	0.00	0.02	0.02	0.04	0.05	0.07
Post-Injection/Pre-Detection	0.01	0.07	0.13	0.19	0.13	0.19	0.26	0.32
Post-Injection	0.35	0.38	0.41	0.44	0.54	0.57	0.59	0.62
Post-Detection	0.40	0.43	0.46	0.49	0.61	0.63	0.65	0.67

Table 3-19
Braidwood 2 Total Co-60 Activity Same Cycle Statistical Assessment Results

Time Period for Comparison to Pre-Zinc Period	Cycle N				Cycle N-1				Cycle N-2			
	α=0.01	α=0.05	α=0.2	α=0.5	α=0.01	α=0.05	α=0.2	α=0.5	α=0.01	α=0.05	α=0.2	α=0.5
Post-Injection/Pre-Detection	-0.16	-0.10	-0.04	0.02	-0.22	-0.20	-0.18	-0.16	-0.31	-0.28	-0.26	-0.23
Post-Injection	0.30	0.32	0.34	0.36	-0.14	-0.12	-0.09	-0.06	-0.24	-0.22	-0.20	-0.18
Post-Detection	0.38	0.40	0.42	0.43	-0.13	-0.10	-0.07	-0.04	-0.23	-0.21	-0.19	-0.17

Table 3-20
Braidwood 2 Total Co-60 Activity Profile Slope Analysis

Period of Analysis	Cycle N		Cycle N-1		Cycle N-2	
	Slope	R^2	Slope	R^2	Slope	R^2
25 Days Pre-Zinc	9.27E-03	0.24	-2.13E-02	0.20	-5.94E-03	0.31
25 Days Post-Injection	1.77E-02	0.30	-3.83E-03	0.15	-2.75E-03	0.03
25 Days Post-Detection	6.48E-03	0.15	1.01E-02	0.20	-7.30E-04	0.00
25 Days Pre-Zinc	1.05E-02	0.33	-2.13E-02	0.20	-5.94E-03	0.31
Detection through EOC	4.28E-03	0.42	4.72E-03	0.12	2.73E-03	0.18

The statistical analyses of the Braidwood 2 data provide strong indications of an increase in radiocobalt concentrations upon zinc injection. These indications include the following:

- Comparison of the first zinc cycle (Cycle N) with the two previous cycles (Cycle N-1 and Cycle N-2) indicate a statistically significant increase in Co-58 and Co-60 in each of the three post-zinc periods considered, but not in the pre-zinc period.
- Comparison of time periods within Cycle N indicates a statistically significant increase in Co-58 and Co-60 after zinc injection. Most prominent is an increase in the post-detection period relative to the pre-injection period, which did not occur in Cycle N-1 or Cycle N-2.
- There is a substantial change in trends upon zinc injection. In the 25-day period prior to zinc injection, Co-58 and Co-60 trends are essentially flat, as they were in Cycle N-1 and Cycle N-2. In the 25-day period following injection, there is a statistically significant ($R^2 > 0.8$) trend in Co-58 (there is a similar but less statistically robust trend in Co-60). These trends are absent in Cycle N-1 and Cycle N-2.

During the post-detection period, the activity of Co-58 is somewhat higher in Cycle 11 (Cycle N-1) relative to Cycle 10 (Cycle N-2), indicating that the increase in Cycle 12 (Cycle N) might have been due to a long term trend in, for example, core design or corrosion product accumulation. However, the higher values in Cycle 11 coincide with a downpower. Thus it is likely that these higher values do not indicate a significant difference from Cycle 10 and that the increase in Cycle 12 is due to zinc injection.

3.4.1.5 Byron 2

Chemistry and operating data from Byron 2 Cycles 11 and 12 were in the CMA Database. Byron 2 began injecting zinc 391 days into the 12th fuel cycle; zinc was detected in the coolant during the fifth week of injection [9] but the exact date of the first detection was unavailable. The average zinc concentration in the coolant was 5.6 ppb [10]. The Byron 2 steam generators are tubed with Alloy 600TT.

Data for Co-58 and plant power are given in Figure 3-10. Data for Co-60 and plant power are given in Figure 3-11. These data were analyzed using the statistical comparisons described in

Section 3.3. The results are given in Table 3-21 through Table 3-23 for Co-58 and Table 3-24 through Table 3-26 for Co-60.

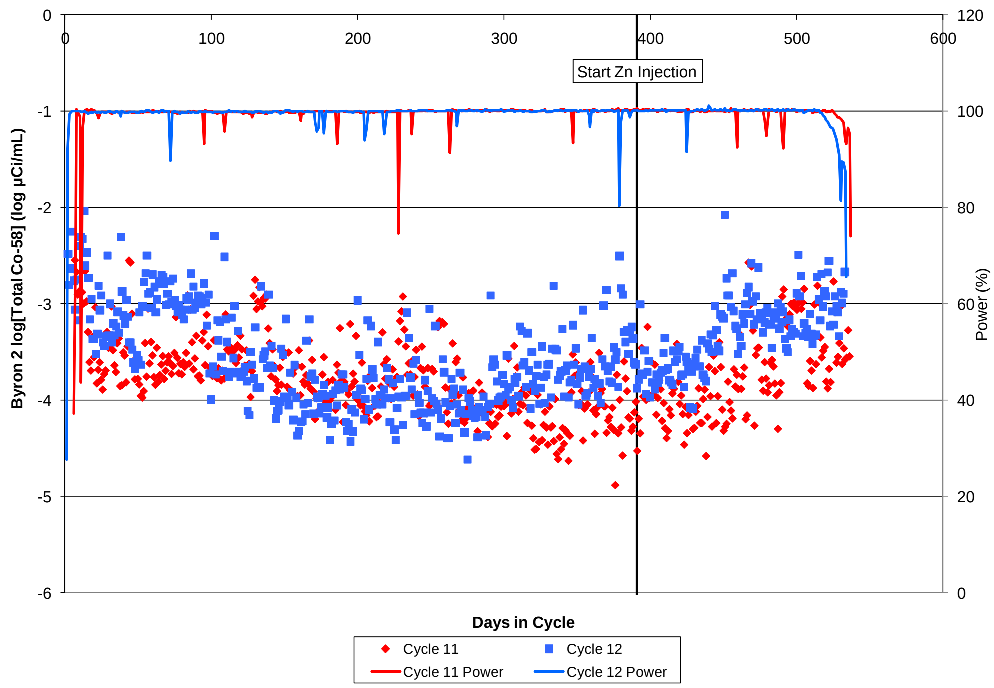

Figure 3-10
Byron 2 Total Co-58 Activity before and during Zinc Injection

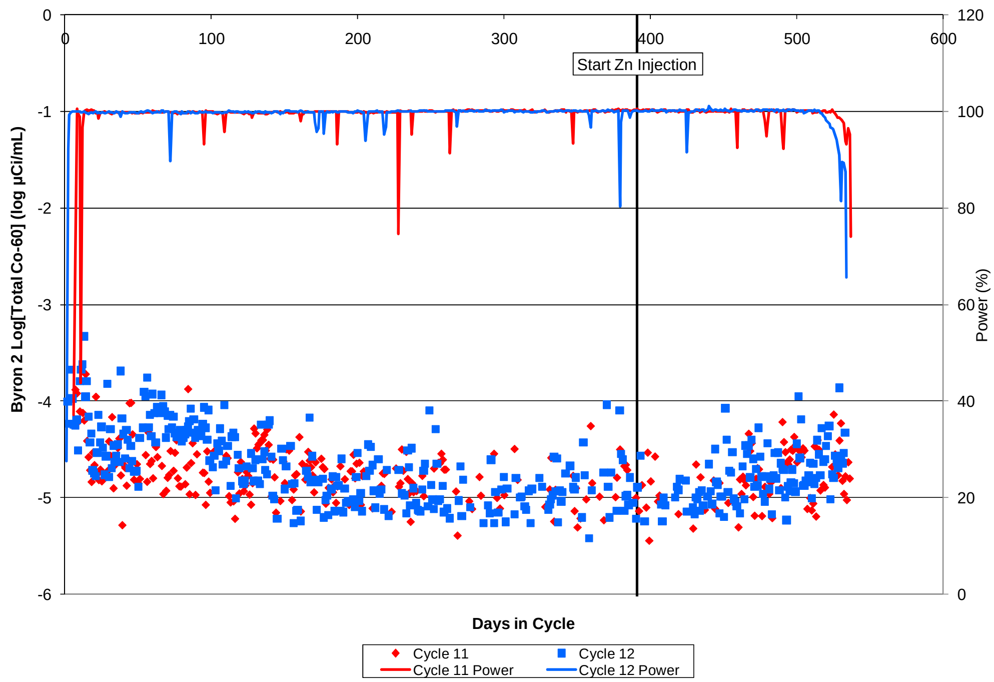

Figure 3-11
Byron 2 Total Co-60 Activity before and during Zinc Injection

Table 3-21
Byron 2 Total Co-58 Activity Multiple Cycle Statistical Assessment Results

Time Period	Change Versus Cycle N-1				Change Versus Cycle N-2			
	α=0.01	α=0.05	α=0.2	α=0.5	α=0.01	α=0.05	α=0.2	α=0.5
Pre-Zinc	0.10	0.12	0.15	0.18	-	-	-	-
Post-Injection/Pre-Detection	-	-	-	-	-	-	-	-
Post-Injection	0.30	0.33	0.37	0.41	-	-	-	-
Post-Detection	-	-	-	-	-	-	-	-

Table 3-22
Byron 2 Total Co-58 Activity Same Cycle Statistical Assessment Results

Time Period for Comparison to Pre-Zinc Period	Cycle N				Cycle N-1				Cycle N-2			
	α=0.01	α=0.05	α=0.2	α=0.5	α=0.01	α=0.05	α=0.2	α=0.5	α=0.01	α=0.05	α=0.2	α=0.5
Post-Injection/Pre-Detection	-	-	-	-	-	-	-	-	-	-	-	-
Post-Injection	0.19	0.22	0.25	0.28	-0.04	-0.01	0.02	0.06	-	-	-	-
Post-Detection	-	-	-	-	-	-	-	-	-	-	-	-

Table 3-23
Byron 2 Total Co-58 Activity Profile Slope Analysis

Period of Analysis	Cycle N		Cycle N-1		Cycle N-2	
	Slope	R^2	Slope	R^2	Slope	R^2
25 Days Pre-Zinc	1.25E-02	0.07	-5.83E-03	0.02	-	-
25 Days Post-Injection	-3.21E-04	0.00	-5.14E-03	0.02	-	-
25 Days Post-Detection	-	-	-	-	-	-
100 Days Post-Injection	1.05E-02	0.43	9.25E-04	0.01	-	-

Table 3-24
Byron 2 Total Co-60 Activity Multiple Cycle Statistical Assessment Results

Time Period	Change Versus Cycle N-1				Change Versus Cycle N-2			
	α=0.01	α=0.05	α=0.2	α=0.5	α=0.01	α=0.05	α=0.2	α=0.5
Pre-Zinc	0.00	0.02	0.04	0.07	-	-	-	-
Post-Injection/Pre-Detection	-	-	-	-	-	-	-	-
Post-Injection	-0.07	-0.04	-0.01	0.02	-	-	-	-
Post-Detection	-	-	-	-	-	-	-	-

Table 3-25
Byron 2 Total Co-60 Activity Same Cycle Statistical Assessment Results

Time Period for Comparison to Pre-Zinc Period	Cycle N				Cycle N-1				Cycle N-2			
	α=0.01	α=0.05	α=0.2	α=0.5	α=0.01	α=0.05	α=0.2	α=0.5	α=0.01	α=0.05	α=0.2	α=0.5
Post-Injection/Pre-Detection	-	-	-	-	-	-	-	-	-	-	-	-
Post-Injection	-0.20	-0.18	-0.15	-0.12	-0.15	-0.12	-0.09	-0.06	-	-	-	-
Post-Detection	-	-	-	-	-	-	-	-	-	-	-	-

Table 3-26
Byron 2 Total Co-60 Activity Profile Slope Analysis

Period of Analysis	Cycle N		Cycle N-1		Cycle N-2	
	Slope	R^2	Slope	R^2	Slope	R^2
25 Days Pre-Zinc	-2.01E-02	0.14	1.39E-02	0.23	-	-
25 Days Post-Injection	-1.48E-02	0.28	1.70E-03	0.00	-	-
25 Days Post-Detection	-	-	-	-	-	-
Days 400-475	6.90E-03	0.26	2.39E-03	0.06	-	-

Statistical comparison between cycles of the post-injection Co-58 and Co-60 activities does not provide strong indications of a zinc effect. Cycle 12 (Cycle N) has significantly higher Co-58 activity than Cycle 11 (Cycle N-1) during the post-zinc period. However, Cycle 12 also has significantly higher Co-58 activity during the pre-zinc period. This provides some indication that the increase is not related to zinc injection. For Co-60 there are no significant differences between Cycle 11 and Cycle 12.

The radiocobalt trends for the 25-day periods before and after zinc injection indicate that there were no significant trends in activity for Co-58 or Co-60.

Consideration of a longer period following zinc injection shows a statistically significant upward trend in Co-58 activity during Cycle 12 (Cycle N). This trend is not evident in Cycle 11 (Cycle N-1). However, the Cycle 11 data are complicated by several power changes during that time which may mask an otherwise significant trend.

In conclusion, there are some indications that the first zinc cycle generally had higher radiocobalt activities unrelated to zinc injection, but there is no strong evidence of a zinc effect.

3.4.1.6 Catawba 1

The first injection of zinc at Catawba 1 took place during the 17th fuel cycle. Data from Cycles 15 and 16 were supplied by EPRI [16], but Cycle 17 data were unavailable, and no analyses were conducted. The Catawba 1 steam generators have Alloy 690TT tubing. (Steam generator replacement occurred after Cycle 9; the original steam generators were tubed with Alloy 600MA [12].)

3.4.1.7 Catawba 2

Catawba 2 first injected zinc during Cycle 15. Data from Cycle 14 were transmitted by EPRI [16], but Cycle 15 data were unavailable, and no evaluations were performed. The Catawba 2 steam generators are tubed with Alloy 600TT.

3.4.1.8 Calvert Cliffs 1

Calvert Cliffs 1 chemistry and operating data were available in the CMA Database [8] and were also provided independently by EPRI [15]. Injection of zinc at Calvert Cliffs 1 was initiated on the 444th day of Cycle 18, the concentration in the RCS was measurable 7 days later, and reached an average concentration of 5.3 ppb. The cycle start and zinc start dates were taken from the CMA Database and from Reference [17]. The Calvert Cliffs 1 steam generators have Alloy 690TT tubing. The Calvert Cliffs 1 steam generators were replaced after Cycle 15; the original steam generators were tubed with Alloy 600HTMA [12]. Calvert Cliffs operates on a 24-month cycle.

Data for Co-58 are given in Figure 3-12. Data for Co-60 are given in Figure 3-13. These data were analyzed using the statistical comparisons described in Section 3.3. The results are given in Table 3-27 through Table 3-29 for Co-58 and Table 3-30 through Table 3-31 for Co-60.

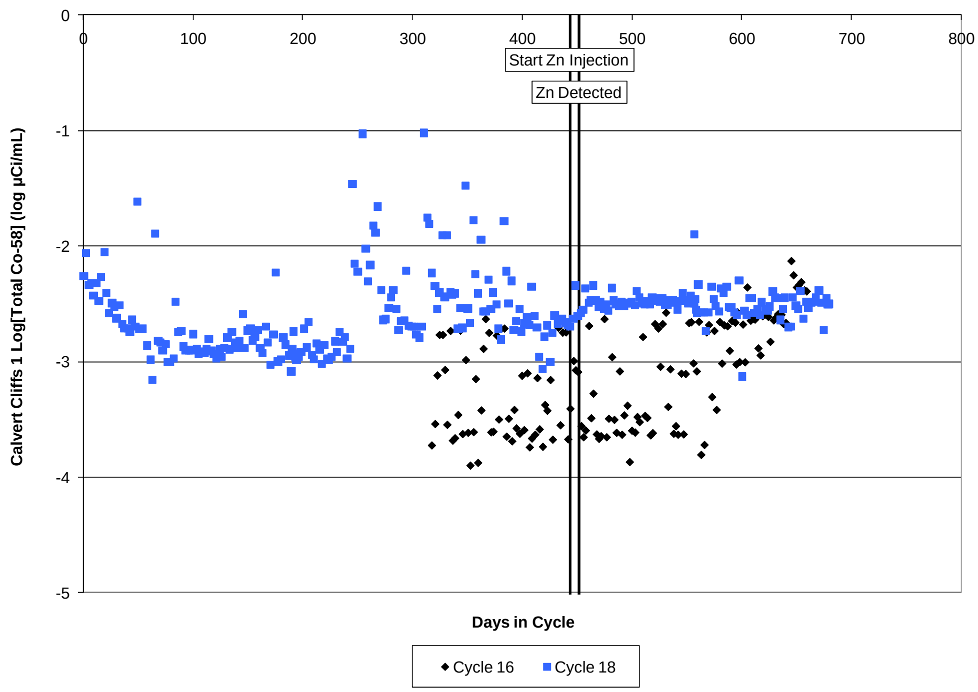

Figure 3-12
Calvert Cliffs 1 Total Co-58 Activity before and during Zinc Injection

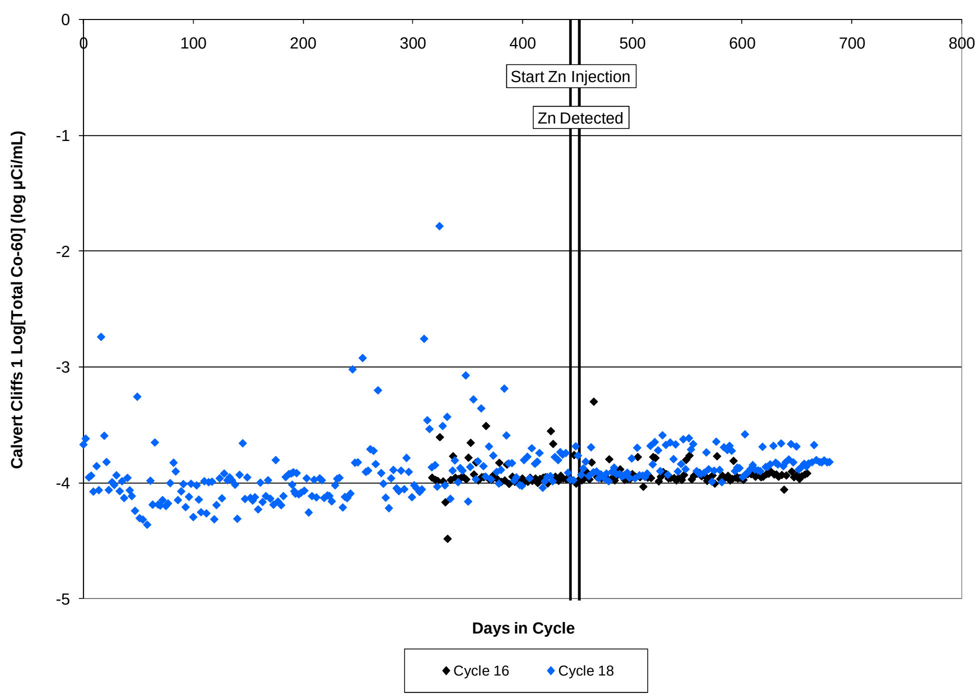

Figure 3-13
Calvert Cliffs 1 Total Co-60 Activity before and during Zinc Injection

Table 3-27
Calvert Cliffs 1 Total Co-58 Activity Multiple Cycle Statistical Assessment Results

Time Period	Change Versus Cycle N-1				Change Versus Cycle N-2			
	α=0.01	α=0.05	α=0.2	α=0.5	α=0.01	α=0.05	α=0.2	α=0.5
Pre-Zinc	-	-	-	-	0.64	0.69	0.75	0.81
Post-Injection/Pre-Detection	-	-	-	-	0.13	0.34	0.50	0.62
Post-Injection	-	-	-	-	0.41	0.45	0.49	0.53
Post-Detection	-	-	-	-	0.41	0.44	0.48	0.52

Table 3-28
Calvert Cliffs 1 Total Co-58 Activity Same Cycle Statistical Assessment Results

Time Period for Comparison to Pre-Zinc Period	Cycle N				Cycle N-1				Cycle N-2			
	α=0.01	α=0.05	α=0.2	α=0.5	α=0.01	α=0.05	α=0.2	α=0.5	α=0.01	α=0.05	α=0.2	α=0.5
Post-Injection/Pre-Detection	-0.58	-0.20	-0.02	0.08	-	-	-	-	-0.19	-0.05	0.07	0.17
Post-Injection	0.04	0.06	0.08	0.11	-	-	-	-	0.11	0.16	0.22	0.28
Post-Detection	0.04	0.06	0.08	0.11	-	-	-	-	0.12	0.17	0.23	0.29

Table 3-29
Calvert Cliffs 1 Total Co-58 Activity Profile Slope Analysis

Period of Analysis	Cycle N		Cycle N-1		Cycle N-2	
	Slope	R^2	Slope	R^2	Slope	R^2
25 Days Pre-Zinc	6.35E-03	0.20	-	-	1.95E-02	0.12
25 Days Post-Injection	3.95E-03	0.09	-	-	-1.02E-02	0.06
25 Days Post-Detection	-1.88E-04	0.00	-	-	5.40E-03	0.01
100 Days Pre-Zinc	-5.77E-03	0.28	-	-	5.33E-04	0.00

Table 3-30
Calvert Cliffs 1 Total Co-60 Activity Multiple Cycle Statistical Assessment Results

Time Period	Change Versus Cycle N-1				Change Versus Cycle N-2			
	α=0.01	α=0.05	α=0.2	α=0.5	α=0.01	α=0.05	α=0.2	α=0.5
Pre-Zinc	-	-	-	-	0.03	0.06	0.11	0.15
Post-Injection/Pre-Detection	-	-	-	-	-0.42	-0.17	0.00	0.11
Post-Injection	-	-	-	-	0.07	0.08	0.09	0.10
Post-Detection	-	-	-	-	0.07	0.08	0.09	0.10

Table 3-31
Calvert Cliffs 1 Total Co-60 Activity Same Cycle Statistical Assessment Results

Time Period for Comparison to Pre-Zinc Period	Cycle N				Cycle N-1				Cycle N-2			
	α=0.01	α=0.05	α=0.2	α=0.5	α=0.01	α=0.05	α=0.2	α=0.5	α=0.01	α=0.05	α=0.2	α=0.5
Post-Injection/Pre-Detection	-0.51	-0.15	0.02	0.12	-	-	-	-	-0.55	-0.22	-0.07	0.02
Post-Injection	0.04	0.06	0.08	0.10	-	-	-	-	-0.04	-0.03	-0.01	0.01
Post-Detection	0.04	0.05	0.07	0.10	-	-	-	-	-0.04	-0.03	-0.01	0.01

Table 3-32
Calvert Cliffs 1 Total Co-60 Activity Profile Slope Analysis

Period of Analysis	Cycle N		Cycle N-1		Cycle N-2	
	Slope	R^2	Slope	R^2	Slope	R^2
25 Days Pre-Injection	5.16E-03	0.14	-	-	-3.81E-03	0.04
25 Days Post-Injection	-3.42E-03	0.06	-	-	9.91E-03	0.14
25 Days Post-Detection	-3.48E-03	0.12	-	-	3.25E-03	0.02
100 Days Pre-Zinc	-1.84E-03	0.06	-	-	-5.09E-04	0.02

The statistical analyses performed on this data set indicated that there are consistently higher Co-58 activities throughout Cycle 18 (Cycle N) relative to Cycle 16 (Cycle N-2). There is no indication that this is due to zinc injection. There are no apparent differences in Co-60 activity.

Analysis of trends during the 25-day periods before and after injection and after detection indicates that there were no trends in Co-58 or Co-60.

Inspection of the data presented in Figure 3-12 indicates that the period of about 50 days before zinc injection started Co-58 activity was relatively constant. After injection started, there was a small increase in activity. Roughly 25 days after the start of injection, a new stable Co-58 activity was reached. These observations would support the conclusion that there was a zinc effect. However, this interpretation does not consider the large variability in the activity about 200 to 50 days prior to zinc injection. During this period the activity varied considerably, with many values exceeding the post-zinc injection plateau.

The Calvert Cliffs 1 data provide an indication that there was an increase in Co-58 (but not Co-60) activity resulting from zinc injection. However, this conclusion cannot be robust because of the following additional observations:

- The zinc cycle generally had significantly higher Co-58 activity than the pre-zinc cycle.
- Pre-zinc periods (not associated with beginning of cycle transients) during the zinc cycle had Co-58 activities in excess of the post-zinc activities.

There were no statistically significant differences or trends in the Co-60 activity associated with zinc.

3.4.1.9 Crystal River 3

Crystal River 3 chemistry and operating data were available in the CMA Database and were also transmitted by EPRI [15]. However, since zinc injection began at Crystal River 3 on January 14, 2009 [12], and Cycle 16 radiocobalt data were available up to September 30, 2008, no analyses were performed. Until replacement in 2009, the Crystal River 3 steam generators were tubed with Alloy 600SR.

3.4.1.10 McGuire 1

Chemistry and operating data were transmitted by Duke personnel and by EPRI. McGuire 1 began injecting zinc 294 days into the 18th fuel cycle, detected zinc in the coolant 21 days later, and averaged 4.2 ppb for the remainder of the cycle after injection was started. McGuire 1 completed full UFC campaigns during the two outages immediately preceding the first injection of zinc, and averaged 4.5 ppb zinc in the coolant during its first cycle of injection. The McGuire 1 steam generators are tubed with Alloy 690TT. The original McGuire 1 steam generators were tubed with Alloy 600MA; steam generator replacement occurred after Cycle 11 [12].

Data for Co-58 and plant power are given in Figure 3-14. Data for Co-60 and plant power are given in Figure 3-15. These data were analyzed using the statistical comparisons described in Section 3.3. The results are given in Table 3-33 through Table 3-35 for Co-58 and Table 3-36 through Table 3-38 for Co-60.

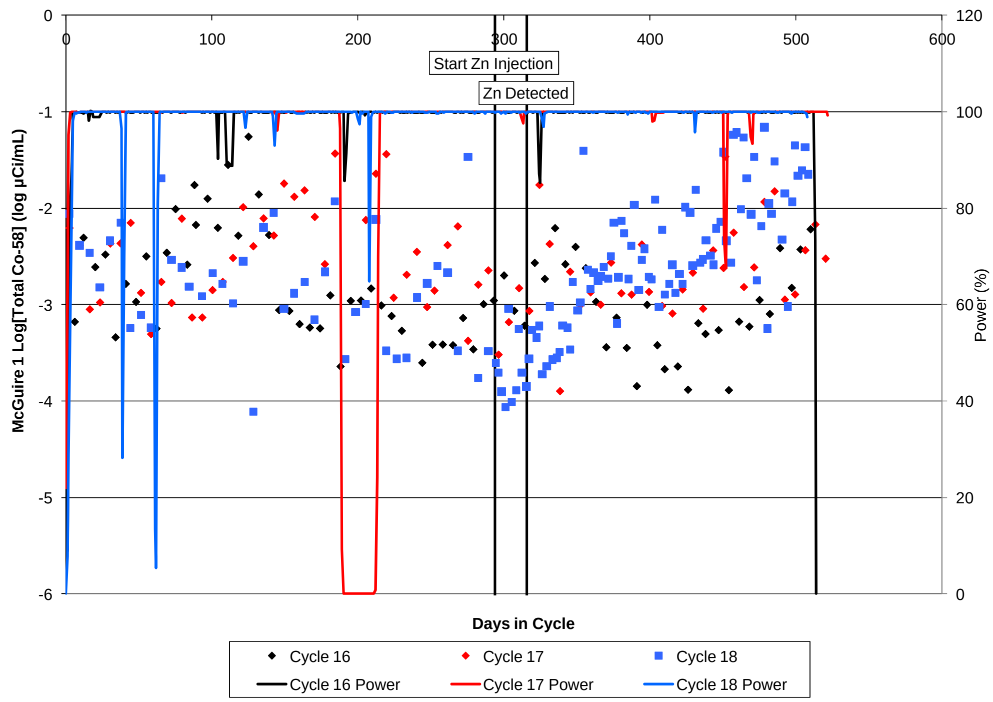

Figure 3-14
McGuire 1 Total Co-58 Activity before and during Zinc Injection

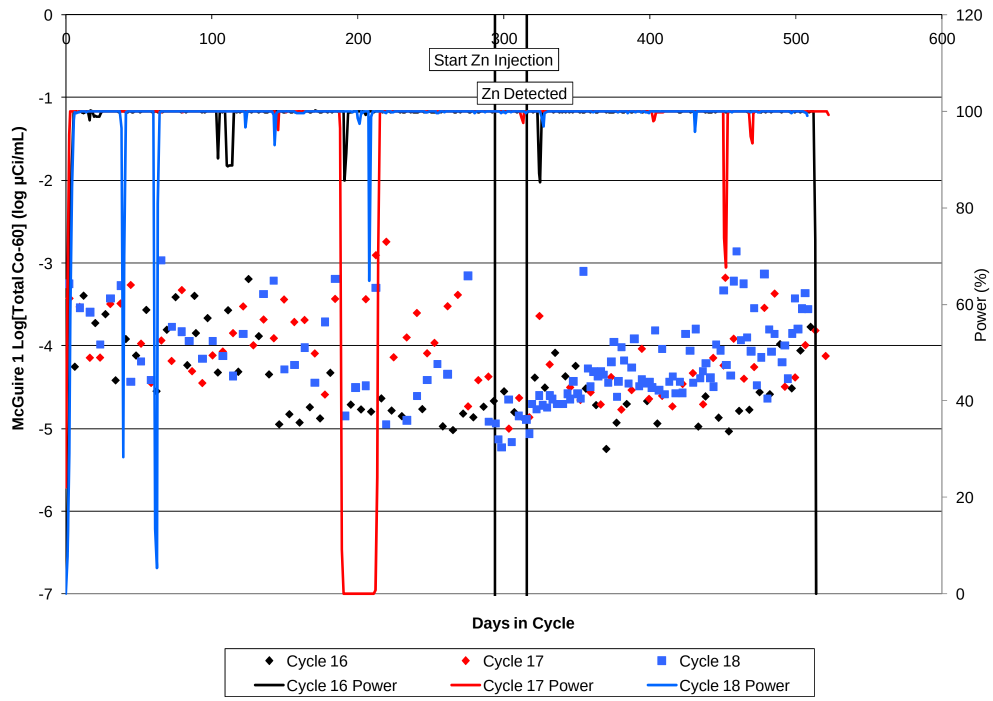

Figure 3-15
McGuire 1 Total Co-60 Activity before and during Zinc Injection

Table 3-33
McGuire 1 Total Co-58 Activity Multiple Cycle Statistical Assessment Results

Time Period	Change Versus Cycle N-1				Change Versus Cycle N-2			
	α=0.01	α=0.05	α=0.2	α=0.5	α=0.01	α=0.05	α=0.2	α=0.5
Pre-Zinc	-0.62	-0.53	-0.43	-0.33	-0.33	-0.24	-0.13	-0.03
Post-Injection/Pre-Detection	-1.55	-1.05	-0.74	-0.51	-1.42	-1.11	-0.88	-0.70
Post-Injection	-0.18	-0.10	0.00	0.09	0.18	0.26	0.36	0.45
Post-Detection	-0.11	-0.03	0.07	0.16	0.29	0.38	0.47	0.58

Table 3-34
McGuire 1 Total Co-58 Activity Same Cycle Statistical Assessment Results

Time Period for Comparison to Pre-Zinc Period	Cycle N				Cycle N-1				Cycle N-2			
	α=0.01	α=0.05	α=0.2	α=0.5	α=0.01	α=0.05	α=0.2	α=0.5	α=0.01	α=0.05	α=0.2	α=0.5
Post-Injection/Pre-Detection	-1.25	-1.13	-1.01	-0.88	-2.20	-1.33	-0.93	-0.71	-1.02	-0.64	-0.39	-0.22
Post-Injection	-0.07	0.02	0.11	0.21	-0.49	-0.41	-0.31	-0.22	-0.57	-0.48	-0.38	-0.27
Post-Detection	0.05	0.13	0.23	0.32	-0.45	-0.36	-0.27	-0.17	-0.59	-0.50	-0.39	-0.28

Table 3-35
McGuire 1 Total Co-58 Activity Profile Slope Analysis

Period of Analysis	Cycle N		Cycle N-1		Cycle N-2	
	Slope	R^2	Slope	R^2	Slope	R^2
25 Days Pre-Zinc	-3.31E-02	0.08	-1.13E-02	0.04	1.44E-02	0.32
25 Days Post-Injection	9.98E-03	0.07	2.44E-02	0.59	-3.72E-02	0.95
25 Days Post-Detection	7.44E-03	0.06	-4.45E-02	0.19	2.58E-02	0.45
100 Days Pre-Injection	-1.09E-04	0.00	-1.09E-02	0.30	-2.71E-03	0.13
50 Days Post-Injection	9.37E-03	0.21	7.89E-03	0.03	1.30E-02	0.34
100 Days Post-Injection	1.58E-02	0.63	3.88E-03	0.06	-8.40E-03	0.29
150 Days Post-Injection	1.00E-02	0.56	1.56E-03	0.03	-7.38E-03	0.44
Detection through EOC	8.55E-03	0.53	2.56E-03	0.11	-6.81E-04	0.01

Table 3-36
McGuire 1 Total Co-60 Activity Multiple Cycle Statistical Assessment Results

Time Period	Change Versus Cycle N-1				Change Versus Cycle N-2			
	α=0.01	α=0.05	α=0.2	α=0.5	α=0.01	α=0.05	α=0.2	α=0.5
Pre-Zinc	-0.44	-0.36	-0.27	-0.17	0.01	0.10	0.21	0.31
Post-Injection/Pre-Detection	-6.75	-1.48	-0.46	-0.18	-0.70	-0.52	-0.37	-0.24
Post-Injection	-0.18	-0.11	-0.04	0.04	0.13	0.19	0.26	0.33
Post-Detection	-0.16	-0.09	-0.02	0.06	0.15	0.22	0.29	0.37

Table 3-37
McGuire 1 Total Co-60 Activity Same Cycle Statistical Assessment Results

Time Period for Comparison to Pre-Zinc Period	Cycle N				Cycle N-1				Cycle N-2			
	α=0.01	α=0.05	α=0.2	α=0.5	α=0.01	α=0.05	α=0.2	α=0.5	α=0.01	α=0.05	α=0.2	α=0.5
Post-Injection/Pre-Detection	-1.31	-1.21	-1.10	-0.99	-7.31	-2.24	-1.25	-0.98	-0.88	-0.70	-0.55	-0.43
Post-Injection	-0.50	-0.43	-0.35	-0.26	-0.72	-0.65	-0.56	-0.47	-0.54	-0.46	-0.37	-0.28
Post-Detection	-0.45	-0.38	-0.29	-0.21	-0.69	-0.62	-0.53	-0.44	-0.53	-0.45	-0.36	-0.26

Table 3-38
McGuire 1 Total Co-60 Activity Profile Slope Analysis

Period of Analysis	Cycle N		Cycle N-1		Cycle N-2	
	Slope	R^2	Slope	R^2	Slope	R^2
25 Days Pre-Zinc	-1.26E-01	1.00	2.58E-02	0.84	8.38E-03	0.75
25 Days Post-Injection	8.75E-03	0.16	9.78E-03	0.13	-2.41E-02	0.93
25 Days Post-Detection	8.81E-03	0.33	4.56E-02	0.27	2.14E-02	0.48
100 Days Pre-Zinc	1.59E-03	0.01	-1.43E-02	0.44	-7.86E-04	0.06
50 Days Post-Injection	9.65E-03	0.40	3.63E-02	0.53	1.20E-02	0.45
100 Days Post-Injection	8.97E-03	0.48	2.06E-03	0.03	-3.28E-03	0.08
150 Days Post-Injection	4.76E-03	0.33	8.06E-04	0.01	-2.60E-03	0.14
Detection through EOC	5.06E-03	0.40	3.06E-03	0.18	8.12E-04	0.02

The following observations can be made from the statistical analysis of the McGuire 1 data:

- The differences in Co-58 activity between Cycle 18 (Cycle N) and Cycle 17 (Cycle N-1) are small or statistically insignificant. Differences between Cycle 18 (Cycle N) and Cycle 16 (Cycle N-2) are larger.
- In the zinc injection cycle, the post-zinc Co-58 activities are significantly higher than the pre-zinc activities. This difference was not present in the prior cycles. However, the Co-58 activity at the beginning of Cycle 18 (Cycle N) was significantly lower than at the beginning of Cycle 17 (Cycle N-1) and Cycle 16 (Cycle N-2). Thus, the difference in Cycle 18 between pre- and post-zinc periods might be ascribed to a low pre-zinc activity, and thus not related to zinc injection.

Inspection of Figure 3-14 indicates that there is a clear trend of increasing Co-58 activity in Cycle 18 (Cycle N) starting at the time when zinc injection started. Comparison to previous cycles indicates that Cycle 17 (Cycle N-1) had no trend in Co-58 during this period. However, Cycle 16 (Cycle N-2) had a decreasing trend during this period. The magnitude and statistical significance of these trends (for example, for the 150 days after injection started) are similar. Therefore, it is possible that the in-cycle increasing trend which followed commencement of zinc injection is part of a larger cycle-to-cycle trend of increases in the end of cycle trends independent of zinc, for example, related to core design changes.

Overall, there appears to have been an effect of zinc addition on radiocobalt releases at McGuire 1, but the data do not provide a basis for a robust assessment.

3.4.1.11 McGuire 2

McGuire 2 chemistry and operating data were available in the CMA database and were transmitted by EPRI. Zinc injection commenced on the 324th day of McGuire 2 Cycle 17, zinc was detected in the coolant on Day 336, and the average concentration following the start of injection was 4.5 ppb. McGuire 2 completed two full UFC campaigns during the two outages immediately preceding the first injection of zinc. McGuire 2 has Alloy 690TT steam generator tubing. (The original McGuire 2 steam generators were tubed with Alloy 600MA; steam generator replacement occurred after Cycle 11[12].)

Data for Co-58 and plant power are given in Figure 3-16. Data for Co-60 and plant power are given in Figure 3-17. These data were analyzed using the statistical comparisons described in Section 3.3. The results are given in Table 3-39 through Table 3-41 for Co-58 and Table 3-42 through Table 3-44 for Co-60.

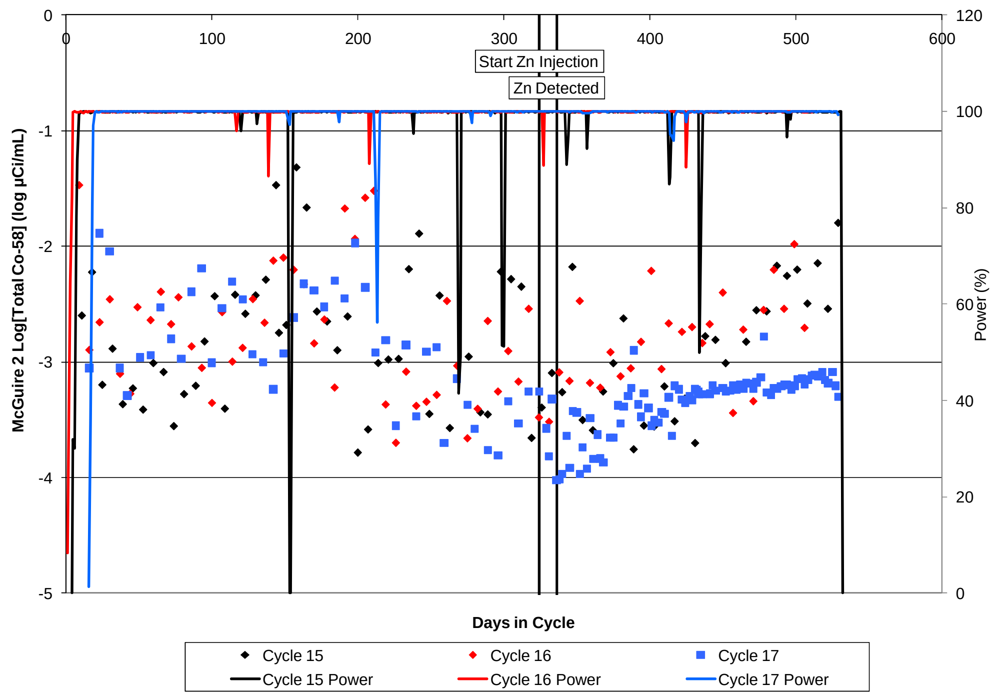

Figure 3-16
McGuire 2 Total Co-58 Activity before and after Zinc Injection

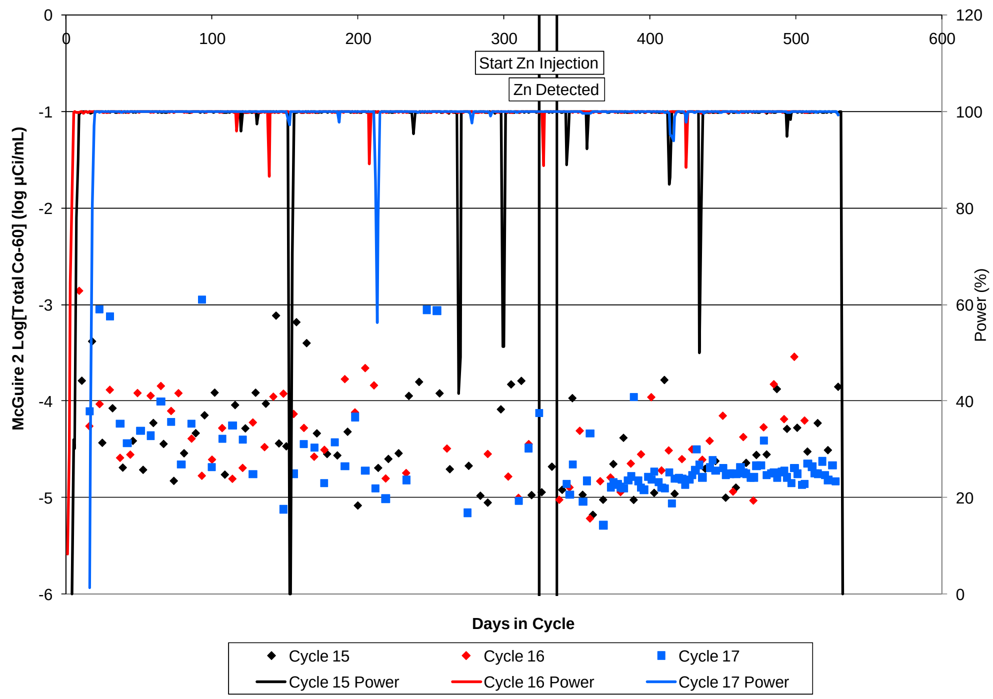

Figure 3-17
McGuire 2 Total Co-60 Activity before and during Zinc Injection

Table 3-39
McGuire 2 Total Co-58 Activity Multiple Cycle Statistical Assessment Results

Time Period	Change Versus Cycle N-1				Change Versus Cycle N-2			
	α=0.01	α=0.05	α=0.2	α=0.5	α=0.01	α=0.05	α=0.2	α=0.5
Pre-Zinc	-0.38	-0.30	-0.21	-0.12	-0.32	-0.24	-0.14	-0.04
Post-Injection/Pre-Detection	-0.58	-0.30	-0.12	0.00	-1.61	-0.82	-0.45	-0.24
Post-Injection	-0.72	-0.66	-0.59	-0.52	-0.69	-0.61	-0.52	-0.43
Post-Detection	-0.76	-0.70	-0.64	-0.57	-0.72	-0.63	-0.54	-0.45

Table 3-40
McGuire 2 Total Co-58 Activity Same Cycle Statistical Assessment Results

Time Period for Comparison to Pre-Zinc Period	Cycle N				Cycle N-1				Cycle N-2			
	α=0.01	α=0.05	α=0.2	α=0.5	α=0.01	α=0.05	α=0.2	α=0.5	α=0.01	α=0.05	α=0.2	α=0.5
Post-Injection/Pre-Detection	-1.12	-0.92	-0.76	-0.62	-0.94	-0.88	-0.81	-0.74	-5.95	-1.52	-0.66	-0.42
Post-Injection	-0.68	-0.63	-0.56	-0.49	-0.35	-0.27	-0.18	-0.09	-0.43	-0.33	-0.22	-0.11
Post-Detection	-0.68	-0.62	-0.56	-0.49	-0.30	-0.22	-0.13	-0.04	-0.41	-0.32	-0.20	-0.08

Table 3-41
McGuire 2 Total Co-58 Activity Profile Slope Analysis

Period of Analysis	Cycle N		Cycle N-1		Cycle N-2	
	Slope	R^2	Slope	R^2	Slope	R^2
25 Days Pre-Zinc	5.92E-03	0.09	3.58E-03	0.97	-9.81E-02	0.79
25 Days Post-Injection	-1.41E-02	0.13	1.96E-02	0.67	4.97E-02	0.67
25 Days Post-Detection	9.84E-03	0.13	6.00E-03	0.03	-3.31E-02	0.21
100 Days Pre-Zinc	-4.00E-03	0.13	5.89E-03	0.20	-3.15E-03	0.02
50 Days Post-Injection	-3.39E-03	0.04	9.93E-03	0.27	-4.17E-03	0.02
100 Days Post-Injection	4.71E-03	0.28	6.93E-03	0.37	-3.61E-03	0.08
150 Days Post-Injection	4.21E-03	0.50	2.70E-03	0.12	1.61E-03	0.03
Detection through EOC	3.50E-03	0.60	3.23E-03	0.20	6.34E-03	0.43

Table 3-42
McGuire 2 Total Co-60 Activity Multiple Cycle Statistical Assessment Results

Time Period	Change Versus Cycle N-1				Change Versus Cycle N-2			
	α=0.01	α=0.05	α=0.2	α=0.5	α=0.01	α=0.05	α=0.2	α=0.5
Pre-Zinc	-0.31	-0.23	-0.13	-0.02	-0.35	-0.26	-0.15	-0.04
Post-Injection/Pre-Detection	-	-	-	-	-	-	-	-
Post-Injection	-0.44	-0.38	-0.31	-0.24	-0.35	-0.29	-0.23	-0.16
Post-Detection	-0.45	-0.39	-0.32	-0.24	-0.39	-0.32	-0.26	-0.19

Table 3-43
McGuire 2 Total Co-60 Activity Same Cycle Statistical Assessment Results

Time Period for Comparison to Pre-Zinc Period	Cycle N				Cycle N-1				Cycle N-2			
	α=0.01	α=0.05	α=0.2	α=0.5	α=0.01	α=0.05	α=0.2	α=0.5	α=0.01	α=0.05	α=0.2	α=0.5
Post-Injection/Pre-Detection	-	-	-	-	-	-	-	-	-5.35	-1.48	-0.73	-0.52
Post-Injection	-0.69	-0.61	-0.52	-0.43	-0.46	-0.38	-0.30	-0.21	-0.56	-0.48	-0.40	-0.31
Post-Detection	-0.70	-0.62	-0.53	-0.43	-0.46	-0.38	-0.30	-0.21	-0.55	-0.47	-0.38	-0.29

Table 3-44
McGuire 2 Total Co-60 Activity Profile Slope Analysis

Period of Analysis	Cycle N		Cycle N-1		Cycle N-2	
	Slope	R^2	Slope	R^2	Slope	R^2
25 Days Pre-Zinc	7.83E-02	1.00	4.73E-05	0.98	-8.18E-02	0.73
25 Days Post-Injection	-3.17E-02	0.80	1.82E-02	1.00	3.83E-02	0.58
25 Days Post-Detection	1.67E-02	0.19	9.99E-05	0.00	-2.54E-02	0.18
100 Days Pre-Injection	-1.22E-02	0.19	-5.70E-04	0.01	-1.35E-03	0.01
100 Days Post-Injection	-2.03E-03	0.05	5.77E-03	0.23	1.33E-03	0.01
Detection through EOC	6.25E-04	0.04	4.81E-03	0.37	3.01E-03	0.20

The statistical analyses performed on the McGuire 2 data indicate the following:

- For all time periods, the zinc cycle (Cycle N) Co-58 activities were significantly lower than those for the preceding cycles (Cycle N-1 and Cycle N-2). (The time period between injection and detection contained too few data for an adequate assessment.) Data for Co-60 were similar.
- The 25-day periods before and after commencement of zinc injection and after zinc detection did not show any significant trends.

Consideration of longer time periods after zinc injection indicate that there was a consistent trend of increasing Co-58 activity from detection through the end of the cycle for all three cycles considered (Cycles N, N-1, and N-2), although the trend in Cycle 17 (Cycle N) was more statistically robust, possibly due to more frequent data reporting).

These data provide a reasonably robust indication that there was no zinc effect on radiocobalts at McGuire 2.

3.4.1.12 Surry 1

Surry 1 chemistry and operating data were provided by EPRI [15, 18]. Zinc injection at Surry 1 was initiated approximately 257 days into the 22nd fuel cycle [10] the concentration reached average of 7.4 ppb [11]; the time of first detection of zinc was unavailable. The Surry 1 steam generators are tubed with Alloy 600TT.

Data for Co-58 and plant power are given in Figure 3-18. Data for Co-60 and plant power are given in Figure 3-19. These data were analyzed using the statistical comparisons described in Section 3.3. The results are given in Table 3-45 through Table 3-47 for Co-58 and Table 3-48 through Table 3-50 for Co-60.

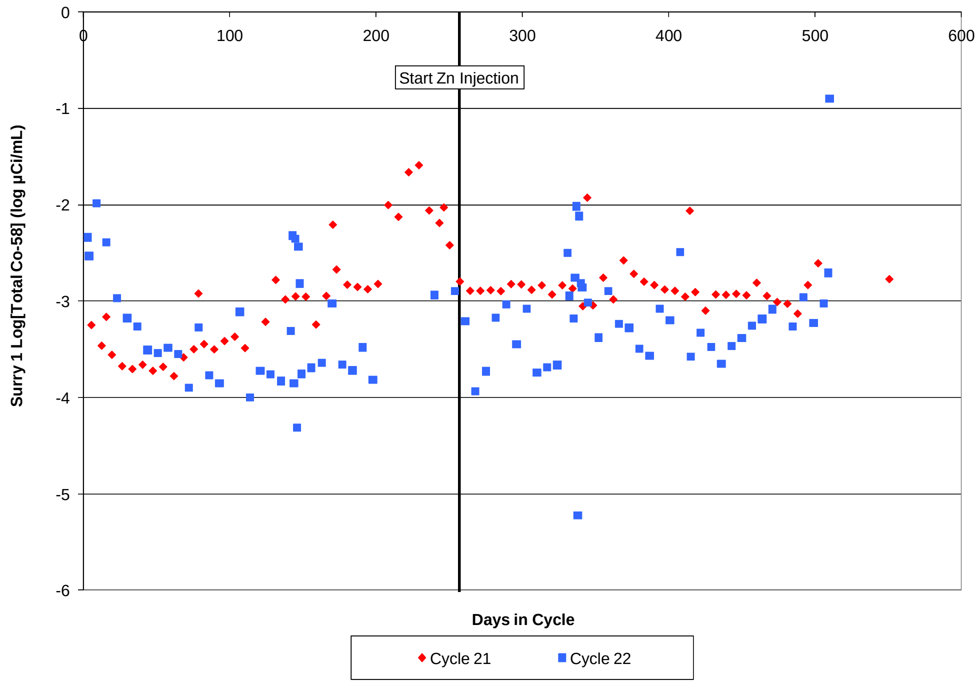

Figure 3-18
Surry 1 Total Co-58 Activity before and during Zinc Injection

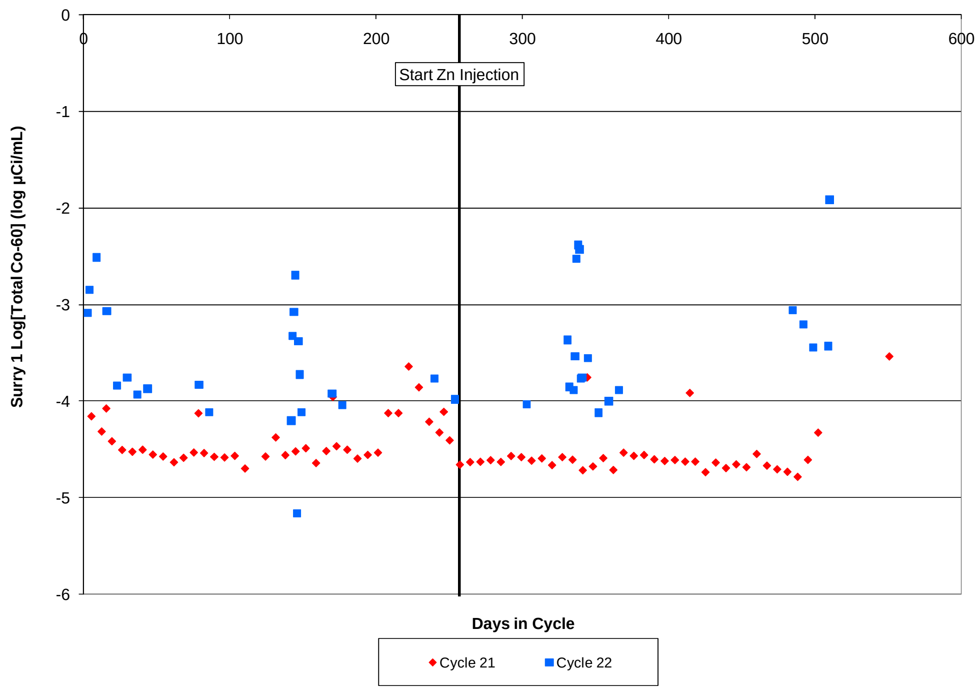

Figure 3-19
Surry 1 Total Co-60 Activity before and during Zinc Injection

Table 3-45
Surry 1 Total Co-58 Activity Multiple Cycle Statistical Assessment Results

Time Period	Change Versus Cycle N-1				Change Versus Cycle N-2			
	α=0.01	α=0.05	α=0.2	α=0.5	α=0.01	α=0.05	α=0.2	α=0.5
Pre-Zinc	-0.67	-0.57	-0.46	-0.34	-	-	-	-
Post-Injection/Pre-Detection	-	-	-	-	-	-	-	-
Post-Injection	-0.57	-0.49	-0.41	-0.33	-	-	-	-
Post-Detection	-	-	-	-	-	-	-	-

Table 3-46
Surry 1 Total Co-58 Activity Same Cycle Statistical Assessment Results

Time Period for Comparison to Pre-Zinc Period	Cycle N				Cycle N-1				Cycle N-2			
	α=0.01	α=0.05	α=0.2	α=0.5	α=0.01	α=0.05	α=0.2	α=0.5	α=0.01	α=0.05	α=0.2	α=0.5
Post-Injection/Pre-Detection	-	-	-	-	-	-	-	-	-	-	-	-
Post-Injection	-0.18	-0.09	0.02	0.13	-0.11	-0.03	0.05	0.14	-	-	-	-
Post-Detection	-	-	-	-	-	-	-	-	-	-	-	-

Table 3-47
Surry 1 Total Co-58 Activity Profile Slope Analysis

Period of Analysis	Cycle N		Cycle N-1		Cycle N-2	
	Slope	R^2	Slope	R^2	Slope	R^2
25 Days Pre-Injection	2.81E-03	1.00	-1.98E-02	0.43	-	-
25 Days Post-Injection	4.72E-03	0.01	-3.86E-03	0.54	-	-
25 Days Post-Detection	-	-	-	-	-	-
150 Days Pre-Zinc	2.63E-03	0.03	1.00E-02	0.64	-	-
Injection through EOC	2.01E-03	0.06	-2.08E-04	0.00	-	-

Table 3-48
Surry 1 Total Co-60 Activity Multiple Cycle Statistical Assessment Results

Time Period	Change Versus Cycle N-1				Change Versus Cycle N-2			
	α=0.01	α=0.05	α=0.2	α=0.5	α=0.01	α=0.05	α=0.2	α=0.5
Pre-Zinc	0.38	0.49	0.61	0.73	-	-	-	-
Post-Injection/Pre-Detection	-	-	-	-	-	-	-	-
Post-Injection	0.80	0.92	1.05	1.18	-	-	-	-
Post-Detection	-	-	-	-	-	-	-	-

Table 3-49
Surry 1 Total Co-60 Activity Same Cycle Statistical Assessment Results

Time Period for Comparison to Pre-Zinc Period	Cycle N				Cycle N-1				Cycle N-2			
	α=0.01	α=0.05	α=0.2	α=0.5	α=0.01	α=0.05	α=0.2	α=0.5	α=0.01	α=0.05	α=0.2	α=0.5
Post-Injection/Pre-Detection	-	-	-	-	-	-	-	-	-	-	-	-
Post-Injection	-0.18	-0.03	0.13	0.30	-0.29	-0.25	-0.21	-0.16	-	-	-	-
Post-Detection	-	-	-	-	-	-	-	-	-	-	-	-

Table 3-50
Surry 1 Total Co-60 Activity Profile Slope Analysis

Period of Analysis	Cycle N		Cycle N-1		Cycle N-2	
	Slope	R^2	Slope	R^2	Slope	R^2
25 Days Pre-Zinc	-1.54E-02	1.00	-8.42E-03	0.15	-	-
25 Days Post-Injection	-	-	2.06E-03	0.92	-	-
25 Days Post-Detection	-	-	-	-	-	-
150 Days Pre-Zinc	-2.03E-03	0.02	3.81E-03	0.34	-	-
Injection through EOC	3.00E-03	0.12	7.00E-04	0.04	-	-

The statistical analysis of the Surry 1 data yielded the following results:

- Both the pre-zinc and post-zinc Co-58 activities were lower during Cycle 22 (Cycle N) than during Cycle 21 (Cycle N-1). Both the pre-zinc and post-zinc Co-60 activities were higher during Cycle 22 (Cycle N) than during Cycle 21 (Cycle N-1).

- In both Cycle 21 and Cycle 22 the Co-58 activity was slightly higher after the time of zinc injection relative to the activity before the time of injection. That is, regardless of zinc, there was a small increase when comparing Co-58 activity after the time of injection to that before the time of injection. Cycle 22 (Cycle N) showed an increase in Co-60 activity, while Cycle 21 (Cycle N-1) showed a decrease, but these changes were relatively small and were less than the scatter in the data.
- There are possible trends in the 25-day period following initiation of injection, but there are very few data in this period.

Inspection of Figure 3-18 and Figure 3-19, indicates that Co-58 was significantly lower in Cycle 22 (Cycle N) than in Cycle 21 (Cycle N-1). This observation was reversed for Co-60. However, there are no indications that this reversal is related to zinc, since these differences were apparent in the pre-zinc period as well.

The data for Surry 1 provide a reasonably robust indication that there was no effect of zinc addition on radiocobalt activities.

3.4.1.13 Surry 2

Chemistry and operating data for Surry 2 were provided by EPRI [15, 18]. Surry 2 began zinc addition at a target concentration of 10 ppb on the 315th day of its 21st fuel cycle, detected zinc 44 days later and averaged about 3.7 ppb zinc [11]. The Surry 2 steam generators have Alloy 600TT tubing.

Data for Co-58 and plant power are given in Figure 3-20. Data for Co-60 and plant power are given in Figure 3-21. These data were analyzed using the statistical comparisons described in Section 3.3. The results are given in for Co-58 and for Co-60.

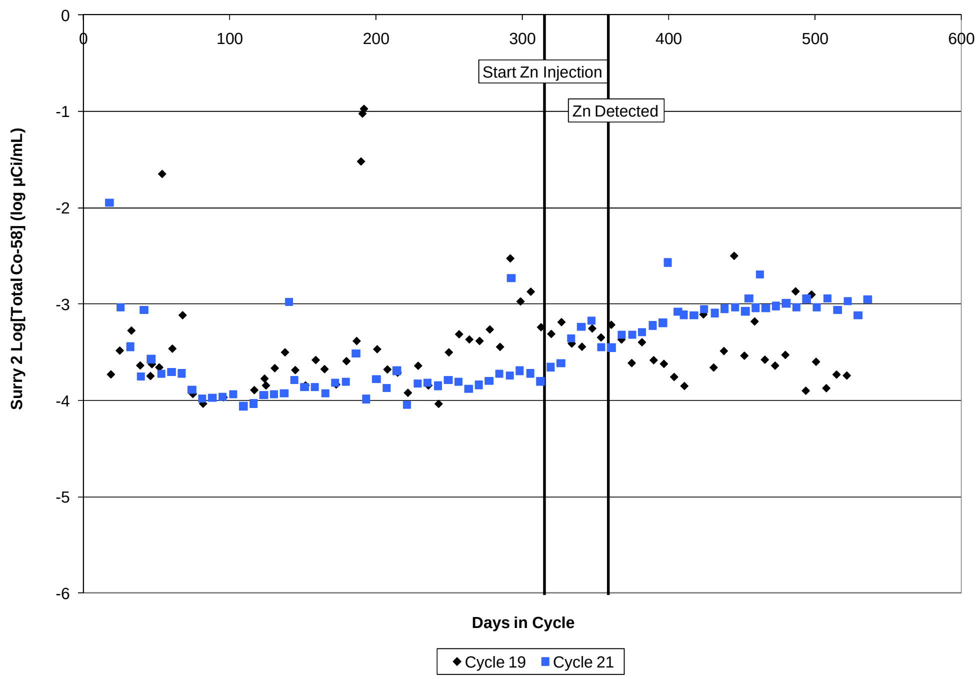

Figure 3-20
Surry 2 Total Co-58 Activity before and during Zinc Injection

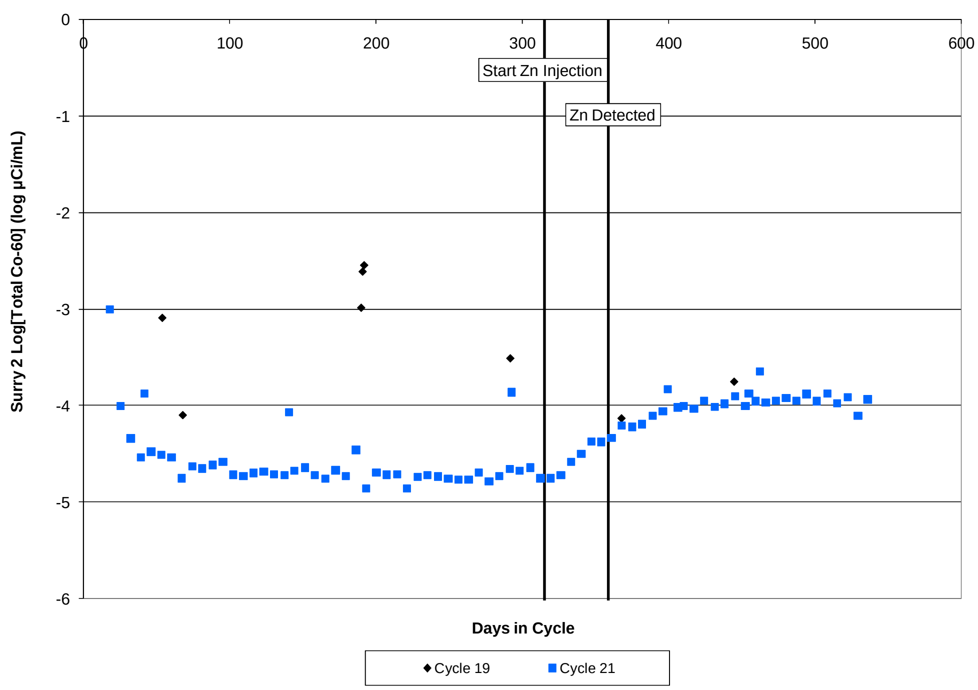

Figure 3-21
Surry 2 Total Co-60 Activity before and during Zinc Injection

Table 3-51
Surry 2 Total Co-58 Activity Multiple Cycle Statistical Assessment Results

Time Period	Change Versus Cycle N-1				Change Versus Cycle N-2			
	α=0.01	α=0.05	α=0.2	α=0.5	α=0.01	α=0.05	α=0.2	α=0.5
Pre-Zinc	-	-	-	-	-0.64	-0.55	-0.45	-0.34
Post-Injection/Pre-Detection	-	-	-	-	-0.35	-0.26	-0.17	-0.09
Post-Injection	-	-	-	-	0.15	0.20	0.26	0.32
Post-Detection	-	-	-	-	0.22	0.28	0.34	0.41

Table 3-52
Surry 2 Total Co-58 Activity Same Cycle Statistical Assessment Results

Time Period for Comparison to Pre-Zinc Period	Cycle N				Cycle N-1				Cycle N-2			
	α=0.01	α=0.05	α=0.2	α=0.5	α=0.01	α=0.05	α=0.2	α=0.5	α=0.01	α=0.05	α=0.2	α=0.5
Post-Injection/Pre-Detection	0.03	0.12	0.21	0.29	-	-	-	-	-0.24	-0.16	-0.06	0.04
Post-Injection	0.42	0.47	0.53	0.59	-	-	-	-	-0.37	-0.28	-0.18	-0.08
Post-Detection	0.49	0.54	0.59	0.65	-	-	-	-	-0.42	-0.32	-0.22	-0.11

Table 3-53
Surry 2 Total Co-58 Activity Profile Slope Analysis

Period of Analysis	Cycle N		Cycle N-1		Cycle N-2	
	Slope	R^2	Slope	R^2	Slope	R^2
25 Days Pre-Zinc	-2.63E-02	0.26	-	-	-2.92E-02	0.80
25 Days Post-Injection	2.15E-02	0.86	-	-	-7.19E-03	0.20
25 Days Post-Detection	6.90E-03	0.75	-	-	-1.13E-02	0.39
200 Days Pre-Zinc	9.66E-04	0.05	-	-	2.27E-03	0.03
100 Days Post-Injection	6.05E-03	0.50	-	-	-5.65E-03	0.67

Table 3-54
Surry 2 Total Co-60 Activity Multiple Cycle Statistical Assessment Results

Time Period	Change Versus Cycle N-1				Change Versus Cycle N-2			
	α=0.01	α=0.05	α=0.2	α=0.5	α=0.01	α=0.05	α=0.2	α=0.5
Pre-Zinc	-	-	-	-	-2.33	-2.00	-1.74	-1.52
Post-Injection/Pre-Detection	-	-	-	-	-	-	-	-
Post-Injection	-	-	-	-	-6.32	-1.37	-0.41	-0.15
Post-Detection	-	-	-	-	-6.12	-1.26	-0.31	-0.05

Table 3-55
Surry 2 Total Co-60 Activity Same Cycle Statistical Assessment Results

Time Period for Comparison to Pre-Zinc Period	Cycle N				Cycle N-1				Cycle N-2			
	α=0.01	α=0.05	α=0.2	α=0.5	α=0.01	α=0.05	α=0.2	α=0.5	α=0.01	α=0.05	α=0.2	α=0.5
Post-Injection/Pre-Detection	-0.12	-0.03	0.04	0.11	-	-	-	-	-	-	-	-
Post-Injection	0.45	0.49	0.53	0.57	-	-	-	-	-1.94	-1.45	-1.09	-0.80
Post-Detection	0.58	0.60	0.64	0.67	-	-	-	-	-1.94	-1.45	-1.09	-0.80

Table 3-56
Surry 2 Total Co-60 Activity Profile Slope Analysis

Period of Analysis	Cycle N		Cycle N-1		Cycle N-2	
	Slope	R^2	Slope	R^2	Slope	R^2
25 Days Pre-Zinc	-2.21E-02	0.28	-	-	-	-
25 Days Post-Injection	1.19E-02	0.89	-	-	-	-
25 Days Post-Detection	5.97E-03	0.66	-	-	-	-
100 Days Pre-Zinc	2.83E-03	0.13	-	-	-	-

The statistical analyses indicate that there was a statistically significant effect of zinc injection on Co-58 activity in that the post-zinc averages were significantly higher than for pre-zinc cycles and that there was a statistically significant increase within the first zinc cycle when zinc was injected (with no significant increase at the same time in the pre-zinc cycle). The within-cycle analysis is similar for Co-60, but the Co-60 data from the pre-zinc cycle are too sparse to make conclusions regarding the existence of differences. The comparison to the pre-zinc cycles is also limited by the availability of only Cycle N-2 data. More cycle to cycle changes would be expected over three cycles than would normally occur over two (i.e., an N to N-2 comparison is less reliable than an N to N-1 comparison).

Inspection of Figure 3-20 and Figure 3-21 show 1) relatively stable radiocobalt activities preceding zinc injection, 2) an increase associated with commencement of zinc injection, and 3) stabilization after about 100 days of zinc injection at activities roughly an order of magnitude higher than the pre-injection period. Extrapolation of the Co-58 trend backward to the pre-zinc period indicates the possibility that this trend started before zinc injection. However, the Co-60 data show much more clearly that the start of this trend coincided with the commencement of zinc injection. Furthermore, during this time during the non-zinc cycle, there was a downward trend in Co-58 data. These observations lead to a robust conclusion that zinc addition did increase the radiocobalt activity at Surry 2.

In summary, there is evidence that allows a very robust conclusion that zinc injection led to an increase in the radiocobalt activity at Surry 2.

3.4.1.14 Three Mile Island 1

Three Mile Island 1 chemistry and operating data were provided by EPRI [16]. Zinc addition at Three Mile Island 1 was initiated approximately 284 days into the 16th fuel cycle and it was detected 127 days later. The average concentration after detection was 5.3 ppb [9]. Prior to replacement in 2009, Three Mile Island 1 had Alloy 600SR steam generator tubing.

Data for Co-58 are given in Figure 3-22. Data for Co-60 are given in Figure 3-23. These data were analyzed using the statistical comparisons described in Section 3.3. The results are given in Table 3-57 through Table 3-59 for Co-58 and in Table 3-59 through Table 3-61 for Co-60.

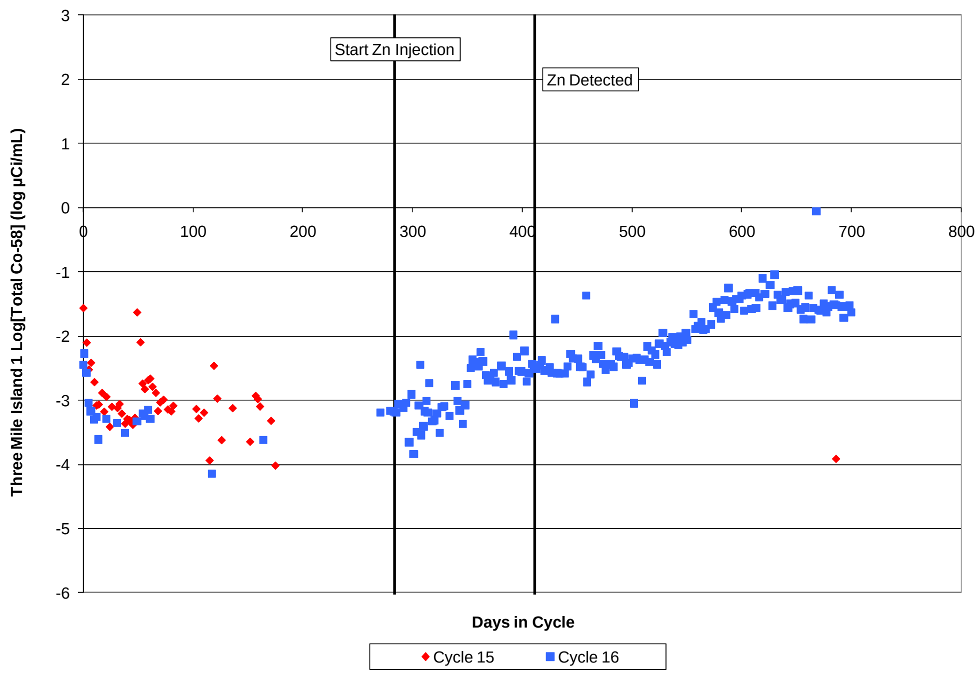

Figure 3-22
Three Mile Island 1 Total Co-58 Activity before and during Zinc Injection

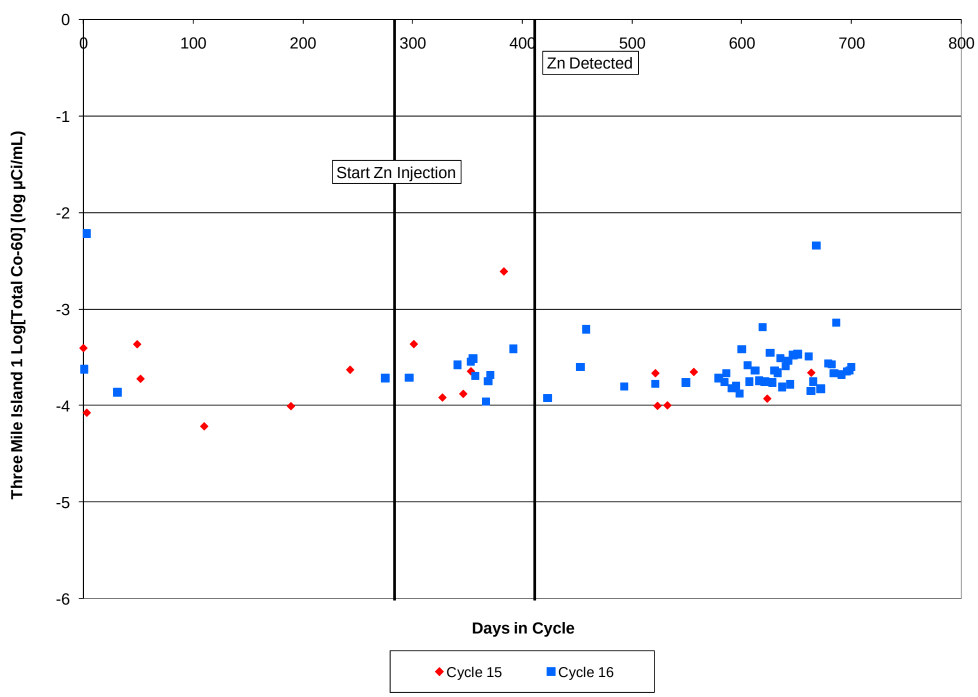

Figure 3-23
Three Mile Island 1 Total Co-60 Activity before and during Zinc Injection

Table 3-57
Three Mile Island 1 Total Co-58 Activity Multiple Cycle Statistical Assessment Results

Time Period	Change Versus Cycle N-1				Change Versus Cycle N-2			
	α=0.01	α=0.05	α=0.2	α=0.5	α=0.01	α=0.05	α=0.2	α=0.5
Pre-Zinc	-0.48	-0.40	-0.31	-0.21	-	-	-	-
Post-Injection/Pre-Detection	-	-	-	-	-	-	-	-
Post-Injection	-	-	-	-	-	-	-	-
Post-Detection	-	-	-	-	-	-	-	-

Table 3-58
Three Mile Island 1 Total Co-58 Activity Same Cycle Statistical Assessment Results

Time Period for Comparison to Pre-Zinc Period	Cycle N				Cycle N-1				Cycle N-2			
	α=0.01	α=0.05	α=0.2	α=0.5	α=0.01	α=0.05	α=0.2	α=0.5	α=0.01	α=0.05	α=0.2	α=0.5
Post-Injection/Pre-Detection	0.08	0.15	0.24	0.33	-	-	-	-	-	-	-	-
Post-Injection	0.76	0.83	0.92	1.00	-	-	-	-	-	-	-	-
Post-Detection	1.06	1.13	1.22	1.30	-	-	-	-	-	-	-	-

Table 3-59
Three Mile Island 1 Total Co-58 Activity Profile Slope Analysis

Period of Analysis	Cycle N		Cycle N-1		Cycle N-2	
	Slope	R^2	Slope	R^2	Slope	R^2
25 Days Pre-Zinc	1.77E-03	0.62	-	-	-	-
25 Days Post-Injection	-3.67E-03	0.01	-	-	-	-
25 Days Post-Detection	4.98E-03	0.03	-	-	-	-
Detection Through EOC	8.11E-03	0.53	-	-	-	-

Table 3-60
Three Mile Island 1 Total Co-60 Activity Multiple Cycle Statistical Assessment Results

Time Period	Change Versus Cycle N-1				Change Versus Cycle N-2			
	α=0.01	α=0.05	α=0.2	α=0.5	α=0.01	α=0.05	α=0.2	α=0.5
Pre-Zinc	-1.01	-0.57	-0.18	0.15	-	-	-	-
Post-Injection/Pre-Detection	-0.46	-0.24	-0.08	0.06	-	-	-	-
Post-Injection	-0.01	0.04	0.10	0.16	-	-	-	-
Post-Detection	0.02	0.08	0.15	0.21	-	-	-	-

Table 3-61
Three Mile Island 1 Total Co-60 Activity Same Cycle Statistical Assessment Results

Time Period for Comparison to Pre-Zinc Period	Cycle N				Cycle N-1				Cycle N-2			
	α=0.01	α=0.05	α=0.2	α=0.5	α=0.01	α=0.05	α=0.2	α=0.5	α=0.01	α=0.05	α=0.2	α=0.5
Post-Injection/Pre-Detection	-1.39	-0.86	-0.48	-0.17	-0.70	-0.48	-0.27	-0.07	-	-	-	-
Post-Injection	-1.35	-0.83	-0.44	-0.14	-0.70	-0.50	-0.32	-0.15	-	-	-	-
Post-Detection	-1.34	-0.82	-0.43	-0.13	-0.74	-0.54	-0.36	-0.19	-	-	-	-

Table 3-62
Three Mile Island 1 Total Co-60 Activity Profile Slope Analysis

Period of Analysis	Cycle N		Cycle N-1		Cycle N-2	
	Slope	R^2	Slope	R^2	Slope	R^2
25 Days Pre-Zinc	-	-	-	-	-	-
25 Days Post-Injection	-	-	-	-	-	-
25 Days Post-Detection	-	-	-	-	-	-
Post-Injection/Pre-Detection	8.49E-04	0.01	-6.59E-03	0.36	-	-

Pre-zinc radiocobalt data for TMI 1 are too sparse to allow strong conclusions regarding the effect of zinc. Furthermore, Exelon personnel have indicated that the increases observed after the injection time (from about Day 300 to Day 500) may have been due to expected changes in core dynamics, i.e., the consumption of burnable poisons and the transition to control of reactivity principally by boron concentration [19].

The data from TMI 1 are inconclusive.

3.4.1.15 Vandellos II

Chemistry and operating data were transmitted in the form of several spreadsheets prepared by Vandellos personnel [15]. Vandellos II averaged about 4.7 ppb zinc, began injecting zinc 278 days into the 15th fuel cycle, and reported a measurable concentration on the 287th day of the cycle. The Vandellos II steam generators are tubed with Alloy 600TT. Vandellos II reduced core boiling duty, lowered T_{avg} and completed its first UFC campaign during the outage prior to the first injection of zinc.

Data for Co-58 and plant power are given in Figure 3-24. Data for Co-60 and plant power are given in Figure 3-25. These data were analyzed using the statistical comparisons described in Section 3.3. The results are given in Table 3-63 through Table 3-65 for Co-58 and Table 3-66 through Table 3-68 for Co-60.

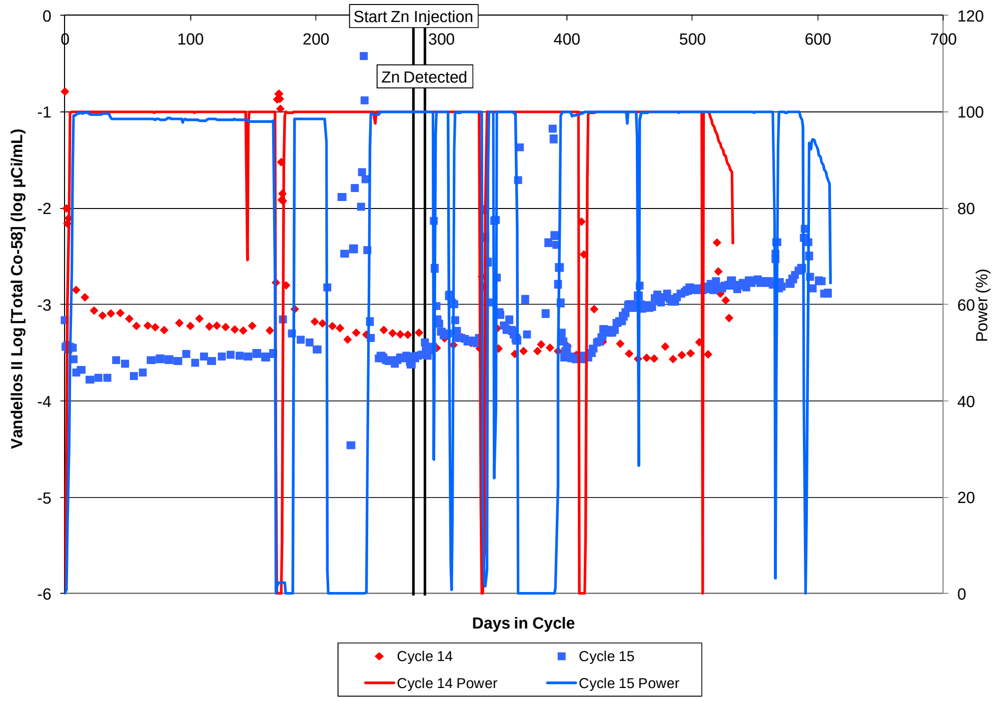

Figure 3-24
Vandellos II Total Co-58 Activity before and during Zinc Injection

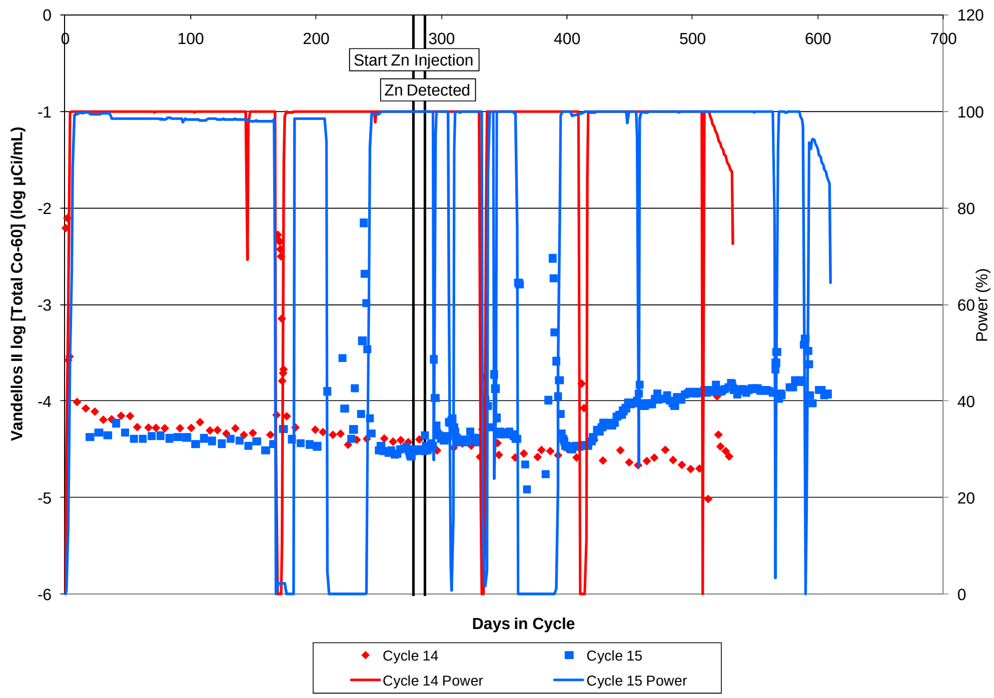

Figure 3-25
Vandellos II Total Co-60 Activity before and during Zinc Injection

Table 3-63
Vandellos II Total Co-58 Activity Multiple Cycle Statistical Assessment Results

Time Period	Change Versus Cycle N-1				Change Versus Cycle N-2			
	α=0.01	α=0.05	α=0.2	α=0.5	α=0.01	α=0.05	α=0.2	α=0.5
Pre-Zinc	-0.92	-0.81	-0.69	-0.56	-	-	-	-
Post-Injection/Pre-Detection	-	-	-	-	-	-	-	-
Post-Injection	0.15	0.19	0.25	0.30	-	-	-	-
Post-Detection	0.16	0.21	0.26	0.32	-	-	-	-

Table 3-64
Vandellos II Total Co-58 Activity Same Cycle Statistical Assessment Results

Time Period for Comparison to Pre-Zinc Period	Cycle N				Cycle N-1				Cycle N-2			
	α=0.01	α=0.05	α=0.2	α=0.5	α=0.01	α=0.05	α=0.2	α=0.5	α=0.01	α=0.05	α=0.2	α=0.5
Post-Injection/Pre-Detection	-0.48	-0.42	-0.35	-0.27	-	-	-	-	-	-	-	-
Post-Injection	0.08	0.15	0.23	0.31	-0.88	-0.79	-0.68	-0.56	-	-	-	-
Post-Detection	0.10	0.16	0.24	0.32	-0.88	-0.79	-0.68	-0.56	-	-	-	-

Table 3-65
Vandellos II Total Co-58 Activity Profile Slope Analysis

Period of Analysis	Cycle N		Cycle N-1		Cycle N-2	
	Slope	R^2	Slope	R^2	Slope	R^2
25 Days Pre-Zinc	2.74E-04	0.01	-2.58E-03	0.87	-	-
25 Days Post-Injection	2.61E-02	0.20	-4.34E-03	0.31	-	-
25 Days Post-Detection	1.07E-02	0.07	2.11E-03	0.07	-	-
Day 241 through Injection	-1.41E-02	0.36	-2.58E-03	0.87	-	-

Table 3-66
Vandellos II Total Co-60 Activity Multiple Cycle Statistical Assessment Results

Time Period	Change Versus Cycle N-1				Change Versus Cycle N-2			
	α=0.01	α=0.05	α=0.2	α=0.5	α=0.01	α=0.05	α=0.2	α=0.5
Pre-Zinc	-0.60	-0.51	-0.42	-0.32	-	-	-	-
Post-Injection/Pre-Detection	-	-	-	-	-	-	-	-
Post-Injection	0.32	0.35	0.39	0.42	-	-	-	-
Post-Detection	0.33	0.36	0.40	0.44	-	-	-	-

Table 3-67
Vandellos II Total Co-60 Activity Same Cycle Statistical Assessment Results

Time Period for Comparison to Pre-Zinc Period	Cycle N				Cycle N-1				Cycle N-2			
	α=0.01	α=0.05	α=0.2	α=0.5	α=0.01	α=0.05	α=0.2	α=0.5	α=0.01	α=0.05	α=0.2	α=0.5
Post-Injection/Pre-Detection	-0.42	-0.38	-0.33	-0.29	-	-	-	-	-	-	-	-
Post-Injection	0.01	0.05	0.10	0.16	-0.85	-0.77	-0.68	-0.59	-	-	-	-
Post-Detection	0.02	0.06	0.11	0.17	-0.85	-0.77	-0.68	-0.59	-	-	-	-

Table 3-68
Vandellos II Total Co-60 Activity Profile Slope Analysis

Period of Analysis	Cycle N		Cycle N-1		Cycle N-2	
	Slope	R^2	Slope	R^2	Slope	R^2
25 Days Pre-Zinc	4.22E-05	0.00	-1.61E-03	0.59	-	-
25 Days Post-Injection	1.33E-02	0.13	-1.79E-03	0.09	-	-
25 Days Post-Detection	3.33E-03	0.02	1.86E-03	0.05	-	-
Day 241 through Injection	-1.30E-02	0.36	-1.61E-03	0.59	-	-

The statistical analyses of the Vandellos II data indicated the following:

- There was a statistically significant increase in Co-58 activity after zinc injection relative to the pre-zinc cycle. This was in contrast to a significantly lower activity in the zinc cycle prior to zinc injection relative to the same period in the previous cycle. Co-60 showed the same behavior.
- There was a statistically significant increase in Co-58 activity after zinc injection relative to the pre-injection activities in the same cycle. In contrast, the same period during the pre-zinc cycle had lower activities than the beginning of cycle period. Co-60 showed the same behavior.

Inspection of Figure 3-24 and Figure 3-25 show that there were significant power transients during both the zinc cycle and the pre-zinc cycle. It was only after a significantly long (~40 days) mid-cycle outage in Cycle 15 (Cycle N) that the radiocobalt activities significantly departed from those in the previous cycle. Therefore, it is difficult to conclude with confidence that there was an effect of zinc on radiocobalt activities.

3.4.2 Assessments from the Literature

To supplement the assessment of the EPRI Zinc Database, a review of the literature was performed to obtain additional data regarding changes in RCS radiocobalt activities in response to zinc injection. The following bullets give the findings of this literature review. A summary of the radiocobalt response data is given in Section 3.4.3.

- *Biblis A*: Reference [20] gives cycle chemistry data for Biblis A, which started zinc injection in January 1998. The zinc concentration was maintained at approximately 3 ppb for the remainder of the cycle (Reference [20] gives data only for the cycle preceding zinc injection and the initial zinc cycle; it is presumed that zinc injection continued at essentially the same target concentration). Biblis A has steam generators with Alloy 800NG tubes.

  The radiocobalt data for Biblis A show no response to the initiation of injection (which occurred about three weeks after the beginning of the cycle) and perhaps a decrease in radiocobalts upon initial detection of zinc (which occurred approximately five weeks after injection started). Radiocobalt activity increased gradually toward the latter half of the cycle with the increase starting about two months after the initial detection of zinc. The author of Reference [20] indicates that this was considered unusual by the utility personnel.

- *Biblis B*: Reference [21] gives cycle chemistry data for Biblis B, which started zinc injection in September 1996. The zinc concentration was maintained at approximately 5 ppb for several cycles. Biblis B has steam generators with Alloy 800NG tubes.

  Reference [21] gives radioisotope activities for Co-58, Co-60, Fe-59, and Zn-65 for a period beginning about one-and-a-half cycles before injection of zinc and for four-and-a-half cycles after injection began. These data are shown in Figure 3-26. Based on these data, there is strong evidence that zinc injection does not affect the RCS Co-60 activity. Likewise, it appears unlikely that zinc injection affects Fe-59 activity. With respect to Co-58, there appears to be a trend of gradually increasing activity during the course of each cycle, beginning with the first cycle of zinc injection. If this trend is independent of zinc injection, then there would appear to be no interruption of this trend due to zinc injection (i.e., zinc injection did not affect the trends in Co-58). However, the only cycle for which data are presented prior to zinc injection contained an extended mid-cycle outage and it is not clear whether the absence of a Co-58 trend during that cycle is the result of the outage or the lack of zinc. The authors of Reference [21] conclude that zinc injection resulted in a five-fold increase in Co-58 activity.

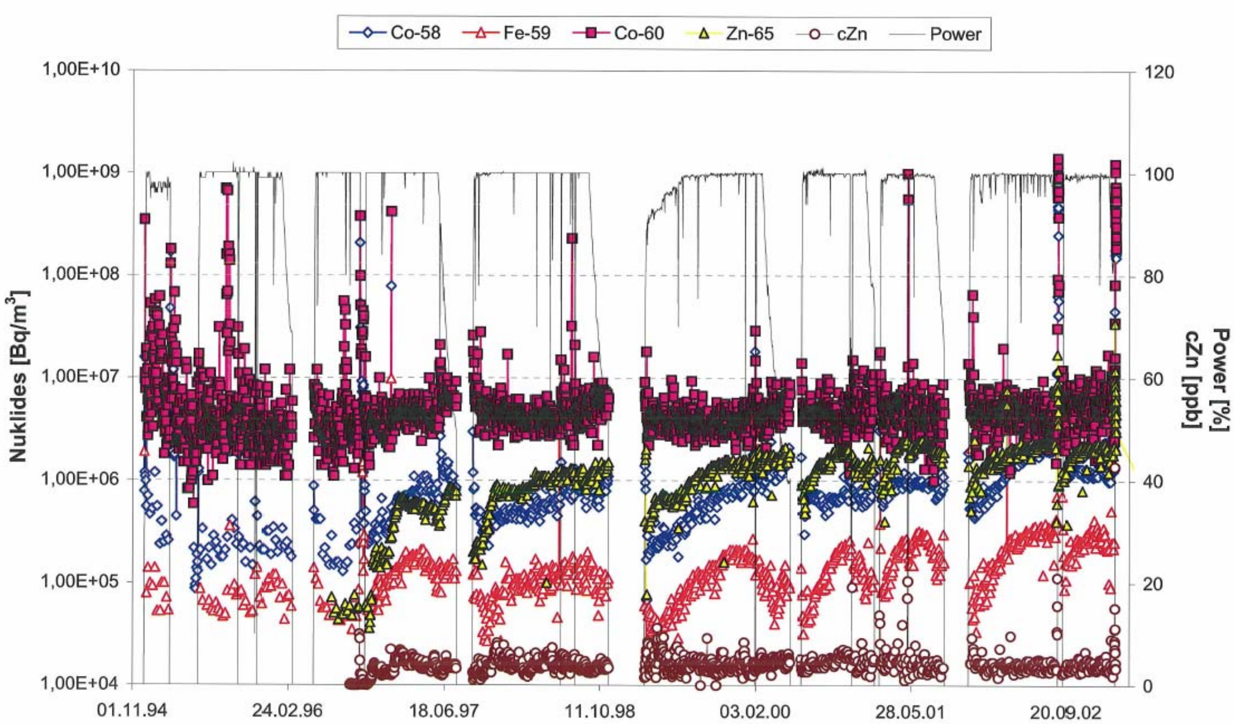

Figure 3-26
Biblis B Isotope Activities before and during Zinc Injection [21]

- *Diablo Canyon 1*: Reference [22] gives cycle chemistry data for Diablo Canyon 1, which started zinc injection in June 1998. Zinc was detected in the coolant 9 days after the start of injection and the average zinc concentration reached during injection was 31 ppb. Before replacement in 2008, Diablo Canyon 1 had steam generators with Alloy 600MA tubes.

Reference [22] provides radioisotope activities for Co-58 and Co-60, and the ratio of the Co-58 to Co-60 activities, presented in Figure 3-27, for the first zinc injection cycle. The data show that the onset of zinc injection corresponded with Co-58 and Co-60 activity increases of about 1.5 and 1 order of magnitude, respectively. The Co-58-to-Co-60 activity ratio increased after the start of injection, which indicates that zinc-induced displacement of radiocobalts from core and ex-core deposits may have been taking place. It should also be noted that large changes in zinc concentration were mirrored by corresponding changes in radiocobalt activity. The author of Reference [22] attributes the increase in cobalt activity after zinc injection to the displacement of cobalt from surface deposits and to a reduction in activity incorporation into these deposits.

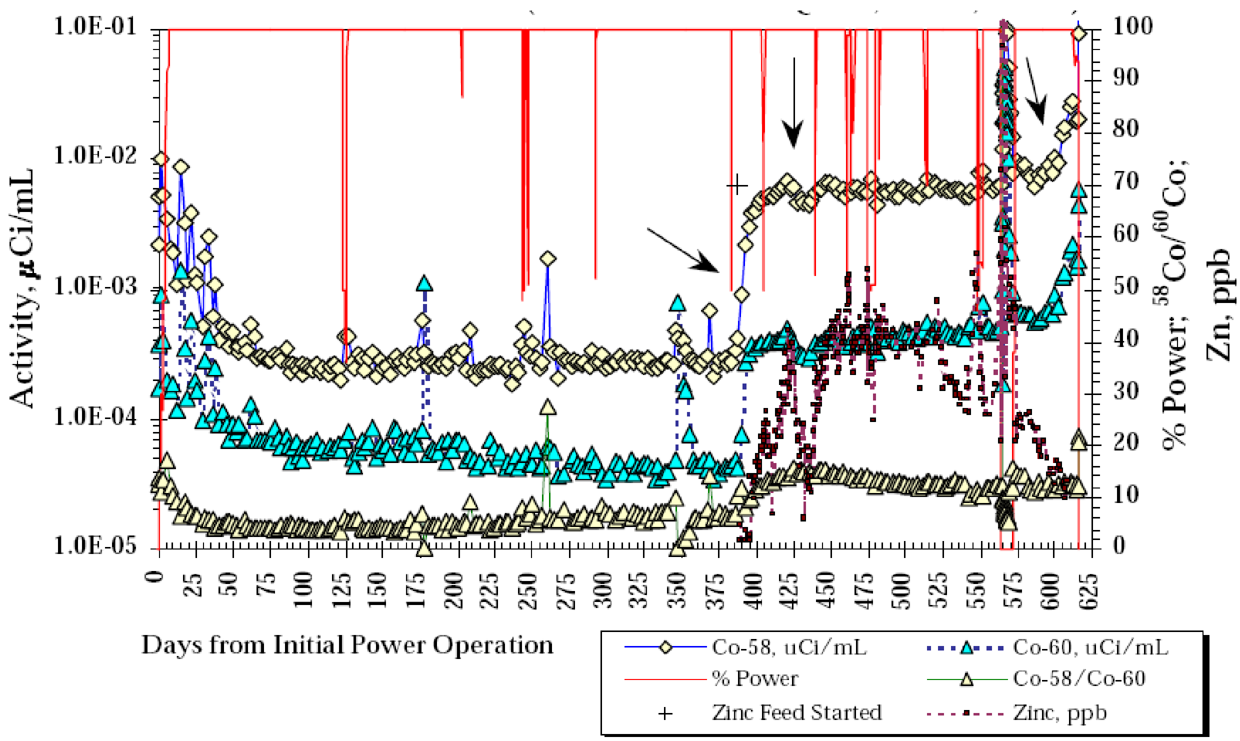

Figure 3-27
Diablo Canyon 2 Isotope Activities and Activity Ratio before and during Zinc Injection [22]

- *Callaway*: Reference [23] gives cycle chemistry data for Callaway, which started zinc injection in May 2003. The average zinc concentration reached during injection was 7.2 ppb. Before replacement in 2005, Callaway had steam generators with some tubes made of Alloy 600MA and others made of Alloy 600TT.

  The isotope data given in Reference [23] are shown in Figure 3-28 (note that there is a Diablo Canyon logo in the lower right-hand corner of this figure because these data were given as part of a Diablo Canyon presentation). The Co-58 and Co-60 activities seem to trend gradually downward for the first month-and-a-half of injection. Co-58 activities later increased during a control rod test and gradually decreased to pre-test values after about two-and-a-half additional months of operation. Upon returning to pre-test values, the Co-58 activity increased through the end of the cycle. The interpretation of the Co-60 activity profile is complicated by the fact that many of the data are below the lower limit of the plot, but it appears that the total Co-60 trend roughly follows that of the total Co-58 activity. At the end of the cycle, the total Co-58 activity increased by more than a factor of 10 and the total Co-60 activity rose by about a factor of 10. These increases support the possibility of an active zinc effect at Callaway, but it was not possible to quantitatively evaluate the effect as the raw data were not available. Additionally, it is well known that there can be significant changes in RCS corrosion product concentrations and activities associated with the end of the cycle, although these changes are not well understood. It should be noted that Callaway completed full UFC campaigns during the two outages preceding the first zinc injection and a partial UFC campaign three outages prior to the first injection. Cycle pH_T and temperature changes were also made during this period.

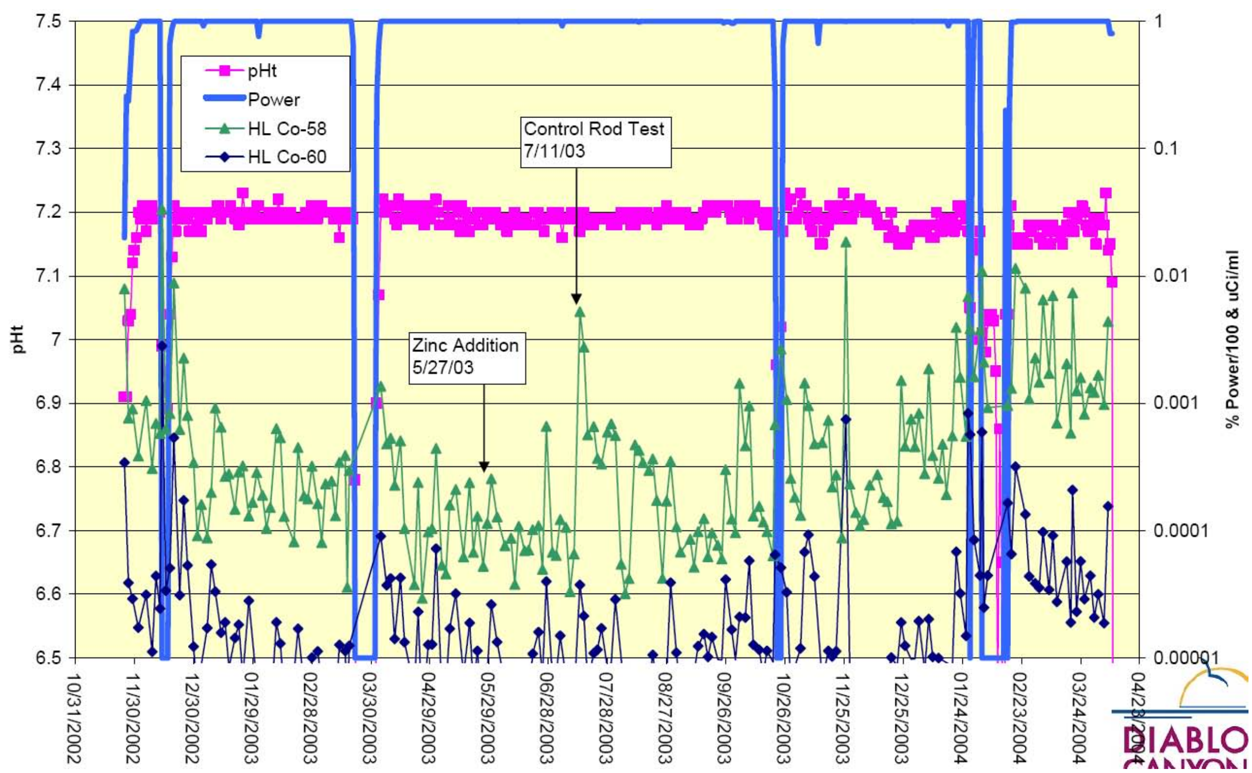

Figure 3-28
Callaway Co-58 and Co-60 Activities before and during Zinc Injection [23]

- *Farley 2*: Reference [24] gives cycle chemistry data for Farley 2, which injected zinc for 9 months starting in June 1994 (during Cycle 10), did not inject zinc during the following cycle, and resumed injection starting in August 1998 [2]. The Cycle 10 average zinc concentration was 35 ppb. Farley 2 had steam generators with Alloy 600MA tubes until they were replaced in 2001.

  Reference [24] provides Co-58, Co-60, and Zn-65 activities for a period spanning from two cycles before the initial injection of zinc to the end of the third cycle following the first injection; the data are given in Figure 3-29 through Figure 3-31 (the Co-60 data are discussed in the following paragraph). The authors note "a clear effect of zinc addition" on the Co-58 activity based on the fact that the activity concentrations increased from about 10^{-4} μCi/mL to roughly 3 x 10^{-3} μCi/mL at the end of the cycle (the peaks observed at the very end of the cycle were attributed to plant shutdowns, rather than to a true increase in Co-58 activity). Relative to Cycles 8 and 9, Co-58 activities remained elevated during Cycle 11 when zinc was not injected, and zinc injection appears to have led to a greater rate of increase in total Co-58 activity during Cycle 12. The onset of the increase observed during Cycle 13 corresponds with the start of injection, and the trend observed was similar to that observed during Cycle 12 until the end of the cycle when the activity decreased by roughly a factor of 5.

The Co-60 activities from the same cycles are given in Figure 3-30. The Co-60 profiles observed during Cycles 8 and 9 were similar in that the beginning of cycle and end of cycle activity levels were approximately equal. Zinc injection corresponded with sharp increases in the rate of increase in total Co-60 activity during Cycles 10, 12, and 13. During Cycle 10 the total Co-60 activity increased by about a factor of ten.

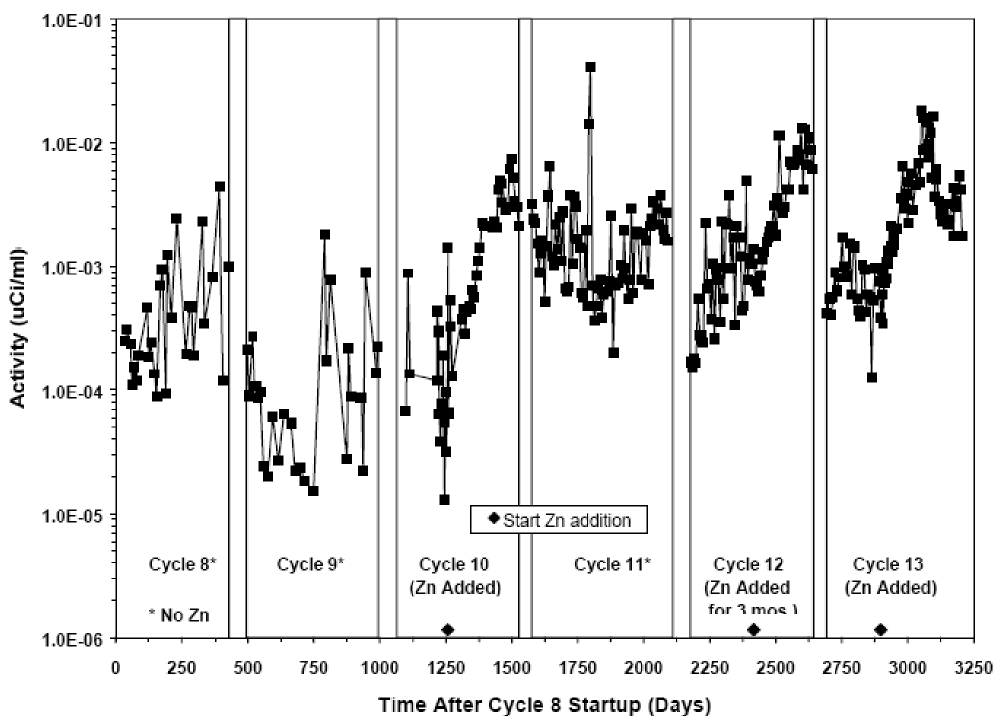

Figure 3-29
Farley 2 Co-58 Activities before and during Zinc Injection [24]

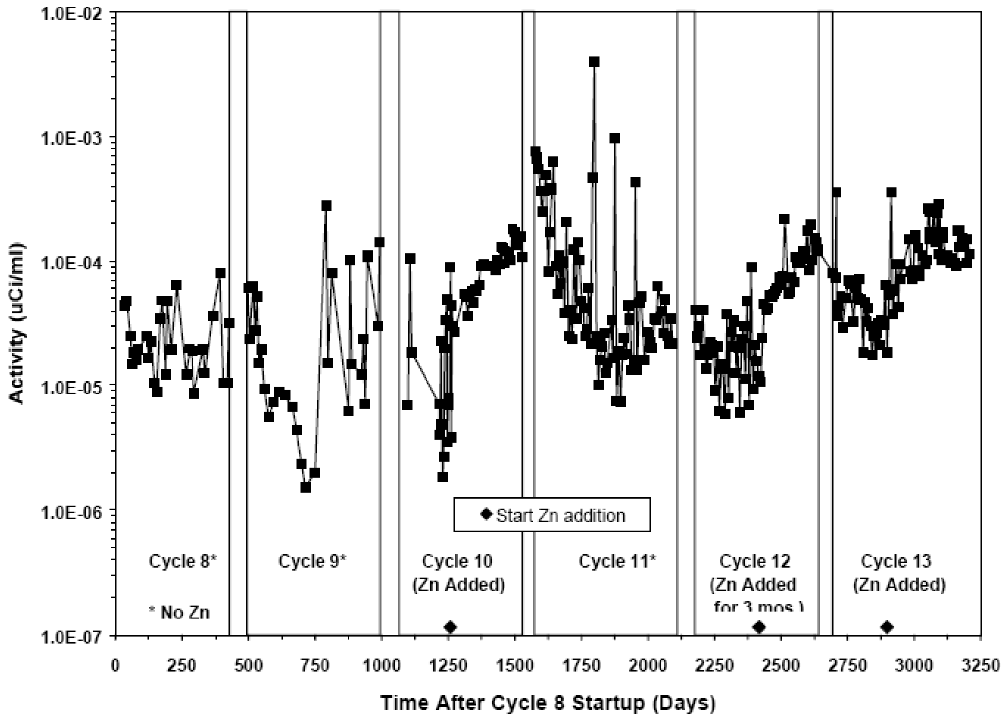

Figure 3-30
Farley 2 Co-60 Activities before and during Zinc Injection [24]

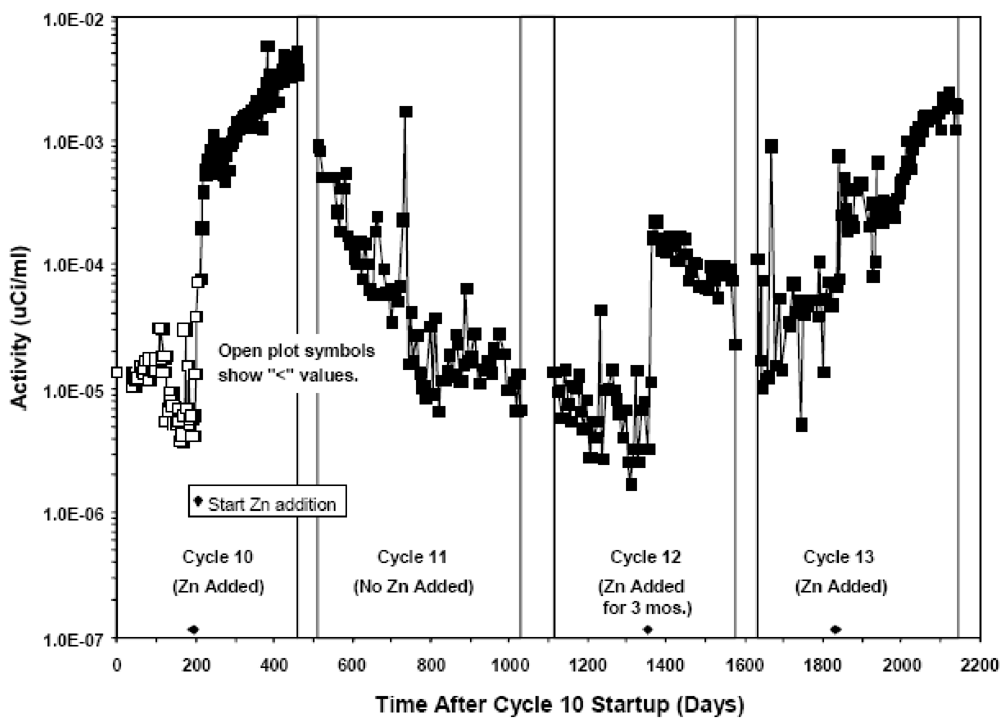

Figure 3-31
Farley 2 Zn-65 Activities before and during Zinc Injection [24]

- *Palisades*: Reference [22] gives cycle chemistry data for Palisades, which started zinc injection in April 1999. The target zinc concentration was 2-5 ppb. Palisades has steam generators with Alloy 600MA tubes.

  Reference [22] gives Co-58 and Co-60 activities for the first zinc injection cycle and for the immediately preceding cycle. The author states that both the total Co-58 and Co-60 activities increased significantly upon the start of zinc addition. The data given in Figure 3-32 show that the Co-58 activity trends were qualitatively very similar for both cycles until roughly 75 days after the initiation of zinc injection (note that the spike in total Co-58 activity beginning near Day 337 of Cycle 14 and subsequent return to the initial trend corresponds with a mid-cycle forced shutdown). At this point in the cycle, the non-zinc cycle Co-58 activities dropped by roughly an order of magnitude and remained depressed for about the next 60 days, at which point the activity increased by about an order of magnitude and increased at roughly the same rate as was observed during the zinc cycle. It is not expected that this difference in behavior between the two cycles resulted from zinc injection. The Co-60 data presented in Figure 3-33 seem to support the presence of an active zinc-displacement mechanism at Palisades as an increasing trend during Cycle 14 was observed after the start of injection while the Cycle 13 activity does not appear to have increased. The relative amounts of radiocobalt removal presented in Figure 3-34 and Figure 3-35 also seem to support the presence of a zinc-displacement mechanism at Palisades, but it should be noted that the chemical and volume control system (CVCS) letdown flow rate was doubled relative to pre-zinc rates after the start of zinc injection.

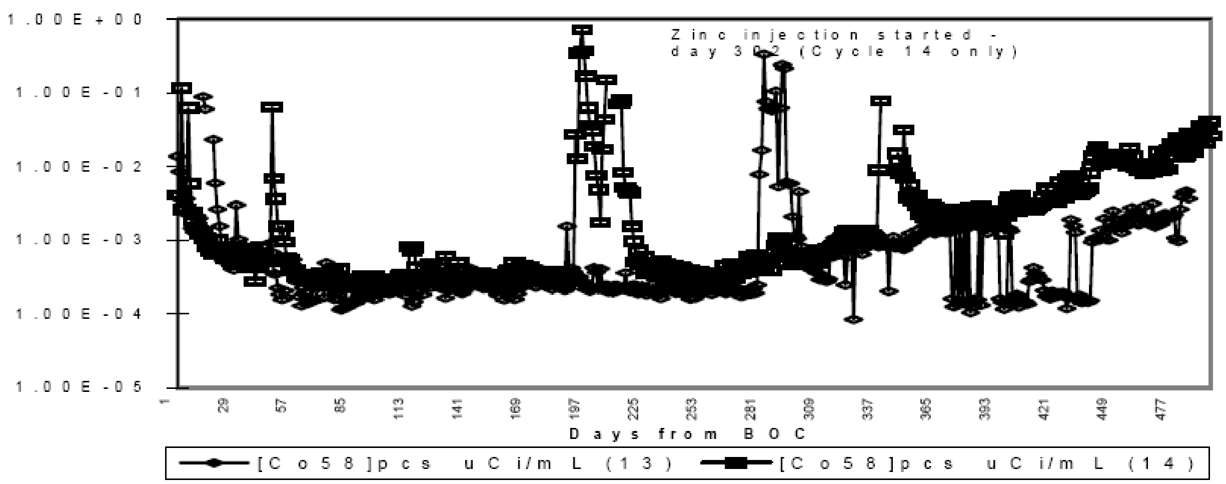

Figure 3-32
Palisades Co-58 Activity before and during Zinc Injection [22]

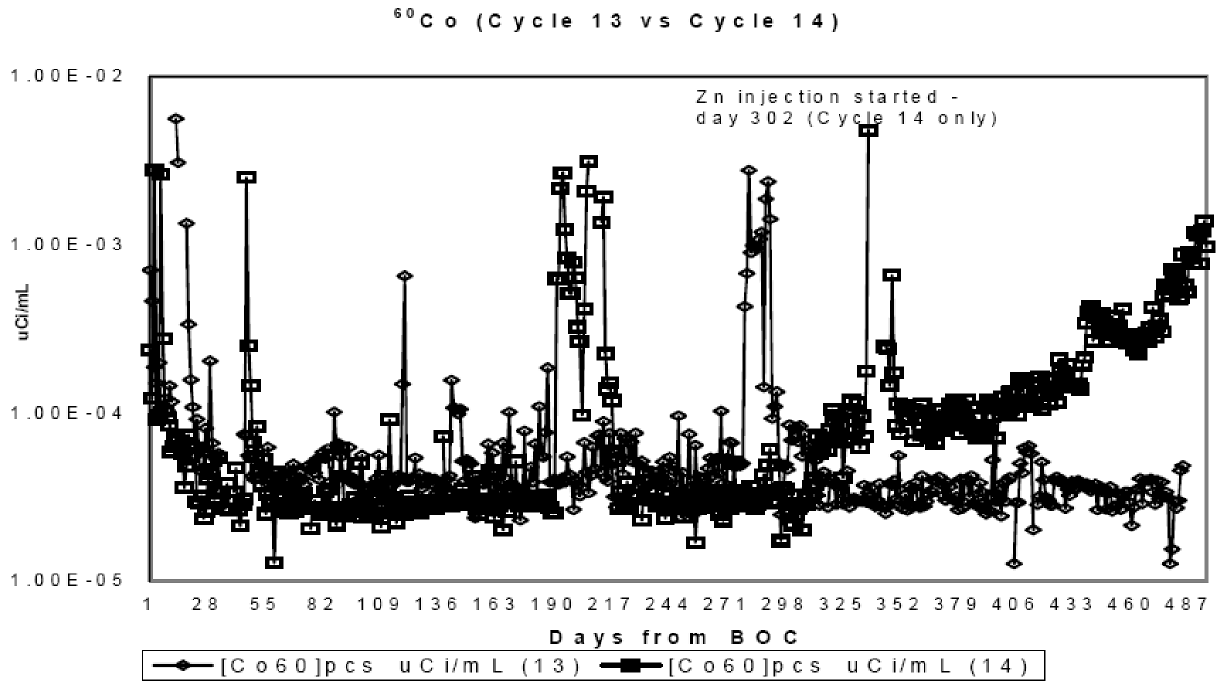

Figure 3-33
Palisades Co-60 Activity before and during Zinc Injection [22]

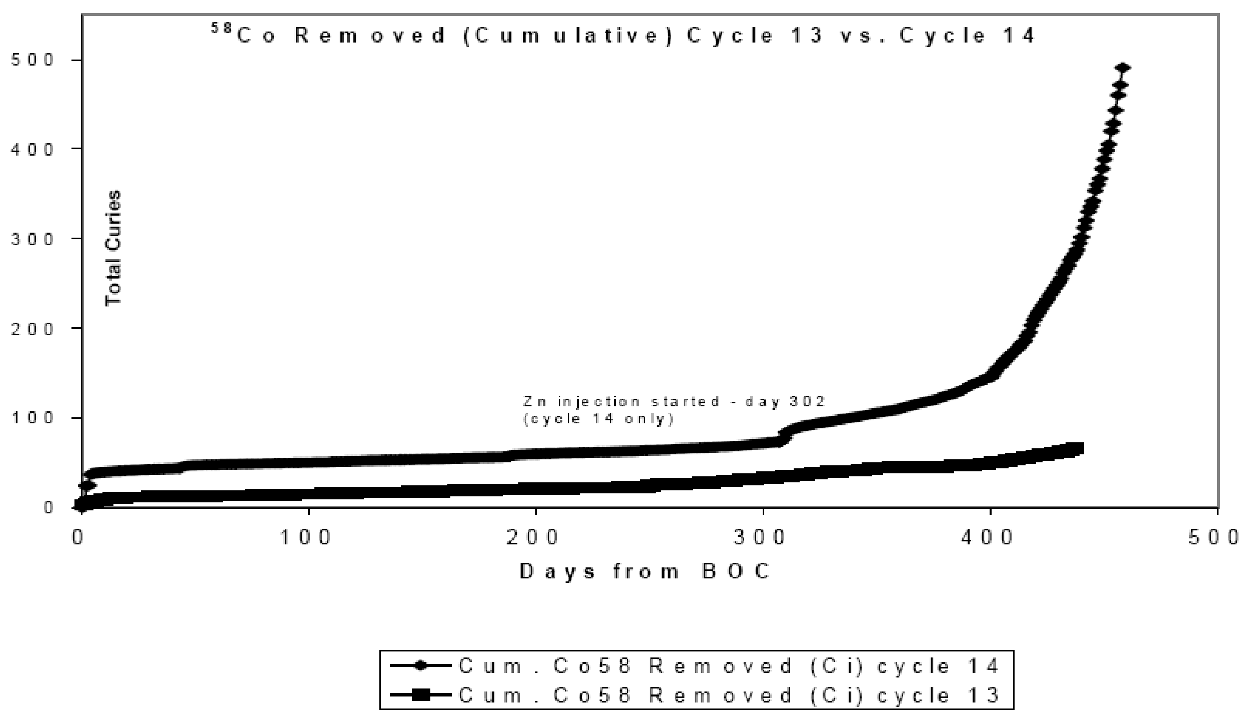

Figure 3-34
Palisades Cumulative Co-58 Activity Removal before and during Zinc Injection [22]

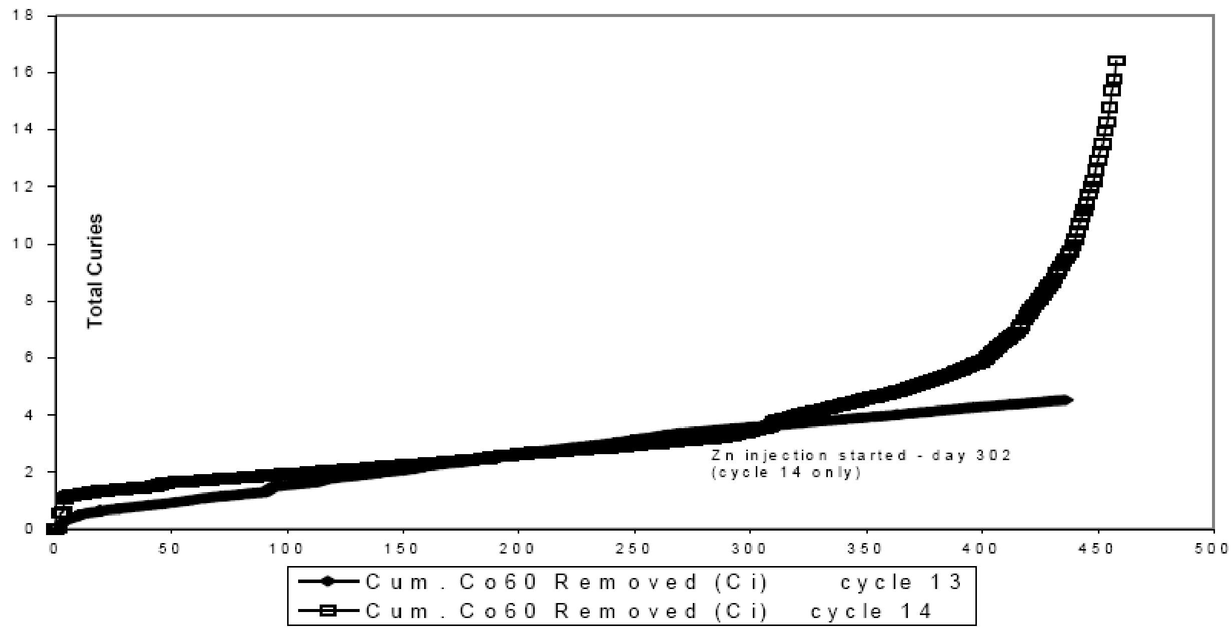

Figure 3-35
Palisades Cumulative Co-60 Activity Removal before and during Zinc Injection [22]

- *Unterweser*: Reference [21] gives cycle chemistry data for Unterweser, which started zinc injection in May 2003. The zinc concentration was maintained at approximately 5 ppb for several cycles. Unterweser has steam generators with Alloy 800NG tubes.

  The isotope data given in Reference [21] are shown in Figure 3-36. From these data, the effect of zinc injection on Co-58 or Co-60 is not easily quantified, but the authors of Reference [21] conclude that zinc injection resulted in a five-fold increase in Co-58 activity and a significant increase in the Co-60 activity. The zinc cycle has significantly and consistently higher activities than the pre-zinc cycle. However, these increases are present before the commencement of zinc injection.

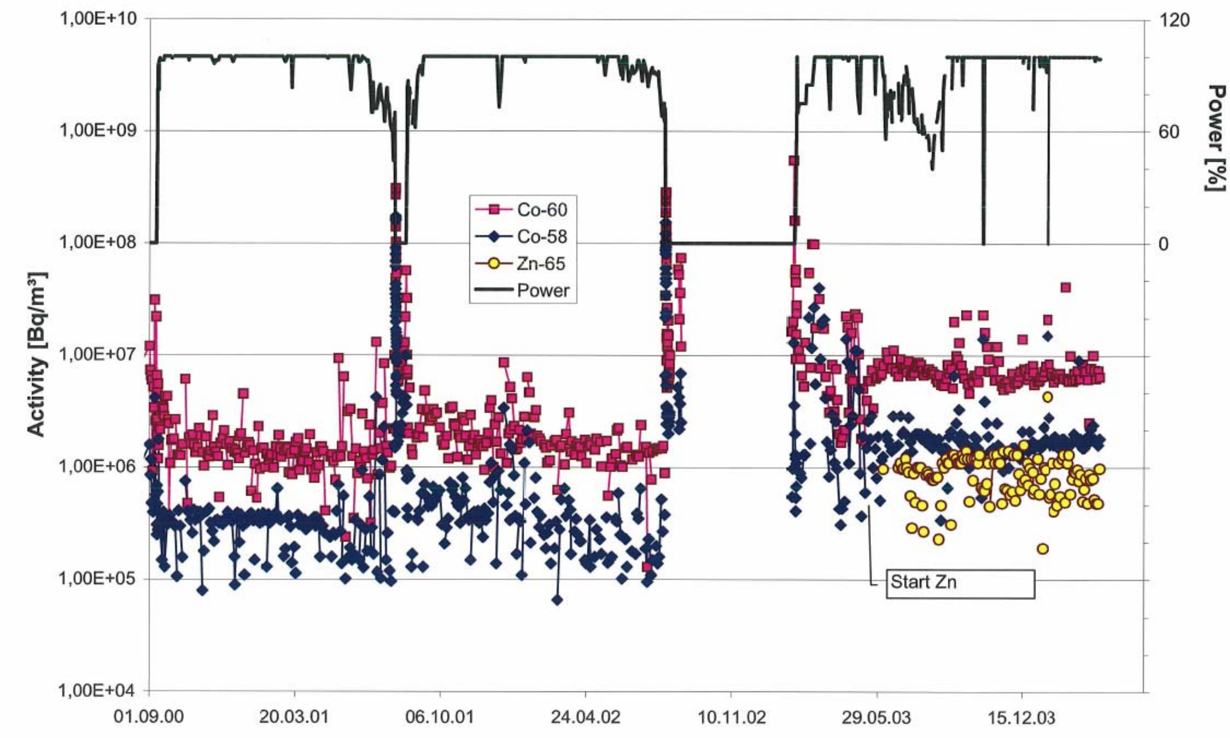

Figure 3-36
Unterweser Isotope Activities before and during Zinc Injection [21]

3.4.3 Summary of Radiocobalt Responses

The impact of the first injection of zinc on primary coolant radiocobalt activities was assessed using raw data from several units and using published data from several others. Table 3-69 summarizes the conclusions for each unit considered. Table 3-70 gives a tally of the results. As these tables indicate, radiocobalt responses have been observed at some units, but not others. A factor that could be correlated to whether or not a unit showed a radiocobalt response could not be identified.

Table 3-69
Summary of Plant Radiocobalt Responses

	Unit	Conclusions Regarding Radiocobalt Response	Comments
Raw Data Available to EPRI	Angra 1	No response.	Reasonably comprehensive data, conclusion robust.
	Asco 1	Increase in radiocobalt due to zinc.	No pre-zinc cycle data available, but correlation with zinc injection transients makes conclusion robust.
	Asco 2	Increase in radiocobalt due to zinc.	No comparison to previous cycles.
	Braidwood 2	Increase in radiocobalt due to zinc.	Reasonably comprehensive data, conclusion robust.
	Byron 2	No response.	Reasonably comprehensive data, conclusion robust.
	Catawba 1		No post-zinc data available at the time of this analysis.
	Catawba 2		No post-zinc data available at the time of this analysis.
	Calvert Cliffs 1	Increase in Co-58, no increase in Co-60 with zinc injection.	Data do not allow a robust conclusion regarding Co-58.
	Crystal River 3		No post-zinc data available at the time of this analysis.
	McGuire 1	Increase in radiocobalt due to zinc.	Data do not allow robust conclusions.
	McGuire 2	No response.	Reasonably comprehensive data, conclusion robust.
	Surry 1	No response.	Reasonably comprehensive data, conclusion robust.
	Surry 2	Increase in radiocobalt due to zinc.	Reasonably comprehensive data, conclusion robust.
	TMI-1	Inconclusive.	Too little pre-zinc data to provide robust conclusions.
	Vandellos 2	Increase in radiocobalt due to zinc.	Evaluation of trends complicated by numerous plant transients.
Data from the Literature	Biblis A	Inconclusive.	No increase was associated with injection or detection, but an increase later in the cycle was observed.
	Biblis B	Possible increase in Co-58. No increase in Co-60.	Based on data presented in the literature. Original authors concluded that there was an increase in Co-58 activity associated with zinc.
	Diablo Canyon 1	Increase in radiocobalt due to zinc.	Based on data presented in the literature. No comparison to previous cycles, but radiocobalts also responded to transients in zinc injection.
	Callaway	Inconclusive.	There was an end of cycle increase possibly associated with zinc, but more likely due to normal changes in core characteristics.
	Farley 2	Increase in radiocobalt due to zinc.	Based on data presented in the literature. Original authors concluded that there was an increase in Co-58 activity associated with zinc and an increase in Co-60 during zinc injection.
	Palisades	Increase in radiocobalt due to zinc.	Based on data presented in the literature.
	Unterweser	Inconclusive.	Based on data presented in the literature. Original authors concluded that there was an increase in Co-58 and Co-60 activity associated with zinc. However, this increase was present before zinc injection commenced.

Table 3-70
Summary of Plant Radiocobalt Responses – All Units Considered

	EPRI Database	Literature	Total
Zinc effect observed	7	3	10
No zinc effect	4	1	5
Inconclusive	1	3	4
No data	3	0	3
Total considered	15	7	22

3.5 Nickel Response

As discussed in Section 3.3 plant data on the coolant concentrations of nickel were evaluated by comparing concentrations before zinc injection with those after zinc injection. Data available in the EPRI Zinc Database are discussed in Section 3.5.1. Additional data available in the literature are discussed in Section 3.5.2. Conclusions based on the unit-specific evaluations in Sections 3.5.1 and 3.5.2 are discussed in Section 3.5.4. While these conclusions are informed by theoretical and modeling considerations discussed in Section 3.7, they are principally based on the plant data.

For the purpose of these analyses, it is assumed that the raw nickel concentrations are approximately normally distributed, and therefore the inputs for the statistical comparisons are the raw concentrations.

3.5.1 Assessments from EPRI Zinc Database

The sections below discuss the analyses performed for each of the data sets available in the EPRI Zinc Database. Data were available for the first zinc cycle for the following units:

- Angra 1
- Asco I
- Asco II
- Braidwood 2
- Calvert Cliffs 1
- Crystal River 3
- McGuire 1
- Surry 1

- Three Mile Island 1
- Vandellos II

3.5.1.1 Angra 1

It was not possible to perform the cycle-to-cycle statistical assessments discussed in Section 3.3 because nickel data from Cycles 10 and 11 (Cycles N-1 and N-2) were not available. The available data, given in Figure 3-37 and Figure 3-38, cannot be used to evaluate possible zinc effects on nickel concentration as there are no data from before the start of zinc addition, there are no prior cycles available for comparison, and the majority of the data were reported as “less than” values. It appears that on Day 174 of Cycle 12, the reported lower limit of detection for nickel decreased from 140 ppb to 2 ppb.

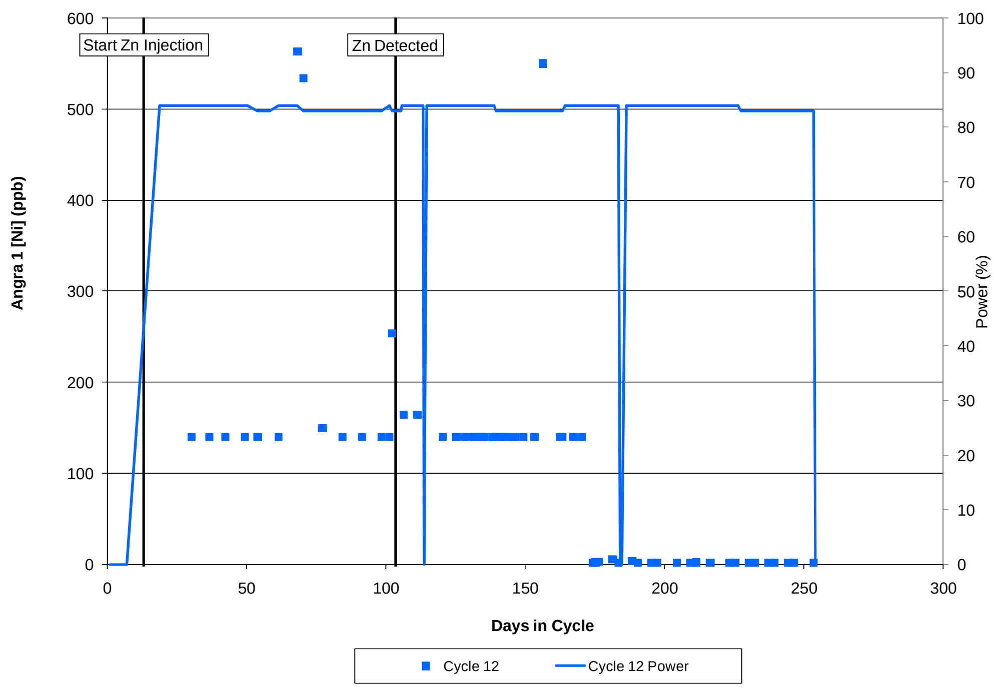

Figure 3-37
Angra 1 Nickel Concentration during Zinc Injection

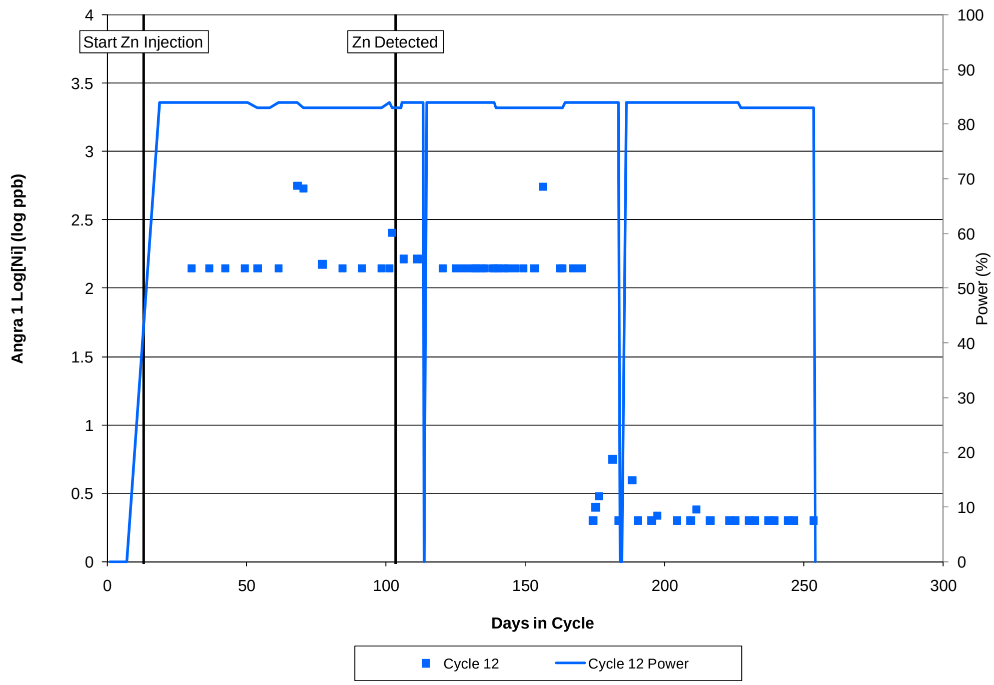

Figure 3-38
Angra 1 Logarithmic Nickel Concentration during Zinc Injection

3.5.1.2 Asco I

Chemistry and operating data were available in the form of several spreadsheets prepared by Asco personnel [15]. Asco I began injecting zinc 125 days into the 19th fuel cycle and a measurable concentration was reported on the 191st day of the cycle. After the initiation of zinc injection during Cycle 19, Asco I operated at an average concentration of 9.5 ppb. The first day of the cycle was taken to be the day of the first at-power data point. The Asco I steam generators have Alloy 800NG tubing.

Data for nickel (along with plant power) are given in Figure 3-39 (normal scale) and Figure 3-40 (log scale). These data were analyzed using the statistical comparisons described in Section 3.3. The results are given in Table 3-71 and Table 3-72.

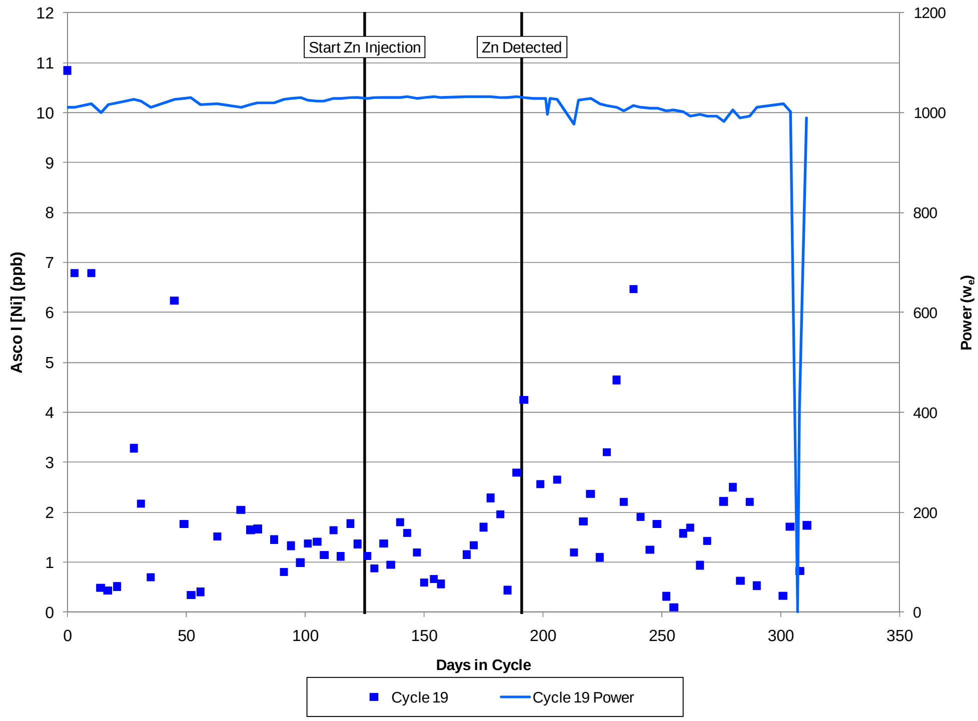

Figure 3-39
Asco I Nickel Concentration before and during Zinc Injection

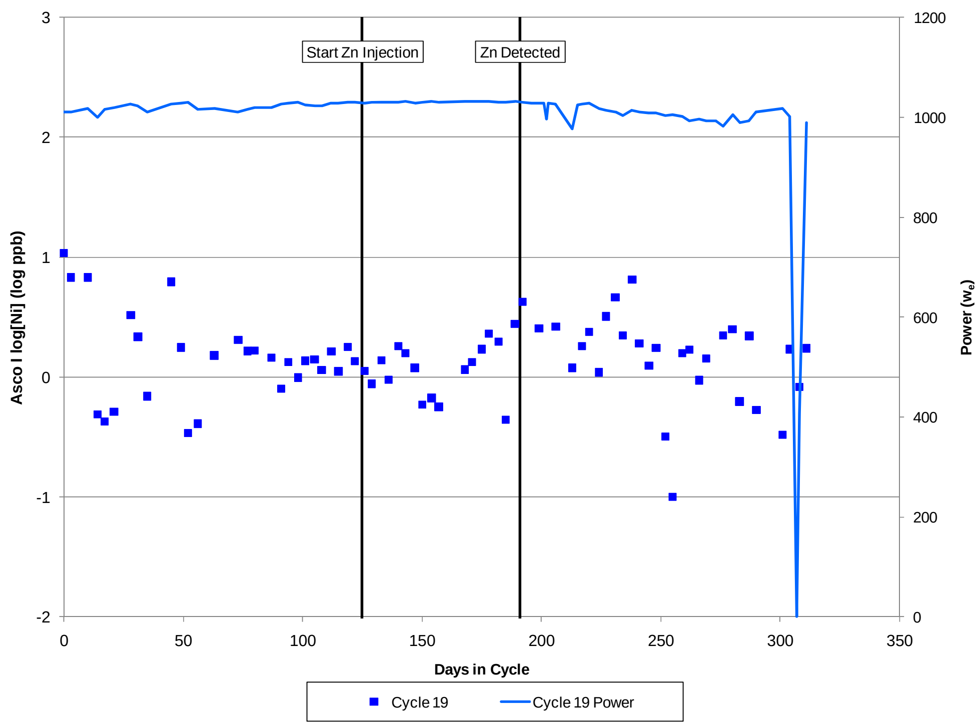

Figure 3-40
Asco I Logarithmic Nickel Concentration before and during Zinc Injection

Table 3-71
Asco I Nickel Concentration Same Cycle Statistical Assessment Results

Time Period for Comparison to Pre-Zinc Period	Cycle N				Cycle N-1				Cycle N-2			
	α=0.01	α=0.05	α=0.2	α=0.5	α=0.01	α=0.05	α=0.2	α=0.5	α=0.01	α=0.05	α=0.2	α=0.5
Post-Injection/Pre-Detection	-2.10	-1.73	-1.31	-0.90	-	-	-	-	-	-	-	-
Post-Injection	-1.72	-1.35	-0.93	-0.51	-	-	-	-	-	-	-	-
Post-Detection	-1.56	-1.17	-0.73	-0.28	-	-	-	-	-	-	-	-

Table 3-72
Asco I Nickel Concentration Profile Slope Analysis

Period of Analysis	Cycle N		Cycle N-1		Cycle N-2	
	Slope	R^2	Slope	R^2	Slope	R^2
25 Days Pre-Zinc	2.15E-03	0.05	-	-	-	-
25 Days Post-Injection	-1.52E-03	0.00	-	-	-	-
25 Days Post-Detection	-1.30E-01	0.88	-	-	-	-
Pre-Zinc	7.87E-03	0.06	-	-	-	-

No nickel data for pre-zinc cycles were available. Analyses of the data from the first zinc cycle indicate the following:

- There was a decrease in the average nickel concentration in all of the zinc periods considered compared to the pre-zinc period.
- There was a significant trend toward lower nickel concentrations in the 25-day period following zinc detection (R^2 ~ 0.9).

These data provide a relatively robust conclusion that there was no measurable increase in nickel following zinc addition.

3.5.1.3 Asco II

Chemistry and operating data were transmitted in the form of several spreadsheets prepared by Asco personnel [15]. Injection of zinc at Asco II was initiated on the 67th day of Cycle 17 and the concentration in the RCS was measurable 11 days later. Zinc concentration during the first injection cycle averaged 9.6 ppb. The first day of the cycle was taken to be the day of the first at-power data point. The Asco II steam generators are tubed with Alloy 800NG.

Data for nickel (along with plant power) are given in Figure 3-41 (normal scale) and Figure 3-42 (log scale). These data were analyzed using the statistical comparisons described in Section 3.3. The results are given in Table 3-73 and Table 3-74.

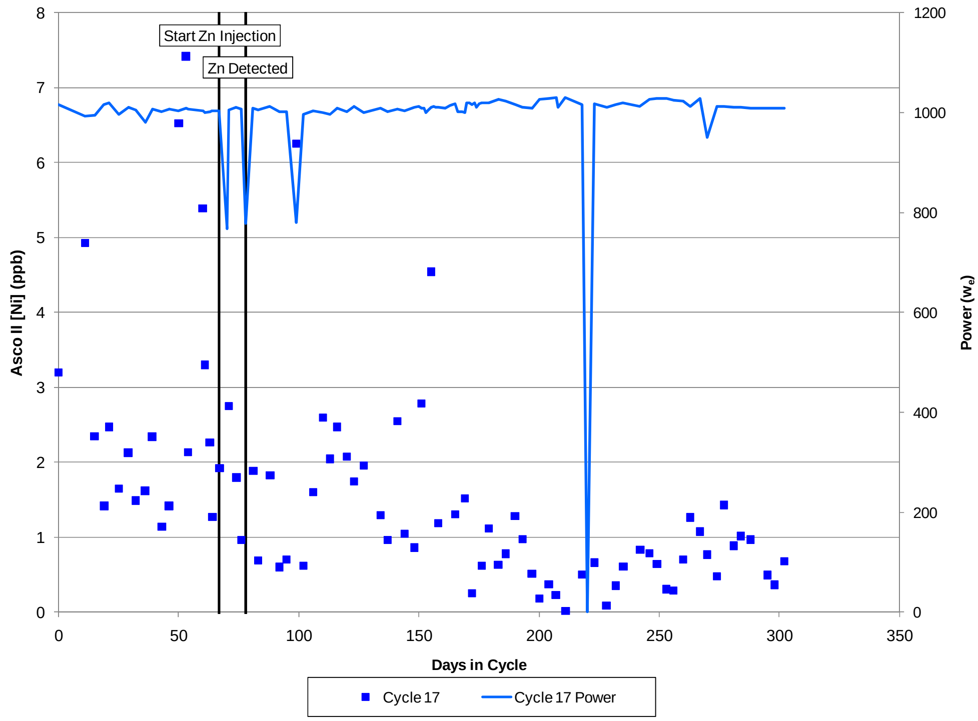

Figure 3-41
Asco II Nickel Concentration before and during Zinc Injection

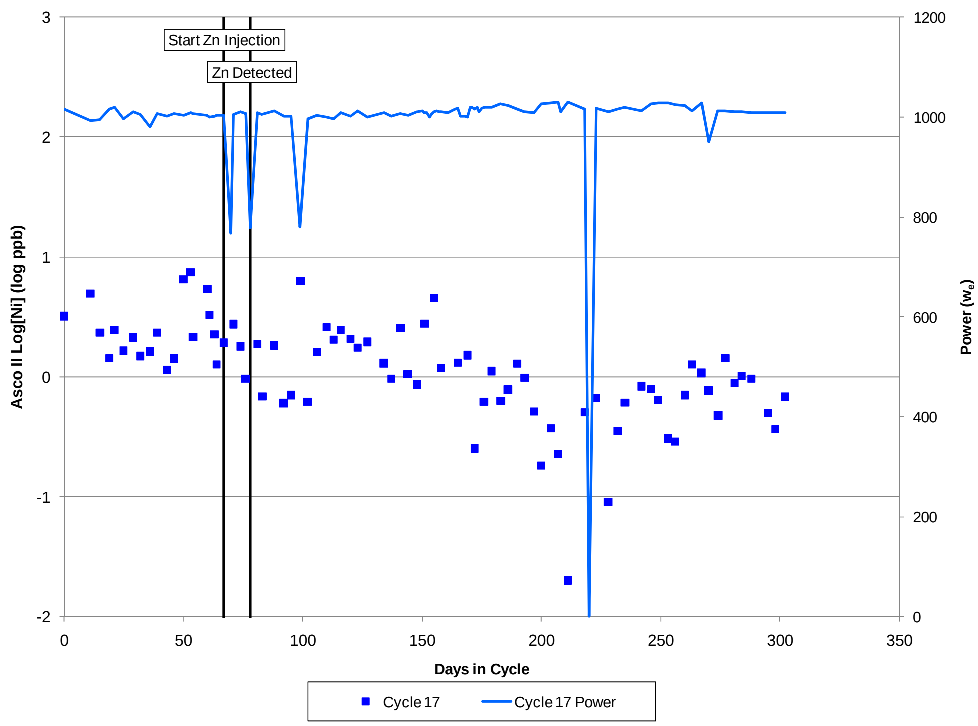

Figure 3-42
Asco II Logarithmic Nickel Concentration before and during Zinc Injection

Table 3-73
Asco II Nickel Concentration Same Cycle Statistical Assessment Results

Time Period for Comparison to Pre-Zinc Period	Cycle N				Cycle N-1				Cycle N-2			
	α=0.01	α=0.05	α=0.2	α=0.5	α=0.01	α=0.05	α=0.2	α=0.5	α=0.01	α=0.05	α=0.2	α=0.5
Post-Injection/Pre-Detection	-2.51	-2.01	-1.50	-1.01	-	-	-	-	-	-	-	-
Post-Injection	-2.78	-2.43	-2.05	-1.68	-	-	-	-	-	-	-	-
Post-Detection	-2.81	-2.46	-2.08	-1.71	-	-	-	-	-	-	-	-

Table 3-74
Asco II Nickel Concentration Profile Slope Analysis

Period of Analysis	Cycle N		Cycle N-1		Cycle N-2	
	Slope	R^2	Slope	R^2	Slope	R^2
25 Days Pre-Zinc	3.58E+00	0.02	-	-	-	-
25 Days Post-Injection	-5.10E-02	0.35	-	-	-	-
25 Days Post-Detection	6.69E-02	0.07	-	-	-	-
Pre-Zinc	1.49E-02	0.02	-	-	-	-

No nickel data for pre-zinc cycles was available. Analyses of the data from the first zinc cycle indicate the following:

- There was a decrease in the average nickel concentration in all of the zinc periods considered compared to the pre-zinc period.

These data provide a relatively robust conclusion that there was no measurable increase in nickel following zinc addition.

3.5.1.4 Braidwood 2

Braidwood 2 chemistry and operating data were available in the CMA Database [8]. Zinc injection at Braidwood 2 was initiated approximately 428 days into the 12th fuel cycle and zinc was detected in the coolant 24 days later.[9] Braidwood 2 operated with an average zinc concentration of 4.6 ppb during its first injection cycle. The Braidwood 2 steam generators have Alloy 600TT tubing.

Nickel (and power) data for Braidwood 2 are shown in Figure 3-43 (normal scale) and Figure 3-44 (log scale). The data for the first zinc cycle (Cycle 12) appear to be reported as lower acceptance limits (i.e., < 5 ppb). Therefore, no analyses were performed.

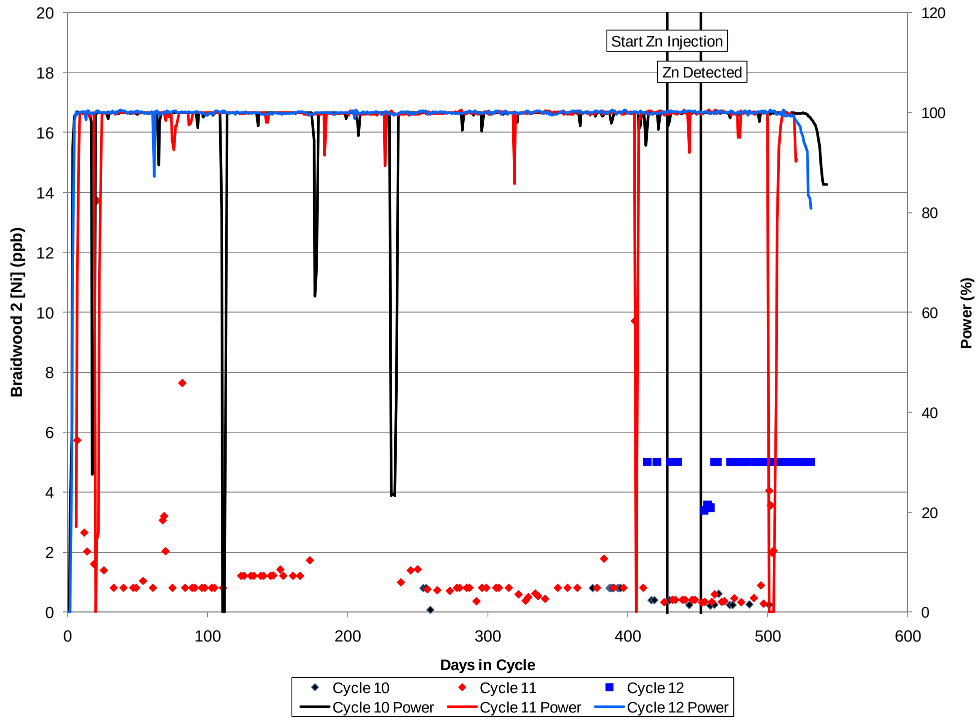

Figure 3-43
Braidwood 2 Nickel Concentration before and during Zinc Injection

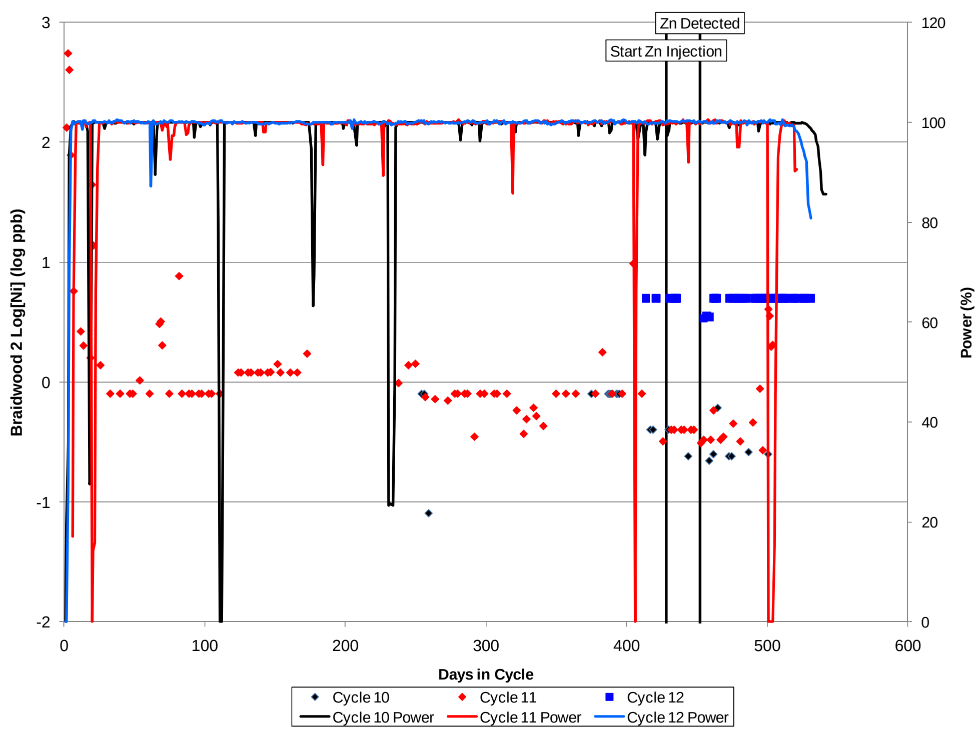

Figure 3-44
Braidwood 2 Logarithmic Nickel Concentration before and during Zinc Injection

3.5.1.5 Catawba 1

The first injection of zinc at Catawba 1 took place during the 17th fuel cycle. Data from Cycles 15 and 16 were supplied by EPRI [16], but Cycle 17 data were unavailable, and no analyses were conducted. The Catawba 1 steam generators have Alloy 690TT tubing. (Steam generator replacement occurred after Cycle 9; the original steam generators were tubed with Alloy 600MA [12].)

3.5.1.6 Catawba 2

Catawba 2 first injected zinc during Cycle 15. Data from Cycle 14 were provided by EPRI [16], but Cycle 15 data were unavailable, and no evaluations were performed. The Catawba 2 steam generators are tubed with Alloy 600TT.

3.5.1.7 Calvert Cliffs 1

Calvert Cliffs 1 chemistry and operating data were available in the CMA Database [8] and were also provided by EPRI.[15] Injection of zinc at Calvert Cliffs 1 was initiated on the 444th day of Cycle 18 and the concentration in the RCS was measurable 7 days later. The cycle start and zinc start dates were taken from the CMA Database and from Reference [17]. The Calvert Cliffs 1 steam generators have Alloy 690TT tubing. The Calvert Cliffs 1 steam generators were replaced after Cycle 15; the original steam generators were tubed with Alloy 600HTMA [12].

Figure 3-45 (normal scale) and Figure 3-46 (log scale) give the nickel data available for Calvert Cliffs 1. No pre-zinc nickel data are available, so no analyses were performed.

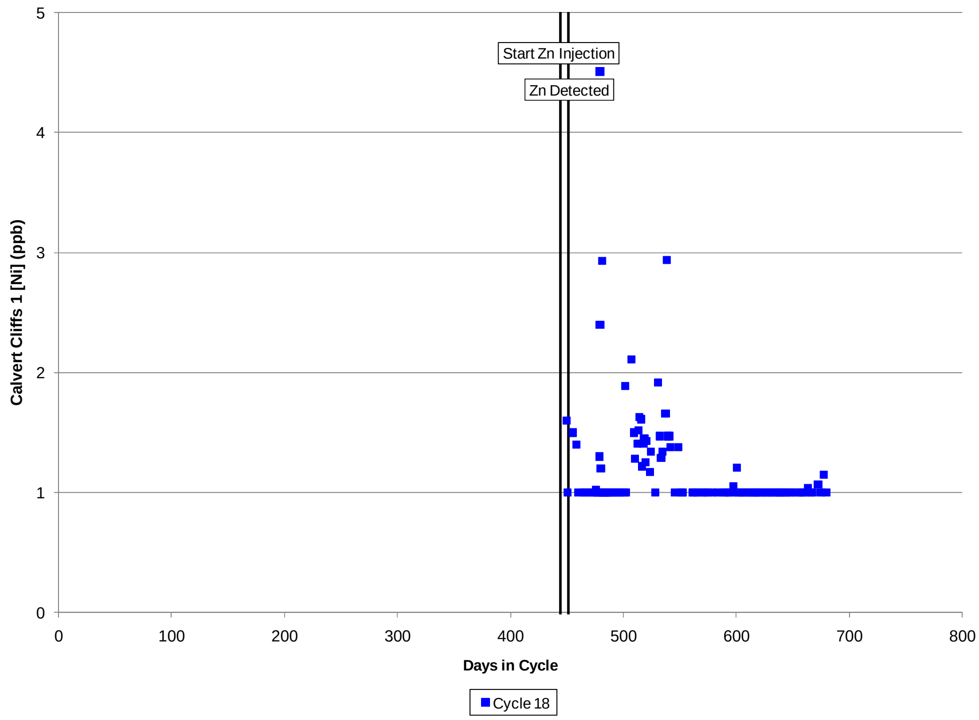

Figure 3-45
Calvert Cliffs 1 Nickel Concentration during Zinc Injection

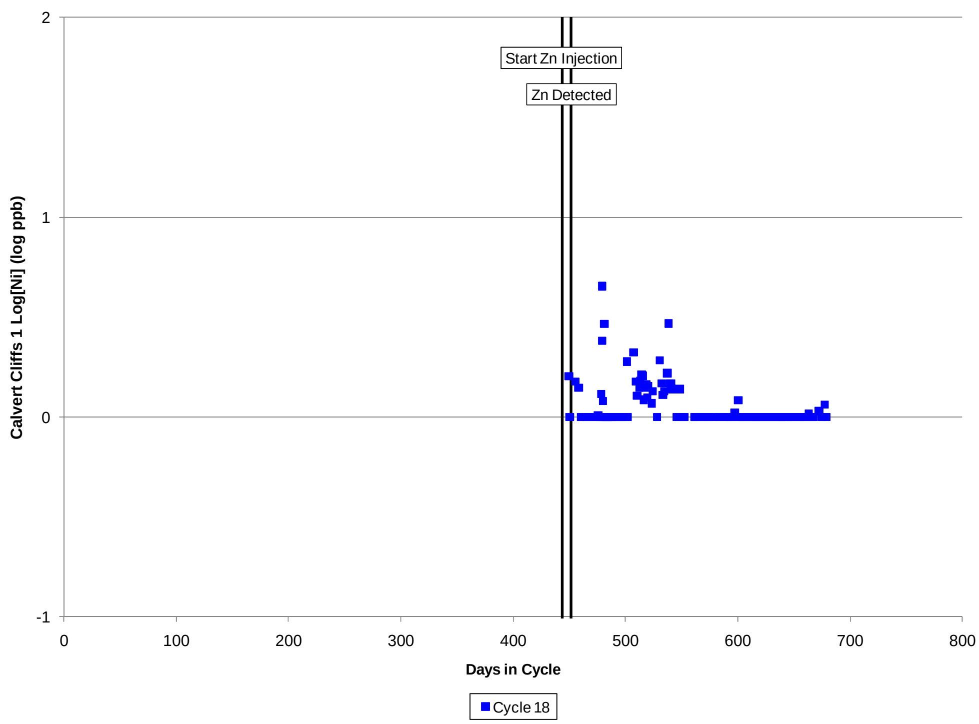

Figure 3-46
Calvert Cliffs 1 Logarithmic Nickel Concentration during Zinc Injection

3.5.1.8 Crystal River 3

Crystal River 3 chemistry and operating data were provided by EPRI [15]. Since zinc injection began at Crystal River 3 on January 14, 2009 [12], and Cycle 16 nickel data were available up to September 25, 2008, no analyses were performed. Until replacement in 2009, the Crystal River 3 steam generators were tubed with Alloy 600SR.

3.5.1.9 McGuire 1

Chemistry and operating data were provided by Duke personnel. McGuire 1 began injecting zinc 294 days into the 18th fuel cycle, detected zinc in the coolant 21 days later, and operated at an average concentration of 4.2 ppb. McGuire 1 completed full UFC campaigns during the two outages immediately preceding the first injection of zinc. The McGuire 1 steam generators are tubed with Alloy 690TT. The original McGuire 1 steam generators were tubed with Alloy 600MA; steam generator replacement occurred after Cycle 11 [12].

Figure 3-47 (normal scale) and Figure 3-48 (log scale) show the available data for nickel (and power). Table 3-75 through Table 3-77 show the results of the statistical analyses described in Section 3.3.

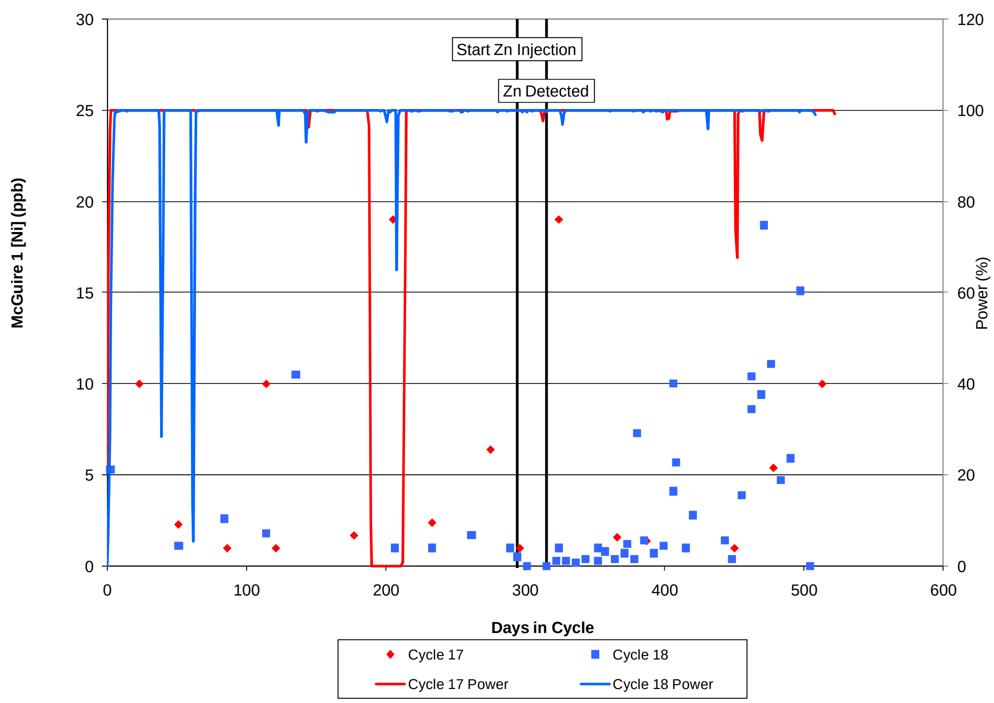

Figure 3-47
McGuire 1 Nickel Concentration before and during Zinc Injection

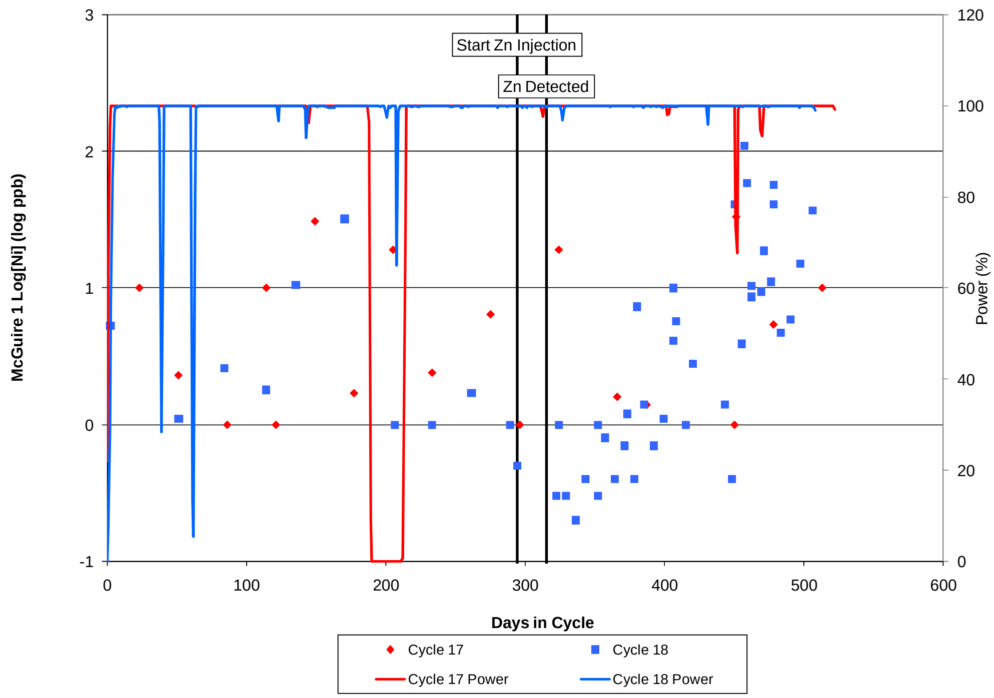

Figure 3-48
McGuire 1 Logarithmic Nickel Concentration before and during Zinc Injection

Table 3-75
McGuire 1 Nickel Concentration Multiple Cycle Statistical Assessment Results

Time Period	Change Versus Cycle N-1				Change Versus Cycle N-2			
	α=0.01	α=0.05	α=0.2	α=0.5	α=0.01	α=0.05	α=0.2	α=0.5
Pre-Zinc	-14.99	-10.88	-6.60	-2.41	-	-	-	-
Post-Injection/Pre-Detection	-	-	-	-	-	-	-	-
Post-Injection	-9.33	-5.40	-1.12	3.17	-	-	-	-
Post-Detection	-10.82	-6.46	-1.80	2.83	-	-	-	-

Table 3-76
McGuire 1 Nickel Concentration Same Cycle Statistical Assessment Results

Time Period for Comparison to Pre-Zinc Period	Cycle N				Cycle N-1				Cycle N-2			
	α=0.01	α=0.05	α=0.2	α=0.5	α=0.01	α=0.05	α=0.2	α=0.5	α=0.01	α=0.05	α=0.2	α=0.5
Post-Injection/Pre-Detection	-15.54	-11.98	-8.65	-5.61	-	-	-	-	-	-	-	-
Post-Injection	-6.41	-2.70	1.37	5.47	-13.22	-8.94	-4.48	-0.11	-	-	-	-
Post-Detection	-6.08	-2.32	1.84	6.02	-13.17	-8.58	-3.83	0.78	-	-	-	-

Table 3-77
McGuire 1 Nickel Concentration Profile Slope Analysis

Period of Analysis	Cycle N		Cycle N-1		Cycle N-2	
	Slope	R^2	Slope	R^2	Slope	R^2
25 Days Pre-Injection	-	-	-	-	-	-
25 Days Post-Injection	-2.03E-02	0.57	-	-	-	-
25 Days Post-Detection	4.50E-03	0.01	-	-	-	-
Detection through EOC	1.70E-01	0.20	4.54E-03	0.00	-	-

The statistical analyses yielded the following results:

- Nickel concentrations after zinc injection were higher than nickel concentrations during the same periods in the pre-zinc cycles. However, this difference was not statistically significant.
- Nickel concentrations before and after zinc injection during the first zinc cycle were not statistically different.
- The only significant trend in the nickel concentrations was a decrease during the 25-day period following commencement of injection.

Inspection of Figure 3-47 and Figure 3-48 indicates that there may have been a trend of increasing nickel concentration after the first detection of zinc. However, the pre-zinc concentrations in the first zinc injection cycle and the previous cycle were too sparse and scattered to draw conclusions regarding the effect of zinc.

In conclusion, it is possible that there was an effect of zinc on nickel concentrations at McGuire 1, but the pre-zinc data are too sparse to draw any conclusions.

3.5.1.10 Surry 1

Surry 1 chemistry and operating data were provided by EPRI [18]. Zinc injection at Surry 1 was initiated approximately 257 days into the 22nd fuel cycle [10] and the average concentration reached was 7.4 ppb [11]; the time of first detection of zinc was unavailable. The Surry 1 steam generators are tubed with Alloy 600TT.

Nickel concentrations are shown in Figure 3-49 (normal scale) and Figure 3-50 (log scale). With this data set, it was possible to perform same-cycle statistical analyses, the results of which are shown in Table 3-78.

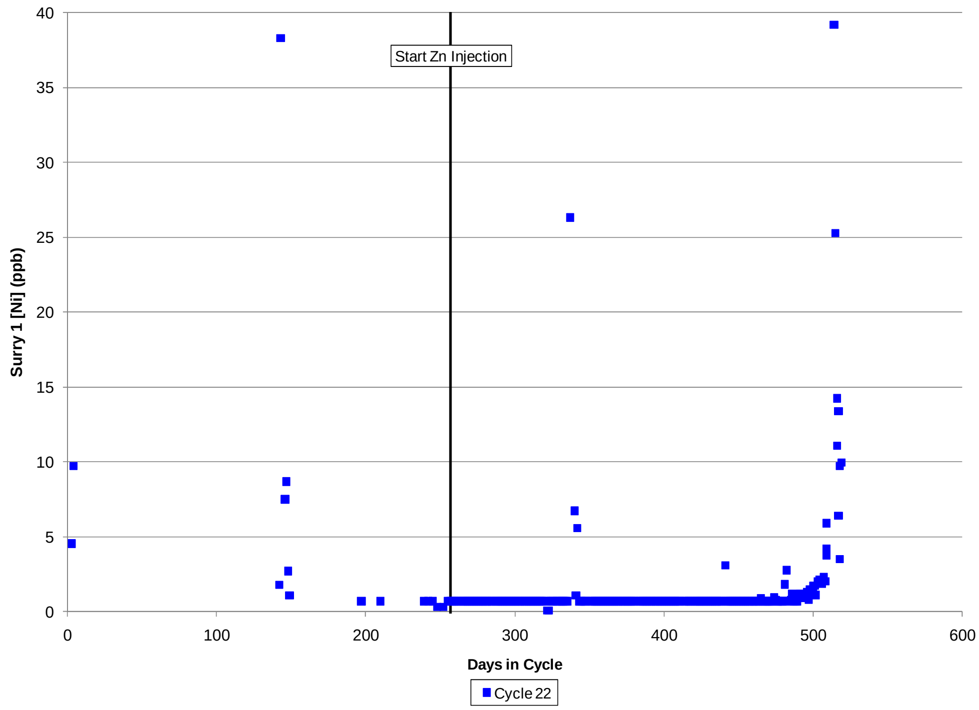

Figure 3-49
Surry 1 Nickel Concentration before and during Zinc Injection

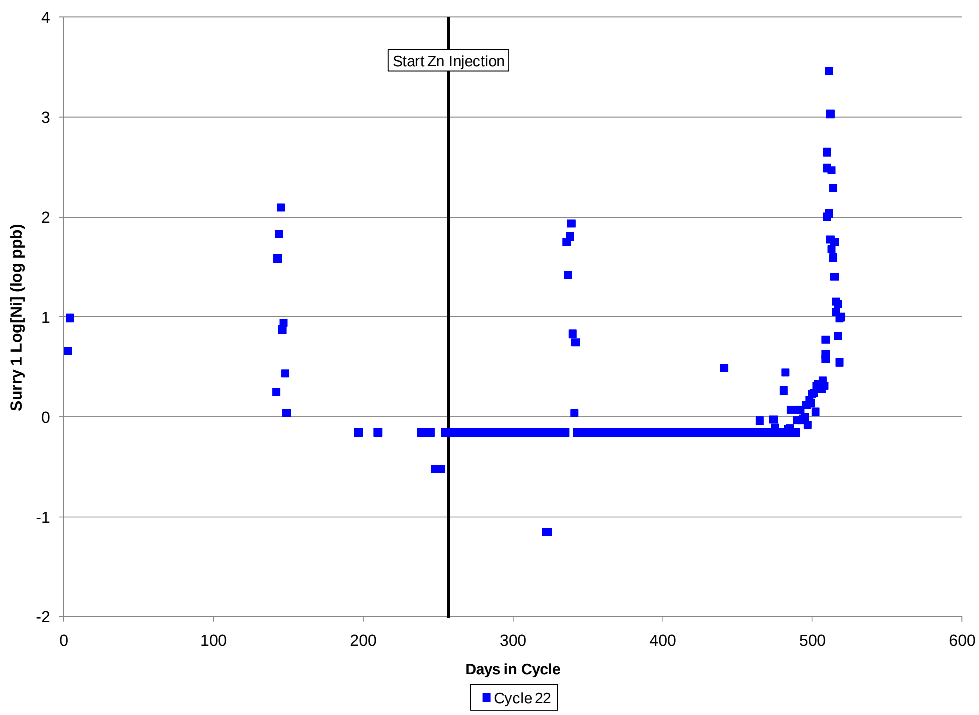

Figure 3-50
Surry 1 Logarithmic Nickel Concentration before and during Zinc Injection

Table 3-78
Surry 1 Nickel Concentration Same Cycle Statistical Assessment Results

Time Period for Comparison to Pre-Zinc Period	Cycle N				Cycle N-1				Cycle N-2			
	α=0.01	α=0.05	α=0.2	α=0.5	α=0.01	α=0.05	α=0.2	α=0.5	α=0.01	α=0.05	α=0.2	α=0.5
Post-Injection/Pre-Detection	-	-	-	-	-	-	-	-	-	-	-	-
Post-Injection	-24.79	-14.98	-3.57	8.31	-	-	-	-	-	-	-	-
Post-Detection	-	-	-	-	-	-	-	-	-	-	-	-

The only statistical assessment possible was a comparison between the pre-injection nickel concentrations and the post-injection nickel concentrations. This comparison indicated that the difference is not statistically significant.

Inspection of Figure 3-49 and Figure 3-50 shows that the nickel concentration was below the lower limit of reportability for the entire cycle (pre- and post-zinc) except for a few brief transients and the end of cycle. It is likely that these transients were associated with factors other than zinc, most likely, to power reductions.

3.5.1.11 Surry 2

Chemistry and operating data for Surry 2 were supplied by EPRI [18]. Surry 2 began injecting zinc at a target concentration of 10 ppb on the 315th day of its 21st fuel cycle, detected zinc 44 days later, and averaged 3.7 ppb zinc following the start of injection [11]. A small number of nickel concentration data from Cycle 20 were available. No assessments were performed as there were no nickel data from Cycle 21. The Surry 2 steam generators have Alloy 600TT tubing.

3.5.1.12 Three Mile Island 1

Three Mile Island 1 chemistry and operating data were available [16]. Zinc addition at Three Mile Island 1 was initiated approximately 284 days into the 16th fuel cycle and zinc was detected in the coolant 127 days later. The average concentration after detection was 5.3 ppb [9]. Prior to replacement in 2009, Three Mile Island 1 had Alloy 600SR steam generator tubing.

It was not possible to assess the effect of zinc on nickel concentration as there were no Cycle 16 data predating the start of zinc injection (Figure 3-52), and there were no data available from previous cycles. Except for the end of cycle, the nickel concentration appears to have been below the lower reportability concentration.

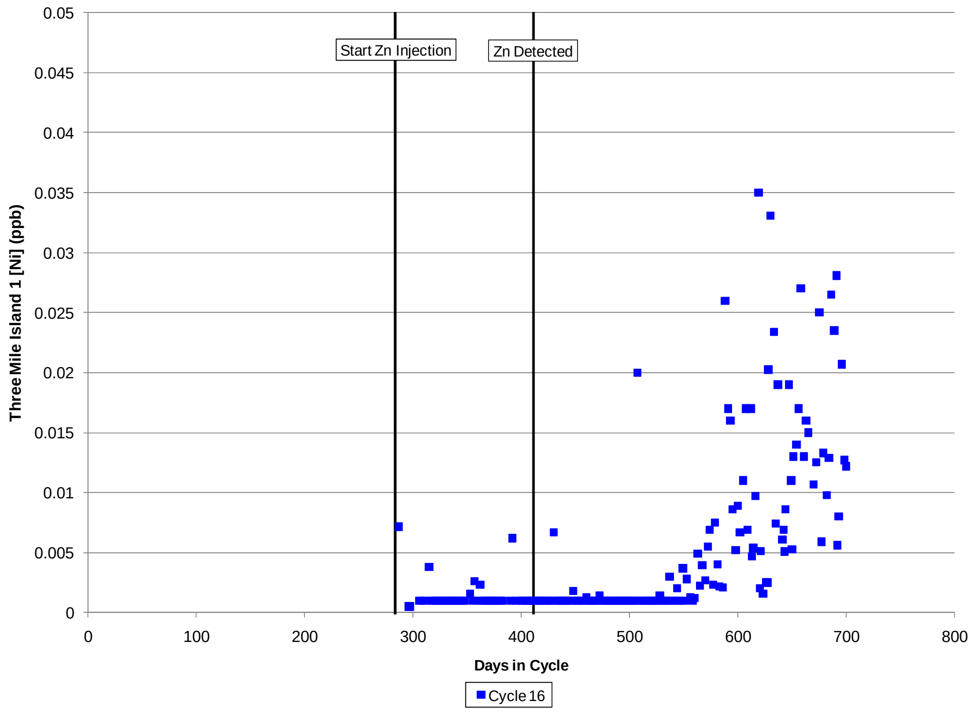

Figure 3-51
Three Mile Island 1 Nickel Concentration before and during Zinc Injection

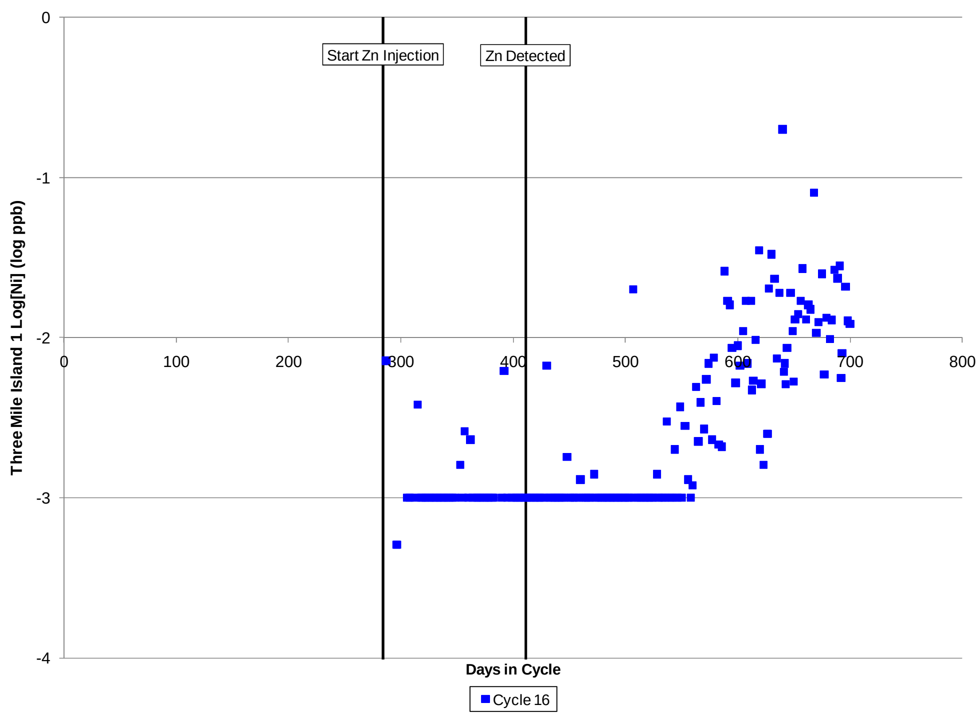

Figure 3-52
Three Mile Island 1 Logarithmic Nickel Concentration before and during Zinc Injection

3.5.1.13 Vandellos II

Chemistry and operating data were transmitted by EPRI in the form of several spreadsheets prepared by Vandellos personnel [15]. Vandellos II began injecting zinc 278 days into the 15th fuel cycle and a measurable concentration was reported on the 287th day of the cycle. The Vandellos II steam generators are tubed with Alloy 600TT. Vandellos II completed its first UFC campaign during the outage prior to the first injection of zinc and after the commencement of injection, operated at an average zinc concentration of about 4.7 ppb.

Figure 3-47 (normal scale) and Figure 3-54 (log scale) show the available data for nickel (and power). Table 3-79 through Table 3-81 show the results of the statistical analyses described in Section 3.3.

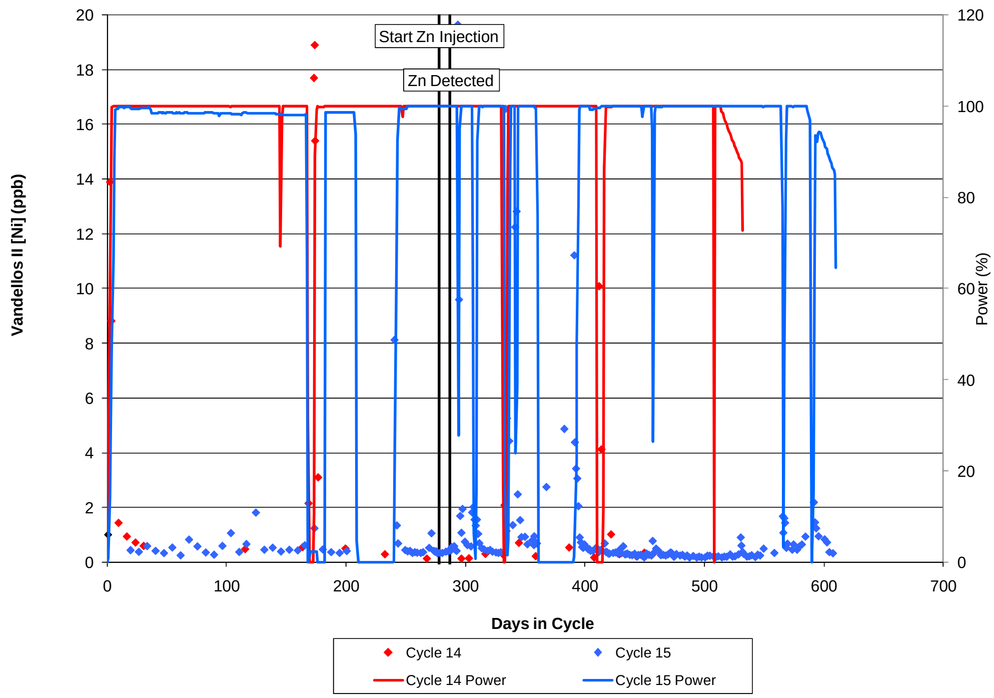

Figure 3-53
Vandellos II Nickel Concentration before and during Zinc Injection

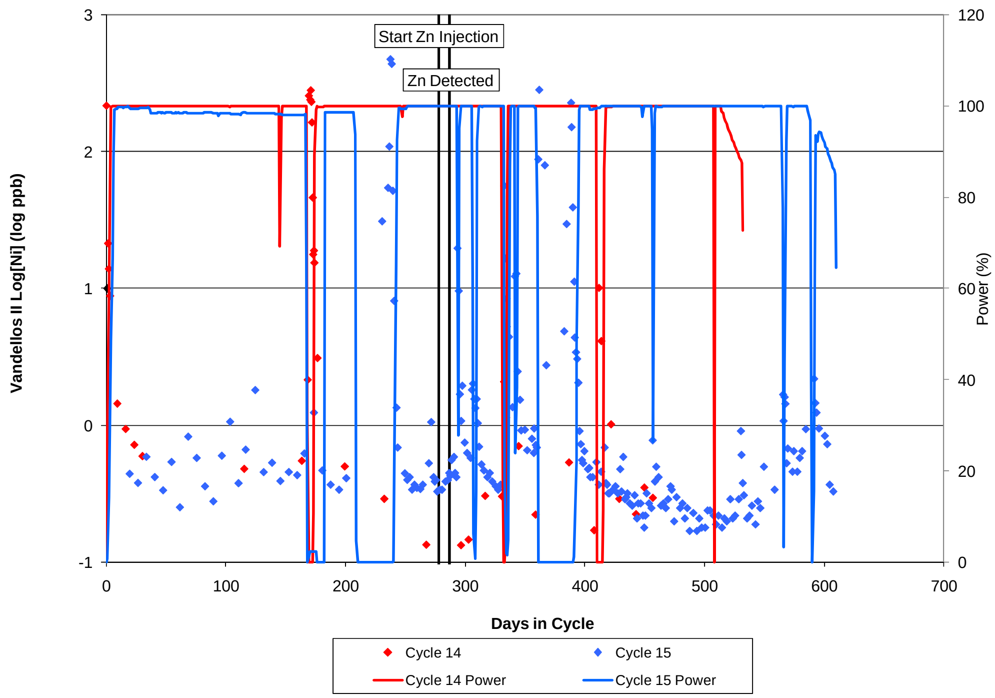

Figure 3-54
Vandellos II Logarithmic Nickel Concentration before and during Zinc Injection

Table 3-79
Vandellos II Nickel Concentration Multiple Cycle Statistical Assessment Results

Time Period	Change Versus Cycle N-1				Change Versus Cycle N-2			
	α=0.01	α=0.05	α=0.2	α=0.5	α=0.01	α=0.05	α=0.2	α=0.5
Pre-Zinc	-110.69	-89.83	-66.78	-43.51	-	-	-	-
Post-Injection/Pre-Detection	-	-	-	-	-	-	-	-
Post-Injection	-0.32	1.40	3.42	5.52	-	-	-	-
Post-Detection	-0.30	1.47	3.53	5.67	-	-	-	-

Table 3-80
Vandellos II Nickel Concentration Same Cycle Statistical Assessment Results

Time Period for Comparison to Pre-Zinc Period	Cycle N				Cycle N-1				Cycle N-2			
	α=0.01	α=0.05	α=0.2	α=0.5	α=0.01	α=0.05	α=0.2	α=0.5	α=0.01	α=0.05	α=0.2	α=0.5
Post-Injection/Pre-Detection	-53.97	-44.66	-34.09	-23.25	-	-	-	-	-	-	-	-
Post-Injection	-48.00	-38.57	-27.83	-16.79	-127.22	-107.53	-86.56	-65.82	-	-	-	-
Post-Detection	-47.87	-38.43	-27.68	-16.64	-127.22	-107.53	-86.56	-65.82	-	-	-	-

Table 3-81
Vandellos II Nickel Concentration Profile Slope Analysis

Period of Analysis	Cycle N		Cycle N-1		Cycle N-2	
	Slope	R^2	Slope	R^2	Slope	R^2
25 Days Pre-Zinc	4.33E-03	0.07	-	-	-	-
25 Days Post-Injection	1.22E-01	0.07	2.08E-03	1.00	-	-
25 Days Post-Detection	-7.19E-02	0.02	2.08E-03	1.00	-	-
Day 241 through Injection	-7.00E-02	0.21	-	-	-	-

The statistical analyses were significantly influenced by the significant variation in the data. For example, Cycle 15 (Cycle N) has (statistically) significantly higher nickel concentrations than Cycle 14 (Cycle N-1) for the periods following zinc injection, but this difference is the result of nickel excursions associated with power transients.

The power transients and the associated nickel transients prevent a determination of whether zinc injection affected nickel release.

3.5.2 Assessments from the Literature

To supplement the assessment of the EPRI Zinc Database, a review of the literature was performed to obtain additional data regarding changes in RCS nickel concentration in response to zinc injection. The following bullets give the findings of this literature review. A summary of the nickel response data is given in Section 3.5.4.

3.5.2.1 Biblis B

Reference [25] gives cycle chemistry data for Biblis B, which started zinc injection in September 1996. The zinc concentration was maintained at approximately 5 ppb for several cycles. Biblis B has steam generators with Alloy 800NG tubes.

RCS nickel concentrations remained below detection capability during the initiation of zinc injection. No detection limit for nickel is reported. However, a detection limit of 0.5 ppb is reported for zinc, and it is considered likely that nickel detection capabilities are comparable.

3.5.2.2 Callaway

Reference [23] gives cycle chemistry data for Callaway, which started zinc injection in May 2003. The average zinc concentration reached during injection was 7.2 ppb. Before replacement in 2005, Callaway had steam generators with some tubes made of Alloy 600MA and others made of Alloy 600TT.

The RCS nickel concentrations from the first zinc cycle at Callaway are given in Figure 3-55 (note that there is a Diablo Canyon logo in the lower right-hand corner of this figure because these data were given as part of a Diablo Canyon presentation). Based on the available figure, it does not appear that there was an impact of zinc on nickel concentration at Callaway, but it was difficult to assess this information as the raw data were not available and there was no discussion included in the presentation.

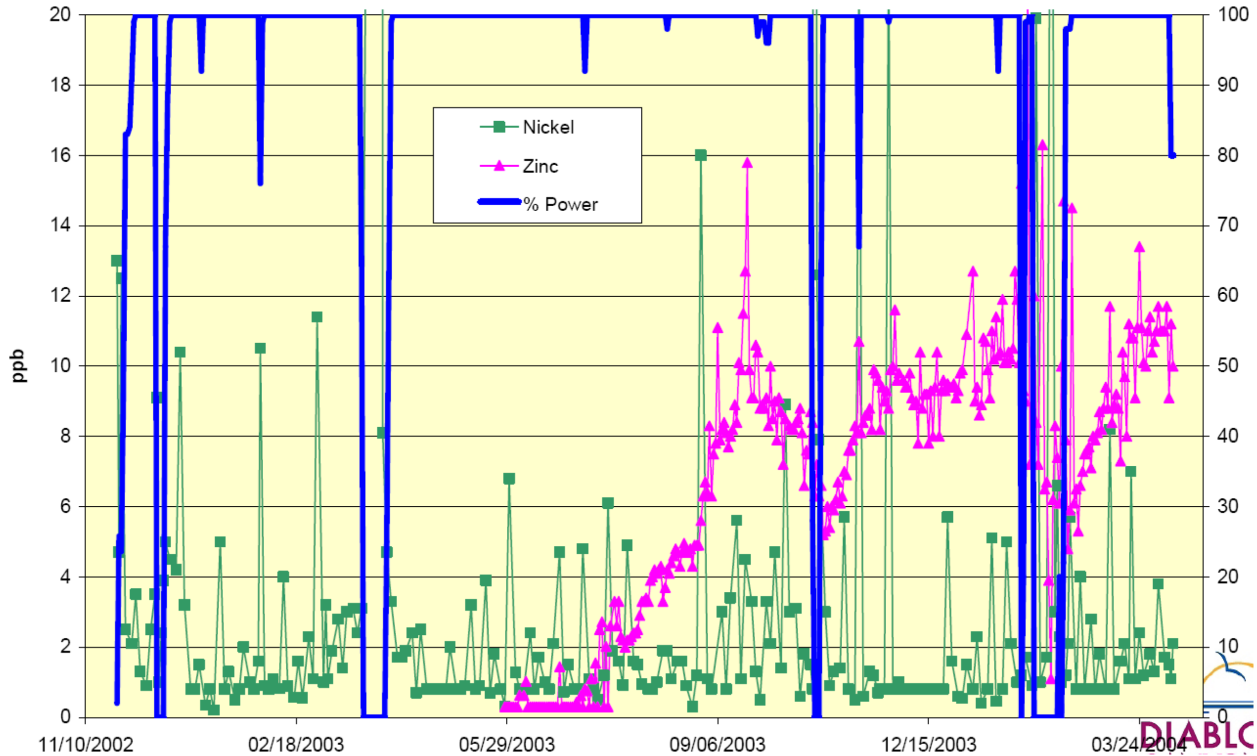

Figure 3-55
Callaway Nickel Concentration before and during Zinc Injection [23]

3.5.2.3 Diablo Canyon 1

Reference [26] gives cycle chemistry data for Diablo Canyon 1, which started zinc injection in June 1998. Zinc was detected in the coolant 9 days after the start of injection and the average zinc concentration reached during injection was 31 ppb. Before replacement in 2008, Diablo Canyon 1 had steam generators tubed with Alloy 600MA.

Very limited nickel data were available in Reference [26] and are presented in Figure 3-56. It appears that the nickel concentration at the times of each of the 5 datum did not exceed the limit of detection of the equipment. Reference [26] does not specify the detection limit for nickel.

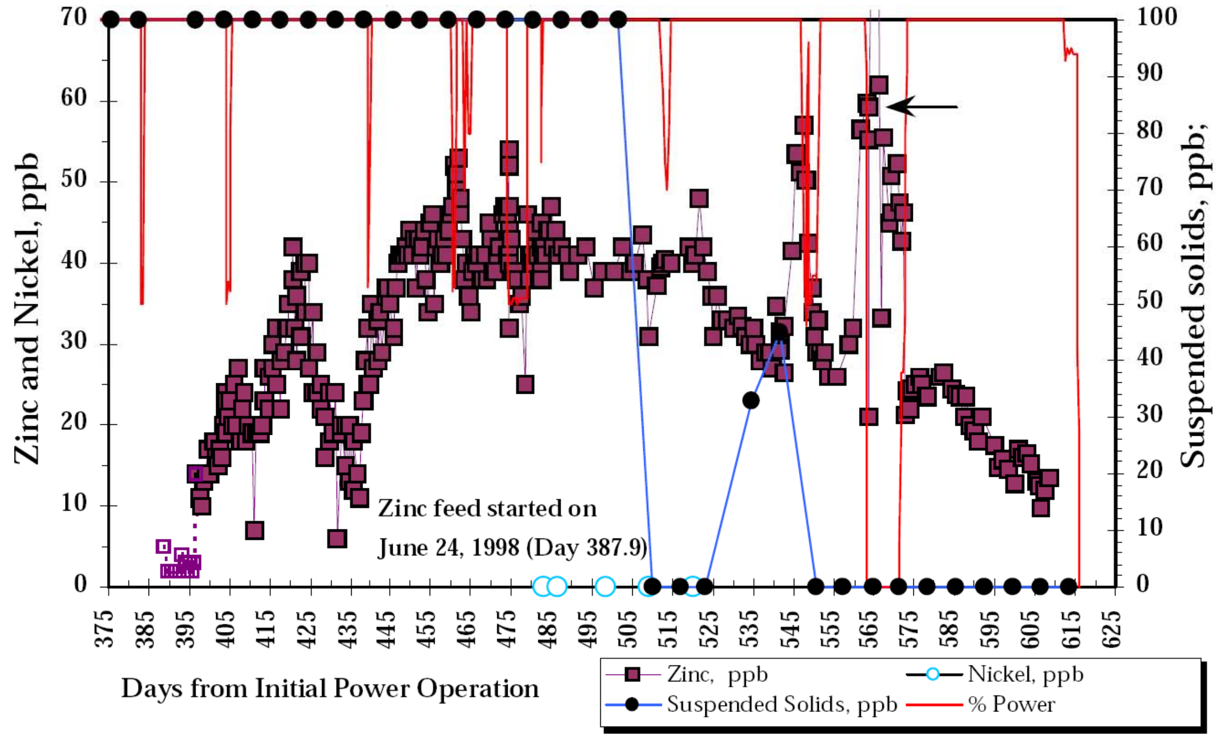

Figure 3-56
Diablo Canyon 1 Nickel Concentration before and during Zinc Injection [26]

3.5.3 Shutdown Nickel Releases

In order to supplement the analyses of RCS nickel concentrations given in Sections 3.5.1 and 3.5.2, the mass of nickel released during refueling outage shutdown chemistry maneuvers was evaluated. If there is a significant release of nickel from ex-core surfaces upon zinc injection, it is expected that some of this nickel will be deposited in the core. At the end of the cycle, some of this nickel is released during shutdown in which decreases in temperature and pH result in much higher nickel solubility.

Shutdown nickel release masses were obtained from the EPRI PWR CMA Database [8] as well as References [27], [28], [29], [30] and [31]. Datasets with shutdown release data from both before and after zinc addition that were amenable to analysis were available for nine units. These data are shown in Figure 3-57 through Figure 3-65. These data show that there is no consistent trend of increased release in the cycles immediately following zinc injection. Although indirect, this provides some evidence that injection of zinc does not significantly increase the mass of nickel depositing on the fuel.

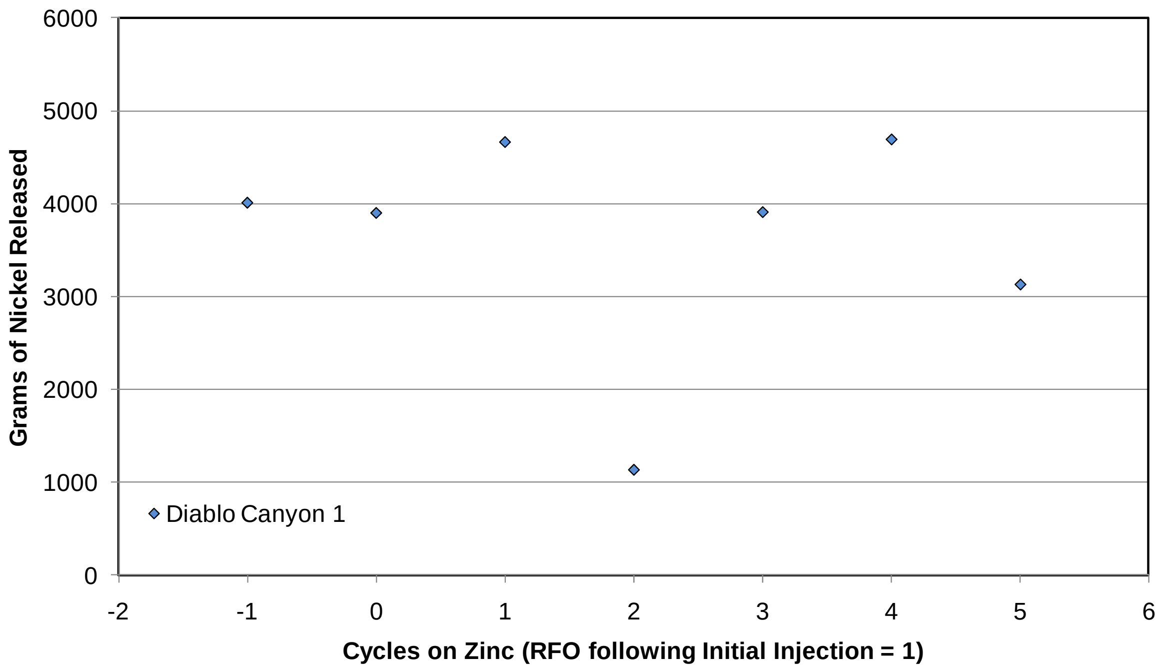

Figure 3-57
Shutdown Nickel Release Masses at Diablo Canyon 1

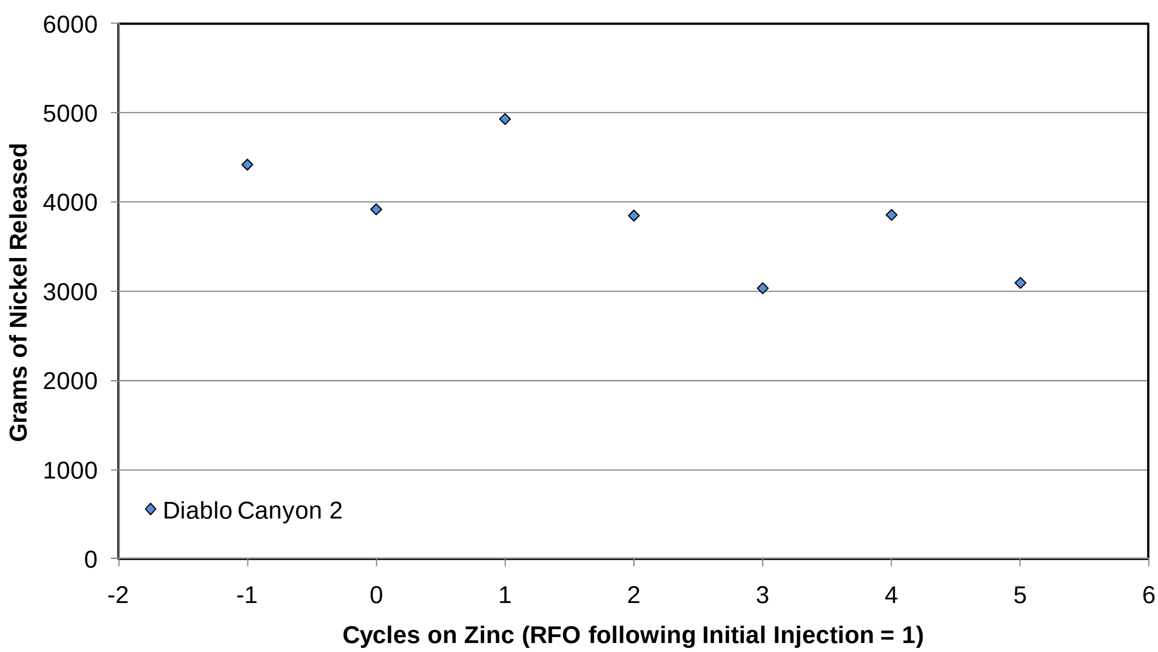

Figure 3-58
Shutdown Nickel Release Masses at Diablo Canyon 2

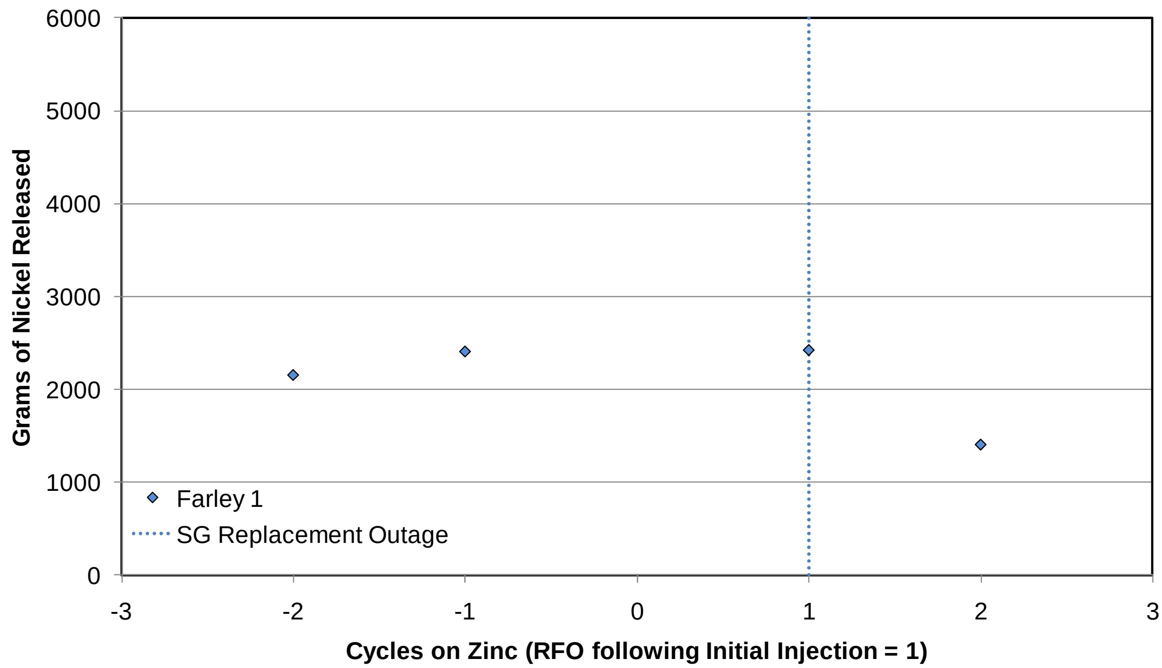

Figure 3-59
Shutdown Nickel Release Masses at Farley 1

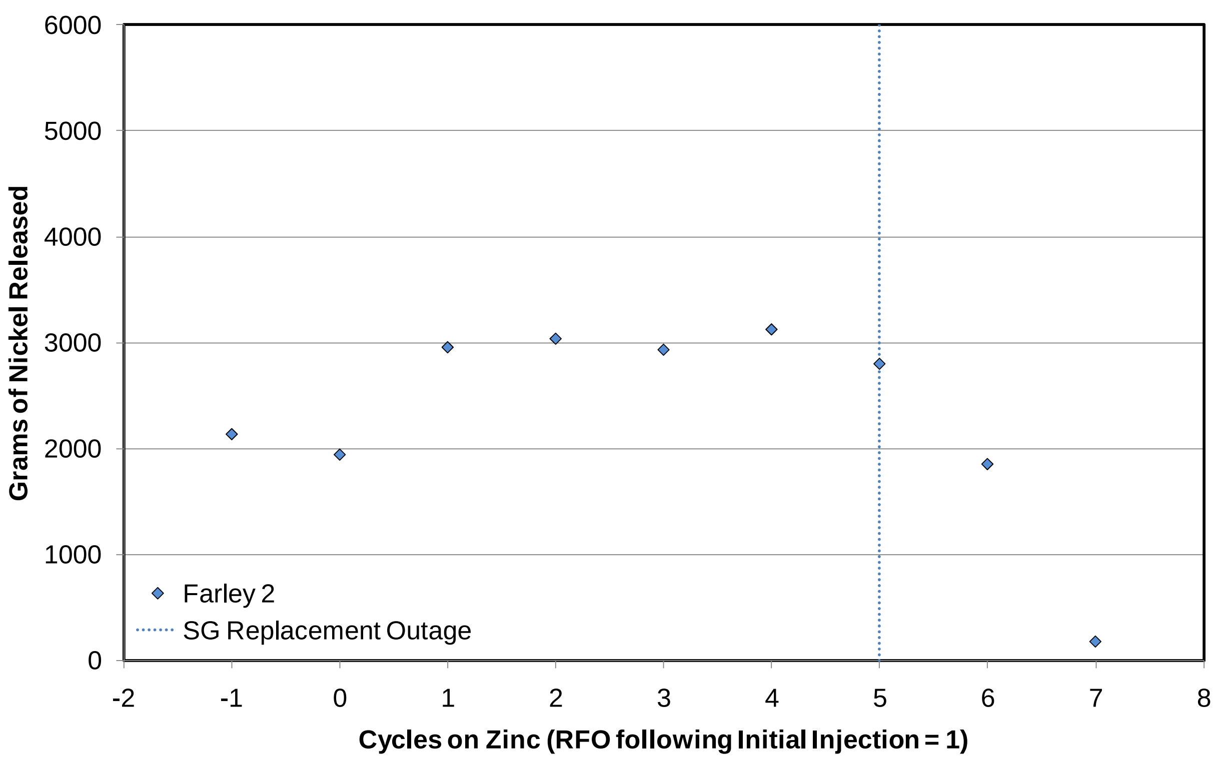

Figure 3-60
Shutdown Nickel Release Masses at Farley 2

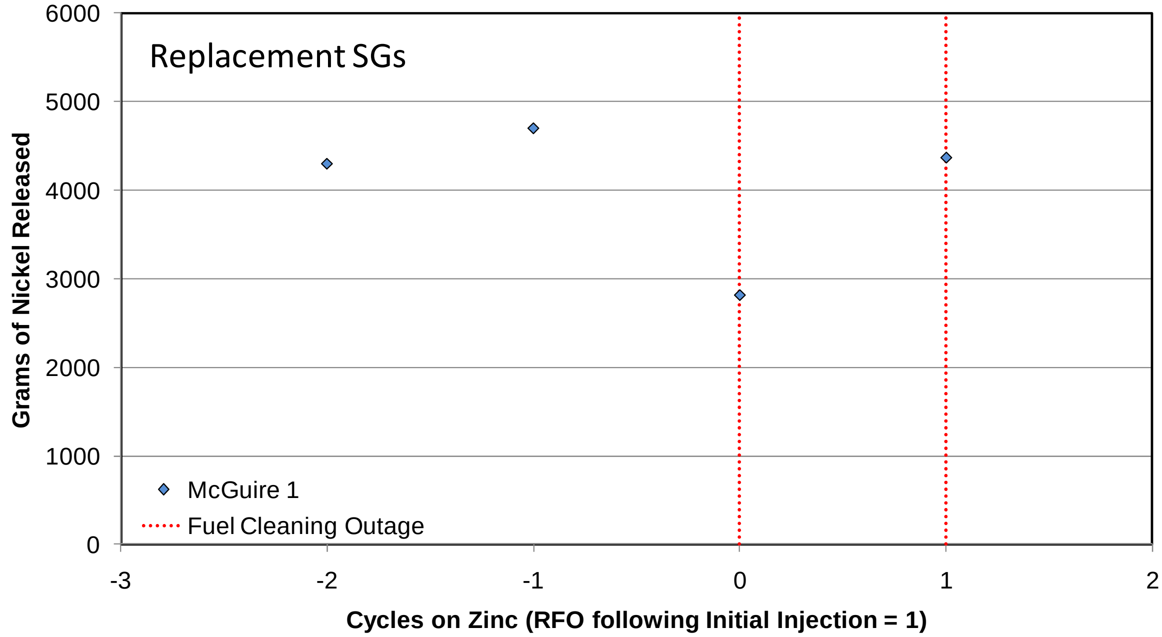

Figure 3-61
Shutdown Nickel Release Masses at McGuire 1

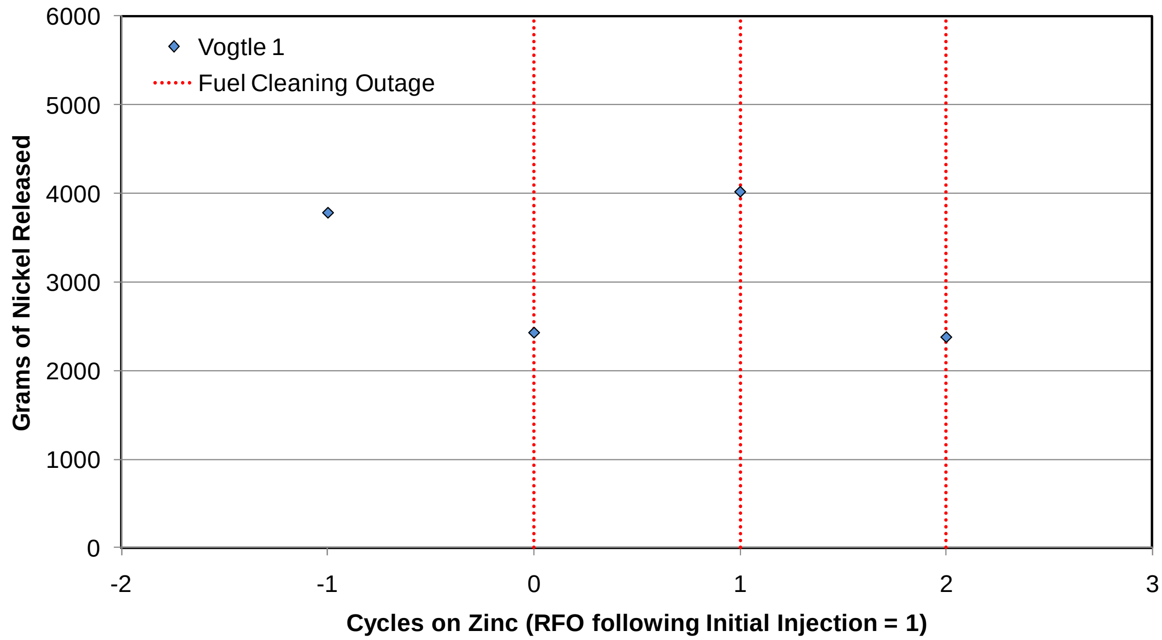

Figure 3-62
Shutdown Nickel Release Masses at Vogtle 1

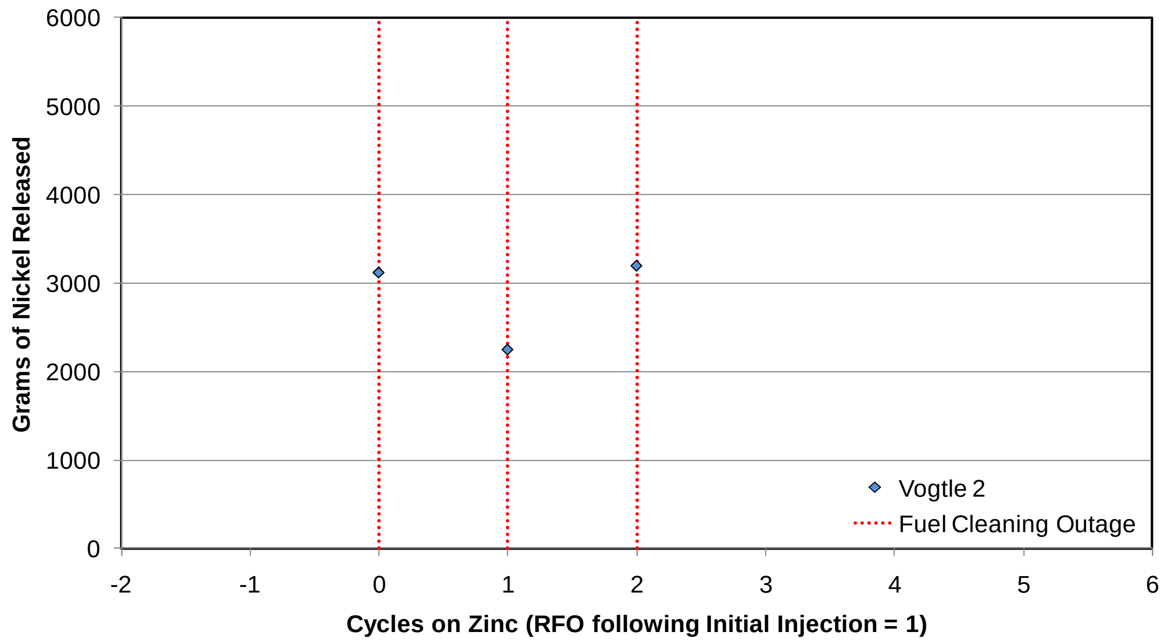

Figure 3-63
Shutdown Nickel Release Masses at Vogtle 2

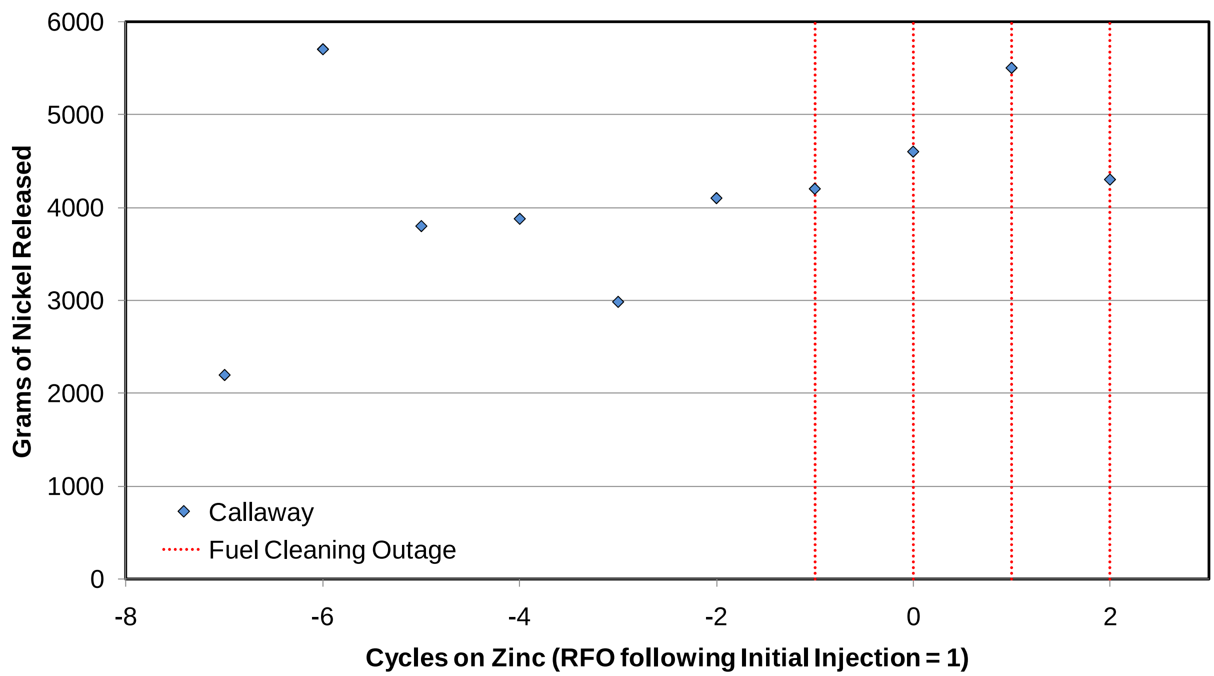

Figure 3-64
Shutdown Nickel Release Masses at Callaway

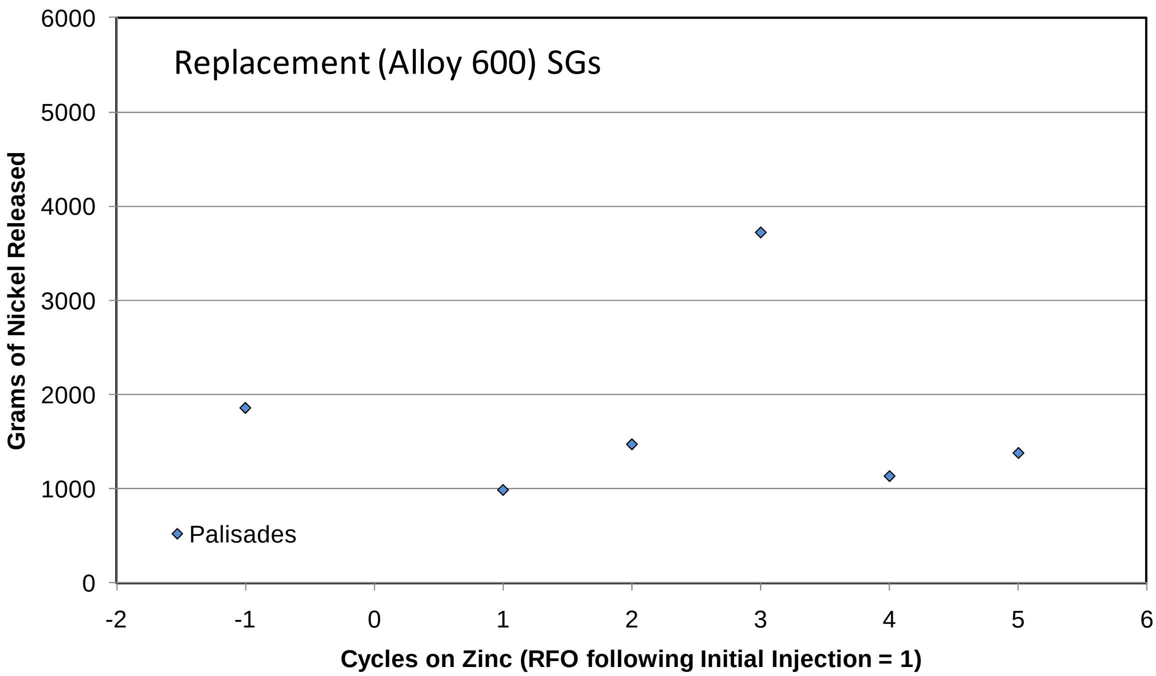

Figure 3-65
Shutdown Nickel Release Masses at Palisades

3.5.4 Summary of Nickel Responses

Nickel data from first zinc cycles and previous cycles were of limited availability due to the limited reporting of data and analytical detection constraints. It was therefore difficult to analyze the impact of the first zinc injection of zinc on nickel concentrations. Data available in the EPRI Zinc Database suggest that the first injection of zinc does not have a statistically significant impact on RCS nickel concentration. Published data from one plant showed that the impact of zinc injection on nickel concentration was insignificant. A summary of the analyses for nickel response is given in Table 3-82. As indicated, there were no data sets which indicated a nickel response, but there were many for which no assessment could be made.

In order to supplement the analysis of the nickel concentrations data, the mass of nickel released during shutdown chemistry maneuvers at zinc plants was assessed. Based on data from nine units, there is no significant systematic difference in the mass of nickel released during shutdowns following the initial injection of zinc.

Table 3-82
Summary of Plant Nickel Responses

	Unit	Conclusions Regarding Nickel Response	Comments
Raw Data Available to EPRI	Angra 1	Indeterminate.	Too little data.
	Asco 1	No nickel release.	Based on data from a single cycle.
	Asco 2	No nickel release.	Based on data from a single cycle.
	Braidwood 2	Indeterminate.	Too little data.
	Catawba 1		No post-zinc data available at the time of this analysis.
	Catawba 2		No post-zinc data available at the time of this analysis.
	Calvert Cliffs 1	Indeterminate.	No pre-zinc data.
	Crystal River 3		No post-zinc data available at the time of this analysis.
	McGuire 1	Indeterminate.	Too little data.
	Surry 2	Indeterminate.	Too little data.
	TMI-1	Indeterminate.	No pre-zinc data.
	Vandellos 2	Indeterminate.	Power transients prevent analysis.
Data from the Literature	Biblis B	Indeterminate.	Nickel below detection before and after zinc injection.
	Callaway	No nickel release.	Limited to reported data.
	Diablo Canyon 1	Indeterminate.	Reported data appear to be a lower detection limit.

Table 3-83
Summary of Plant Nickel Responses — All Units Considered

	EPRI Database	Literature	Total
Zinc effect observed	0	0	0
No zinc effect	2	1	3
Indeterminate	7	2	9
No data	3	0	3
Total considered	12	3	15

3.6 Iron Response

3.6.1 Assessments from EPRI Zinc Database

In general, RCS iron concentrations were not reported in the EPRI database. This is due primarily to the fact that iron concentrations are of greater interest at units with Alloy 800NG steam generator tubing. Most units participating in the EPRI database programs have Alloy 600 or Alloy 690 steam generator tubing, for which nickel concentrations are of greater interest.

3.6.2 Assessments from the Literature

To supplement the assessment of the EPRI Zinc Database, a review of the literature was performed to obtain additional data regarding changes in RCS iron concentration in response to zinc injection. The following bullets give the findings of this literature review. A summary of the iron response data is given in Section 3.6.3.

3.6.2.1 Unnamed Siemens Plant

Reference [32] presents data from an unnamed Siemens plant (which started injection in January 2005). The steam generators at this unit are tubed with Alloy 800NG. Power level data included in Reference [32] indicate relatively stable power operation both before and after zinc injection began. The target zinc concentration was 5 ppb, but there was significant variation around this concentration during the period for which data are presented.

The data include the RCS iron concentration one half cycle before initial zinc injection, the remainder of the initial zinc cycle, and three subsequent cycles. The data for iron concentrations indicates a recurring trend of high iron (6-10 ppb) at the beginning of the cycle which gradually tapers off (to about 1 ppb). Because data for the initial portion of the first zinc cycle are not presented, it is not possible to determine if the beginning of cycle elevated iron values were typical before injection. However, comparison of the iron concentrations at the end of the first zinc cycle, the end of the first complete zinc cycle, and the ends of the three subsequent cycles to iron concentrations before zinc injection indicate that there was no increase in iron concentration when zinc injection was started.

3.6.2.2 Biblis A

Reference [20] gives cycle chemistry data for Biblis A, which started zinc injection in January 1998. The zinc concentration was maintained at approximately 3 ppb for the remainder of the cycle (Reference [20] gives data only for the cycle preceding zinc injection and the initial zinc cycle; it is presumed that zinc injection continued at essentially the same target concentration). Biblis A has steam generators with Alloy 800NG tubes.

The data for iron concentration indicate no significant change in RCS iron concentration. Relative to the previous cycle, iron concentrations appear to have been both more consistent and lower.

3.6.2.3 Biblis B

Reference [21] gives cycle chemistry data for Biblis B, which started zinc injection in September 1996. The zinc concentration was maintained at approximately 5 ppb for several cycles. Biblis B has steam generators with Alloy 800NG tubes.

The data for iron (shown in Figure 3-66) indicate that before zinc injection iron concentrations were on the order of 1-2 ppb. For about 1-2 months after zinc injection began, the iron concentration increased to 8-10 ppb. After the first two months, the iron concentration decreased steadily to about 2-3 ppb over the course of about 6 months. It remained at that concentration for at least the next four cycles. Note that data for only about five months exist before injection. The estimate of 1-2 ppb iron before zinc injection began is therefore not very robust, and it is not clear that the long-term concentration is truly higher than it was before injection began. However, the immediate short-term increase appears to be statistically significant.

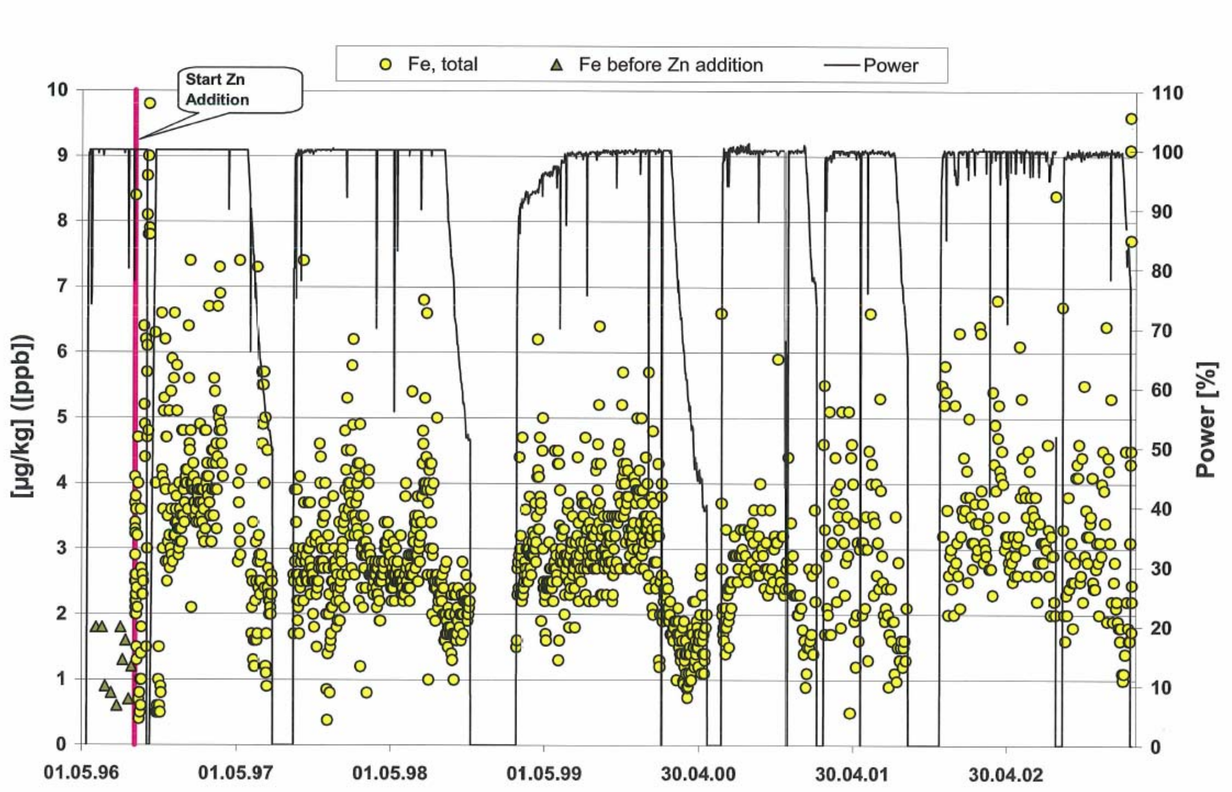

Figure 3-66
Biblis B Iron Concentrations before and during Zinc Injection [21]

3.6.2.4 Unterweser

Reference [21] gives cycle chemistry data for Unterweser, which started zinc injection in May 2003. The zinc concentration was maintained at approximately 5 ppb for several cycles. Unterweser has steam generators with Alloy 800NG tubes.

Data from Reference [21] are given in Figure 3-67. For the first 2-3 weeks following zinc injection there was an increase in iron concentrations (from 2-4 ppb to about 4-8 ppb). After the first six weeks of injection, the concentration returned to the pre-injection values. Note, however, that the increase in iron also corresponded to a period of plant power transients.

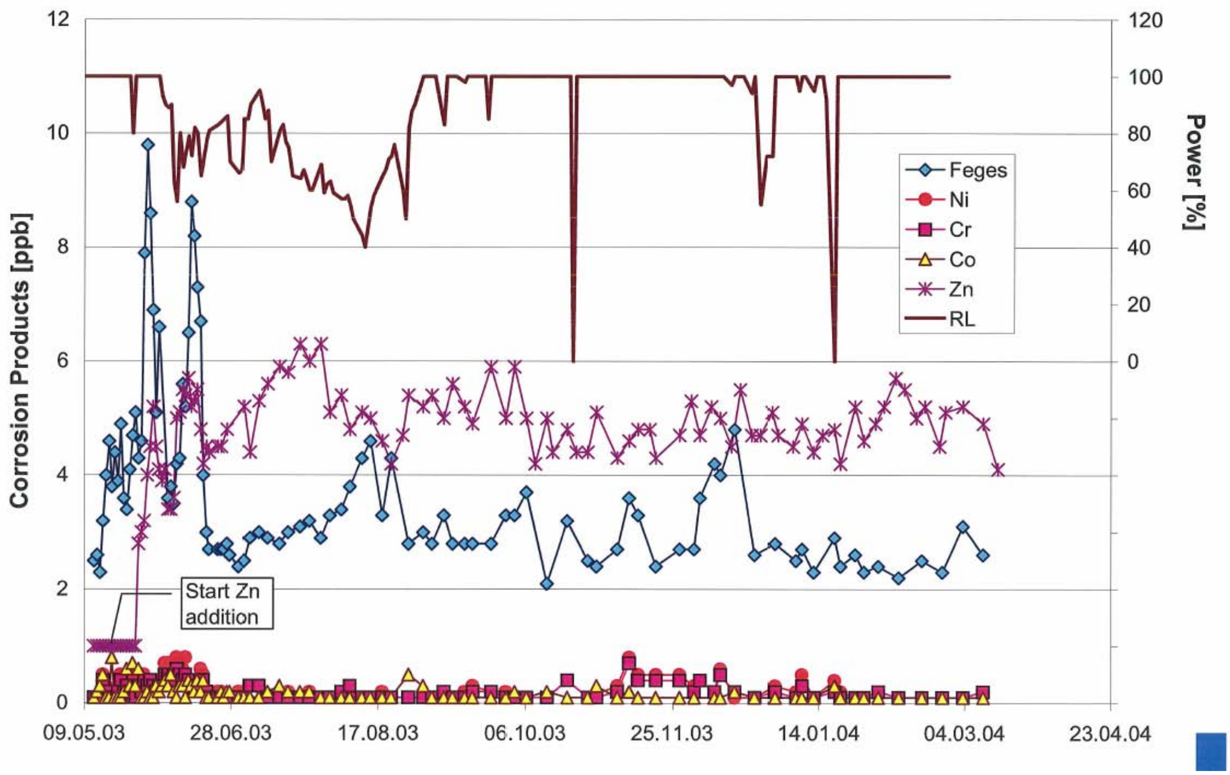

Figure 3-67
Unterweser Iron Concentrations before and during Zinc Injection [21]

3.6.3 Summary of Iron Responses

Iron response data were only available for four units. All of these units had steam generators tubed with Alloy 800NG. In two cases, there was a significant short-term increase in the iron concentration upon initiation of zinc injection. In one case, there was no iron response. In the last case, there was not enough data to determine if there was a response. A summary of these observations is given in Table 3-84.

Table 3-84
Summary of Plant Iron Responses

Unit	Conclusions Regarding Iron Response	Comments
Unnamed Siemens Plant	Inconclusive.	Very little pre-zinc data.
Biblis A	No increase.	No change with zinc addition. No change from previous cycle.
Biblis B	Increase in iron.	Short-term increase (1-2 months) and then a return to near previous values.
Unterweser	Increase in iron.	Short-term increase, but complicated by transient.

3.7 Theoretical Considerations

A number of theoretical considerations were evaluated to determine whether there was an a priori expectation of accelerated release of radiocobalts, nickel, and/or iron upon initial exposure of the RCS to zinc. These considerations are discussed individually in the following subsections. Overall conclusions based on these considerations as well as plant experience are discussed in Section 3.7.

3.7.1 Ex-Core Decontamination

Reference [33] gives ex-core Co-60 activities for several locations in the Biblis B primary system over the course of four outages, three of which follow the initiation of zinc injection. These measurements were made with shielded detectors and are thought to accurately represent the actual Co-60 activity. As shown in Figure 3-68, in most cases, the Co-60 activity after two-and-a-half cycles on zinc is roughly uniformly distributed about the activity that would have resulted from decay of the activity present before zinc injection. During this time there were substantial reductions in surface activity, indicating that the net rate of incorporation of new contamination was reduced or halted by the use of zinc. Similar data from Obrigheim are shown in Figure 3-69, which likewise shows that ex-core surface activity essentially followed the Co-60 decay curve.

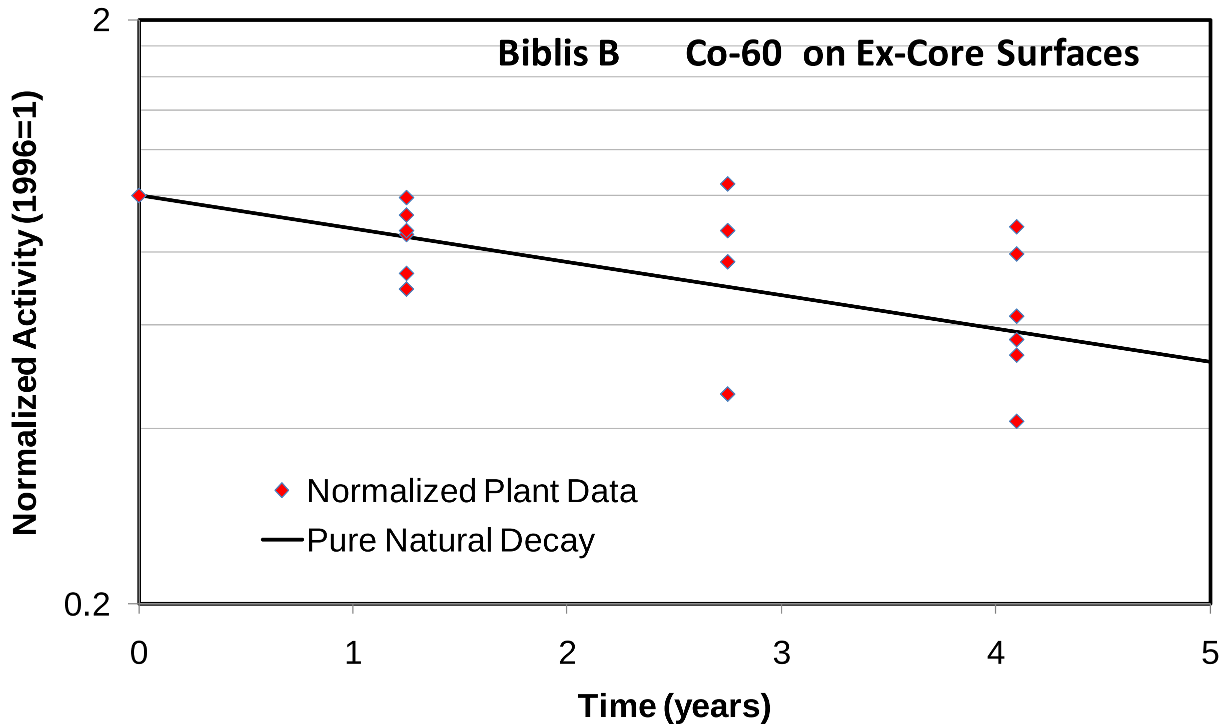

Figure 3-68
Ex-Core Surface Co-60 Activity at Biblis B (Initial Zinc Injection prior to 1997 Outage)

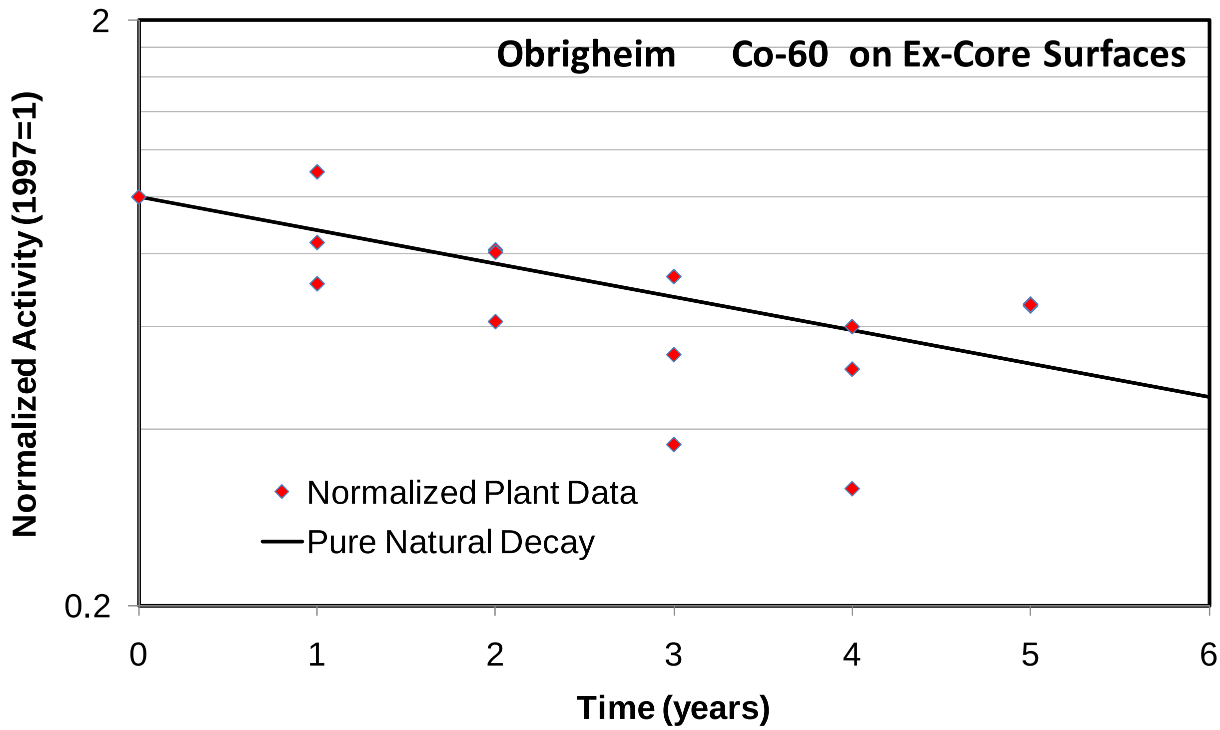

Figure 3-69
Ex-Core Surface Co-60 Activity at Obrigheim (Initial Zinc Injection prior to 1998 Outage)

3.7.2 Mixed Spinel Solubilities

Reference [21] presents the results of solubility calculations for mixed spinels, which are reproduced in Table 3-85. Note that these calculations assume an infinite source of the solid species and then determine the resulting soluble concentrations. An alternative approach would be to determine the stoichiometry of the spinel precipitated at given concentrations of the various metals. From the results in Table 3-85, it could be concluded that under conditions of thermodynamic equilibrium, if the nickel concentration in solution were held constant and the zinc concentration in solution were increased, then iron concentrations in solution would increase. However, since spinels are fairly stable at RCS conditions, it is unlikely that thermodynamic equilibrium would be achieved and interpretation of these results is somewhat more complicated. Nonetheless, they do provide an indication that the iron response to zinc is likely to be much more significant than the nickel response. This is an indication that experience with iron releases from PWRs with Alloy 800NG tubed steam generators cannot be used to predict nickel responses in PWRs with Alloy 600 or 690 tubed steam generators.

Table 3-85
Calculated Solubilities of Various Zinc Spinels [21]

Spinel		Solubility at pH_T=6.9 (ppb)				Solubility at pH_T=7.0 (ppb)			
		Fe	Ni	Cr	Zn	Fe	Ni	Cr	Zn
$Zn_0Cr_{1.29}Fe_{1.26}Ni_{0.45}O_4$	0% Zinc	2.4	0.4	0.4	0	2.9	0.3	0.7	0
$Zn_{0.3}Cr_{1.29}Fe_{1.11}Ni_{0.30}O_4$	10% Zinc	3.5	0.4	0.2	2.9	4.3	0.3	0.3	0.9
$Zn_{0.6}Cr_{1.29}Fe_{0.90}Ni_{0.21}O_4$	20% Zinc	4.5	0.4	0.1	14	5.4	0.3	0.2	4.6

3.7.3 Chemical Behavior of Radiocobalts

In consideration of the effects of zinc injection on the behavior of radiocobalts, it is worthwhile to quickly review the ways in which cobalt is expected to behave in the reactor coolant system. Co-60 is present in the RCS due to the following reaction:

$$^{59}\mathrm{Co}\left(\mathrm{n},\gamma\right)\,^{60}\mathrm{Co} \qquad \textbf{Eq. 3-1}$$

Therefore, Co-60 may be expected to behave chemically like cobalt in all locations. However, Co-58 is formed by the following scheme:

$$^{58}\mathrm{Ni}\left(\mathrm{n},\beta\right)\,^{58}\mathrm{Co} \qquad \textbf{Eq. 3-2}$$

Therefore, when incorporated into core deposits, Co-58 may be expected to behave like nickel and is considered a sister isotope. That is, it is deposited in the core while still nickel and is thus embedded in a nickel matrix. The chemical concentration of cobalt formed by Equation [3-2] is very small. Thus release of Co-58 is generally believed to mimic that of nickel.

Once released from the core, it is expected that Co-58 and Co-60 would both react with ex-core surfaces as cobalt. Thus, consideration of isotopic differences in radiocobalt responses to zinc injection can provide clues regarding the source of changes. For example, increases in Co-58 and Co-60 but not nickel, would imply release from ex-core surfaces. Likewise, an increase in Co-58 and nickel but not Co-60 would imply release from in-core deposits.

3.7.4 Potential Implications of Low Nickel Solubility

As discussed in Reference [34], the first step in the incorporation of zinc into deposit and oxide structures is likely to be adsorption. For zinc incorporation, this hypothesis is well founded, since concentrations of zinc are well below the solubility limits (typical applications are less than 40 ppb, while the solubility is greater than 200 ppb and probably about 250 ppb [35]). Similarly, cobalt is expected to be incorporated into surfaces only through adsorption since the chemical concentrations of the radiocobalts are extremely small and will thus not result in deposition. For nickel, adsorption may not be the dominant mechanism since nickel concentrations in the RCS [36] are often significantly in excess of the calculated solubility [37]. (Note that new calculations of nickel solubility confirm that under conditions in which nickel metal is stable, nickel solubility is on the order of 60 ppt and that when nickel oxide is stable nickel solubility is on the order of 200 ppt or less [38, 39].)

Given the extremely low solubility of nickel relative to cobalt and zinc, it would appear unlikely that zinc can displace nickel from RCS surfaces. That is, the mechanisms by which nickel and zinc are bound to system surfaces are expected to be very different. Nickel is expected to be in the solid phase, fully incorporated into a deposit or oxide film. Zinc is expected to deposit as an adsorbed film (which may, with time, be incorporated into a growing oxide or deposit layer).

In contrast to nickel, cobalt is not expected to exist in the RCS at concentrations that challenge its solubility. Therefore, cobalt on surfaces is most likely adsorbed (with incorporation into the solid phase occurring as oxides continue to grow or new deposits form on top of the adsorbed species).

The difference in deposition mechanisms makes it likely that nickel and radiocobalts will respond differently to zinc injection, with the most plausible result being a cobalt release but no nickel response.

3.7.5 Quantification of Adsorbed Nickel and Cobalt

Reference [34] gives the following relationship between the extent to which adsorption sites are filled (*x*) and the concentration (*C*):

$$C = \frac{\left(\frac{x}{2}\right)^2 \left[H_2O\right]\left[H^+\right]}{\left(1-x\right)^2 k_{ads}} MW \qquad \textbf{Eq. 3-3}$$

where k_{ads} is a function of the adsorbing species and the temperature, and *MW* is the molecular weight of adsorbing species.

The methodology of Reference [34] was used to determine k_{ads} at different temperatures for nickel, cobalt, and zinc. As inputs, the values of k_{ads} at 234°C for these species on hematite were taken from Reference [40], and the values of the solubility products were taken from Reference [41] for zinc and nickel and from Reference [42] for cobalt. The results are given in Table 3-86.

Table 3-86
Adsorption Coefficients for Nickel, Cobalt, and Zinc

Metal	Adsorption Coefficient (mol/kg)		
	234°C	300°C	343°C
Ni	0.00025	0.025	2.89
Co	0.0032	0.62	406.5
Zn	0.0025	0.81	611

From the adsorption coefficients given in Table 3-86, curves relating the liquid phase concentration to the extent of adsorption were calculated using Equation [3-3]. The results are given in Figure 3-70, Figure 3-71, and Figure 3-72. Note that the fraction of occupied adsorption sites is directly proportional to the adsorbed mass. The range of concentrations shown in Figure 3-70 was chosen to demonstrate trends. The range in Figure 3-71 and Figure 3-72 is somewhat more realistic with respect to actual concentrations in PWR primary coolant.

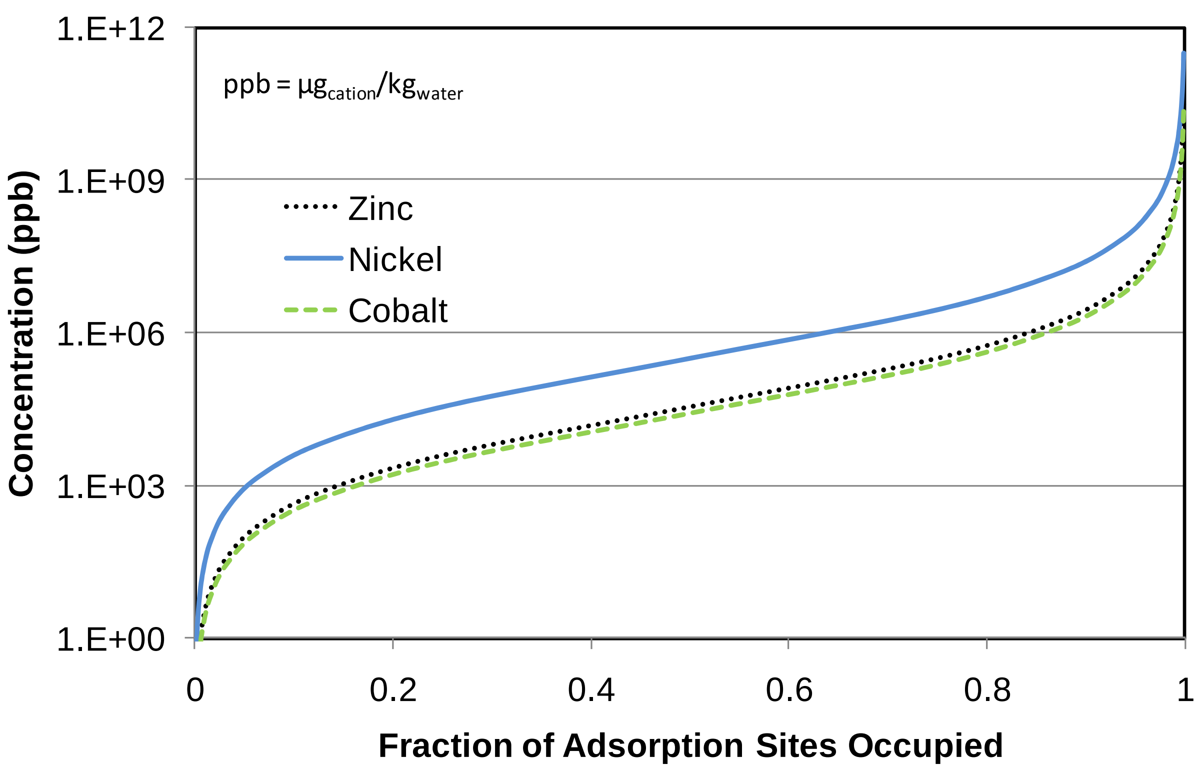

Figure 3-70
Adsorption Equilibria for Nickel, Cobalt, and Zinc at 234°C (pH_T~7)

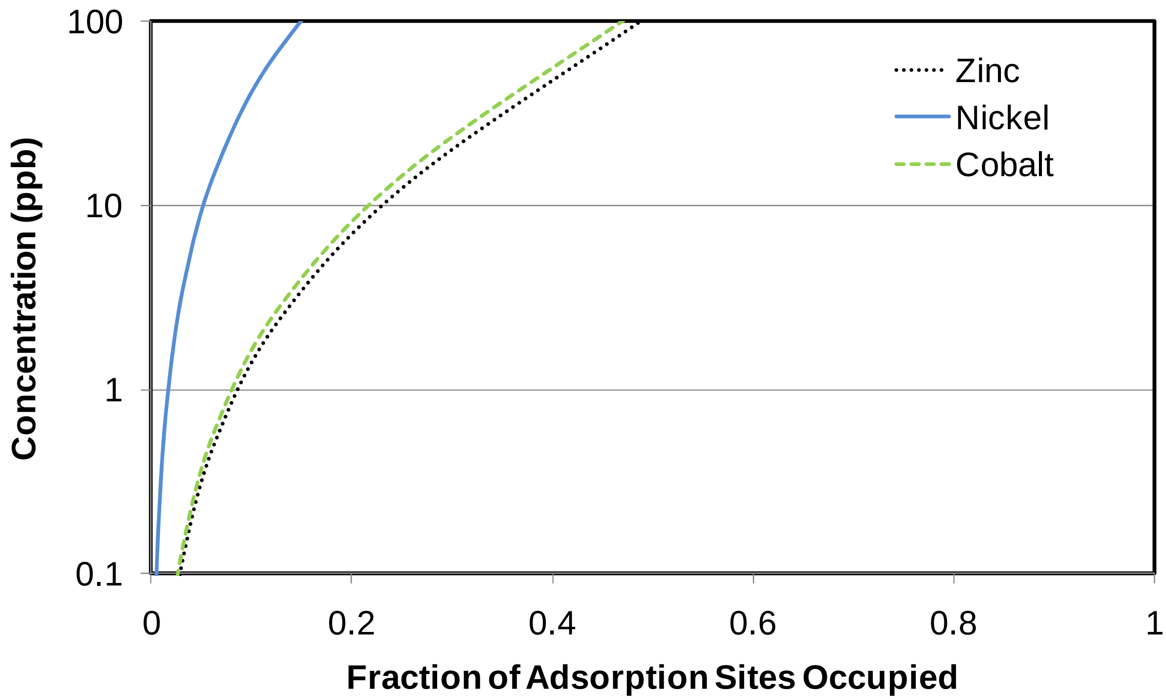

Figure 3-71
Adsorption Equilibria for Nickel, Cobalt, and Zinc at 300°C (pH_T~7)

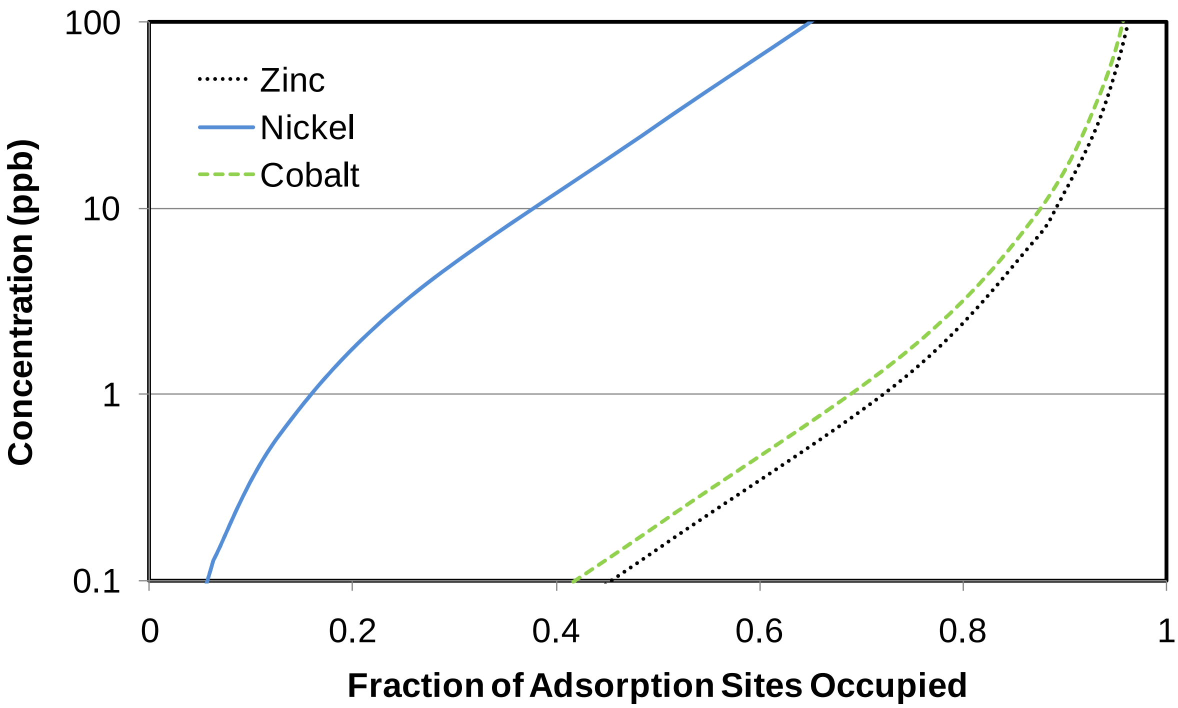

Figure 3-72
Adsorption Equilibria for Nickel, Cobalt, and Zinc at 343°C (pH_T~7)

Note that for significant masses of nickel or cobalt to be adsorbed, high liquid concentrations are ostensibly required. However, significant masses of zinc could adsorb at concentrations that are typical of zinc application concentration targets (e.g., around 10 ppb).[2]

Reference [34] provides estimates for the surface areas in a typical PWR as well as adsorption site densities. From these estimates, the maximum adsorption capacities for nickel, cobalt, and zinc were calculated. The results of this calculation are shown in Table 3-87. Using these capacities, prototypical primary coolant concentrations, and Equation [3-3], the adsorbed mass of each cation was calculated. The concentration estimates were made as follows:

- Nickel was assumed to be present at 100 ppt. This is considered a reasonable upper bound on the solubility of nickel metal under primary side conditions when unit-to-unit differences in temperatures and hydrogen concentrations are taken into account [38].
- The cobalt concentration was assumed to be 10 ppt.
- The zinc concentration was taken as 10 ppb, based on typical zinc injection programs.

The results of these calculations are shown in Table 3-88. Note that at a zinc concentration of 10 ppb, most sites (at 343°C) are expected to be filled by zinc, indicating that there is a high likelihood that zinc addition will displace other adsorbed cations. However, due to lower concentrations and lower tendencies to adsorb, the masses of nickel and cobalt desorbed will be about an order of magnitude less than the masses of zinc adsorbed.

[2] Although unrelated to this discussion, this observation provides an explanation for the different distribution of zinc deposits versus non-zinc deposits. It has been observed [2] that after cycles with zinc addition, fuel deposits cover a larger portion of the fuel, are generally darker, and can even deposit on non-heat transfer surfaces (for example fuel assembly grids and nozzles). These phenomena can all be explained by the difference in deposition mechanisms between zinc and nickel. Because of its low solubility, nickel never reaches the concentrations required for significant adsorption, and deposition takes place by particulate deposition in the boiling regions. Zinc, which has a high solubility and is present at concentrations resulting in significant adsorption, is deposited by chemisorption, which does not require boiling or heat flux.

Table 3-87
Adsorption Capacity of a Typical RCS

Metal	Adsorption Capacity		
	mg/m^2	Core (g)	SGs (g)
Ni	0.11	0.61	2.24
Co	0.11	0.61	2.25
Zn	0.12	0.68	2.50

Note that unrealistically high concentrations are required to achieve these masses.

Table 3-88
Adsorbed Masses at Prototypical RCS Concentrations (343°C)

Metal	Assumed Concentration (ppb)	Fraction of Adsorption Sites	Adsorbed Mass (g)
Ni	0.1	0.056	0.16
Co	0.01	0.182	0.52
Zn	10	0.891	2.83

The desorbed mass of nickel (0.16 g) would correspond to a change of about 0.6 ppb if it were instantaneously released to the coolant. If instead, it were estimated that the release took place over the course of a week as zinc gradually replaced the nickel, the maximum increase would be on the order of 0.1 ppb, assuming a cleanup time (RCS volume divided by the letdown flowrate) of 24 hours. Note that under these assumptions the coolant nickel concentration would begin to return to its original values after the release was complete, i.e., after seven days. As this simple calculation indicates, since there is a fixed mass of nickel available for desorption, the larger changes in RCS concentration are associated with a shorter burst and less time during which the elevated concentrations are experienced.

These model calculations lead to the following important conclusions:

- The behavior of nickel and radiocobalt upon initial zinc injection are likely to be different, due to different solubilities and concentrations in the reactor coolant.
- The mass of nickel that could be displaced by zinc may be very small and would be unlikely to cause measurable increases in the coolant nickel concentration.

3.8 Conclusions

The following conclusions are supported by the data analyses discussed in this chapter:

- There is strong evidence that at some units there is an increase in primary coolant radiocobalt activity upon initiation of zinc injection, and there are some units for which the data clearly indicate that there has been no response.
- There were no units for which a definitive increase in coolant nickel concentration was observed upon initial zinc injection. However, there were numerous units evaluated for which a determination could not be made.
- For some units (with Alloy 800NG steam generator tubes) there was a short-term increase in iron concentrations upon initial zinc injection.
- There is no evidence of increased nickel release during shutdown chemistry maneuvers following the initial injection of zinc.

These results are far from definitive due to the known significant problems with obtaining representative PWR reactor coolant system samples.[2, 7] These problems may be somewhat less for radiocobalts (activity measurements) than for iron and nickel (concentration measurements). However, there is also some theoretical evidence that the nickel and radiocobalt responses may actually be different. Specifically, a priori considerations predict a radiocobalt response but not a nickel response, primarily due to the low solubility of nickel relative to its concentration in the primary coolant.

Other factors were evaluated to determine if plant-specific conditions could be used to predict whether or not there would be a cobalt response. The following conclusions were reached in this evaluation:

- There was no correlation between the time required before zinc was first detected and whether or not there was a radiocobalt response.
- There was no correlation between the tubing material and whether or not there was a cobalt response.
- There was no correlation between the hot leg temperature and whether or not there was a radiocobalt response.
- There was no correlation between the number of steam generators and whether or not there was a radiocobalt response.

While it is appropriate, given the data available, to conclude that there may be, depending upon plant-specific conditions, radiocobalt and iron responses but that there is probably not a nickel response, the collection of additional data would be beneficial. Specifically, determination of the best nickel measurement methodologies and their implementation at numerous plants would greatly increase the confidence in the conclusions drawn above.

4
EFFECTS OF SYSTEM CONFIGURATION AND PARAMETERS

4.1 Introduction

Each PWR unit is unique, and it is to be expected that each unit will have a unique response to zinc injection. This chapter discusses several system configuration and parameter differences that might be expected to affect the response to zinc. Despite the differences between units, it is possible to make reasonable predictions regarding plant responses based on a theoretical understanding of how and why units respond in different ways. Major conclusions from these analyses are summarized in Section 4.7.

4.2 Effect of Boiling Duty

4.2.1 Background Regarding Boiling Duty

In a PWR, the reactor coolant system pressure is maintained by a steam bubble in the pressurizer, which operates at saturation and is the highest fluid temperature in the system. In many modern day core designs, some fuel cladding surface temperatures slightly exceed saturation and produce local subcooled nucleate boiling (SNB). However, the fluid in the core is always subcooled, even at the exit of the highest powered channels. Historically, a significant concern regarding boiling in the core is the accelerated deposition of corrosion products, which has the potential to increase the risk of accelerated corrosion of the clad and to increased deposition of boron (leading to AOA/CIPS). There are similar concerns regarding the deposition of zinc.

The rate of steam production (boiling rate) in the core is highly plant specific and may vary from cycle to cycle as core designs are changed. The boiling rate also changes with time as the cycle progresses. A significant complication is that the boiling rate is not typically measured, but must be calculated, for example using EPRI's Boron-Induced Offset Anomaly Risk Assessment Tool (BOA).[4]

Because core boiling rates vary from unit to unit and cycle to cycle, a *typical* value cannot be given. Figure 4-1 shows example values for four different cycles at a Westinghouse 4-loop unit. An alternative example would be a unit which had no SNB, i.e., in which the core boiling was zero for the entire cycle.

While the solubility of zinc in primary coolant is relatively high (on the order of 200-250 ppb versus upper-bound application concentrations, which are not intended to exceed 50 ppb), the solubility in steam is relatively low (on the order of 1 ppb at 350°C) [35]. Therefore, the zinc present in the liquid coolant cannot enter the steam phase when boiling occurs. Various hypotheses regarding the mode by which zinc is removed are discussed in Section 4.2.2. A summary of the conclusions reached regarding the effect of boiling duty on plant responses to zinc injection are discussed in Section 4.2.3.

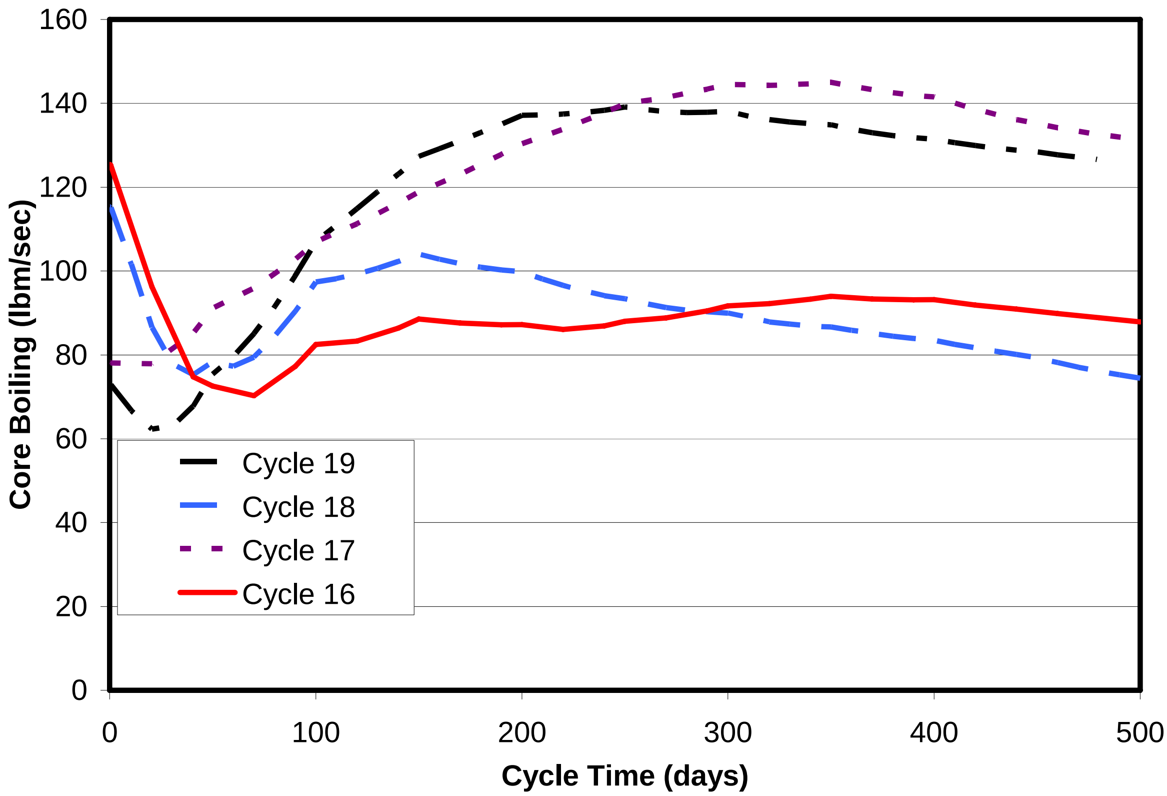

Figure 4-1
Total Core Boiling as a Function of Time for Four Cycles at a Westinghouse 4-Loop Unit

4.2.2 Modeling of Boiling

In this section, the following hypotheses regarding the removal of zinc from the boiled water are explored:

- Deposition on the fuel cladding
- Precipitation in the bulk water
- Diffusion away from the surface

As discussed in Section 4.2.1, the steam may contain up to 1 ppb zinc. In PWRs where zinc is added at concentrations below 5 ppb, evaporation may account for a significant, but substantially incomplete, fraction of the zinc present in the boiled water. Therefore, steam phase zinc is not considered further. Nonetheless, it should be noted that this implies that if the zinc concentration is maintained below 1 ppb boiling duty will have no effect on deposition of zinc on the fuel. That is, although broader concentration ranges can be justified by reasonable assumptions regarding boiling duty and deposit thickness, a zinc concentration of 1 ppb should not result in deposition as long as the pressurizer maintains 2250 psi (i.e., as long as the temperature of boiling surfaces is 343°C).

4.2.2.1 Deposition on the Cladding

One testable hypothesis regarding the effect of boiling duty on zinc deposition is to assume that all of the zinc in the boiled water deposits on the heated surface. As shown in Figure 4-1, boiling rates in PWR cores can be on the order of 100 lb/s or about 50 kg/s. Assuming a RCS concentration of 4 ppb (which is less than most concentration targets), this boiling rate can be used to calculate a total zinc deposition rate as follows:

$$R_{boiling} = \left(50\ \frac{kg_{water}}{s}\right)\left(4 \text{ x } 10^{-9}\ \frac{kg_{zinc}}{kg_{water}}\right)\left(\frac{1000\ g}{kg}\right)\left(\frac{3600\ s}{hr}\right)\left(\frac{24\ hr}{day}\right) = 17\ \frac{g}{day} \qquad \textbf{Eq. 4-1}$$

This deposition rate, based on the assumption that all of the zinc present in the boiled water deposits, significantly exceeds the typical rates inferred from plant data, which are on the order of 1-5 g/day [34]. This implies that deposition due to boiling is not adequately modeled by assuming that all the zinc in the boiled water deposits.

4.2.2.2 Precipitation in the Bulk Water

For relatively clean surfaces, bubble formation is thought to occur at nucleation sites. As the initial vapor phase grows in size, it forms a bubble, which eventually detaches, leaving a vapor phase nucleus behind to grow into a new bubble. This process is shown schematically in Figure 4-2. Note that when bubbles grow by this process, evaporation (boiling) is occurring at the bubble/bulk interface, such that any high concentrations of dissolved species are created in the bulk fluid. Therefore, boiling occurring on clean surfaces is expected to deposit very little zinc on the fuel surface. Zinc precipitated in the bulk would be quickly redissolved, since concentrations would only approach saturation at the bubble interface, and as discussed in Section 3.7.4, the bulk concentration is well below the solubility limit.

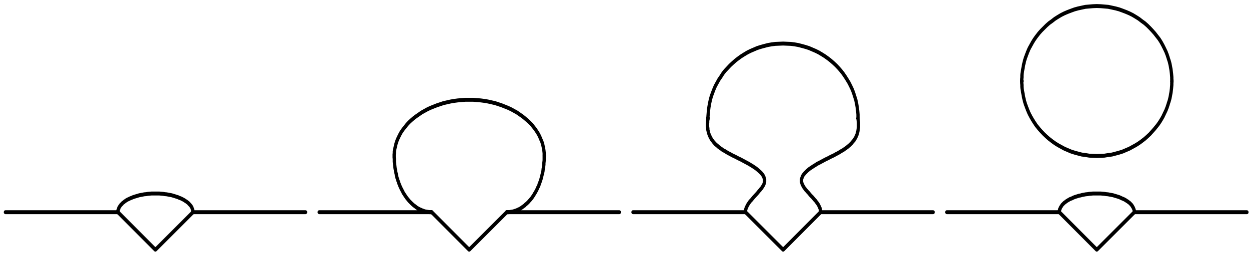

Figure 4-2
Bubble Formation on a Clean Surface

In some cases of clean-surface boiling, it is possible for a liquid film to form between the surface and the growing bubble (i.e., at the vertex where the bubble grows along the surface). This can result in high concentrations of impurities trapped between the steam phase in the bubble and the hot surface. This mechanism could lead to deposition in rings around nucleation sites.

4.2.2.3 Diffusion away from the Surface

An alternative model of boiling that is likely to be more relevant at PWR fuel cladding surfaces is wick boiling in which a porous deposit results in small channels bringing liquid nearer the hot surface and large channels, referred to as chimneys, allowing steam to escape. A schematic of the deposit structure associated with this model is shown in Figure 4-3. In this model of boiling, zinc can escape deposition only if the diffusional flux away from the surface is greater than the convective flux toward the surface.

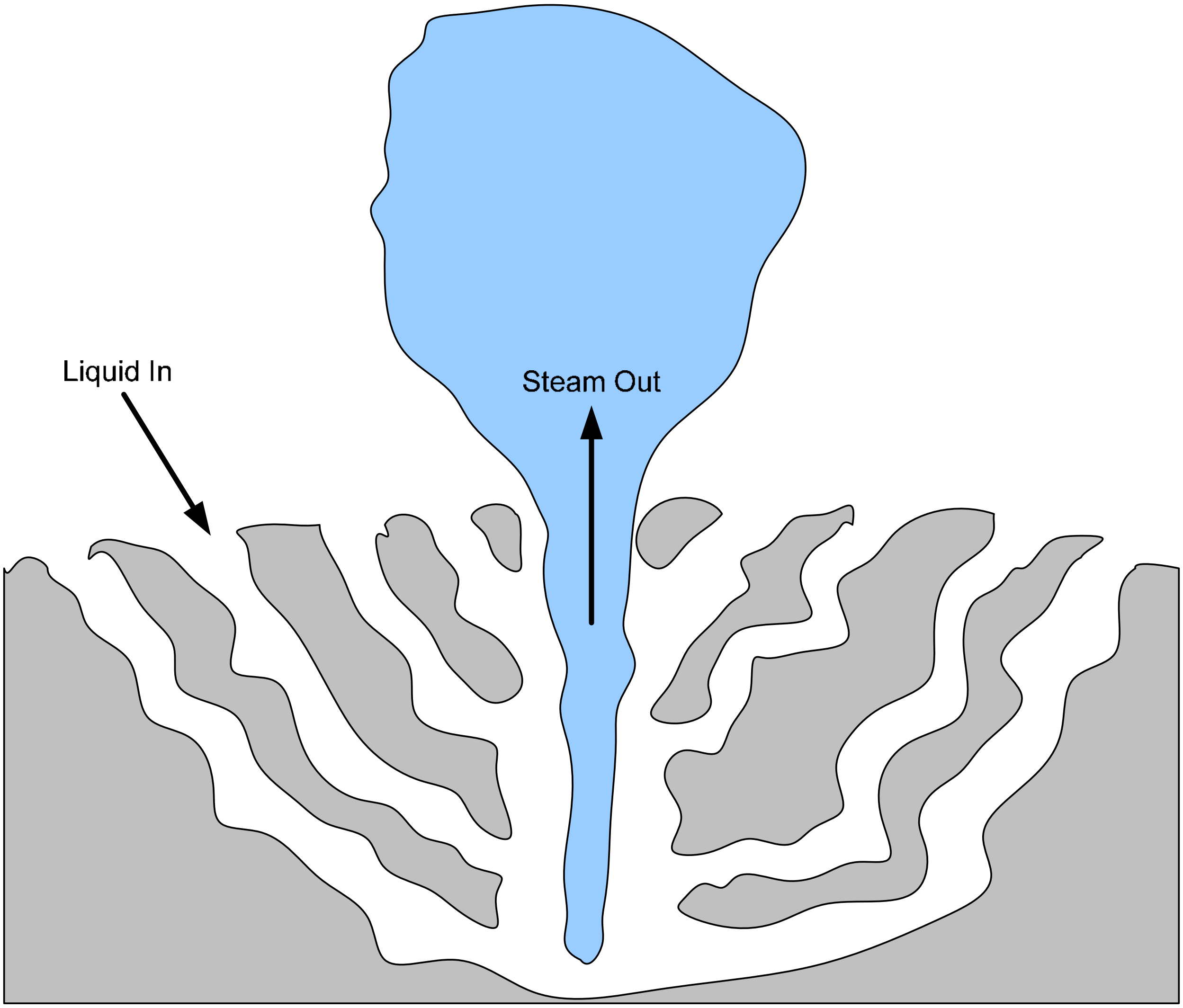

Figure 4-3
Bubble Formation on a Fouled Surface

The diffusional flux can be estimated as follows:

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

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

$$= 2.5 \text{ x } 10^{-5}\,\frac{g}{m^2 s}$$

The concentration at the fuel surface is taken as 250 ppb, the approximate solubility of zinc under these conditions [2]. The thickness of the deposit layer is taken as 100 μm, a high but reasonable value for deposits derived from crud scrapes of relatively high duty cores that will provide a reasonable lower bound estimate on the diffusion rate [43]. The density of water can be found in many references, such as Reference [44].

The diffusion of zinc in water is characterized by the diffusion coefficient, $D_{Zn\text{-}H2O}$. The diffusion coefficient of zinc ions in water at 25°C is 0.72 x 10^{-5} cm^2/s [45]. For temperatures other than 25°C, the Stokes-Einstein relationship [44] is used to adjust this value, according to the following equation:

$$D_{Zn-H_2O}\left(343°C\right) = D_{Zn-H_2O}\left(25°C\right)\frac{T}{298.15}\frac{\mu_{25°C}}{\mu_{343°C}}$$

$$= \left(0.72 \text{ x} 10^{-5}\,\frac{cm^2}{s}\right)\left(\frac{616.15\,K}{298.15\,K}\right)\left(\frac{9.18 \text{ x } 10^{-4}\,\dfrac{kg}{m-s}}{8.34 \text{ x } 10^{-5}\,\dfrac{kg}{m-s}}\right) \qquad \textbf{Eq. 4-3}$$

$$= 1.64\, x\, 10^{-8}\,\frac{m^2}{s}$$

where T is the absolute temperature and μ is the at-temperature viscosity (per Reference [44]).

The convective flux may be approximated as follows:

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

$$= 6.8 \text{ x } 10^{-6}\,\frac{g}{m^2 s} \qquad \textbf{Eq. 4-4}$$

where 500 lb/ft^2hr was selected as a high but reasonable value [2] for a core with significant boiling for the local boiling rate, $\dot{m}_e$. This value will provide a reasonable upper bound estimate of the convective flux.

Comparing Equation [4-2] and Equation [4-4] shows that the diffusional flux is nearly four-times the convective flux, indicating that the concentration will not reach the postulated value of 250 ppb.

The calculations shown in Equation [4-2] and Equation [4-4] can be combined to derive a relationship between the local boiling rate and the bulk concentration required to precipitate zinc oxide. Specifically, equating the two fluxes defines the point of incipient precipitation. The combined equation can then be rearranged to find either the bulk concentration for a given boiling rate or the boiling rate for a given concentration, as shown in the following equations, respectively:

$$\dot{m}_e \geq \frac{D\left(C_{sat} - C_{RCS}\right)\rho_{water}}{\delta_{deposit\ thickness} C_{RCS}} \quad for\ \ precipitation \qquad \textbf{Eq. 4-5}$$

$$C_{RCS} \geq \frac{\dfrac{D C_{sat} \rho_{water}}{\delta_{deposit\ thickness}}}{\dot{m}_e + \dfrac{D\rho_{water}}{\delta_{deposit\ thickness}}} \quad for\ \ precipitation \qquad \textbf{Eq. 4-6}$$

It is possible to validate the analyses given above by comparison to laboratory data generated in a Westinghouse study performed for EPRI. Reference [46] describes a heated rod test in which zinc solutions were boiled in the pores of a deposit on a heated rod. The relevant test parameters are as follows:

- $\delta_{deposit\ thickness}$ = 50-75 μm (taken as 60 μm)
- $\dot{m}_e$ = 460 lb/ft^{2}hr
- T = 625°F (329°C)

At this temperature, Equation [4-3] yields a diffusion coefficient of 1.55 x 10^{-8} m^2/s. The density of water is 656 kg/m^3 [44]. Substituting these values into Equation [4-6] yields the following:

$$C_{RCS} \geq \frac{\dfrac{\left(1.55 \text{ x } 10^{-8}\ \dfrac{m^2}{s}\right)\left(250 \text{ x } 10^{-9}\ \dfrac{kg_{zinc}}{kg_{water}}\right)\left(656\ \dfrac{kg_{water}}{m^3}\right)}{\left(60 \text{ x } 10^{-6}\ m\right)}}{\left(460\ \dfrac{lb_{water}}{ft^2 hr}\right)\left(\dfrac{0.454\ kg_{water}}{lb_{water}}\right)\left(\dfrac{ft}{0.3048\ m}\right)^2\left(\dfrac{hr}{3600\ s}\right) + \dfrac{\left(1.55 \text{ x } 10^{-8}\ \dfrac{m^2}{s}\right)\left(656\ \dfrac{kg_{water}}{m^3}\right)}{\left(60 \text{ x } 10^{-6}\ m\right)}} \qquad \textbf{Eq. 4-7}$$

$$\geq 53 \text{ x } 10^{-9}\ \frac{kg_{zinc}}{kg_{water}} = 53\ ppb$$

This evaluation indicates that, for the conditions tested by Westinghouse [46], a bulk concentration of 53 ppb is necessary to precipitate zinc. The actual tests under these conditions resulted in precipitation at 60 ppb and no precipitation at 40 ppb, in agreement with the predicted results.

Another test series [47] provides additional confirmation of this model, although the conditions tested provide a less rigorous test of the model. Tests with SNB at the Halden Reactor demonstrated deposition of zinc when the concentration was about 130 ppb, but no deposition at a concentration of 40 ppb. The boiling rate during these tests was approximately 200 lb/ft^{2}hr (based on the void fractions reported in Reference [47]). These points are also shown in Figure 4-4.

Note that in this regard the behavior of nickel, which is known to deposit heavily in boiling regions of PWR cores, is expected to be substantially different from that of zinc. Specifically, the solubility of nickel under primary chemistry conditions is thought to be on the order of 0.05 ppb [37]. The ~4 orders of magnitude higher solubility of zinc allows concentrations to form in the deposit layer which are sufficient to drive significant diffusion fluxes countering the convective flux due to boiling. Concentration gradients of this size are not possible with nickel because of its low solubility. The behavior of iron is somewhat intermediate, with solubilities from nickel ferrite on the order of 5 ppb [48].

A more detailed model of wick boiling has been developed by Cohen [49], and is discussed in detail in Reference [50]. Note that other models in addition to the Cohen model are also discussed in Reference [50]. The Cohen model is expressed as follows:

$$C_{RCS} \geq C_{sat} e^{-\left\{ Pe_{\delta} \left[(1-\xi) - \frac{\sinh\left[Bi_m (1-\xi) \right]}{Bi_m \cosh(Bi_m)} \right] \right\}} \quad for\ precipitation \qquad \textbf{Eq. 4-8}$$

where:

- ξ is the normalized axial coordinate along a boiling chimney
- Pe_{δ} is the Peclet number based on layer thickness
- Bi_m is the modified Biot number

The above parameters are defined as follows:

$$\xi = \frac{z}{\delta_{deposit\ thickness}} \qquad \textbf{Eq. 4-9}$$

$$Pe_{\delta} = \frac{\delta_{deposit\ thickness} U_{\ell}}{D} \qquad \textbf{Eq. 4-10}$$

$$Bi_m = \delta_{deposit\ thickness} \sqrt{\frac{2\pi N_v}{f} \square \frac{h_e r_v}{k_m}} \qquad \textbf{Eq. 4-11}$$

where:

- z is the axial coordinate (distance from heating surface)
- U_L is the scaling velocity:

$$U_{\ell} = \frac{q_0^{''}}{f h_{fg} \rho_{\ell}}$$ **Eq. 4-12**

– where $q_0^{''}$ is the imposed heat flux at the heating surface, f is the fraction of heating surface not occupied by heating surface (calculated as the ratio of the surface excluding chimneys to the total surface), h_{fg} is the latent heat of vaporization of water, and ρ_L is the density of saturated liquid water

- D is the effective diffusion coefficient of solute in porous matrix (as suggested by Pan, Jones, and Machiels [51]):

$$D = \tau \varepsilon D_{\ell}$$ **Eq. 4-13**

– where τ is the tortuosity of the porous medium (outside the chimney), ε is the porosity of the porous medium (outside the chimney), and D_L is the molecular diffusivity of zinc in water

- N_v is the chimney population density
- h_e is the evaporative heat transfer coefficient at the chimney wall according to the Schrage model from kinetic theory [52], which is valid for small evaporation rates:

$$h_e = \left(\frac{2E}{2-E}\right)\left(\frac{M}{2\pi R}\right)^{1/2} \frac{h_{fg}^2}{T_{sat}^{3/2} v_{fg}}$$ **Eq. 4-14**

– where E is the evaporation coefficient constant (conservative value 0.04 [51]), M is the molecular mass of water, R is the universal gas constant, T_{sat} is the absolute saturation temperature at system pressure, and v_{fg} is the specific volume change upon vaporization

- r_v is the chimney radius
- k_m is the effective thermal conductivity of porous medium saturated with liquid water (may be calculated using Maxwell's formula or Bruggeman's equation)

$$\text{Bruggeman's Equation: } \left[\frac{k_m - k'}{k_{sk} - k'}\right] \square \left[\left|\frac{k_{sk}}{k_m}\right|\right]^{(1/3)} = 1 - \varepsilon$$ **Eq. 4-15**

– where k' is the thermal conductivity of saturated liquid water and k_{sk} is the skeletal thermal conductivity of the deposit (assumed to be the nominal value given in Reference [50] for magnetite)

Based on prototypical values of the input parameters, given in Table 4-1, a curve of boiling duty versus bulk zinc concentration can be developed to delineate conditions under which deposition will occur from those under which it would not be expected.

Table 4-1
Cohen Model Input Parameter Values

Parameter	Value	Unit
z	0	m
$\delta_{deposit\ thickness}$	6.00E-05	m
f	9.51E-01	-
h_{fg}	990000	J/kg
ρ_l	600.6	kg/m^3
τ	3	-
ε	0.6	-
D_l	1.55E-08	m^2/s
N_v	2.50E+09	m^{-2}
E	0.04	-
M	0.018015	kg/mol
R	8.3145	J/mol-K
h_{fg}	990000	J/kg
T_{sat}	343	°C
v_{fg}	0.008505	m^3/kg
r_v	2.50E-06	m
k'	0.4622	W/m-K
k_{sk}	1	W/m-K

Figure 4-4 shows this curve, which indicates a somewhat higher likelihood of precipitation than the model developed above, but appears also to be somewhat conservative relative to the available experimental data and most of the operational experience data.

4.2.3 Conclusions Regarding the Effects of Boiling Duty

In general, the concern over boiling deposition has been a major consideration in the use of zinc injection at high duty plants. However, as demonstrated in Section 4.2.2.3, deposition of zinc oxide by boiling is not expected to be relevant in most zinc applications (other possible precipitates are discussed below). The following equations give bulk concentration and local boiling duty requirements for boiling deposition:

$$\dot{m}_e \geq \frac{D\left(C_{sat} - C_{RCS}\right)\rho_{water}}{\delta_{deposit\ thickness} C_{RCS}} \quad for\ \ precipitation \qquad \textbf{Eq. 4-16}$$

$$C_{RCS} \geq \frac{\dfrac{DC_{sat}\rho_{water}}{\delta_{deposit\ thickness}}}{\dot{m}_e + \dfrac{D\rho_{water}}{\delta_{deposit\ thickness}}} \qquad for\ \ precipitation \qquad \textbf{Eq. 4-17}$$

Evaluation of available experimental data supports the validity of the models used to generate Equations [4-16] and [4-17]. This analysis suggests that the vulnerability to zinc deposition on fuel surfaces during a cycle should be assessed not just as a function of duty (steaming rate) but also as a function of concentration. Figure 4-4 shows a simplified plot of a sampling of US cycles with zinc giving the local boiling rate and the average zinc concentration (for the time during which a zinc residual was present) [2]. Equation [4-16] (or equivalently, Equation [4-17]) is also plotted in Figure 4-4. The results of the Westinghouse WALT loop tests [46] and the Halden reactor tests [47] are also shown and are consistent with the model predictions.

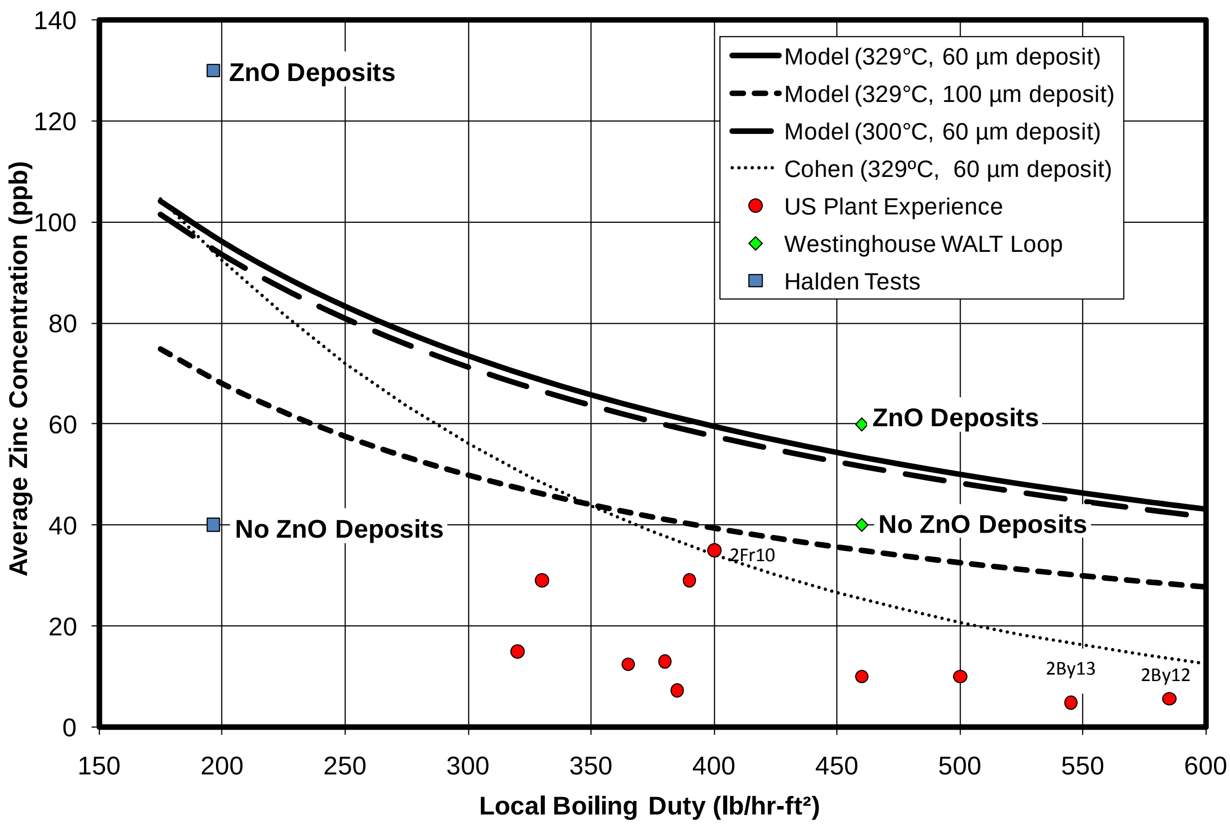

Figure 4-4
US Zinc Experience Relative to the Risk of Zinc Deposition by Boiling Precipitation

It should be noted that the presentation of data in Figure 4-4 is somewhat simplistic. For example, Equations [4-16] and [4-17] contain terms that are dependent on temperature (the density and viscosity of water). The model equation in Figure 4-4 is given at 329°C (for comparison to the Westinghouse WALT data), but temperature will vary from unit to unit. As indicated by the curve for 300°C in Figure 4-4, the temperature effect is not particularly large.

Another simplification in Figure 4-4 is the use of a single deposit thickness (again, the selected value, 60 µm, was chosen for comparison to the WALT data, which were generated on a surface with a 60 µm deposit layer, and to the Halden data, which were generated with a deposit thickness of about 65 µm). As can be seen from the 100 µm curve, reasonable variations in deposit thickness could have a significant effect on the thresholds for zinc deposition. (Note that this is the local deposit thickness in the region of peak boiling.) Eliminating this simplification would require analyses outside the scope of this project. Possible means of addressing this issue would be the inclusion of deposit thicknesses for individual cycles (either from crud scrapes or from deposition models, e.g., BOA [4]). It is also likely that there is a strong correlation between deposit thickness and boiling duty which would allow redrawing the model curve to implicitly incorporate a predicted thickness. This would likely result in a somewhat steeper slope.

One interesting observation from Figure 4-4 is that the Byron 2 cycles (2By12 and 2By13), which have been considered to bound most of the US fleet in terms of zinc injection programs, were actually at less risk of zinc deposition than the early Farley 2 cycle (2Fr10). While the incorporation of deposit thickness variations into the model is likely to reduce the apparent margin that existed during the Byron cycles, it is unlikely that the apparent margin would be eliminated by a more refined calculation.

Finally, a major assumption in the analysis given above is that zinc deposition occurs by precipitation of zinc oxide. In many fuel deposit analyses, zinc has been detected in fuel deposits, indicating that zinc does deposit in the core. Possible mechanisms could include precipitation of other zinc compounds (a likely candidate would be a zinc-substituted nickel ferrite) or adsorption (which would tend to more evenly distribute zinc through the core than a boiling deposition process).

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

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

4.3 Effect of Fuel Cleaning

Numerous utilities have implemented ultrasonic fuel cleaning (UFC) to remove corrosion deposits from fuel assemblies during refueling outages. At several units (about 15), both UFC and zinc injection have been used. This group includes a wide variety of implementation experiences including the following:

- Implementation of UFC before zinc (in some cases, immediately before the first zinc cycle so that the effects of zinc and UFC are not separable)
- Implementation of UFC after zinc
- Units with steam generator tubing made of Alloy 600, Alloy 690, and Alloy 800
- Units that had previously experienced AOA and units which had not

Because of this variety of conditions, it is not possible to draw conclusions with confidence to address whether units that implement UFC will respond differently to zinc based on plant experience (although, as noted in Section 3.7, none of the units which performed UFC experienced an increase in radiocobalts upon initiation of zinc injection). However, theoretical consideration of the phenomena involved provides some insight.

Addition of zinc is theorized to modify the oxide films formed on ex-core surfaces such that the films are more protective and there is a lower corrosion product release rate. This lower release rate results in a reduction in the accumulation of corrosion products in the core.

Typical PWR core designs use fuel assemblies for three (sometimes four) cycles. Approximately one third of the fuel assemblies in each core design are replaced at each refueling outage. The remaining two thirds are reloaded into the core for the next cycle. In the past, residual deposits on reload fuel are thought to have been a significant source of mobile corrosion products. Since the development of UFC, utilities have the option of removing a significant mass of these deposits before beginning a new cycle.

For example, UFC at Millstone 3 Refuel 12 removed approximately 1.2 kg of deposits from reload fuel [53]. Assuming that this mass was primarily nickel oxide, this is equivalent to about 0.9 kg of nickel. During the shutdown preceding fuel cleaning, approximately 2.8 kg of nickel were removed [54]. This implies that at least one third of the deposits on the fuel at the end of the cycle were carried forward from the previous cycle.

Figure 4-5 shows the distribution of nickel releases for units which have reported this data to EPRI's PWR CMA database [8] and in References [27, 28 , 29 , 30, 31, 55 , 56]. Very limited data (three units) indicates that the mass of nickel removed during UFC is about 20-40% of the mass removed during shutdown.

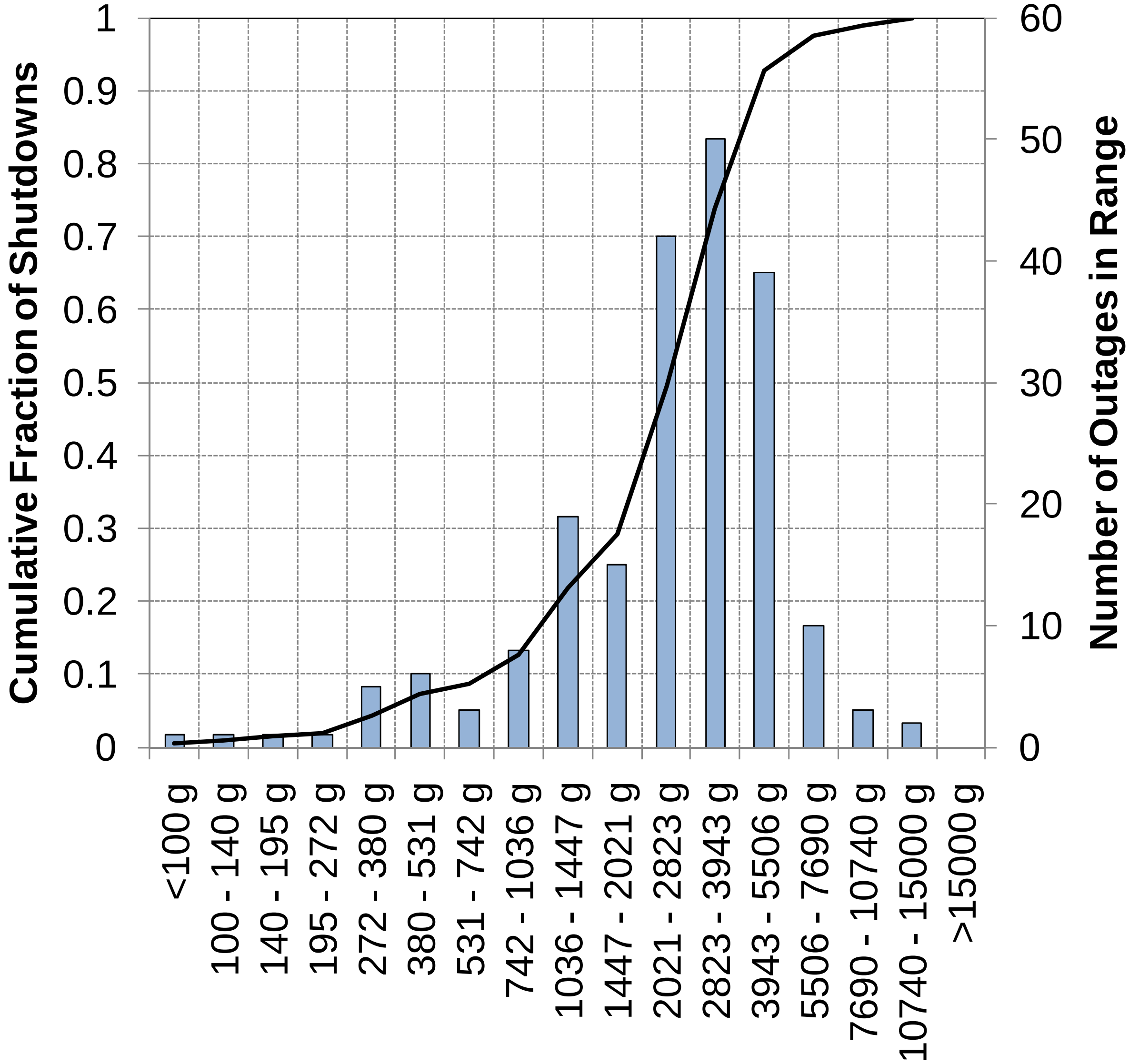

Figure 4-5
Total Nickel Release during End of Cycle Shutdown

The effects of zinc injection and UFC are therefore complementary. Zinc is thought to reduce the release of new corrosion products. UFC removes existing corrosion products. There appear to be no theoretical considerations which would imply an interaction other than an additive effect. That is, zinc injection and UFC are not likely to be substitutes for each other, nor are they likely to enhance each other.

4.4 Effect of Steam Generator Surface Area

4.4.1 Introduction

Zinc injection is performed in order to modify the oxides on ex-core surfaces to prevent corrosion product release and uptake of radiocobalts. Since this involves the uptake of zinc on ex-core surfaces, the area of those surfaces might be expected to affect the overall behavior of zinc in the primary system. Section 4.4.2 discusses some of the theoretical (i.e., model) predictions of the effect of steam generator surface area on zinc behavior. Section 4.4.3 reviews plant experience. Overall conclusions, based on models and experience, are discussed in Section 4.4.4.

4.4.2 Theoretical Considerations

As discussed in Reference [34] and Section 3.7.5, zinc is expected to become incorporated into primary system surfaces through a mechanism that begins with adsorption. The capacity of the surface to adsorb zinc is expected to be directly proportional to the surface area. Thus, for units with larger steam generator surface areas, a larger mass of zinc is expected to adsorb. However, the mass of zinc required to saturate a typical RCS system surface (including fuel and steam generator surfaces) is estimated to be on the order of 1-2 grams. This is much less than is fed to the system during the period (days to weeks) before zinc is detected (Figure 4-6 shows industry data on zinc feed rates). This implies that zinc must be removed from the system by some means other than adsorption.

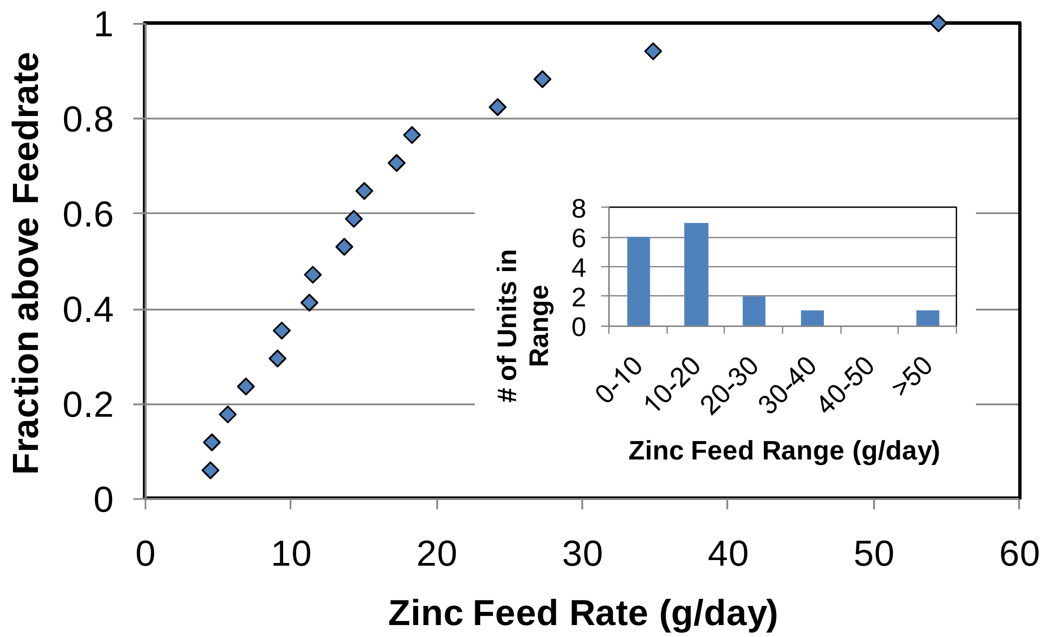

Figure 4-6
Zinc Feed Rates (Data from Reference [57])

After zinc is adsorbed onto system surfaces, it becomes incorporated into the growing oxide layer. Reference [58] gives data on zinc incorporation which was fitted to the following equation for the mass incorporated per area (m_{inc} in g/m^2):

$$m_{inc} = 0.0053\ln(t) - 0.0088 \qquad \textbf{Eq. 4-18}$$

where t is the time in days. For a typical time until zinc detection of 20 days (see Section 4.4.3 for a discussion of plant experience with time until zinc detection), Equation [4-18] would predict a loading of approximately 0.007 g/m^2. This corresponds to an average incorporation rate of approximately 9 g/day (for a prototypical system area of 25,000 m^2 for fuel and steam generators). This represents reasonable agreement with typical injection rates which are on the order of 10-20 g/day given the scatter in the original laboratory data (reproduced in Figure 4-7).

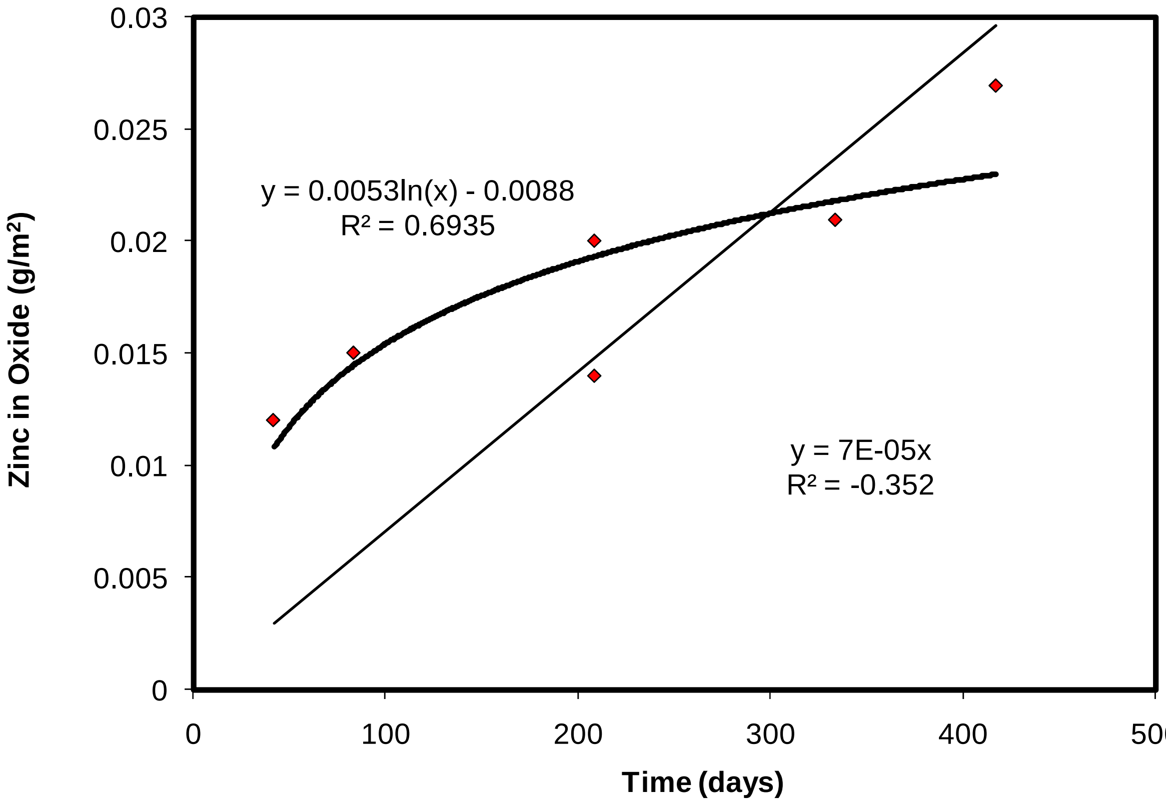

Figure 4-7
Incorporation of Zinc into Oxide Films on Alloy 600 (Data from Reference [58])

These modeling calculations indicate that it is reasonable to conclude that the detection of zinc is governed by the incorporation of zinc into oxide and deposit films, and not by the initial adsorption of zinc onto surfaces. This implies that the time until detection of zinc (i.e., the mass required to bring the solid phase concentrations into equilibrium with detectable liquid phase concentrations) is more likely to be a function of oxide and deposit mass than of system surface area.

4.4.3 Plant Experience

The EPRI Zinc Database was evaluated to determine if steam generator surface area (the total surface area of all the steam generators at a given unit) had an effect on the following parameters:

- Time until first zinc detection
- Fraction of added zinc retained in the system

The results of these analyses are discussed below.

4.4.3.1 Effect of SG Surface Area on Time to First Zinc Detection

The time between the start of injection and the first detection of zinc in the RCS is plotted against steam generator surface area (total for all steam generators) in Figure 4-8. In general, there is no correlation between the time to first detection and the steam generator surface area. This lack of a correlation would be expected if utilities take measures to compensate for differences in steam generator area when determining a zinc addition rate. However, as shown in Figure 4-9, there is, in general, no correlation between the mass rate of zinc injection and the steam generator surface area.

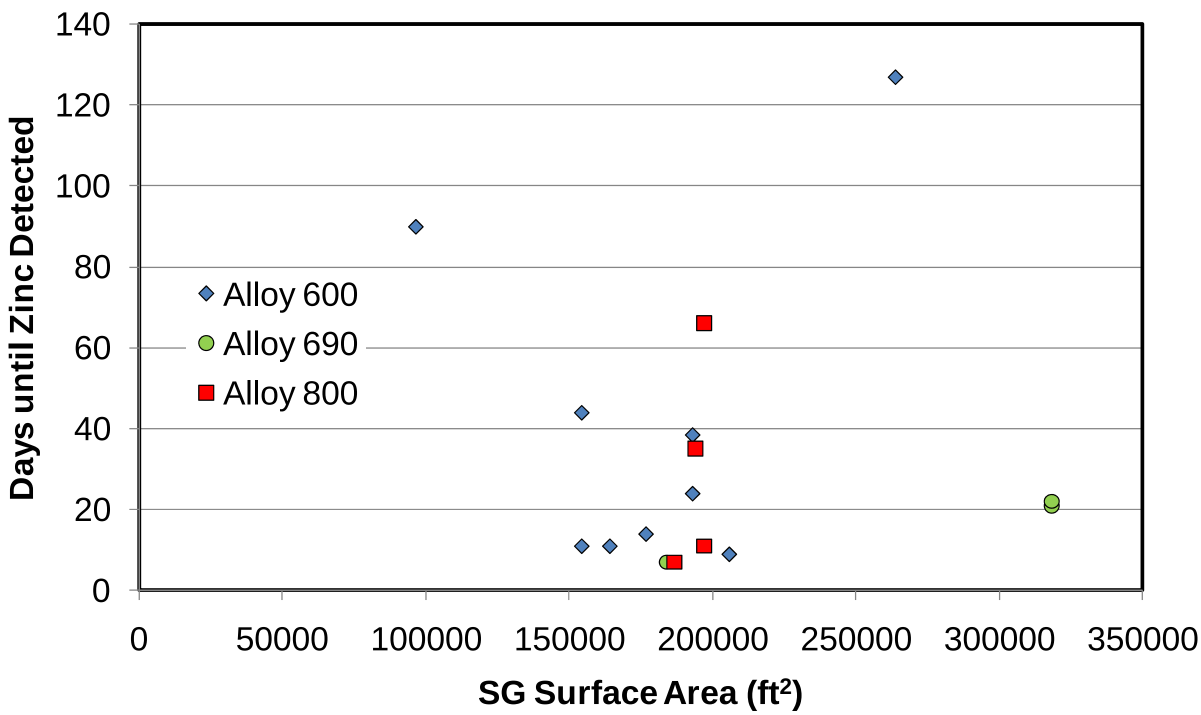

Figure 4-8
Time of First Zinc Detection versus Steam Generator Area

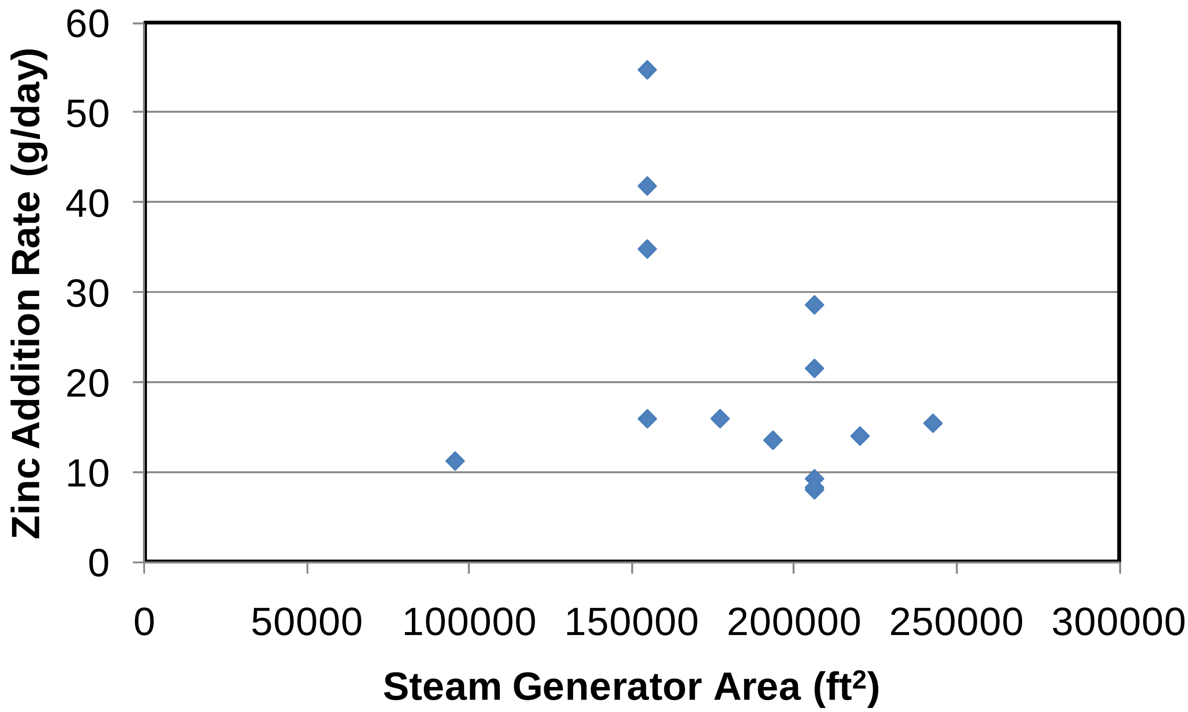

Figure 4-9
Zinc Addition Rate versus Steam Generator Area

A further indication that steam generator area is not a factor in the time to first zinc injection is that there is no correlation between the product of the zinc target concentration and the days to exposure (essentially the total mass of zinc accumulated before detection) and the steam generator area, as shown in Figure 4-10.

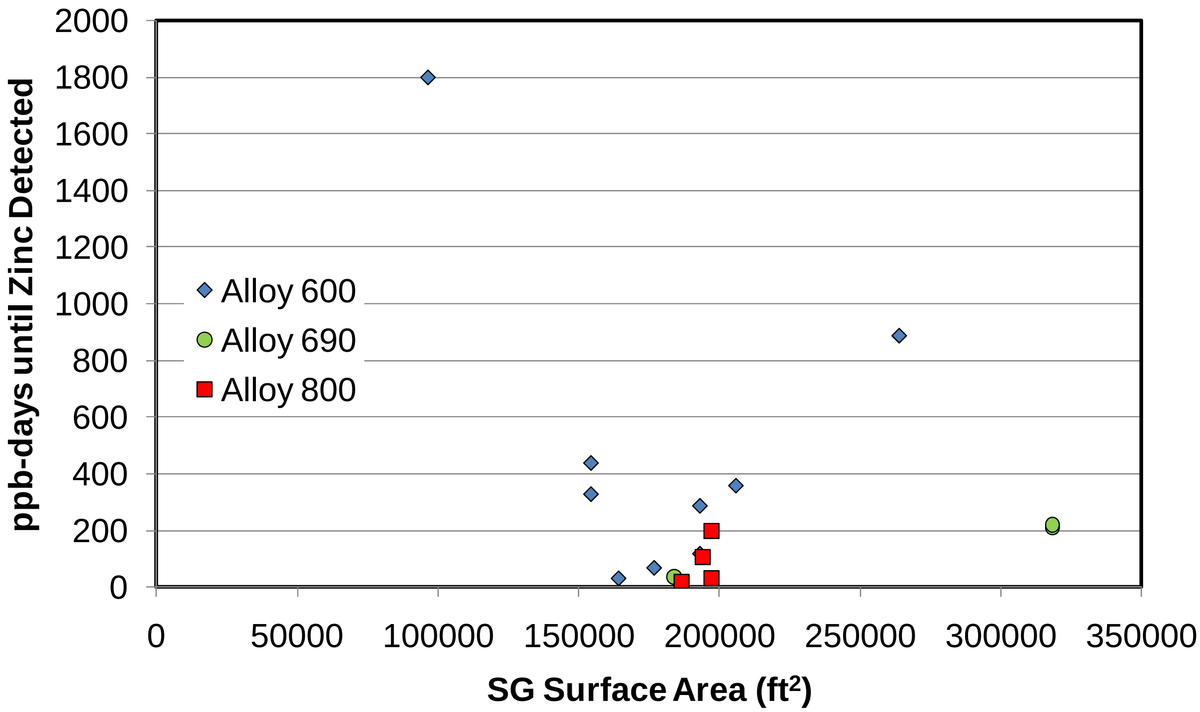

Figure 4-10
Zinc Exposure at First Zinc Detection versus Steam Generator Area

Note that these evaluations would be more useful if the actual mass injected were available. However, this data was not available at the time of this analysis.

4.4.3.2 Zinc Uptake during Operation

As discussed in Section 4.4.2, there is an expectation from laboratory testing that the uptake of zinc by system surfaces will be proportional to the surface area. To evaluate this hypothesis, the fraction of zinc that was retained in the system was evaluated against steam generator surface area. The fraction of zinc held is defined as follows:

$$x_{held} = \frac{m_{added} - m_{removed}}{m_{added}} \qquad \textbf{Eq. 4-1}$$

where m_{added} is the mass added and $m_{removed}$ is the mass removed (i.e., by letdown purification). The fraction of zinc held is plotted against steam generator area for a number of cycles at several units in Figure 4-11. As illustrated in this figure, there is no correlation between the fraction of zinc held in the primary system and the steam generator surface area.

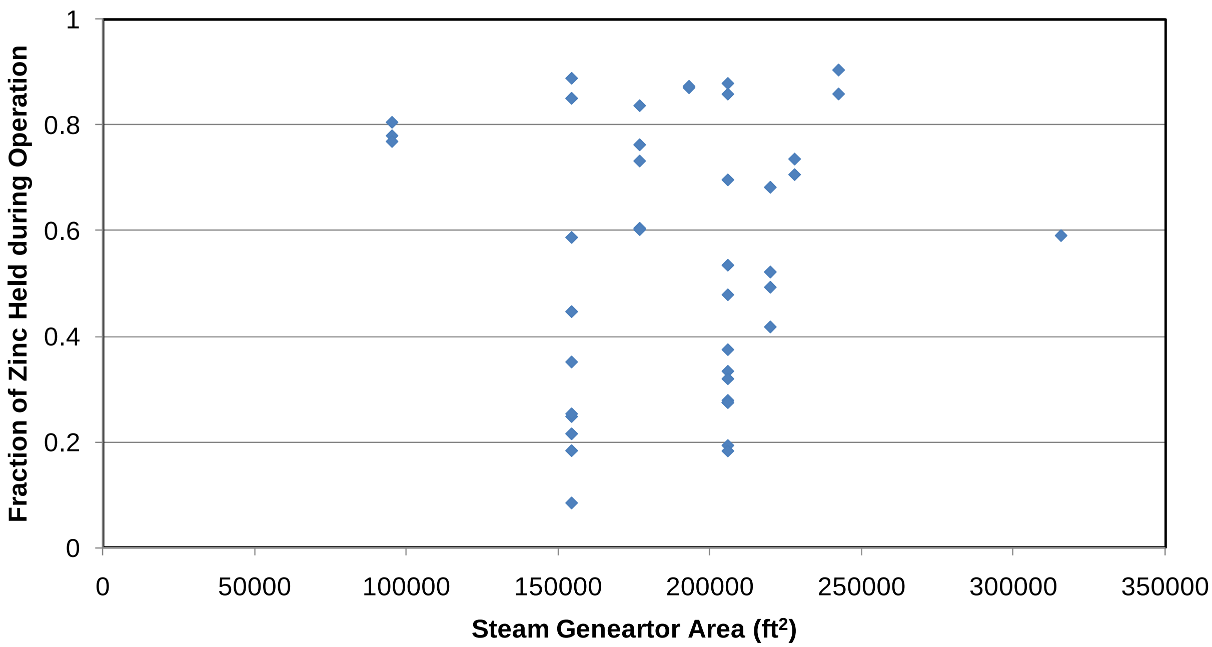

Figure 4-11
Fraction of Zinc Held during Operation (Data from Reference [57])

4.4.4 Conclusions Regarding Steam Generator Surface Area

Plant experience was evaluated to determine if there was an effect of steam generator surface area on the time to first zinc detection or the fraction of zinc retained in the system, two surrogate measurements of the uptake of zinc on system surfaces. There was no correlation evident from the data. The steam generators account for a majority of the primary system surface (on the order of 75% of the surface [34]). The absence of a correlation indicates that uptake is not solely a function of available surface area. For example, the condition of the surface prior to zinc injection (deposit loading, porosity, crystalline structure, etc.) is likely to be a factor in determining how much and at what rate zinc is taken up by the surface.

4.5 Effect of Fuel Surface Area

In general, fuel surface area does not vary significantly from unit to unit within relatively large groups of common design (for example, most Westinghouse four loop plants have the same nominal fuel surface area). Within these common design groups, there are significant differences in the response to zinc. At this time, no effect of fuel surface area is observable in the plant experience data base. Likewise, no effect is considered likely to be derivable from modeling.

4.6 Effect of Operating Temperature

Plant experience was assessed against the operating temperatures (T_{hot}) of the units in the EPRI Zinc Database. No correlation between operating temperature and the plant response to zinc was observable. In general, the temperature differences between units are small compared to the uncertainty in modeling predictions. Therefore, no effect is considered likely to be derivable from modeling without significant refinement (with additional experimental work) of the available models.

4.7 Conclusions

The following conclusions were reached regarding plant-specific factors:

- Core boiling duty: Operating experience indicates that plants have not had significant issues with zinc deposition due to boiling. Theoretical considerations, with limited experimental validation, indicate that both the zinc concentration and the boiling duty should be considered in assessing the risk of zinc deposition in the core. The operating cycle most at risk for zinc deposition was Farley 2 Cycle 10.
- Ultrasonic fuel cleaning: Operating experience with both zinc addition and ultrasonic fuel cleaning is too limited to draw conclusions due to differences in when the two measures were taken (i.e., zinc first, then UFC, UFC first then zinc, etc.). Theoretical considerations indicate that the two measures should be complimentary, but not necessarily synergistic. That is, the advantages are expected to be additive not multiplicative.
- Steam generator surface area: Operating experience provides no indication that steam generator area significantly affects the plant response to zinc.
- Fuel surface area: Differences in fuel surface area are relatively limited within groups of similar plant designs. Therefore, it is not likely to be possible to observe effects of fuel surface area.
- Operating temperature: Operating experience indicates no effect of operating temperature. In general, temperature differences between plants are small, and the effect of these differences, if any, would be expected to be smaller than differences arising from other sources.

5 PREDICTIONS OF RESPONSES TO PLANT TRANSIENTS

In general, it is desirable for plant chemists to understand the manner in which their plants will respond to zinc injection. Such an understanding allows for advanced preparation of other plant personnel for changes in observed plant behavior and for efficient responses to plant transients. In this chapter, the chemistry response to plant transients is discussed.

5.1 Introduction

In order to predict plant responses to transients, the following two approaches were used:

- Assessment of transients reported in the literature or available in the EPRI database
- Assessment of modeling considerations

The assessments using these approaches are discussed in Sections 5.2 and 5.2, respectively. Conclusions from these assessments, i.e., predictions and prediction methods, are discussed in Section 5.4.

5.2 Data Analysis

Responses to transients, primarily power transients or loss of zinc injection, were identified in a review of the literature (focusing mostly on papers presented at technical conferences and EPRI workshops) and in a review of the data in the EPRI Zinc Database. Individual cases are reviewed in the sections below. General conclusions regarding transients are discussed in Section 5.4.

5.2.1 Trend Evaluations

As a tool for assessing the effects of plant transients, a simple lumped parameter model of the RCS system was used. This model describes the change in concentration as a function of the rates at which zinc enters and leaves the system. The rate of zinc entering the system in the injection feed (m_{inj}) is calculated as follows:

$$m_{inj} = q_{inj} C_{inj} \quad \textbf{Eq. 5-1}$$

where q_{inj} is the injection flow rate and C_{inj} is the concentration of zinc in the injection solution.

The removal of zinc is assumed to occur through two mechanisms, letdown purification and uptake by the system. The removal by letdown purification ($m_{letdown}$) is calculated as follows:

$$m_{letdown} = q_{letdown} C_{RCS} \quad \textbf{Eq. 5-2}$$

where $q_{letdown}$ is the purification flow rate and C_{RCS} is the RCS zinc concentration. The removal by uptake by the system is modeled such that uptake is linearly correlated to the RCS concentration. This one-parameter model was chosen to capture essential features, but is essentially arbitrary. Other hypotheses were considered (for example, uptake depending on the rate of concentration change) but were rejected because the fit to the data was not improved by the added complexity. The uptake rate (m_{uptake}) is given as follows:

$$m_{uptake} = aC_{RCS} \quad \textbf{Eq. 5-3}$$

where a is an arbitrary constant. The RCS concentration which follows a change in plant conditions can be modeled as follows:

$$C_{RCS} = \left(\frac{m_{inj}}{q_{letdown} + a}\right) + \left(C_0 - \frac{m_{inj}}{q_{letdown} + a}\right) e^{-\left(\frac{q_{letdown} + a}{M}(t - t_0)\right)} \quad \textbf{Eq. 5-4}$$

where M is the RCS mass and C_0 is the concentration at time t_0, the start of the transient.

Note that at steady state (i.e., infinite t), Equation [5-4] can be used to calculate the uptake rate (aC). In the special case of no uptake (a is zero) and no addition (m_{inj} is zero) Equation [5-4] reduces to the theoretical cleanup curve for the RCS.

5.2.2 Bugey 2

Data from Cycle 23 of EDF's Bugey Unit 2 were presented in Reference [32]. Bugey Unit 2 is a load following plant which frequently reduces power. During load following maneuvers, the rate of zinc injection is adjusted [59]. A qualitative review of the available data does not indicate a relationship between the load following maneuvers and the reactor coolant zinc concentration. However, the zinc data may not be not frequent enough to capture a zinc transient response. EDF concluded from comparison of the zinc experience at Bugey and other industry data, that frequent power transients have reduced the extent to which zinc addition has mitigated radiation fields.

5.2.3 Farley 1

Data from Cycle 20 of Southern Nuclear's Farley Unit 1 were evaluated to investigate the effects of transients. Figure 5-1 shows the data available for the entire cycle. Two specific transients were evaluated: a power transient at around Day 260 and a change in letdown flow rate at around Day 332. These transients are discussed in the following paragraphs.

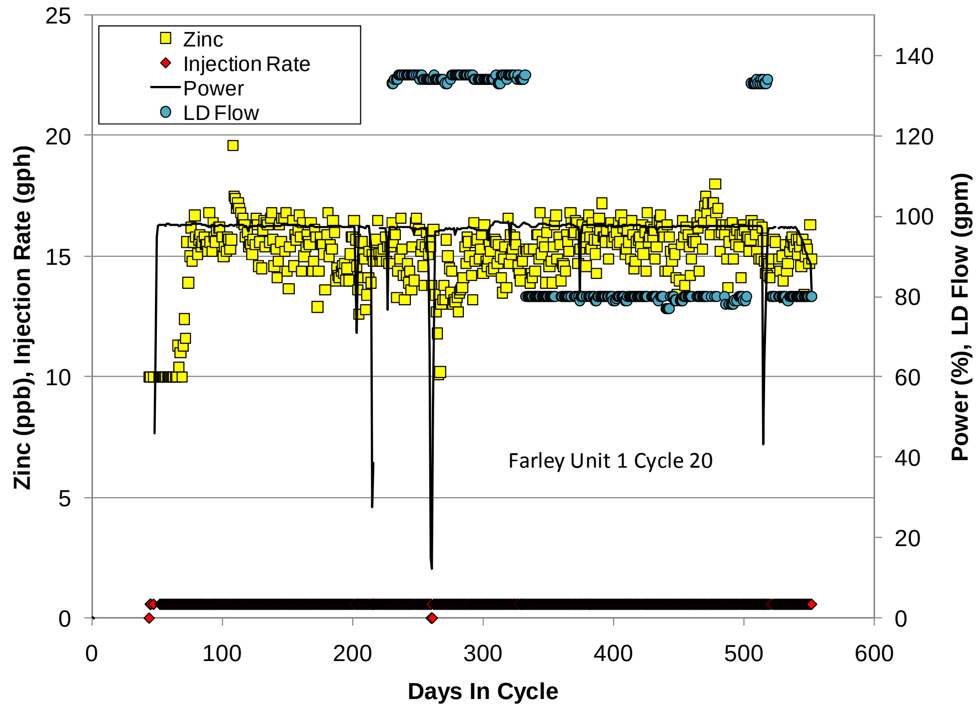

Figure 5-1
Farley Unit 1 Cycle 20: Complete Cycle Data

At about Day 257 of Cycle 20, Farley Unit 1 began to reduce power. After the power reduction, full power was restored on about Day 263. During this time the letdown flow rate was maintained at a nearly constant value of 134 gpm. Zinc injection was secured on Day 260 and returned to service in about a day. Although temperature data were not available, it is likely, given the short length of the downpower and the rapid return to full power, that system temperatures were not significantly reduced (except on the fuel surface, where cessation of boiling would be expected and the temperature probably dropped from the pressurizer temperature (343°C) to the hot leg temperature (305°C).

Zinc concentrations in the RCS appear to have been unaffected by this transient. As discussed in Reference [34] and summarized below in Section 5.3.1, a zinc response to the small temperature change caused by power reduction is not expected.

The total mass of zinc removed from the system during the period when zinc was suspended can be calculated as follows:

$$\begin{aligned} m_{removed} &= q_{letdown} C_{zinc} t \\ &= (134\ gpm)(15\ ppb)(2\ days)\left(\frac{3785\ g}{gal}\right)\left(\frac{10^{-9}}{ppb}\right)\left(\frac{1440\ \text{min}}{day}\right) \\ &= 22\ g \end{aligned} \qquad \textbf{Eq. 5-5}$$

A typical mass of zinc in the RCS coolant can be calculated per the following equation:

$$m_{RCS} = V_{RCS}\rho_{water}C_{zinc} = \left(265\ m^3\right)\left(700\frac{kg}{m^3}\right)\left(15\ ppb\right) = 2.8\ g \qquad \textbf{Eq. 5-6}$$

where V_{RCS} is the system volume (265 m^3 was taken as typical for a Westinghouse three-loop plant) and ρ_{water} is the density of water (approximated as 700 kg/m^3). Comparison of the results of Equation [5-5] with Equation [5-6] indicates that during this suspension of zinc injection, letdown purification would have been sufficient to remove essentially all of the zinc in the RCS coolant. Figure 5-3 shows the plant data at the time of zinc injection suspension. Also shown is a theoretical cleanup curve derived assuming that no zinc is added to the system and that it is removed from the system by the letdown cleanup flow. The difference between the theoretical cleanup curve and the actual zinc measurements indicates that there is either an additional source of zinc (i.e., zinc incorporated into the system surfaces was released) or that there is some other time averaging of the data (e.g., zinc is released from the surfaces of the sampling line). Comparison of the mass removed (22 g per Equation [5-5]) to estimates of the adsorbed zinc (~2.8 g per Table 3-88) indicates that the stability of the zinc concentration during this transient was not the result of desorption of zinc.

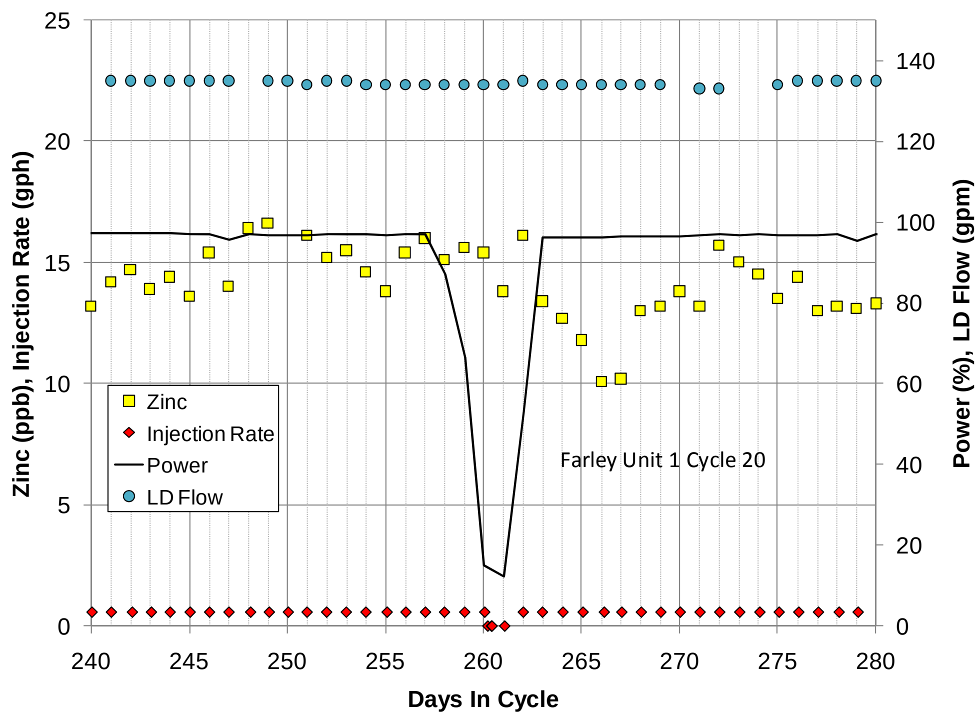

Figure 5-2
Farley Unit 1 Cycle 20: Power Transient

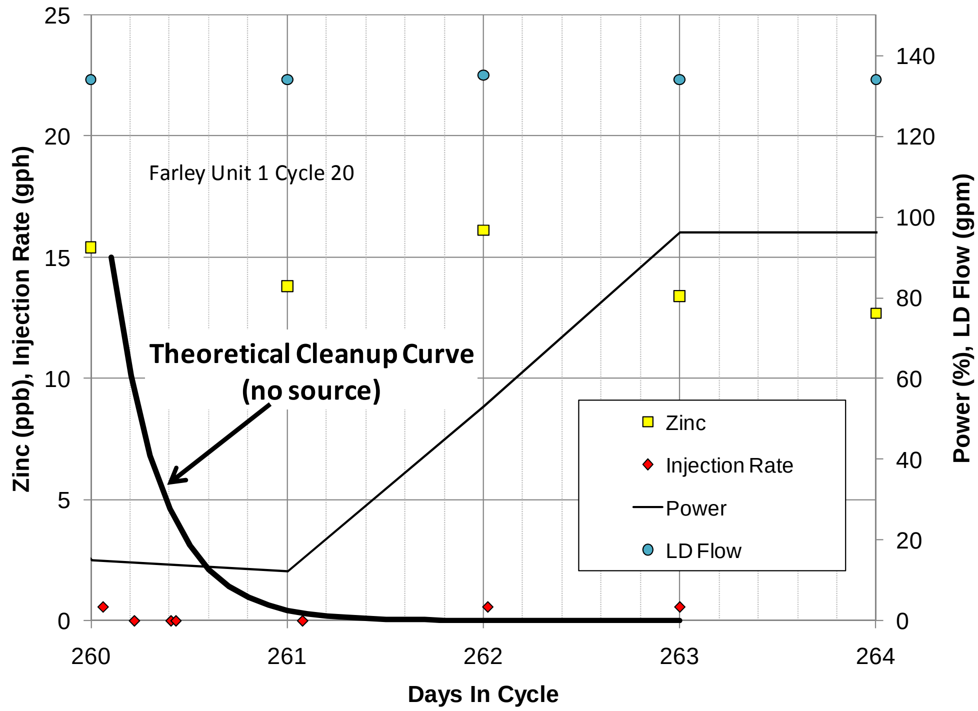

Figure 5-3
Farley Unit 1 Cycle 20: Power Transient with Theoretical Cleanup Curve

At about Day 332 of Cycle 20 the letdown flow rate was decreased from 134 gpm to about 80 gpm. At the time of this change in letdown flow rate, there were no significant changes in plant power or zinc injection rate. These operating parameters as well as zinc concentration measurements are shown in Figure 5-4. Note that there was no observable change in the zinc concentration due to the change in letdown flow rate.

The rates of various processes before and after the change in letdown flow are summarized in Table 5-1. These values indicate that the rate at which zinc was removed from the system was reduced by about half (directly proportional to the reduction in letdown flow rate, since the concentration of zinc was unchanged). Because there was no change in the injection rate, the rate at which zinc was taken up by the system increased when the removal by letdown was reduced.

Cycle 20 was the fifth cycle with zinc injection for Farley Unit 1. As discussed in Section 6.2.3, the fraction of zinc retained by the system has been shown to decrease steadily with time on zinc for all of the units for which more than three cycles of zinc data were available. This is thought to be due to gradual saturation of the RCS surfaces. Therefore, a sudden change in the zinc uptake rate, as implied by the calculated values in Table 5-1, is not expected.

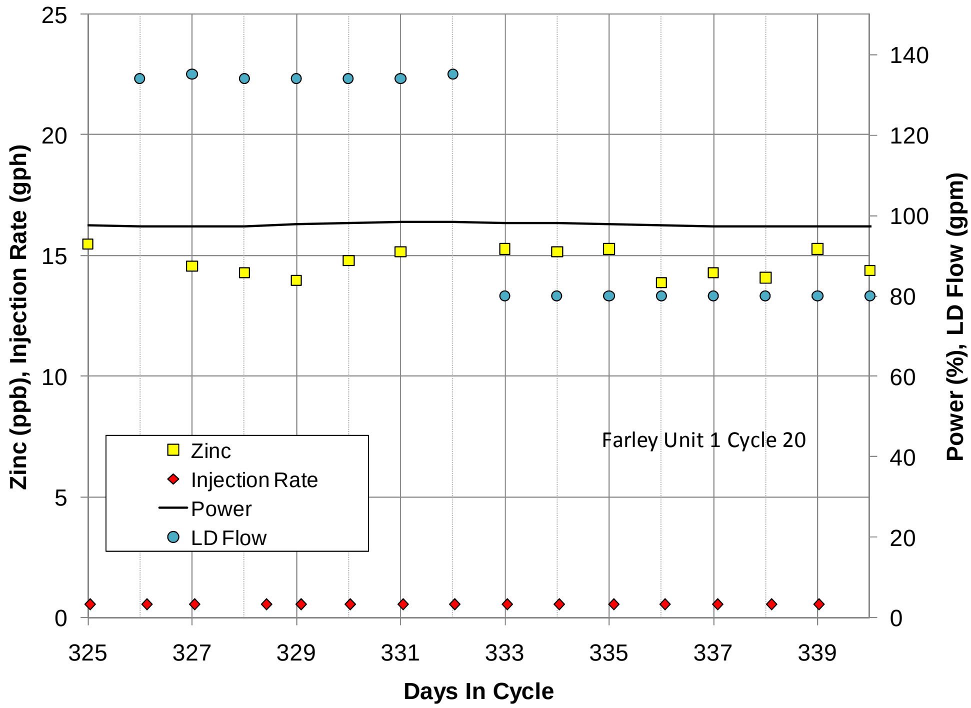

Figure 5-4
Farley Unit 1 Cycle 20: Letdown Flow Rate Transient

Table 5-1
Process Rates before and after the Change in Letdown Flow Rate

	Before	After
Letdown Flow Rate (gpm)	134	80
Zinc Injection Rate (g/hr)	0.568	0.568
Zinc Concentration (ppb)	15	15
Zinc Removal by Letdown (g/hr)	*0.46*	*0.27*
System Uptake Rate (g/hr)	*0.11*	*0.30*
Fraction Retained by System	*0.20*	*0.52*

Values in *italics* were calculated.

5.2.4 Callaway

During Callaway Cycle 14 there was a transient during which the zinc injection rate was increased so that a higher RCS zinc concentration could be obtained. Once the new higher concentration was obtained, a downpower occurred (unrelated to zinc injection) during which zinc injection was halted but letdown purification flow was maintained. Data for all of Cycle 14 are shown in Figure 5-5. Data for only the transient period are shown in Figure 5-6. Zinc was first injected at Callaway during Cycle 13.

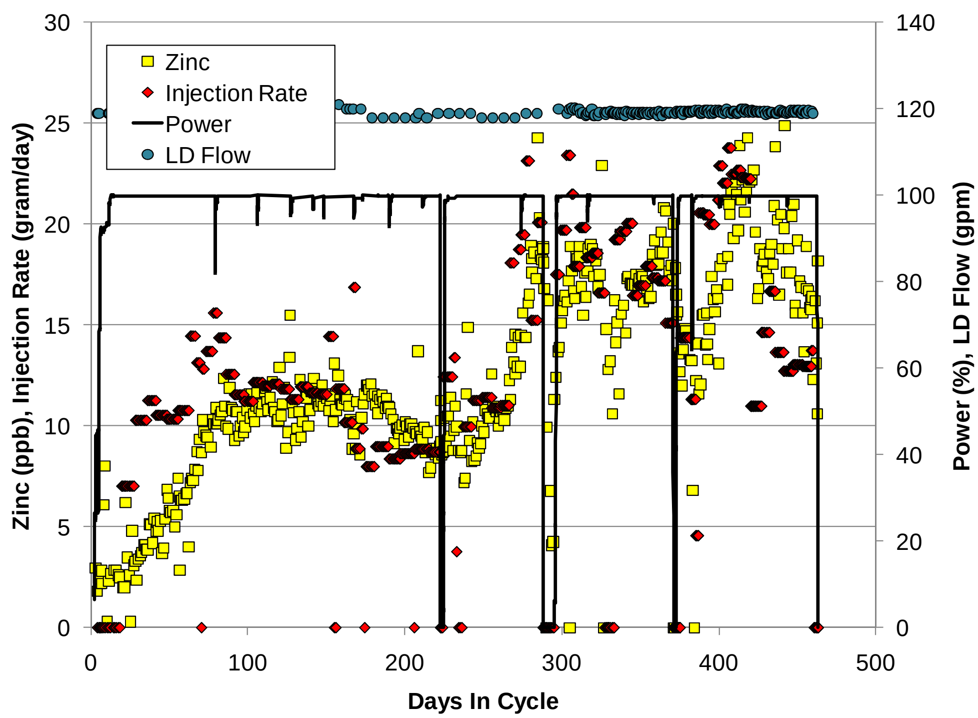

Figure 5-5
Callaway Cycle 14: Power and Zinc Injection Transient – Full Cycle Data

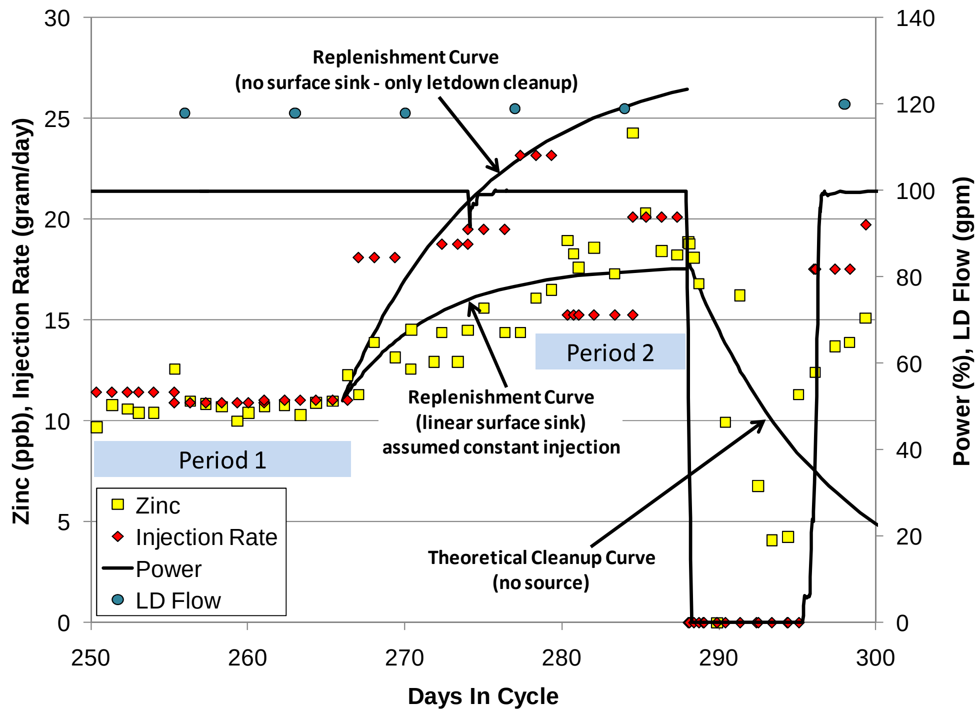

Figure 5-6
Callaway Cycle 14: Power and Zinc Injection Transient – Data during Transient

Two different periods were evaluated as being at steady state (i.e., the zinc concentration in the RCS was not changing with time). These periods are shown in Figure 5-6. Note that while it is not certain that Period 2 represents an actual steady state, it is convenient to treat it as such for analysis of how the transient affected zinc concentration.

During the two steady state periods, it is possible to calculate zinc uptake and letdown cleanup rates using Equation [5-4]. These are shown in Table 5-2. Per the model discussed in Section 5.2.1, at steady state the removal of zinc is the product of the concentration and the letdown flow rate. The calculated uptake rate did not increase as much as either the injection rate or the removal rate, although it did increase significantly. Thus the uptake rate was not proportional to the concentration, but did increase.

Table 5-2
Callaway Cycle 14: Process Rates before and after Increase in Injection Rate

		Period 1	Period 2
Letdown Flow Rate (gpm)		118	119
Zinc Injection Rate	(g/hr)	0.46	0.76
	(g/day)	11.1	18.2
Zinc Concentration (ppb)		10.9	19.0
Zinc Removal by Letdown (g/hr)		*0.29*	*0.51*
System Uptake Rate (g/hr)		*0.17*	*0.25*
Fraction Retained by System		*0.37*	*0.32*

Values in *italics* were calculated.

Between Period 1 and Period 2, the zinc concentration was increasing. Figure 5-6 shows two curves for this time generated using Equation [5-4]. One curve (labeled no surface sink) was generated by assuming that both constants governing the surface uptake (*a* in Equation [5-4] was zero), i.e., the zinc was removed from the system only by letdown purification. This curve overshoots the measured zinc concentration, indicating that there is additional removal by another mechanism. The second replenishment curve in Figure 5-6 assumed that the constant a (relating zinc uptake to the concentration) was given by the uptake rate during Period 1. In other words, it was assumed that the system uptake was proportional to the concentraiton and that the proportionality constant (*a*) could be derived from the steady state period preceding the transient. This curve (which assumed that the new injection rate was constant at the average value) provides a reasonable prediction of the actual zinc concentrations. Note that this curve was a prediction in the sense that it was derived using only the information known in advance of the transient.

Following the (planned) increase in zinc concentration, there was an unrelated downpower during which zinc injection was terminated. This period is shown in Figure 5-6 along with a cleanup curve generated using Equation [5-4] assuming no surface uptake or release (i.e., *a* was zero). This curve overpredicts the measured zinc concentrations implying that there is an additional removal mechanism. During this period there is no boiling in the core (no power is being generated). As discussed in Section 5.3.1, a reduction in temperature (such as would occur during a downpower) is likely to result in the release of zinc, not deposition. Therefore, the additional removal is not likely to be due to a temperature effect. The solubility of zinc is not thought to be challenged by these concecntrations, so there is not expected to be any precipitation. The additional removal mechanism has not been determined.

5.2.5 ANO 1

During ANO 1 Cycle 20, there were two system transients amenable to evaluation. During the first transient, zinc injection was terminated for about seven days before resumption. In the second transient there was an increase in the letdown purification flow rate. Data from the full cycle are shown in Figure 5-7. Data from the zinc injection transient are given in Figure 5-8. Data from the letdown flow transient are shown in Figure 5-9.

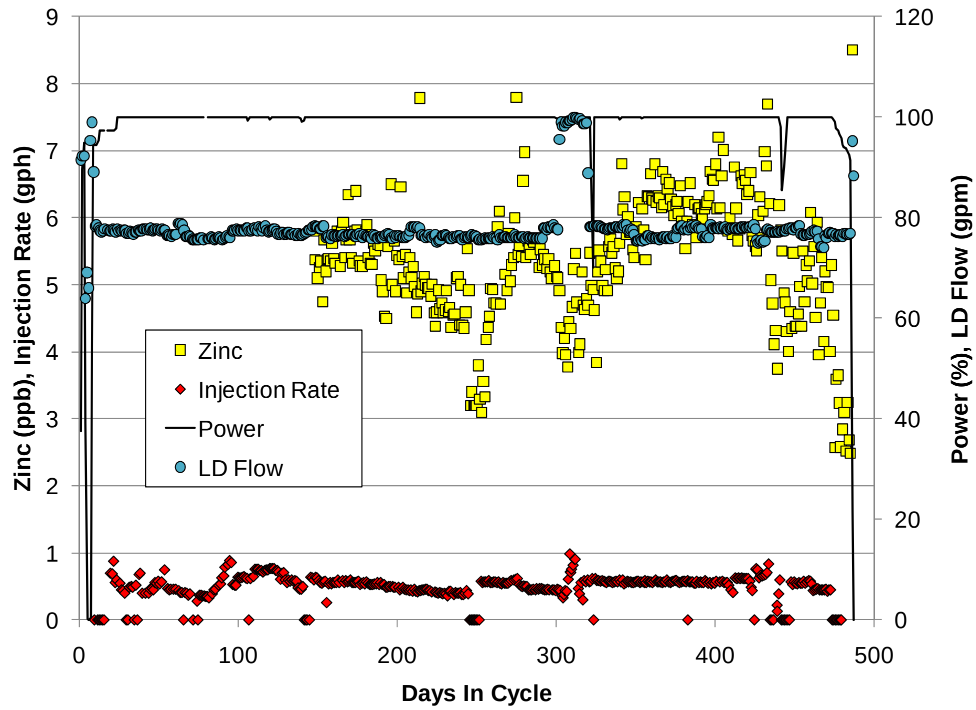

Figure 5-7
ANO 1 Cycle 20: Letdown Flow and Zinc Injection Transients – Full Cycle Data

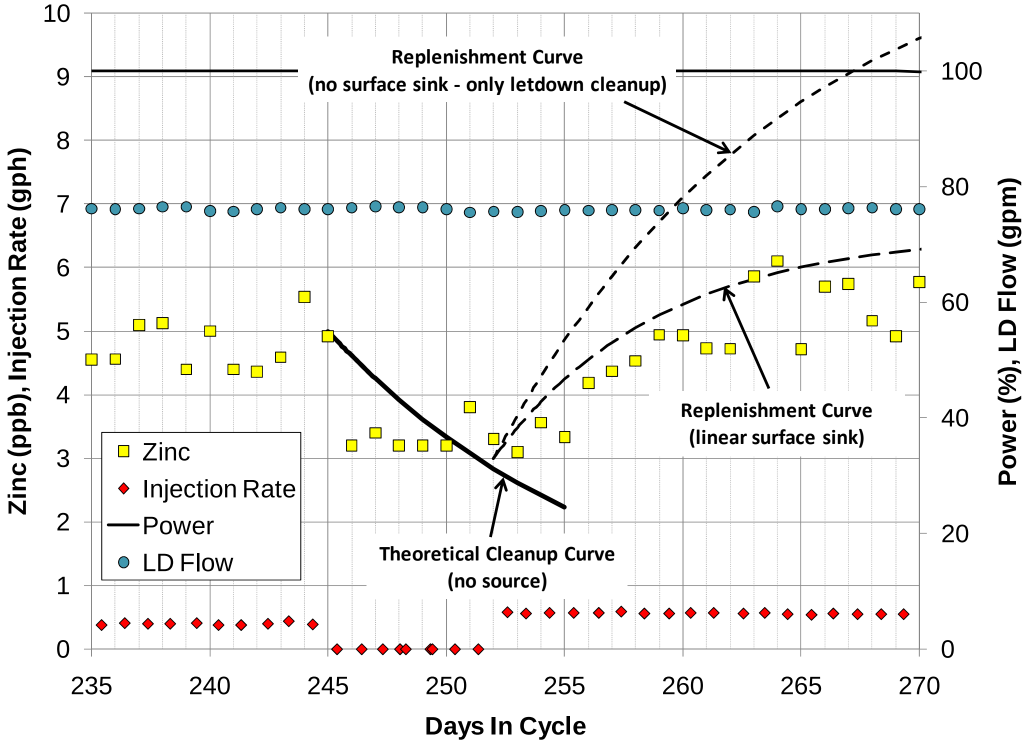

Figure 5-8
ANO 1 Cycle 20: Zinc Injection Transient

As shown in Figure 5-8, when injection of zinc was terminated there was a decrease in zinc concentration that was essentially a step change to a lower concentration. Because the concentration was essentially constant, a constant uptake rate could be calculated for this period as well as the steady state period preceding the termination of zinc. The results of these calculations are given in Table 5-3 along with rate information for these periods and the period after zinc was restored. These results indicate that there was a significant release of zinc from the system surfaces maintained over the course of the whole transient. This release added zinc to the coolant at a rate that was about one quarter the rate at which injection had been adding zinc.

Upon resumption of zinc injection, the zinc concentration gradually increased. Figure 5-8 shows three calculated replenishment curves based on concentrations calculated using Equation [5-4]. The first curve assumes no surface uptake (i.e., a was zero). This curve overpredicts the zinc concentration, implying that there is surface uptake during this period. The second curve assumes a linear uptake rate based on the uptake rate before injection was stopped (i.e., a is based on the value calculated from concentrations before the transient). This curve predicts a steady-state concentration more similar to the concentration actually reached, but predicts arriving at that concentration slightly sooner than was observed.

Table 5-3
ANO 1 Cycle 20: Process Rates before, during, and after Cessation of Zinc Injection

	Before	During	After
Letdown Flow Rate (gpm)	76	76	76
Zinc Injection Rate (g/hr)	0.14	0.00	0.20
Zinc Concentration (ppb)	4.6	3.2	Increasing
Zinc Removal by Letdown (g/hr)	*0.08*	*0.06*	*Increasing*
System Uptake Rate (g/hr)	*0.06*	*-0.06*	*Increasing*
Fraction Retained by System	*0.44*	—	—

Values in *italics* were calculated.

The second transient evaluated for ANO 1 Cycle 20 was an increase in letdown flow. Data taken during this transient are shown in Figure 5-9.

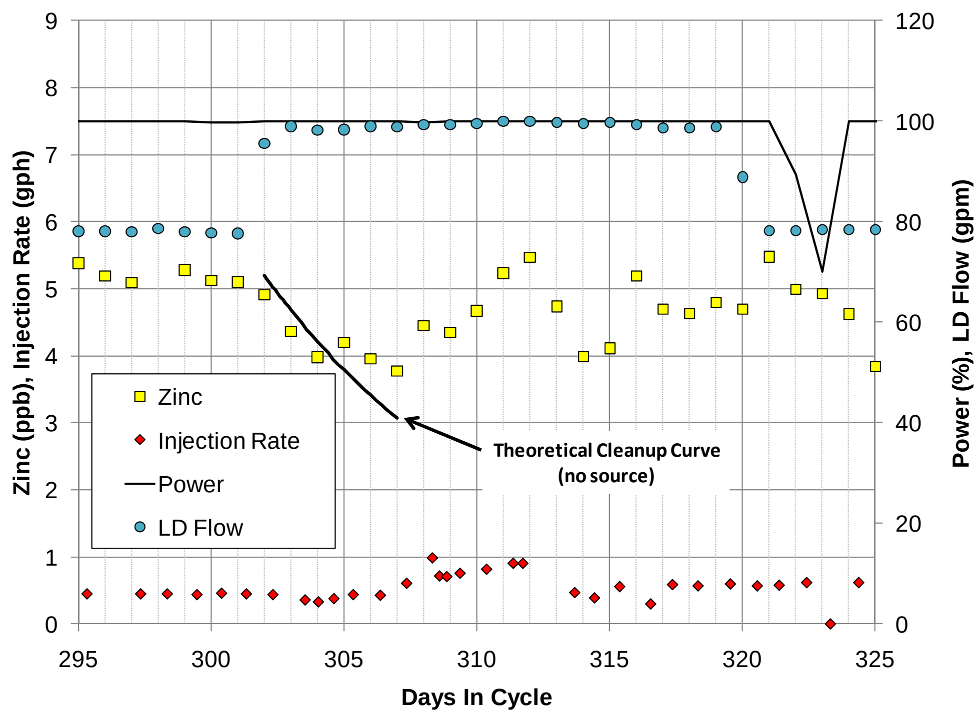

Figure 5-9
ANO 1 Cycle 20: Letdown Flow Transient

Table 5-4
ANO 1 Cycle 20: Process Rates before and after Increase in Letdown Flow

	Before	After
Letdown Flow Rate (gpm)	78	99
Zinc Injection Rate (g/hr)	0.16	Increasing
Zinc Concentration (ppb)	5.2	Decreasing
Zinc Removal by Letdown (g/hr)	*0.09*	*Decreasing*
System Uptake Rate (g/hr)	*0.07*	—
Fraction Retained by System	*0.42*	—

Values in *italics* were calculated.

5.3 Theoretical Considerations

Models of system responses to power transients were developed in Reference [34]. The major findings of that work are discussed in Sections 5.3.1 through 5.3.4. Additional considerations, new to this project, are given in Section 5.3.5.

5.3.1 Zinc Return on Temperature Reduction

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

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

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

5.3.2 Deposition of Zinc Returns

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

5.3.3 Significance of Boiling

The most important result of this modeling effort is the elimination of boiling precipitation as a likely mode of zinc deposition on the fuel surfaces. Evaluation of diffusion of zinc out of deposits where it has been concentrated by boiling indicates that concentrations at the fuel surface will generally not reach saturation. The model developed to demonstrate this lack of precipitation was benchmarked against laboratory testing with good results, giving high confidence to the computed limits on precipitation. An evaluation of the zinc concentrations and boiling duty for several US units indicated that none of the plants were operating under conditions where zinc precipitation was a significant risk. (The cycle at most risk for zinc precipitation, Farley 2 Cycle 10, would have required deposits thicker than 100µm to have zinc precipitate, as discussed in Section 4.2).

5.3.4 Time Scales of Zinc Incorporation

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

5.3.5 Nickel Solubility Considerations

Previous analyses of the response of zinc concentrations to temperature transients (Reference [34] and Sections 5.3.1 through 5.3.4) considered the adsorption/desorption of zinc from deposit surfaces. It is also possible that zinc incorporated into deposits may be released upon dissolution of the deposits. In general, for systems with Alloy 600 or Alloy 690 steam generators it is assumed that dissolution of deposits is governed by nickel chemistry (i.e., the deposits are composed primarily of nickel-based compounds such as nickel metal, nickel oxide, and nickel ferrite). Therefore, it is of value to consider the extent of nickel dissolution during transients, since the dissolution of nickel compounds would be expected to release any zinc previously incorporated into the deposit.

As discussed in Section 3.7.4, the solubility of nickel under primary coolant conditions is at most on the order of 200 ppt and is generally much less at operating conditions. This limit is valid down to temperatures on the order of 270°C. In this range, the dissolution of nickel due to increases in solubility is very limited. For example, a change in solubility from 0 to 200 ppt would result in the release of only about 50 mg. Typical fuel deposit loadings are at least 1 kg (core wide loading) [53] and probably range up to 10 kg. Thus the nickel dissolved due to a solubility increase due to temperature decreases down to 270°C will result in negligible nickel dissolution and thus negligible zinc release from fuel deposits.

5.4 Conclusions

Evaluation of plant data collected during a number of plant transients yielded varying results, including the following:

- During a power transient with suspension of zinc injection during Farley 1 Cycle 20 resulted in no perceptible change in zinc concentration, despite letdown rates that would have rapidly reduced the concentration.
- During a letdown flow rate transient during Farley 1 Cycle 20 resulted in no perceptible change in zinc concentration. The constant zinc concentration during the change in letdown flow rate implies a threefold increase in the zinc uptake rate, implying that the system uptake rate had been limited because zinc was being removed by letdown.
- During Callaway Cycle 14, an increase in the zinc injection rate led to a gradual increase in the zinc concentration that was consistent with a system uptake rate proportional to the zinc concentration, with the proportionality constant observed before the transient governing the period after the injection rate change and consistent with the new steady state achieved after the injection rate increase.
- During Callaway Cycle 14, a down power and concurrent cessation of zinc injection led to a decrease in the zinc concentration that was greater than would be predicted by the theoretical cleanup curve.
- During ANO 1 Cycle 20, zinc injection was halted, leading to a step change in zinc concentration to a lower concentration. The concentration change, even if assumed to be continuous between the concentrations measured, exceeded the theoretical cleanup rate.
- Upon restoration of zinc injection after the ANO 1 Cycle 20 transient, the zinc concentration gradually increased in a manner that was consistent with the uptake rate being proportional to the concentration and the proportionality constant being equal to that derived from the pre-transient uptake rate.
- An unrelated letdown flow rate transient during ANO 1 Cycle 20 resulted in a decrease in zinc concentration which was roughly consistent with the theoretical cleanup curve.

In general, the above observations indicate that the increase in zinc concentration resulting from an increase in the injection rate (whether from resumption of a halted feed or from an increase in the federate associated with increasing the zinc concentration) is consistent with an uptake rate that is linearly proportional to the zinc concentration. Furthermore, the proportionality constant relating concentration and the uptake rate remains constant through the transient, allowing a prediction of the zinc concentration.

In contrast, other types of transients (letdown flow rate changes or decreases in the zinc feed rate) led to unpredictable and inconsistent changes, with some transients leading to no change and others to unexplained step changes

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6
PREDICTIONS OF RESPONSES IN FUTURE CYCLE

6.1 Introduction

The *EPRI Zinc Guidelines* [2] provide ample support for utilities considering initiation of zinc injection. However, during Zinc Users Group meetings, utility personnel have requested additional guidance regarding how zinc programs should evolve with additional cycles. This chapter evaluates the EPRI Zinc Database for information that would be useful in predicting the behavior of plants in future zinc cycles.

6.2 Data Analysis

Evaluations of plant data were performed to assess the long-term response of the primary system to injection of zinc. These evaluations included consideration of the effect of continuing injection on the following:

- PWSCC mitigation
- Dose rate reduction
- Zinc retention

The extent to which plant experience can be used to predict the ongoing response of other units to zinc addition is discussed for each of these effects in the sections below.

6.2.1 PWSCC Mitigation

PWSCC mitigation is discussed in detail in Section 7.3 in the context of its use as a performance indicator. Based on the plant data discussed in that section, PWSCC mitigation is expected to be enhanced as additional cycles of addition are accumulated. However, there are few plants which are able to monitor ongoing PWSCC initiation in a quantitative manner. Quantification of a plant-specific PWSCC benefit would require the presence of statistically significant PWSCC initiation before zinc injection commenced or a steam generator design with a known susceptibility to PWSCC.

6.2.2 Dose Rate Reduction

Dose rate reduction is discussed in Section 7.2 in the context of its use a performance indicator. As discussed in that section, zinc injection leads to a statistically significant increase in the rate of ex-core dose rate reduction. However, the reduction rate is highly variable.

6.2.3 Zinc Retention

As zinc injection continues, it is expected that system surfaces will complete a transformation to a more protective structure which will lead to lower rates of nickel release. Upon completion of this transformation, it is expected that additional zinc will no longer be incorporated into the RCS surfaces. In order to test this hypothesis, data on zinc retention [57] were evaluated for four units in the EPRI Zinc Database for which data were available for four or more cycles. As discussed in Section 4.4.3.2, the fraction of injected zinc retained in the system is given by the following equation:

$$x_{held} = \frac{m_{added} - m_{removed}}{m_{added}} \qquad \textbf{Eq. 6-1}$$

where m_{added} is the mass of zinc added over the course of the cycle and $m_{removed}$ is the mass of zinc removed during operation (i.e., through purification). Note that the mass removed during shutdown evolutions is not considered, since this mass is expected to largely be released as part of a nickel dominated deposit (i.e., its removal does not add capacity for zinc uptake to the system since the deposits into which zinc would be incorporated are removed at the same time).

Long-term trends in the fraction of zinc retained during operation are shown in Figure 6-1. Note that these data are subject to several caveats, including the following:

- Not all cycle lengths are the same
- Target zinc concentrations were different between plants and sometimes between cycles at the same plants
- The plant designs are different
- The plant conditions were different at the time of initial zinc injection

Nonetheless, there appears to be a consistent trend in which the retention of zinc is reduced as zinc injection continues. That is, as zinc is injected for more cycles, more of the zinc is removed by letdown, or, equivalently, lower federates are required to maintain the same RCS concentrations.

Although the trends shown in Figure 6-1 are entirely empirical, they are qualitatively consistent with expectations based on the current understanding of zinc modification of system oxide surfaces. Although initial retention fractions appear to be plant specific, the subsequent reductions in retention (the slopes in Figure 6-1) are consistent enough to conclude that these trends might occur at other plants.

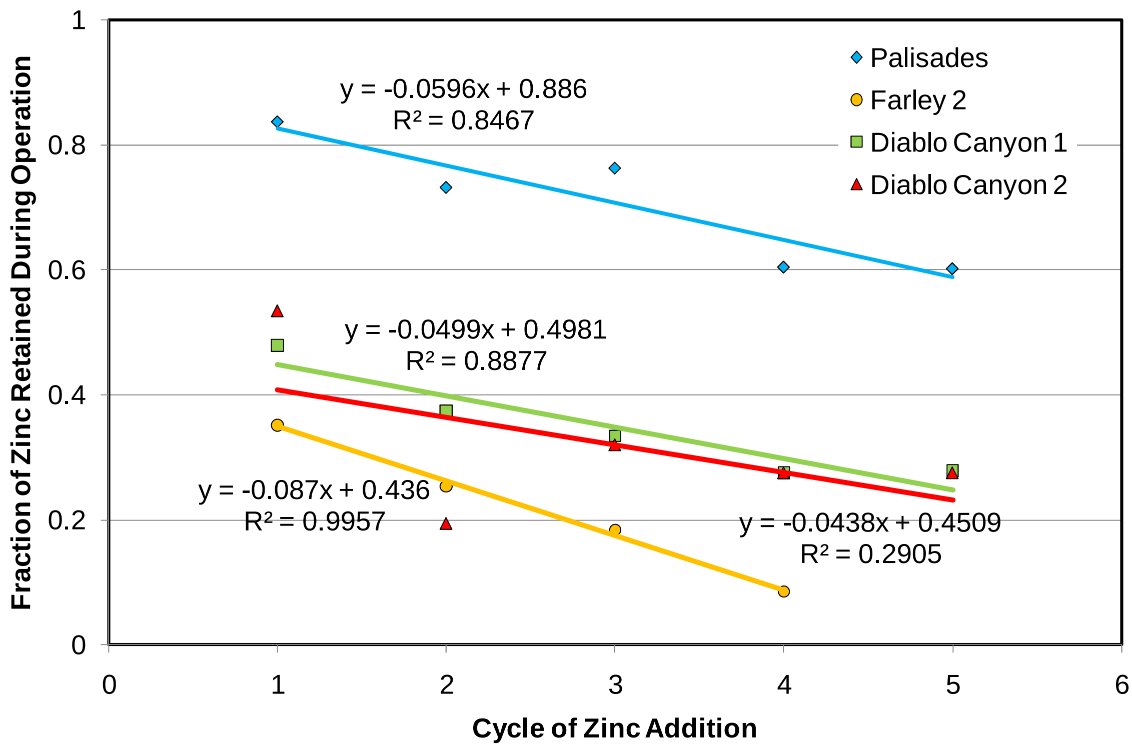

Figure 6-1
Long—Term Zinc Retention Trends

6.3 Conclusions

Examination of plant data revealed the following trends:

- PWSCC mitigation continues to increase (i.e., PWSCC continues to slow) with ongoing zinc application.
- Ex-core dose rates decrease with additional cycles of zinc injection at rates that are significantly greater than the rates of decrease without zinc addition.
- The fraction of zinc incorporated into system surfaces decreases with time.

In no case was there a significant effect of zinc concentration noted, although the available data were not necessarily sufficient to distinguish such an effect.

7
PERFORMANCE INDICATORS

7.1 Introduction

The EPRI Primary Water Chemistry Guidelines [7] mandate that each plant have a Strategic Water Chemistry Plan. The Plan is meant to be a living document that is periodically updated to reflect research and plant experience. In this context, it would be useful for utilities to have performance indicators to evaluate their zinc programs. The following sections consider performance indicators based on the four following program goals:

- Dose rate reduction (Section 7.2)
- PWSCC mitigation (Section 7.3)
- AOA/CIPS susceptibility minimization (Section 7.4)
- Program compliance (Section 7.5)

7.2 Dose Rate Reduction

One of the principle goals of zinc injection is the reduction of ex-core dose rates. In order to provide a benchmark against which utilities could compare reductions at individual units, the industry experience with dose rate reductions by zinc injection was evaluated. This evaluation proceeded through the following steps:

- For each unit with dose rate data in the PWR CMA Database [8], a decay constant for each ex-core dose rate was determined.
- The decay constants were analyzed using a variety of statistical techniques

The details of this evaluation are given Sections 7.2.1 through 7.2.7. Conclusions regarding the potential for using dose rate reductions as a performance indicator are given in Section 7.2.8.

7.2.1 Standard Radiation Monitoring Program Data Collection Points

EPRI work on radiation-field buildup, covering the various phases of plant construction and operation, began more than 25 years ago. More recent EPRI studies have emphasized technology transfer through capturing utility experiences and lessons learned in reports, guidelines, and seminar proceedings. The Standard Radiation Monitoring Program (SRMP) began as an initiative focused on data collection and evaluation, and on the continuation of work started by NSSS vendors.[60] The standardized radiation measurement points corresponding to the dose rate data in the CMA Database for Babcock and Wilcox (B&W), Combustion Engineering, and Westinghouse plants are given in Figure 7-1 through Figure 7-3, respectively.

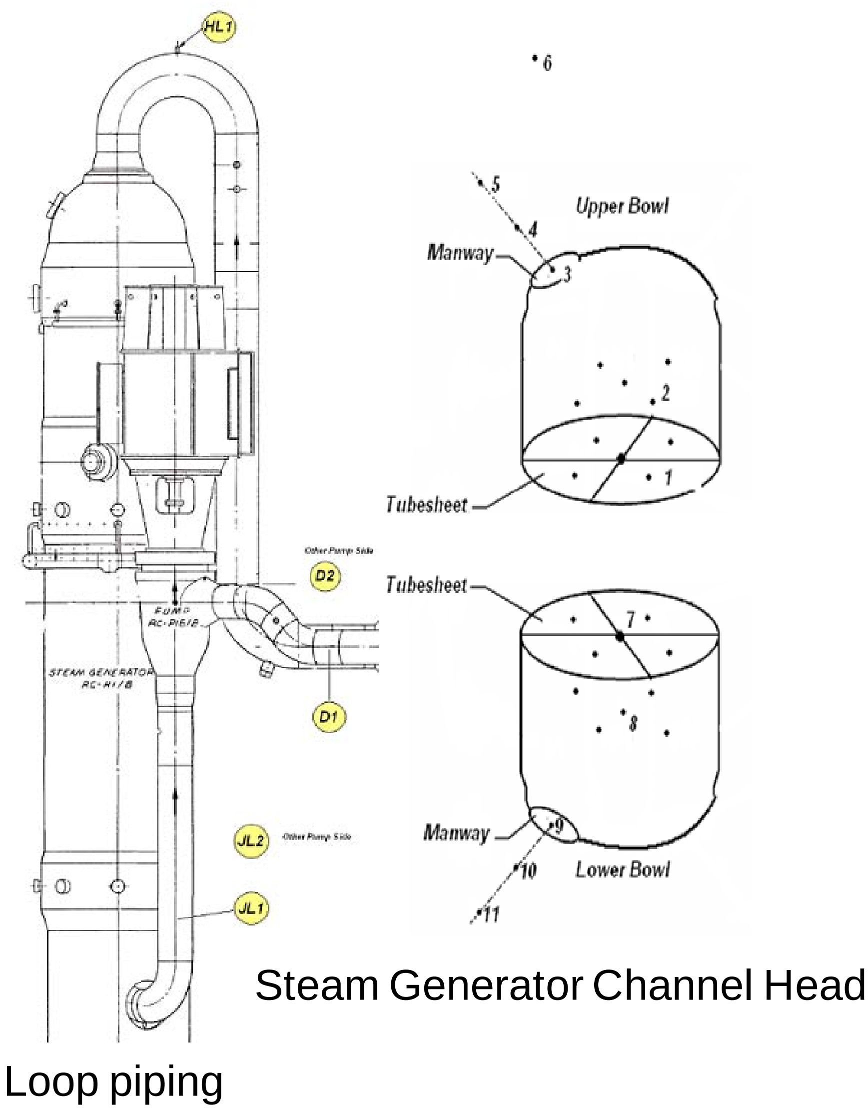

Figure 7-1
Babcock and Wilcox Monitoring Points [61]

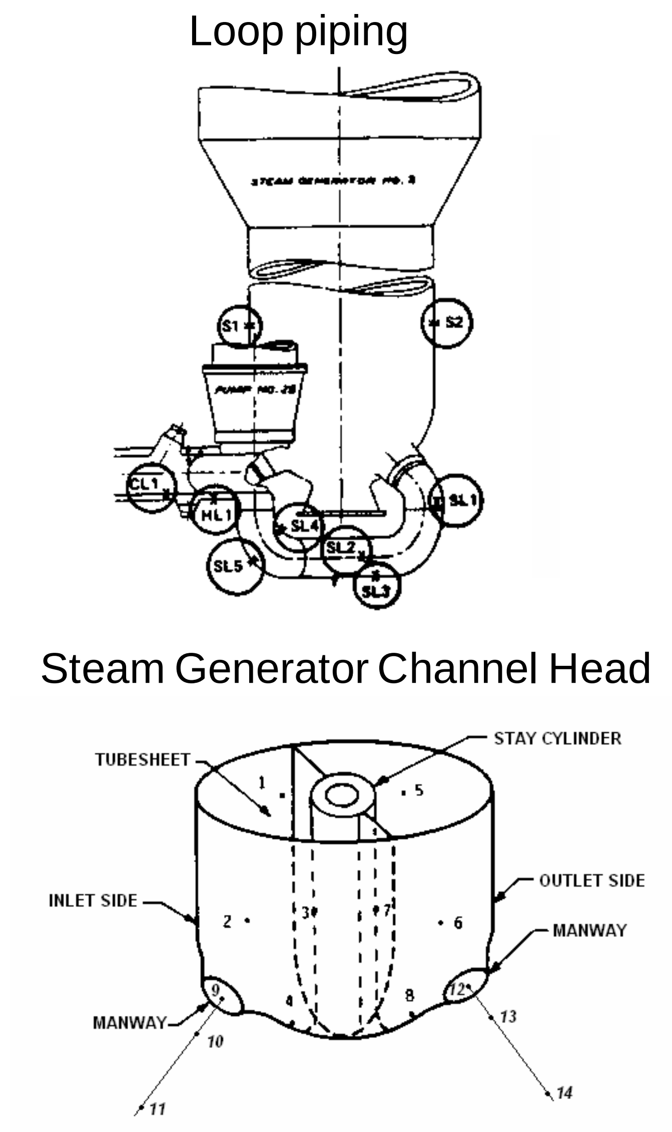

Figure 7-2
Combustion Engineering Monitoring Points [61]

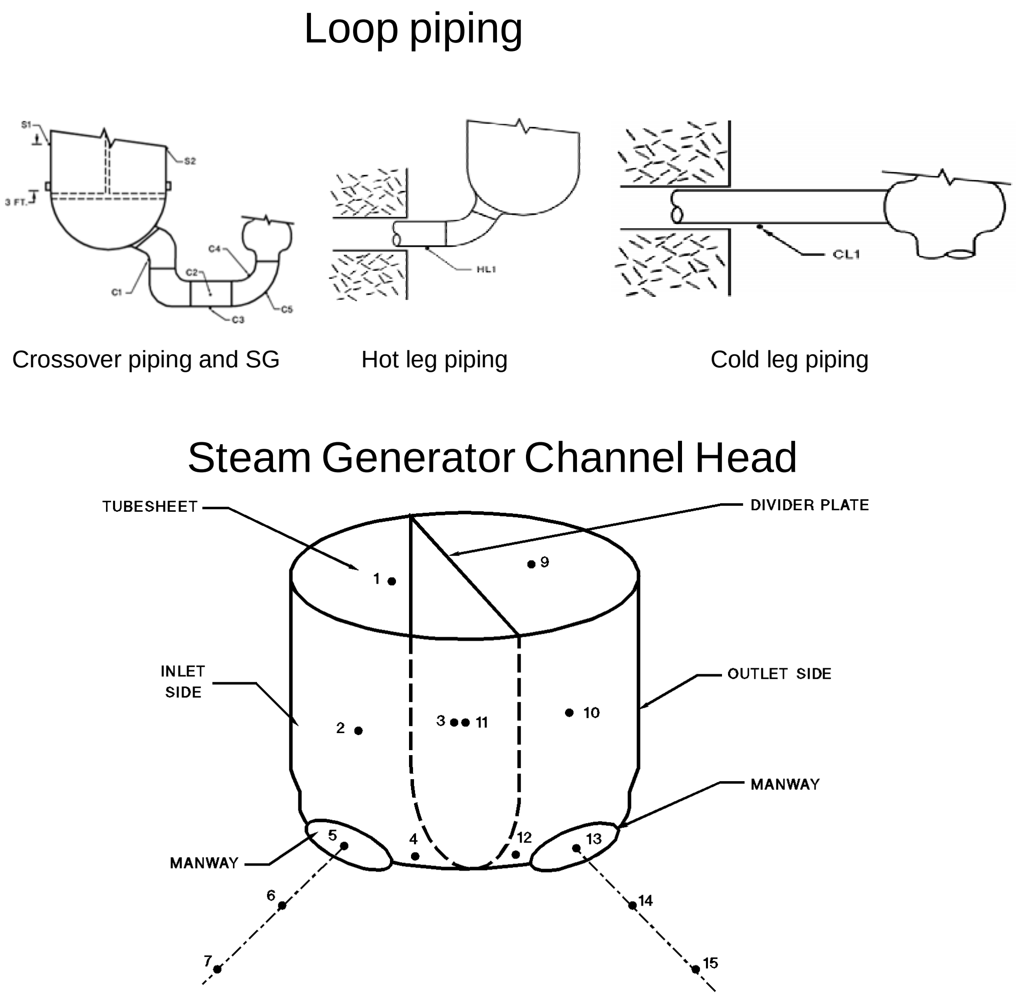

Figure 7-3
Westinghouse Monitoring Points [61]

7.2.2 PWR CMA Database Contents for SRMP Data

The number of outages for which there were data was determined for each measurement location at each unit to characterize the distribution of zinc units injecting across the various plant designs.

The SRMP Database contains radiation monitoring data from seven B&W units with 16 measurement points per outage data set, five Combustion Engineering units with 29 measurement points per outage data set, and 36 Westinghouse units with 23 measurement points per outage data set. The contents of the database for each plant design are summarized on a radiation-monitoring-point-specific basis for each unit in Table 7-1 through Table 7-3.

Table 7-1
Number of Outages with Reported Data per Measurement Point, B&W Units

	JL1pt	JL2pt	D1pt	D2pt	HL1pt	Pt1	Pt2	Pt3	Pt4	Pt5	Pt6	Pt7	Pt8	Pt9	Pt10	Pt11
Arkansas Nuclear One 1	1	1	1	1	1	1	1	1	1	1	0	1	1	1	1	1
Crystal River 3	0	0	0	0	0	7	7	0	0	0	0	7	7	0	0	0
Davis Besse	10	10	10	10	10	10	10	0	0	0	0	9	7	0	0	0
Oconee 1	7	7	5	5	7	6	6	6	6	0	0	6	6	6	6	0
Oconee 2	8	8	7	7	7	7	7	7	6	0	0	7	7	7	6	0
Oconee 3	7	7	5	5	5	6	6	6	6	0	1	6	6	6	6	1
Three Mile Island 1	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4

Table 7-2
Number of Outages with Reported Data per Measurement Point, Combustion Engineering Units

	S1pt	S2pt	SL1 A	SL1 B	SL2 A	SL2 B	SL3 A	SL3 B	SL4 A	SL4 B	SL5 A	SL5 B	HL1	CL1 A	CL1 B	Pt1	Pt2	Pt3	Pt4	Pt5	Pt6	Pt7	Pt8	Pt9	Pt10	Pt11	Pt12	Pt13	Pt14
Fort Calhoun	1	1	1	1	1	1	1	1	1	1	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Millstone 2	5	4	5	5	5	5	4	4	4	4	4	4	5	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4
San Onofre 2	0	0	4	4	4	4	4	4	4	4	4	4	0	0	0	13	13	13	0	13	13	13	0	13	0	0	13	0	0
San Onofre 3	0	0	4	4	4	4	4	4	4	4	4	4	0	0	0	13	13	13	0	13	13	13	0	13	0	0	13	0	0
Waterford 3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	6	6	6	6	6	6	6	6	6	5	0	6	5	0

Table 7-3
Number of Outages with Reported Data per Measurement Point, Westinghouse Units

	S1	S2	C1	C2	C3	C4	C5	HL1	CL1	Pt1	Pt2	Pt3	Pt4	Pt5	Pt6	Pt7	Pt9	Pt10	Pt11	Pt12	Pt13	Pt14	Pt15
Beaver Valley 1	4	4	4	4	4	4	4	4	3	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Beaver Valley 2	3	3	3	3	3	3	3	3	3	10	10	10	10	10	10	10	10	10	10	10	10	10	10
Braidwood 1	0	0	0	0	0	0	0	0	0	10	10	10	10	10	10	10	10	10	10	10	10	10	10
Braidwood 2	0	0	0	0	0	0	0	0	0	12	12	12	12	12	12	12	12	12	12	12	12	12	12
Byron 1	0	0	0	0	0	0	0	0	0	9	9	9	8	9	8	8	9	9	9	8	9	8	8
Byron 2	0	0	0	0	0	0	0	0	0	11	11	11	8	11	8	8	12	12	12	9	12	9	9
Callaway	14	14	14	12	0	0	0	14	14	14	14	14	14	1	14	1	14	14	14	14	1	14	1
Catawba 1	0	0	0	2	0	0	0	1	2	2	2	1	1	2	2	0	2	2	1	1	2	2	0
Catawba 2	0	0	0	1	0	0	0	1	1	4	4	2	2	4	4	0	4	4	2	2	4	4	0
Comanche Peak 1	10	10	10	10	10	10	10	10	10	9	9	9	7	9	9	7	9	9	9	8	9	9	7
Comanche Peak 2	9	8	8	8	8	8	9	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8
DC Cook 1	4	4	4	4	4	4	4	4	4	4	3	3	3	3	3	3	3	3	3	3	3	3	3
DC Cook 2	5	5	5	5	5	5	5	5	5	4	4	4	4	4	4	4	4	4	4	4	4	4	4
Diablo Canyon 1	6	6	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7
Diablo Canyon 2	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7
Farley 1	4	4	4	4	4	4	4	4	4	2	2	2	2	2	2	0	2	2	2	2	2	2	0
Farley 2	6	6	6	6	6	6	6	6	6	2	2	1	1	1	1	0	2	2	1	1	1	1	0
Indian Point 3	1	1	1	1	1	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
McGuire 1	1	1	1	3	1	1	1	3	3	4	4	4	4	4	3	1	4	4	4	4	4	3	1
McGuire 2	2	2	2	3	2	2	2	3	3	2	2	2	2	2	1	1	2	2	2	2	2	1	1
Millstone 3	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5
North Anna 1	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8
North Anna 2	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6
Prairie Island 1	8	8	8	8	8	8	8	8	8	8	8	7	8	8	8	8	8	8	7	8	8	8	8
Prairie Island 2	5	5	5	5	5	5	5	5	5	5	5	4	5	5	5	5	5	5	4	5	5	5	5
Robinson	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	3	4	4	4	4	4	4	3
Seabrook 1	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2
Shearon Harris	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
South Texas Project 1	10	10	10	10	10	10	10	10	10	9	9	9	9	9	9	9	9	9	9	9	9	9	9
South Texas Project 2	11	11	12	12	12	12	12	12	12	9	9	9	9	9	8	9	9	9	9	9	9	8	9
Surry 1	13	13	13	13	13	13	13	13	13	12	12	12	12	12	11	11	12	12	12	12	12	13	11
Surry 2	12	12	12	12	12	12	12	12	12	13	13	13	13	13	13	13	13	13	13	13	13	13	13
Turkey Point 3	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2
Turkey Point 4	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Watts Bar 1	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2
Wolf Creek	3	3	3	3	3	3	3	3	3	3	3	3	3	3	0	0	3	3	3	3	3	0	0

Of the seven available B&W units, Arkansas Nuclear One 1 (ANO1) was the only unit that injected zinc in the previous cycle (ANO1 did both), but only one outage was reported. Fort Calhoun (FC) was the only Combustion Engineering unit to inject zinc in the previous cycle, but again only one outage was reported. Due to this lack of data, no further analyses were conducted for B&W and Combustion Engineering plants. Of the 36 Westinghouse units present, 33 reported data from at least two outages.

7.2.3 Data Collection Techniques

Typical SRMP dose rate measurements are made from the exterior of primary system piping. This can lead to significant measurement variability that does not reflect true differences in the contamination of system surfaces. Some issues that lead to measurement variability include the following [62]:

- Particulate contamination
- Lack of shielding
- Insulation thickness variability

It is not possible from the data available to segregate these effects from actual variability. Therefore, all forms of variability were treated in common.

7.2.4 Calculation of Decay Constants

Radiation fields detected during shutdown are the result of the presence of activated corrosion products from primary system components and, generally to a much lesser extent, fission products released from fuel cladding defects. Activated corrosion products are the primary long-term source of radiation fields, primarily due to the presence of Co-58 and Co-60 early in the life of the plant and Co-60 late in the life of the plant. Following activation in the core, these species are deposited on several different surfaces within the core and outside of the core, including the fuel rods, reactor pressure vessel, steam generator channel head, and primary system piping. Following deposition onto any of these surfaces, activated corrosion products can again be released and deposited elsewhere in the primary system [60].

Zinc injection began in the U.S. PWRs in 1994 in an effort to mitigate PWSCC of primary system components. The first plants to inject zinc also observed major decreases in shutdown radiation dose rates. This added benefit is consistent with the ability of zinc to stabilize primary oxide films and a subsequent decrease of future cobalt incorporation into the oxide. PWRs have historically added natural or depleted zinc to primary coolant, with depleted zinc yielding a greater dose reduction benefit. Natural zinc leads to smaller dose rate reductions as a result of its Zn-64 content, which gives rise to the radioisotope Zn-65 when irradiated in the core. The Zn-64 content of depleted zinc is greatly reduced relative to that present in natural zinc, and as a result, the formation of Zn-65 has a minimal effect on dose rate at units injecting depleted zinc [2].

If the injection of zinc leads to a stabilization of RCS oxide films (reducing the incorporation of additional radiocobalt activity present in the coolant) it is expected that the measured dose rate would decrease at the natural rate of decay of the radioisotopes present. If zinc also displaces radioisotopes from RCS oxide films, the measured dose rate would decrease more rapidly than would be observed from natural decay. Assuming that Co-60 is the primary contributor to shutdown dose rates it is expected that the decay constants calculated from the zinc outage data would be comparable to the natural decay constant of Co-60. The decay constant of Co-60 is given as follows:

$$\lambda_{Co-60} = \frac{\ln(2)}{t_{1/2,Co-60}} = \frac{\ln(2)}{(5.271 \text{ yr})\left(\frac{365 \text{ days}}{\text{yr}}\right)} = 3.60\text{x}10^{-4} \text{ day}^{-1}$$ **Eq. 7-1**

where $\lambda_{Co\text{-}60}$ is the decay constant of Co-60 in reciprocal days and $t_{1/2,Co\text{-}60}$ is the half-life of Co-60 (5.271 years [63]).

Unique decay constants were calculated for each monitoring location at each unit and, when relevant, before and after the first zinc injection and/or before and after steam generator replacement. Note that since UFC is expected to impact shutdown dose rates, outages before which a UFC campaign was completed were excluded from the analysis. The exponential function given in Equation [7-2] was fit to each set of SRMP data and was used to characterize the progression of measured dose rates as a function of time.

$$D_i(t) = Ce^{-\lambda_i t}$$ **Eq. 7-2**

In Equation [7-2] D_i is the measured dose rate at location i in mSv/hr, C is a fitted constant, λ_i is the decay constant at location i in reciprocal days, and t is the time days. The decay constant is greater than zero when the measured dose rate decreases over time (i.e., the rate of removal of the already present radioisotopes by decay or redistribution is greater than the rate of incorporation of additional source).

7.2.5 Comparison of Zinc and Non-Zinc Decay Constants at Each Location

A comparison of the descriptive statistics (i.e., the mean and standard deviation) of the calculated decay constants at each measurement location was the first step in the analysis of the effect of zinc injection on shutdown dose rate based on the SRMP data. Note that this comparison was intended to provide a qualitative description of the impact of measurement location and zinc injection on the calculated decay constant; the quantitative analyses of these data are discussed in Sections 7.2.6 and 7.2.7. The mean and standard deviation of the decay constants calculated for each measurement location for no-zinc and zinc outages at each unit are presented graphically in Figure 7-4.

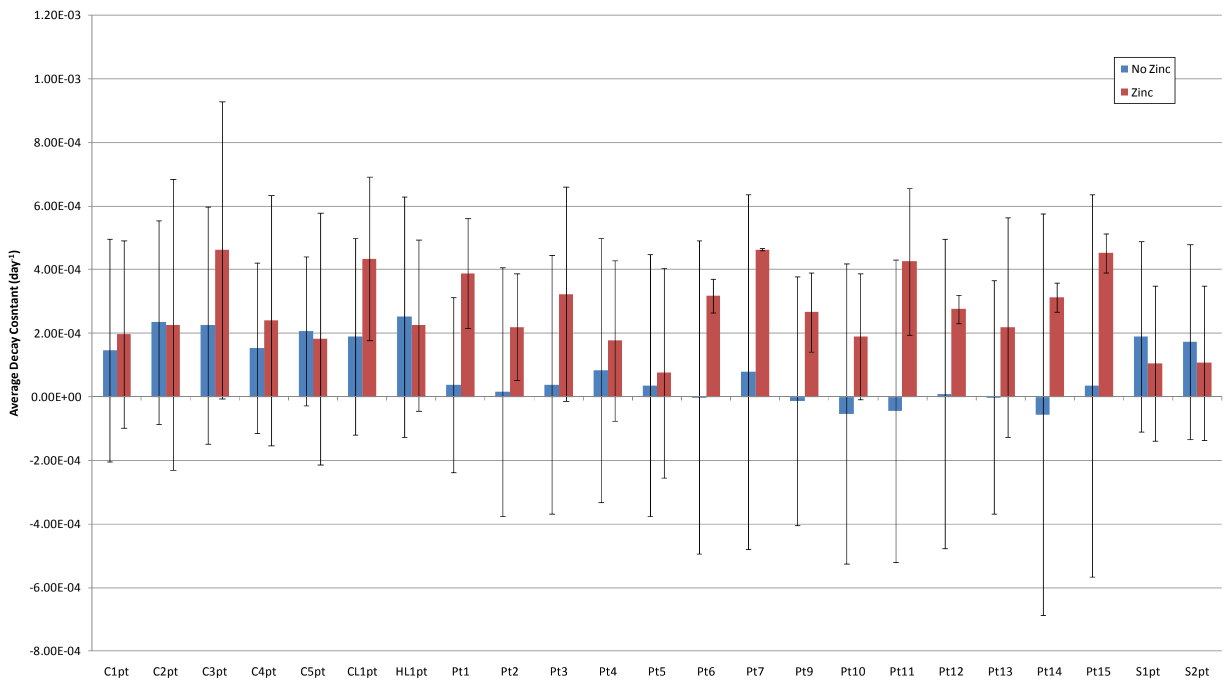

Figure 7-4
Average Decay Constant by SRMP Location for No-Zinc and Zinc Outages

Figure 7-4 shows that the calculated decay constants were highly variable irrespective of zinc injection and the measurement location. The plot also shows that the average decay constant calculated for zinc outages was greater than the corresponding no-zinc decay factor at the same location at more than ¾ of the locations. Due to the high degree of variability in the data, the significance of this result is not immediately apparent and it is explored further in Section 7.2.6.

7.2.6 Statistical Assessment of the Significance of Location and Zinc Addition

The goal of the statistical assessment of the decay constants derived from the SRMP data was to analyze the contribution of the measurement location and zinc injection, each is a unique categorical factor composed of a number of individual categories, to the variability present in the set of calculated decay constant values. A population of categorical data can be divided into smaller groups using categorical factors, in this case measurement location and zinc injection status.

Based on the data presented in Figure 7-4, the relationship between the calculated decay constant, the measurement location, and zinc injection is not immediately apparent. It was therefore of interest to determine if there was a location- and/or zinc-specific effect on the calculated decay constant. The location factor is made up of 23 categories (i.e., one category for each measurement location) and the zinc factor is made up of 2 categories (i.e., one category of data for non-zinc outages and one for zinc outages). If the impacts of location and zinc injection were both statistically significant, the decay constant data would be composed of 46 unique populations, one for each combination of location and zinc injection status. If there were a location effect only, the set of decay constants would consist of 23 unique populations and if there were a zinc effect only, the set of decay constants would be made up of 2 unique populations.

The statistical software package known as Statgraphics [64] has the ability to manipulate and analyze categorical data and is therefore well suited for this type of analysis. The individual decay constant values used to generate Figure 7-4 were input to Statgraphics and were organized by location and by zinc injection status. The location and zinc factors were then analyzed using an analysis of variance technique. This analysis showed that there was a statistically significant effect of zinc at 95% confidence and that the impact of location was not significant. The data were then fit to the following model:

$$\lambda_j = A + f_{Zn} \qquad \textbf{Eq. 7-3}$$

where λ_j is the calculated decay constant with zinc injection status j, A is a constant, and f_{Zn} is the zinc factor. This simple model was chosen to isolate the effect of zinc on the calculated decay constant. The model fits to this equation and the 95 and 85% confidence intervals, based on a t-distribution, for the no-zinc and the zinc decay constants are given in Table 7-4.

Table 7-4
Calculated Decay Constant Model Fits and Confidence Limits

Decay Constant	A	f_{Zn}	$\lambda_{Average}$	95% Confidence		85% Confidence	
				$\lambda_{Lower\ Limit}$	$\lambda_{Upper\ Limit}$	$\lambda_{Lower\ Limit}$	$\lambda_{Upper\ Limit}$
$\lambda_{No\ Zn}$	1.67E-04	-9.54E-05	7.16E-05	3.69E-05	1.06E-04	4.61E-05	9.71E-05
λ_{Zn}	1.67E-04	9.54E-05	2.62E-04	1.82E-04	3.43E-04	2.03E-04	3.22E-04

The table shows that the no-zinc and the zinc decay constants are significantly different at 95% confidence as their confidence intervals do not overlap. This result implies that the net removal rate of activity contributing to shutdown dose rates was more rapid at zinc units than at non-zinc units. Note that the ranges spanned by the 85% confidence intervals are smaller than those of the 95% intervals. This result can be explained by the fact that a confidence interval must be widened to reduce the probability that the true population mean will fall outside of the interval (i.e., increase the level of confidence that the value of the true mean is within the interval). It should also be noted that these confidence limits were derived using a one-sample t-test because the calculated decay constants were approximately normally distributed and the true variances were unknown.

7.2.7 Statistical Assessment of the Relationship to the Co-60 Decay Curve

The decay constant of Co-60 is contained within the 95% confidence interval of neither the no-zinc nor the zinc decay constant. Specifically, the Co-60 decay constant, 3.60E-04, is greater than the upper limits of both confidence intervals. This result shows that despite the faster removal rates of activity source at zinc units relative to those of non-zinc units, the measured dose rates decrease more slowly over time at zinc units than would be expected by Co-60 decay alone. Based on the differences between the zinc and the no-zinc decay constants and their relationship to the decay of Co-60, it is likely that zinc injection stabilized surface oxide films and reduced the rate of incorporation of activity source into those films. Since this analysis did not attempt to isolate the impact of natural zinc (leading to Zn-65 production) versus depleted zinc, it is possible that a greater increase in decay constant relative to non-zinc units would have been observed at depleted zinc units. The difference between the zinc decay constant and the decay constant of Co-60 suggests that zinc injection did not lead to significant displacement of Co-60 from oxide films.

7.2.8 Conclusions Regarding Dose Rate Reduction Metrics

While there is a strong statistical indication that long-term use of zinc significantly lowers ex-core dose rates relative to units that do not use zinc, there is too much variability in the data arising from unknown sources for dose rate reduction to be used as a performance metric.

7.3 PWSCC Mitigation

The evidence for the mitigation of PWSCC by zinc injection has been reviewed in detail in References [65] and [66]. Reference [65] reviews experience with steam generator tube degradation. Reference [66] addresses steam generator data as well as laboratory data and experience with thickwall components and welds. Based on these reviews, there is ample evidence of mitigation of PWSCC of Alloy 600MA steam generator tubes. Figure 7-5 shows the mitigation factor φ as a function of the cumulative operating time since the first injection of zinc. The mitigation factor, φ, is defined such that the degradation that occurs in time t without zinc occurs in time t/φ with zinc. That is, the rate of degradation with zinc occurs at φ times the rate at which degradation would occur without zinc.

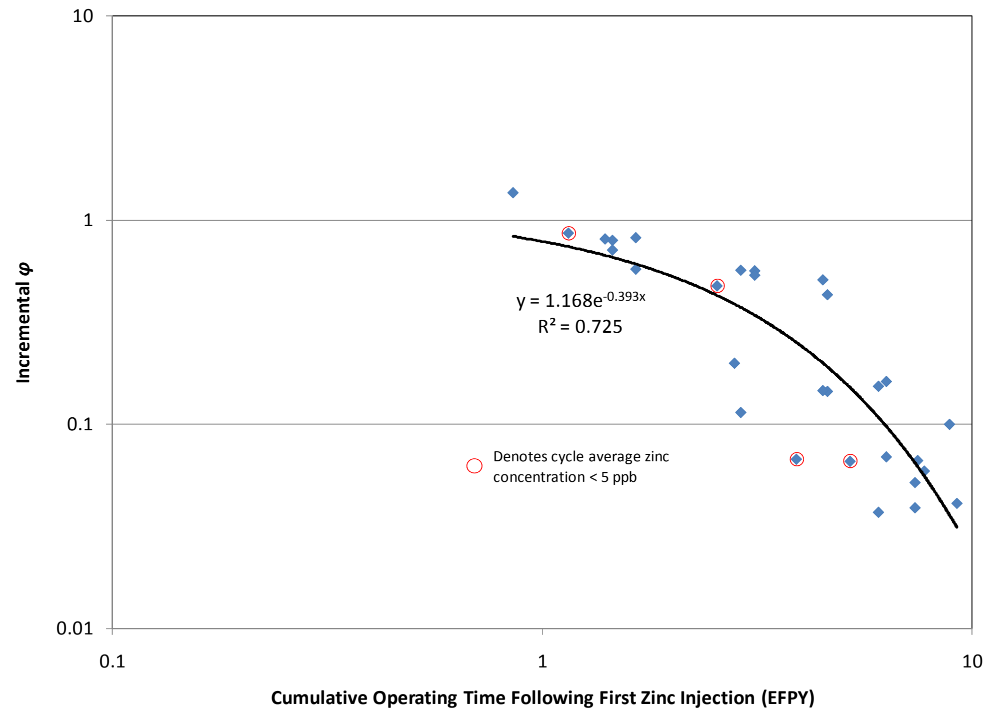

Figure 7-5
Incremental φ vs. Cumulative Operating Time Following First Zinc Injection

As demonstrated in Figure 7-5, the mitigative effect of zinc continues to increase with continued use. Also, the mitigative effect appears to be independent of zinc concentration.

Reference [66] reviews operating experience with thickwall components. There is no discernable effect of zinc on PWSCC of thickwall components or welds.

PWSCC of Alloy 600TT steam generator tubes is not sufficiently prevalent to develop statistical analyses that would address the effects of zinc. PWSCC of Alloy 690TT has not occurred in plants. It is possible that a zinc effect on PWSCC might be observed if PWSCC of Alloy 600TT tube ends and tube welds were evaluated. However, such an evaluation has not been performed and is outside the scope of this report.

Because most plants injecting or considering injecting zinc do not have Alloy 600MA tubing, there is little basis for the development of a performance indicator for PWSCC mitigation. Prior experience and laboratory testing provide a robust basis for concluding that there is a mitigating effect on PWSCC initiation, but no feasible measure of ongoing performance is available.

EPRI's Materials Reliability Program has endorsed the following definition of an acceptable zinc PWSCC mitigation program:

- Zinc has been injected for at least 4 years (calendar time, beginning with initial injection and with no interruptions exceeding 6 months).

- RCS zinc concentrations have been at least 3 ppb for at least 90% of the time that RCS $T_{average}$ has exceeded 250°F.

While these criteria are not a performance indicator as such, they still represent an industry consensus regarding the program elements necessary to demonstrate PWSCC mitigation. That is, although no PWSCC based performance indicator can be defined at this time, it is generally accepted that zinc application will mitigate PWSCC to a significant extent.

7.4 AOA/CIPS Susceptibility Minimization

There is a general industry consensus that axial offset anomaly (AOA, the occurrence of an axial discrepancy between the predicted and measured power profiles of a reactor core) is due to the accumulation of boron in the corrosion product deposits on fuel clad, hence the alternative name of crud induced power shift (CIPS). However, the following issues have prevented accurate quantification of AOA/CIPS susceptibility:

- The mechanism of boron accumulation has not been conclusively determined. Laboratory experiments have confirmed that lithium and boron will precipitate as Li_2BO_7 on fuel cladding under subcooled nucleate boiling conditions. Bonaccordite (Ni_2FeBO_5) was measured in fuel deposits at one unit and strongly suspected at another. However, there are almost certainly other processes or species, either kinetically or thermodynamically driven, that play a role in the development of AOA. Uncertainty regarding these processes in uncertainties regarding susceptibility.
- Most current models of AOA/CIPS susceptibility (e.g., EPRI's BOA code [4]) are tools for maintaining margin against AOA/CIPS and are therefore conservative estimates rather than best estimates of susceptibility. In general, the extent of conservatism has not been well quantified.

Because of these issues, no AOA/CIPS susceptibility based performance indicator can be formulated at this time.

In previous assessments of EPRI's data collection efforts [36], it has been recommended that measurements of actual axial offsets (and not just whether or not the offset is in excess of a utilities threshold) be included in the PWR CMA Database. This information is collected in the EPRI Fuel Reliability Program database, FRED.

7.5 Program Compliance

As with other chemistry programs, utilities should monitor compliance with the program requirements.

7.6 Conclusions

None of the performance indicators considered is a good candidate for short-term (single cycle) performance indicators. However, the following considerations may be feasible:

- There is sufficient industry experience for bench marking long-term trends in dose rate reductions.
- It is not anticipated that there will ever be enough data regarding PWSCC of SG tubes to use this as a performance metric in current steam generators (i.e., tubed with Alloy 600TT or Alloy 690TT). It is possible that evaluation of PWSCC of Alloy 600TT tube ends might provide an indication of the efficacy of zinc injection in mitigating PWSCC, but such an evaluation has not been performed.

The occurrence of AOA (CIPS) may be a useful performance metric in the future if other factors affecting AOA can be separated whether a unit is injecting zinc or not.

8
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A
DISCUSSION OF STATISTICAL METHODS

A.1 Statistical Methods

As discussed in Section 3.3.4, the statistical analyses performed for this project were essentially comparisons of data collected when injecting zinc with data collected before injecting zinc (either earlier in the cycle or from previous cycles). The principal statistical tool was therefore a test of the significance of the difference between two populations, which in this case was a two-sample, upper-tailed heteroscedastic Student's t test. The fundamental theory behind the methods used and why they were chosen are discussed in A. This section gives a qualitative overview of how the results presented are to be interpreted.

Hypothesis testing of mean values provides a measure of confidence in the calculated difference between a sample mean and a given value or between the mean values of two unique samples. The goal of such a hypothesis test is to compare the mean of a sample of measured data (or in this case the difference in the means of two samples of data) to a value that is assumed to be true under "normal" circumstances, and to determine the level of confidence that can be placed in the difference between the sample mean and the assumed value. If the level of confidence in the difference between these two values is below some threshold confidence level determined by the investigator performing the test, the calculated difference is not considered to be statistically significant (i.e., the calculated difference was the result of random variability in the data and not a true difference), the null hypothesis (i.e., that the sample mean is equal to the assumed value) is accepted, and the alternate hypothesis (i.e., that the sample mean is, depending on the test, greater than or equal to, less than or equal to, or not equal to the assumed value) is rejected. However, if there is sufficiently high confidence that the mean of a sample of data is different from the assumed (null) value, the calculated difference is considered to be statistically significant, the null hypothesis is rejected, and the alternate hypothesis is accepted.

For a given sample of data and null value, there is an associated level of significance, referred to as the α-value (also known as a p-value), which is defined as the probability that the null hypothesis will be rejected when it is true. For example, if the α-value calculated for a given test were 0.05, there would be a 5% probability that the null hypothesis would be rejected when it was true. It is important to note that the confidence level of a given test is inversely related to the α-value because the confidence in a calculated difference increases as the probability of errantly rejecting the null hypothesis decreases. In this example, an α-value of 0.05 corresponds to the 95% confidence level (i.e., confidence level = $(1- \alpha)100\%$).

The plant data analyses presented in this chapter employ two-sample hypothesis testing to assess the differences between the means of various zinc and pre-zinc data sets. For illustrative purposes, consider two normally distributed populations with sample means, μ_1 and μ_2 ($\mu_1 < \mu_2$), in which both populations have narrow distributions as presented in Figure A-1, and in which both have broad distributions as presented in Figure A-3. It is of interest to describe the significance level (α-value) of the difference between μ_2 and μ_1 as a function of the null value, $\Delta\mu_{hyp}$. This analysis provides insight into not only the significance of the difference between the two means, but also into the confidence level that can be applied to a given magnitude of the difference. In this case the null value of the test corresponding to a given confidence level represents the upper bound on the magnitude of the difference between μ_2 and μ_1. For example, at 95% confidence (i.e., $\alpha = 0.05$), the difference between μ_2 and μ_1 is less than or equal to $\Delta\mu_{hyp}(\alpha = 0.05)$.

For an upper-tailed test (i.e., $\mu_2 - \mu_1 > \Delta\mu_{hyp}$), the significance level as a function of the null value is plotted for narrow and broad populations in Figure A-2 and Figure A-4, respectively. As shown on the plots, the maximum (i.e., most positive) null value considered is the difference of μ_2 and μ_1. Since this is the greatest null value considered, it can be stated with the lowest level of confidence that this is the upper bound on the true magnitude of the difference between the two population means. This scenario has an associated confidence level of 50% (i.e., there is a 50% probability that the null hypothesis will be errantly rejected).

The level of confidence in the magnitude of the difference between the mean values increases as the difference between the calculated difference in the mean values and the null value increases (i.e., as the null value decreases relative to a fixed calculated difference between the sample means). Recalling that the null hypothesis represents an upper bound on the true difference between the values of the sample means, increasing the required confidence level of the test requires a decrease in the upper bound estimate of the true difference between the two means because there is random variability in the data. The confidence level corresponding to $\Delta\mu_{hyp} = 0$ for an upper-tailed test represents the greatest level of confidence at which the alternate hypothesis can be accepted. Note that Figure A-2 and Figure A-4 show that the confidence level continues to increase as $\Delta\mu_{hyp}$ decreases below 0, but a negative value of $\Delta\mu_{hyp}$ implies that μ_1 is greater than μ_2, and, therefore, that μ_2 is not statistically greater than μ_1.

Both narrow and broad distributions were included in this discussion to demonstrate the impact of random variability (scatter) on hypothesis testing. A given difference observed between two populations with a small degree of scatter is more likely to be the result of true differences between the two populations, while an equal difference observed between highly scattered populations is more likely to be due to random variability rather than to actual differences in the populations. Applying this principle to the current example, at a given value of $\Delta\mu_{hyp}$ the level of significance of the difference between μ_2 and μ_1 is greater for the narrow distributions than for the broad distributions. In other words a given difference observed between highly variable (broad) populations is less significant than an equal difference observed between less variable (narrow) populations. This relationship is presented graphically in Figure A-2 and Figure A-4.

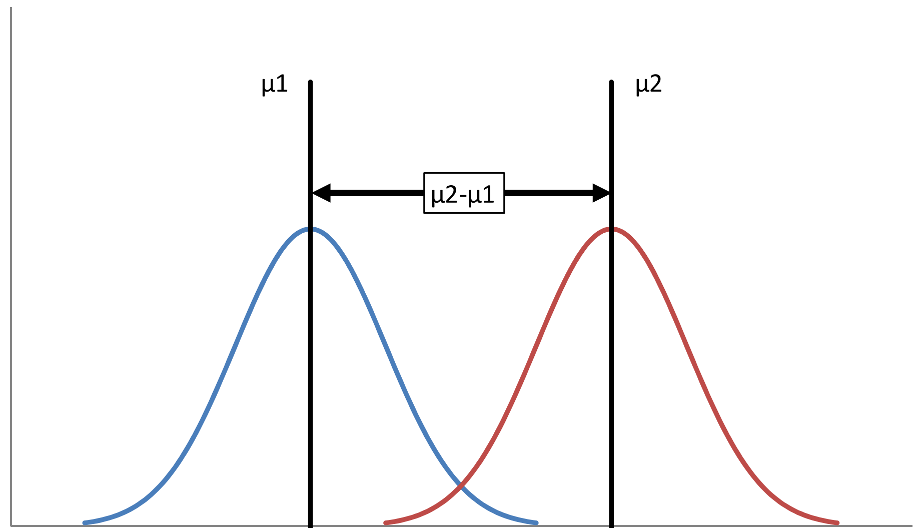

Figure A-1
Normal Populations with Narrow Distributions

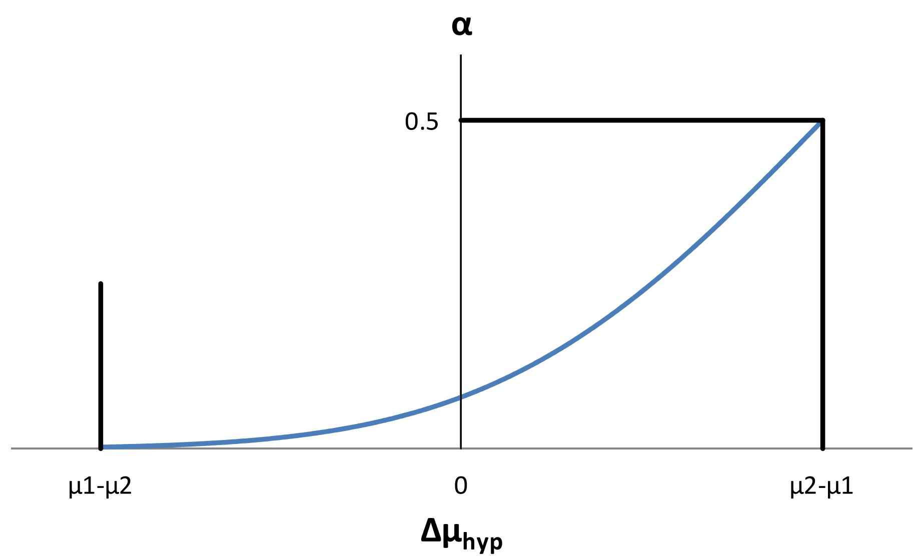

Figure A-2
Hypothesis Testing Significance Level for Narrow Distributions

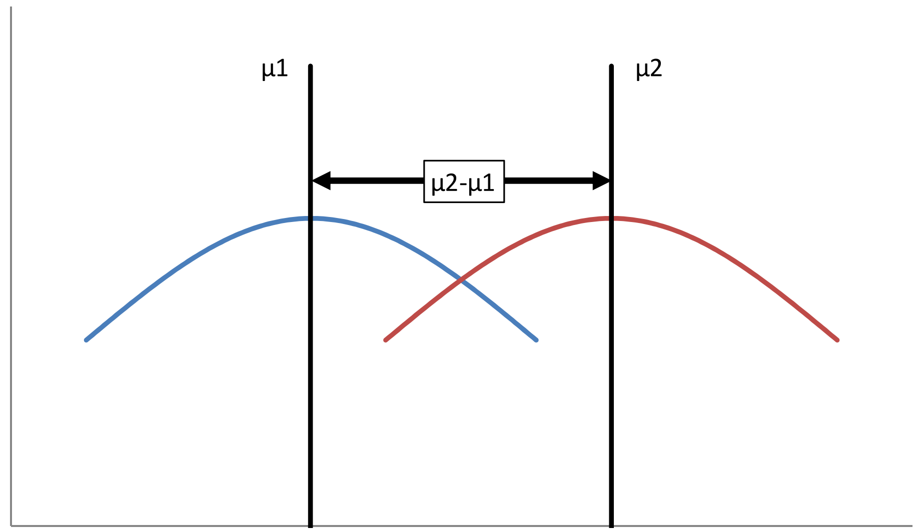

Figure A-3
Normal Populations with Broad Distributions

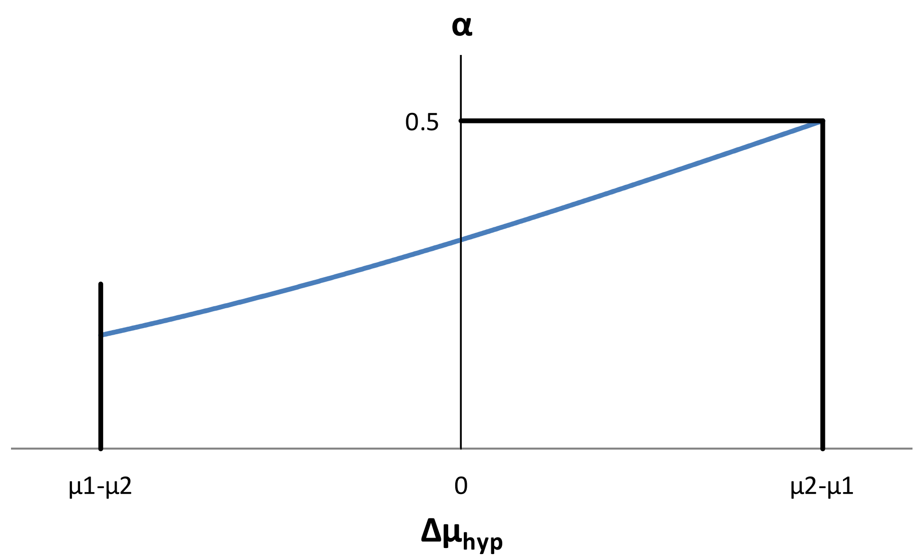

Figure A-4
Hypothesis Testing Significance Level for Broad Distributions

A.2 Evaluation of Appropriateness of the Methods Selected

Statistical hypothesis testing was used in Sections 3 and 7 to quantitatively analyze the impact of the first injection of zinc on radiocobalt activities and nickel concentration, and the impact of zinc injection on shutdown dose rates measured at the SRMP measurement points.

Heteroscedastic two-sample upper-tailed Student's t-tests were used for the analyses discussed in Section 3 to determine if the averages of the chemistry data measured during the first zinc cycle were statistically significantly different from the various pre-zinc data sets. The standardized test statistic, the degrees of freedom, the alternate hypothesis, and the upper-tailed rejection region of this test, respectively, are given by the following equations [67]:

$$t = \frac{m_2 - m_1 - \Delta\mu_{hyp}}{\sqrt{\frac{s_1^2}{n_1} + \frac{s_2^2}{n_2}}} \qquad \textbf{Eq. A-1}$$

$$\nu = \frac{\left(\frac{s_1^2}{n_1} + \frac{s_2^2}{n_2}\right)^2}{\frac{\left(s_1^2/n_1\right)^2}{n_1 - 1} - \frac{\left(s_2^2/n_2\right)^2}{n_2 - 1}} \qquad \textbf{Eq. A-2}$$

$$\mu_2 - \mu_1 > \Delta\mu_{hyp} \qquad \textbf{Eq. A-3}$$

$$t \geq t_{\alpha,\nu} \qquad \textbf{Eq. A-4}$$

where t is the standardized test statistic, m_1 and m_2 are the sample means of data sets 1 and 2, respectively, $\Delta\mu_{hyp}$ is the null value, s_1 and s_2 are the sample standard deviations of data sets 1 and 2, respectively, n_1 and n_2 are the number of data in data sets 1 and 2, respectively, ν is the number of degrees of freedom of the test, μ_1 and μ_2 are the true means of data sets 1 and 2, respectively, and $t_{\alpha,\nu}$ is the value of the t distribution at the α significance level with ν degrees of freedom. Curves analogous to those given in Figure A-2 and Figure A-4 can be generated by combining Equations [A-2] through [A-4] and solving for $\Delta\mu_{hyp}$, yielding the following inequality:

$$\Delta\mu_{hyp} \leq m_2 - m_1 - t_{\alpha,\nu}\sqrt{\frac{s_1^2}{n_1} + \frac{s_2^2}{n_2}} \qquad \textbf{Eq. A-5}$$

where all parameters are as previously defined.

This method is valid for normally distributed data, and unlike a pooled (homoscedastic) t-test, it does not require equality of the true variances of the two populations of data [67]. An upper-tailed test was chosen to evaluate if the post-zinc data were statistically greater than the pre-zinc data. It was chosen in lieu of a comparable z-test or a pooled t-test because it can accommodate small sample sizes and it does not require knowledge of the true variances of the sample populations. It should be noted that the Student's t-test approaches the z-test with increasing sample size.

In order to correctly apply this method, normality tests were performed on representative samples of the measured radiocobalt data evaluated in Section 3. Specifically, periods of approximately constant activity (i.e., there was no apparent upward or downward trend) were identified at a representative sample of units and cycles for Co-58 and Co-60. The measured activity values (raw data as opposed to logarithmic activity) were then tested for normality and lognormality using Statgraphics. The results of these analyses are presented graphically. Each set of raw data is presented followed by a histogram showing the normal and lognormal distributions fit to that set of data in Figure A-5 through Figure A-12.

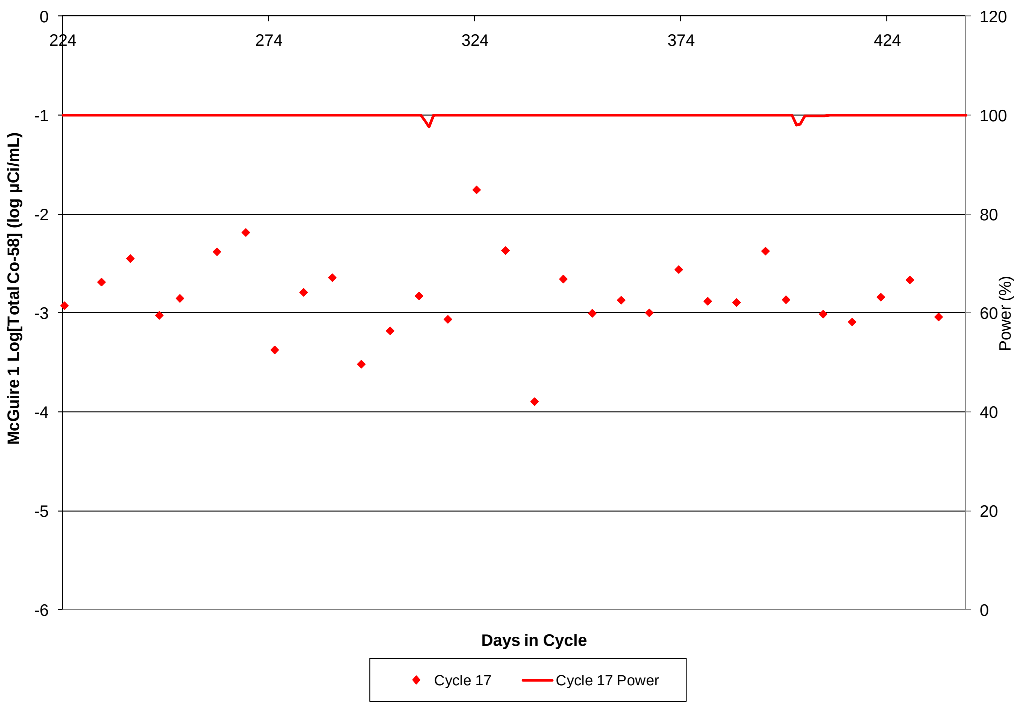

Figure A-5
McGuire 1 Cycle 17 Logarithmic Total Co-58 Activity

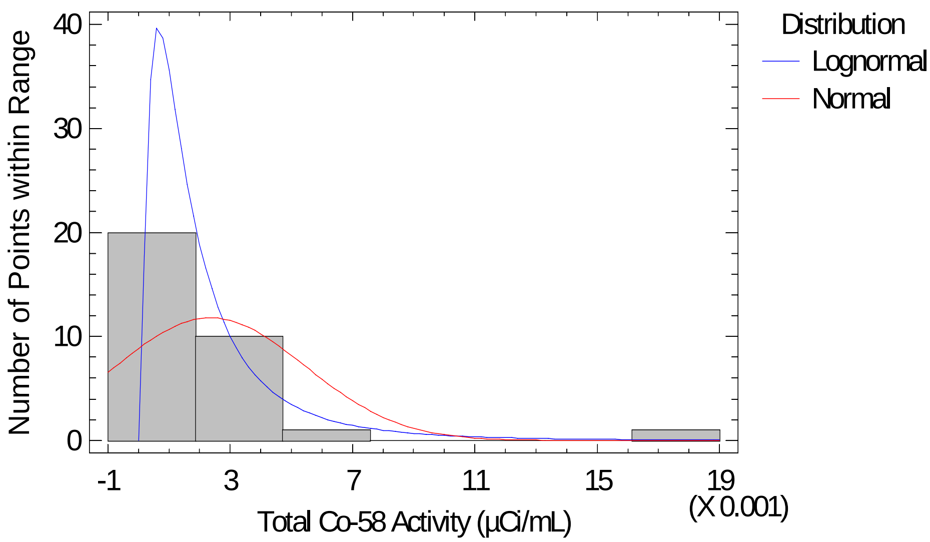

Figure A-6
McGuire 1 Cycle 17 Total Co-58 Statistical Distribution Fitting

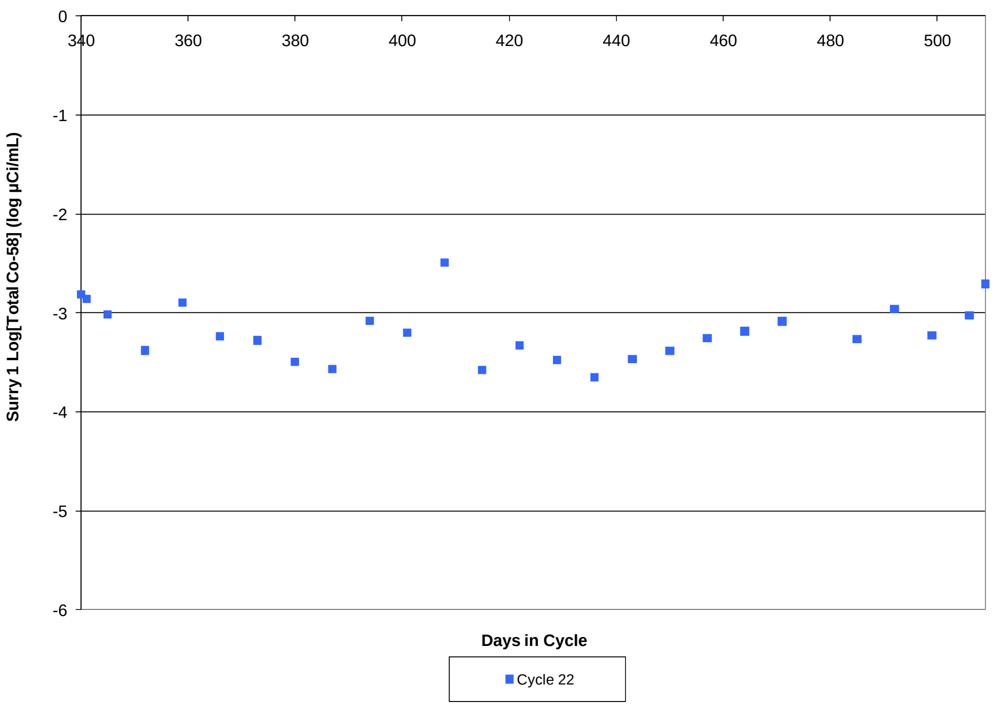

Figure A-7
Surry 1 Cycle 22 Logarithmic Total Co-58 Activity (post-Zn)

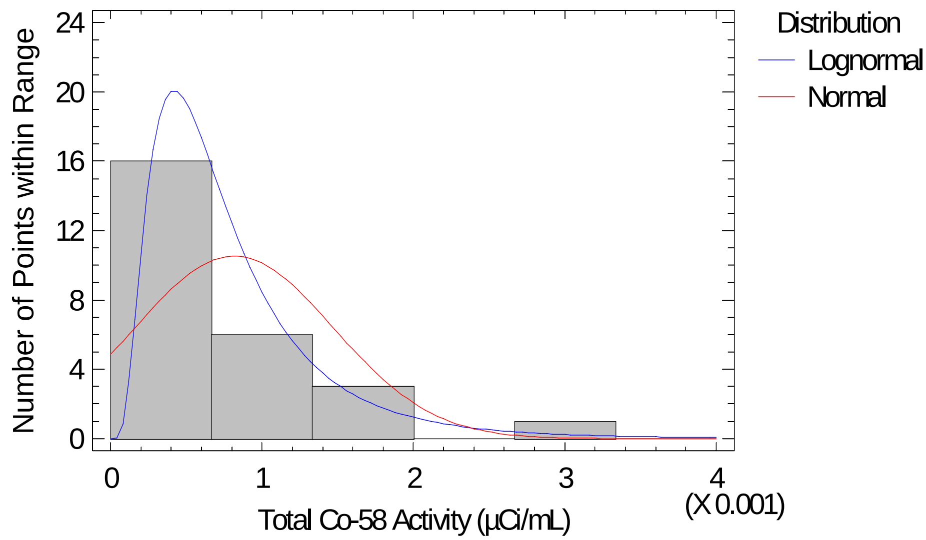

Figure A-8
Surry 1 Cycle 22 Total Co-58 Statistical Distribution Fitting (post-Zn)

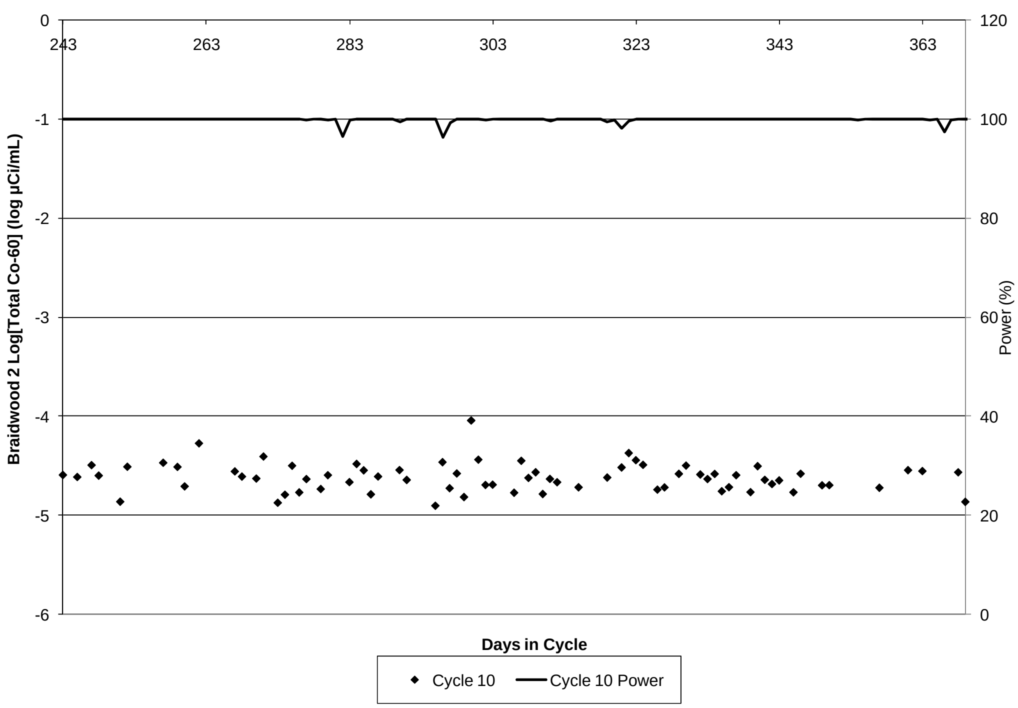

Figure A-9
Braidwood 2 Cycle 10 Logarithmic Total Co-60 Activity

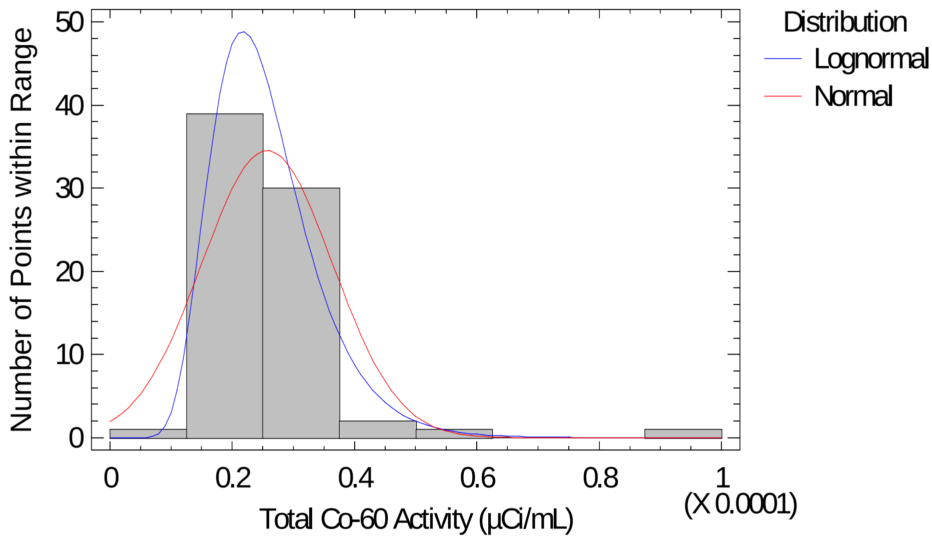

Figure A-10
Braidwood 2 Cycle 10 Total Co-60 Statistical Distribution Fitting

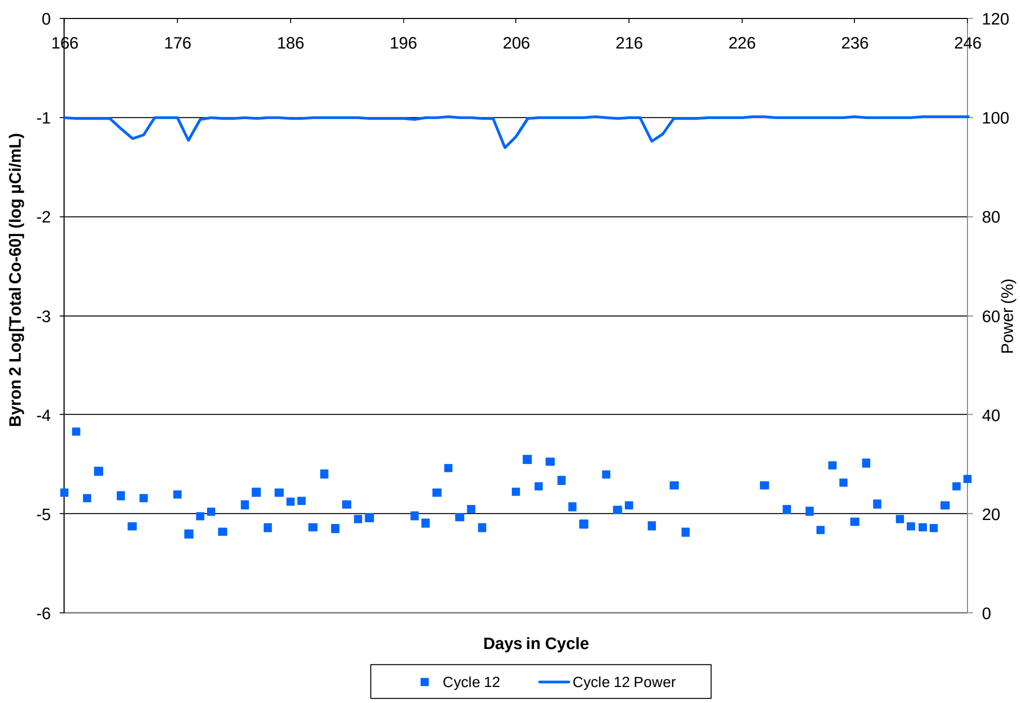

Figure A-11
Byron 2 Cycle 12 Logarithmic Total Co-60 Activity

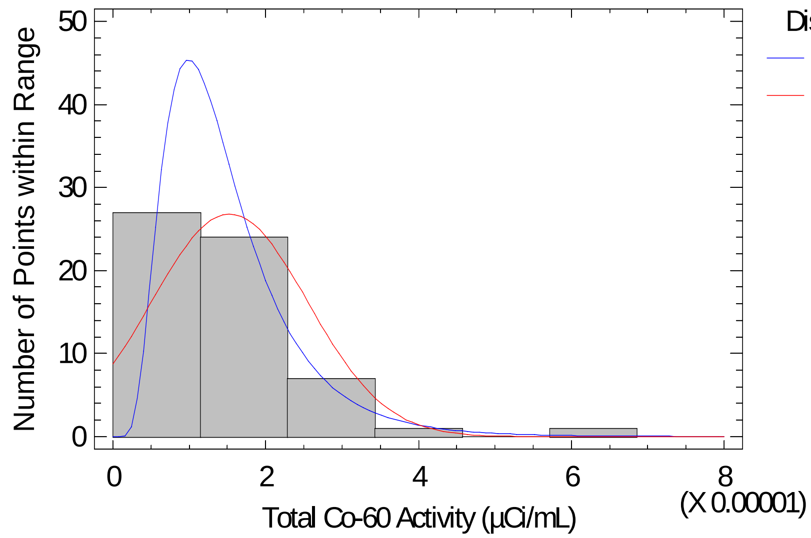

Figure A-12
Byron 2 Cycle 12 Total Co-60 Statistical Distribution Fitting

The figures presented above show that the total Co-58 and Co-60 activities are generally better described by a lognormal distribution (i.e., the logarithm of activity is normally distributed) rather than by a normal distribution as the lognormal probability density functions (PDFs) fit to each data set show better agreement with the histogram bars than do the normal PDFs. Based on the limited available nickel data, it appears that the nickel concentration is generally adequately described by a normal distribution. These results are important because they show that the hypothesis testing methods discussed above, which are valid for normally distributed data, must be applied to the logarithmic Co-58 and Co-60 activities (as opposed to the measured activities) and to the measured nickel concentration (as opposed to the logarithmic concentration.

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