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Pressurized Water Reactor Fuel Impact Assessment for Injecting Zinc at a High-Duty PWR: Callaway

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Technical Report

Pressurized Water Reactor Fuel Impact Assessment for Injecting Zinc at a High-Duty PWR: Callaway

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Interim Report, October 2003

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REPORT SUMMARY

Zinc injection is an effective technique for lowering shutdown dose rates in pressurized water reactors (PWRs). Another potential benefit provided by zinc injection is the reduction in crack initiation and possibly crack propagation of Alloy 600. Further benefits may be provided by a long-term reduction in plant corrosion rates and general improvement in the material condition of a PWR plant.

Background

To date, PWRs considered to be high-duty have been unable to realize the benefits associated with zinc injection. The lack of participation by this class of plants arises, in part, from the fact that zinc injection, in the short-term, will exacerbate mechanisms that can result in an axial offset anomaly (AOA) or crud-induced power shift (CIPS). This report describes the Westinghouse evaluation performed for Callaway to allow that unit to inject zinc during Cycle 13. The specific emphasis of this report concerns zinc's potential impact on fuel. Callaway is a high-duty unit that experienced varying degrees of AOA between Cycles 4 - 11. Callaway's interest in zinc injection stems from a desire to reduce plant radiation fields in anticipation of replacing steam generators following Cycle 14. EPRI's Robust Fuel Program (RFP) sponsored this evaluation for Callaway as part of a multi-cycle demonstration program.

Objectives

To describe from a fuel impact standpoint the evaluation issues and process that allow a high-duty PWR to inject zinc and, secondarily, to outline issues that are evaluated for non-fuel primary components when a PWR is considering zinc injection.

Approach

Using existing operational experience with zinc injection, corrosion models, and AOA risk assessment tools, evaluations with varying degrees of complexity were performed to confirm that zinc injection could be implemented at the Callaway plant without a significant risk to fuel performance. Other evaluations addressed non-fuel safety-related and operational considerations to further assure that zinc injection would be accomplished successfully.

Results

The evaluations demonstrate that, along with prescribed operational monitoring, zinc injection is viable for Callaway Cycle 13. A step sequence injection program is recommended in the first cycle due to anticipated elevated corrosion product levels when injection commences. AOA risk analysis suggests little susceptibility to AOA. The calculated maximum best estimate oxide thickness for the fuel clad was predicted in second-cycle fuel and was less than 40 microns even with a zinc penalty applied.

EPRI Perspective

In addition to proven benefits of zinc addition on reducing radiation fields and a potential benefit in the area of primary water stress corrosion cracking (PWSCC), EPRI's Robust Fuel Program views zinc addition as a possible mitigation strategy for AOA. From an AOA perspective, the benefits may arise from two factors:

- Laboratory studies have demonstrated that zinc reduces corrosion rates for primary system materials. Therefore, in the long term this should have a positive impact on the corrosion product source term in the reactor coolant system.
- Based on fuel crud measurements and observations from the existing zinc experience base, crud is relatively thin and uniform and has a tendency to deposit along the entire length of the fuel assembly. If this pattern holds for high-duty units, then the requisite thick crud for boron to deposit in for AOA may be avoided.

The Westinghouse evaluation reported in this document was sponsored by the Robust Fuel Program and paves the way to broaden the experience base for utilities wishing to add zinc. Callaway has encountered AOA in a number of previous operating cycles. To reduce this propensity for AOA and reduce the risk for fuel-related problems from adding zinc, AmerenUE has taken several measures to abate a chronic crud inventory burden. These measures include reducing overall core duty, ultrasonically cleaning all reinsert assemblies over the past two refueling outages, and operating at a constant pH_t 7.2 reactor coolant system (RCS) chemistry level since Cycle 11. These measures have positioned Callaway as a good demonstration candidate for high-duty plants that wish to inject zinc.

Callaway began injecting zinc in May 2003. Post-zinc injection fuel examinations will be performed in 2004 following the completion of Cycle 13. If the post-cycle examinations are satisfactory, injection will continue in Cycle 14 with additional fuel examinations planned in 2005. Results of these poolside campaigns and operating cycle data will confirm whether zinc can be added to a high-duty PWR without detriment to fuel performance.

Keywords

PWR
Zinc injection
Radiation reduction
PWSCC
Axial Offset Anomaly
AOA
Crud

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FUEL EVALUATIONS

Reactor Coolant Chemistry and Corrosion Product Behavior

Depending on the initial rate of injection, the first measurable detection of zinc in the reactor coolant generally occurs 10 to 20 days after the start date of injection. In some reported cases, a period of four weeks has elapsed from the start of zinc injection to the first detectable result. The initial addition of zinc to the RCS also results in an increase in the radiocobalt activity concentrations in the coolant. The "equilibrium" radiocobalt concentrations that are attained appear to be plant-specific and dependent on the pre-zinc values. However, there is some evidence of a relationship between how high the radiocobalt increases are from the pre-zinc coolant values to post-zinc concentrations and the average zinc level in the coolant. The magnitude of increase in ^{58}Co activity is greater than the increase in ^{60}Co activity, suggesting that zinc may be affecting the release of nickel from ex-core corrosion films to a greater extent than cobalt.

The degree to which coolant nickel levels can be expected to increase should be available from measurements made at plants that are operating with zinc addition. Unfortunately, very little pre-zinc nickel data is available. This makes it difficult to project the anticipated increase at other units. Nickel data from the first two cycles of zinc addition at Farley 1 are shown in Figures 1-1 and 1-2 to illustrate this point. Cycle 16 added zinc at a concentration of about 30 ppb. Steam generators were replaced after Cycle 16, and the zinc concentration was reduced to about 12 ppb in Cycle 17.

The few values available prior to the start of zinc addition at Farley 1 (Figure 1-1) are all less than the laboratory detection limit of 1 ppb. For most of the cycle, these values remained at this level until about 360 days from the beginning of the cycle. It is noted that at about 360 days the reported laboratory measured values changed from soluble nickel to total nickel. Since nickel saturation under PWR primary coolant conditions may be anywhere from 0.1 – 0.5 ppb, detectable nickel levels at Farley are considered to be largely in the form of particles or colloids. The observed increase in nickel concentrations during the last month of the cycle could be either due to a true increase or due to the change in the measured (and reported) value from soluble to total nickel. Assuming that the values before 360 days represent total nickel at a level of 1.0 ppb, an increase due to zinc by a factor of two (e.g. from ~1 to ~2 ppb) could be inferred from the Cycle 16 data.

The Farley 1 Cycle 17 data presented in Figure 1-2 represent a second cycle of zinc addition. As noted on the figure, zinc injection started about 50 days into the cycle and several baseline nickel samples were obtained and analyzed beforehand. However, since there was residual zinc in the system from the previous cycle, the nickel concentration before the start of zinc addition likely reflects some zinc "memory effect", and the measured nickel values may not represent true baseline (no zinc) conditions. The data indicate that the nickel concentration may have increased by about a factor of two (~1.5 to ~3) after the resumption of zinc addition. Another complicating factor regarding Cycle 17 is that it was the first cycle after steam generator replacement. Higher coolant nickel levels are expected due to higher corrosion product release rates from the new steam generator tubing material.

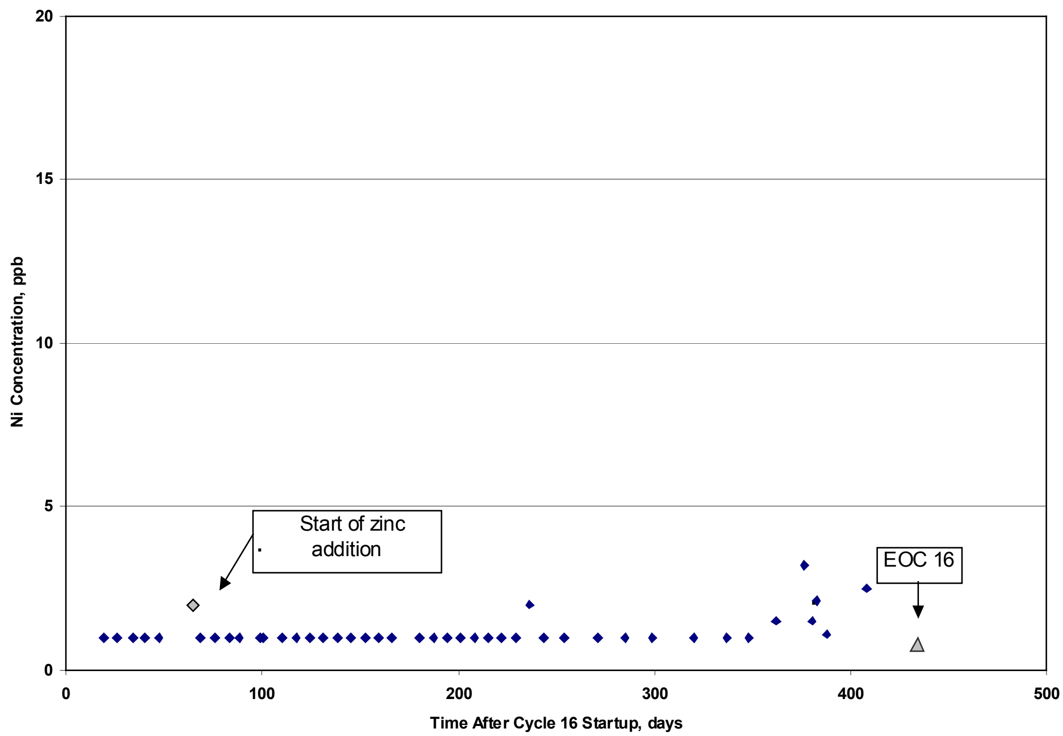

Figure 1-1
Farley 1 Cycle 16 RCS Nickel Concentrations (First Cycle of Zinc Addition – 30 ppb)

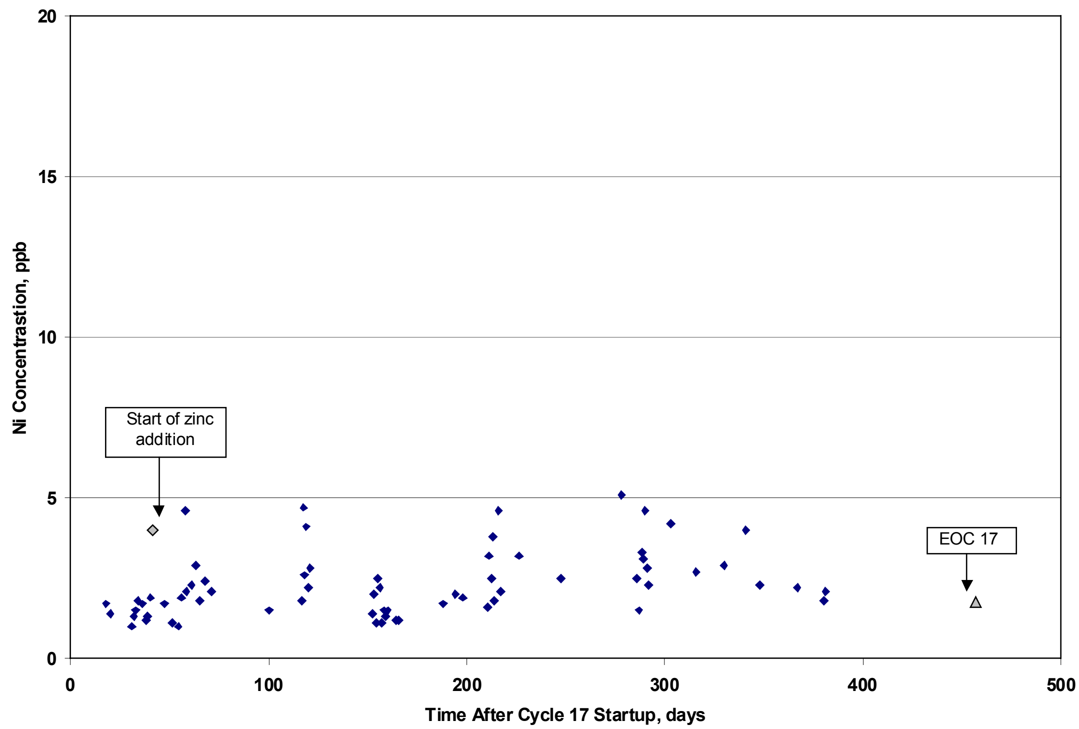

Figure 1-2
Farley 1 Cycle 17 RCS Nickel Concentrations (Second Cycle of Zinc Addition – 12 ppb)

Even though the data are incomplete in the sense that an absolute increase in coolant nickel concentration cannot be ascribed after the injection commenced, some general observations are made regarding the Farley-1 experience:

- A factor of two increase in the nickel concentrations is likely with zinc concentrations of about 15 ppb.
- Total nickel concentrations range from about 1 to 3 ppb after two-to-three cycles of zinc addition.
- Increases in coolant nickel concentration at EOC, coinciding with increases in the insoluble ^{58}Co concentrations, are commonly observed in many operating PWR plants.
- A sampling program must be in place to follow the nickel behavior.

Experience learned from Farley 2 during Cycle 14 showed that if the coolant nickel concentration does rise above undesired levels (in this case approximately 9 ppb), isolating zinc injection will cause the nickel levels to return to more acceptable values.

Crud Induced Power Shift (AOA) Evaluation

The expected increase in coolant nickel concentration as a result of adding zinc is assumed, at least initially, to increase the risk of CIPS (Crud Induced Power Shift, or AOA). Plants that have added zinc to the coolant in the 10-40 ppb range have not experienced AO differences in excess of 3% attributed to CIPS. However, most of the zinc addition experience is in cores with lower boiling duty compared to Callaway. Callaway has experienced CIPS and has measured crud thicknesses in excess of 2 mils (50 microns) in previous cycles. Plants such as Farley and Diablo Canyon that have added zinc have not had a history of thick crud. The Callaway High Duty Core Index (HDCI) and mass evaporation rates calculated with the VIPRE code are compared in Table 1-1.

Table 1-1
Fuel Duty Comparison

Plant	VIPRE-W Maximum Mass Evaporation Rate (lb/hr-ft2)	High Duty Core Index[1] (HDCI)
Farley 1 and 2	Not Available	116-126
Diablo Canyon 1 and 2	300-345	108-119
Callaway Cycle 13	390	173

In Callaway and other plants that have experienced CIPS, the crud is thickest in the areas of the core undergoing sub-cooled nucleate boiling. This is generally in the upper spans of the assemblies operating with the highest heat flux. For cores adding zinc to the coolant in excess of 10 ppb, a different type of deposit has occurred. The deposit appears to more uniform over the height of the assemblies and is also present on the grids and nozzles. The deposit appears to be thin and black in color. After several months in the spent fuel pit, the deposit is not longer visible on the fuel indicating it is not firmly attached to the clad. Crud scrapes at Diablo Canyon indicate that the crud present contains carbon and appears to be more filmy and pliable than other core crud. The carbon may come from the acetate material as zinc was added to the coolant in the form of zinc acetate.

A Callaway-specific CIPS analysis was performed to quantify the potential increased CIPS risk in the initial cycles of zinc addition. Various assumptions regarding the amount of zinc being added were evaluated. The results from these various assumptions were used to define the amount of zinc to add in order to balance the risk of CIPS with the potential benefits of zinc addition.

While coolant nickel concentrations are expected to rise in the first few cycles following zinc addition, little actual pre-zinc addition data is available from the existing experience base to establish a baseline and further determine the magnitude of increase in nickel concentrations attributable to zinc addition. Other plant zinc addition data are available that can be used to estimate the expected initial increase in nickel release to the coolant. Zinc uptake data have been used in the Callaway analysis in order to determine the expected increase in corrosion product release to the coolant for the initial cycles of zinc addition**.** Zinc displaces cobalt and other transition metals (notably nickel) when it is incorporated in the corrosion films. The amount of zinc retained in the primary system, or the zinc uptake, is determined from a mass balance. The total zinc mass added to the system is measured during the cycle. The amount removed by the CVCS can also be reliably estimated. The zinc uptake for a given cycle is therefore determined from the amount added to the RCS and the amount removed via the CVCS. Zinc uptake can be parameterized as a function of total zinc exposure. In the Callaway analysis, nickel release was inferred from this assuming each atom of zinc displaces an atom of nickel from the corrosion films. In this manner, nickel release via displacement from the corrosion film can also be parameterized as a function of zinc exposure.

The zinc uptake method may not account for all modes of nickel release, however. In addition to displacement of nickel from the corrosion films, the reduction in corrosion film thickness may lead to release of loosely attached corrosion products, primarily nickel ferrite, from the outer layer of the plant corrosion films. Available plant data was used to estimate the total nickel release, resulting from incorporation of zinc and displacement of nickel in the inner layer of the corrosion film, as well as thinning of the outer layer of the corrosion film. The corrosion products attributed to the thinning of the corrosion films were included in the Callaway CIPS analyses. An estimate of the expected nickel release during the first cycle of zinc addition, including the effects of corrosion layer thinning is provided in Figure 1-3.

The Westinghouse BOB code[2] was used to evaluate CIPS risk. BOB models the various processes leading to CIPS including corrosion product release, crud deposition, and boron deposition in the crud layer. BOB quantifies CIPS risk based on the maximum expected boron mass deposited in the crud. The difference between measured and predicted axial offset is directly proportional to this maximum boron mass. The amount of boron mass calculated by BOB is directly proportional to the level of risk for CIPS. Mild CIPS would be detectable in the plant but would be expected to have minimal impact on plant operations. This level of CIPS would result in a maximum difference between measured and predicted AO of 2-3%. Moderate CIPS would be consistent with a maximum AO difference of 5% lasting for several months of the cycle. Plants experiencing moderate CIPS would still be expected to be able to operate at full power for the planned duration of the cycle, but with additional evaluations and operational requirements. Severe CIPS would be consistent with AO differences as large as 10%, or more. Continued operation at 100% power operation may be jeopardized.

An acceptable risk level was established based upon a boron mass expected to result in a relatively small change in axial offset (<1%). For a four loop core, this corresponds to about 0.2 lb boron mass deposited. Various zinc injection scenarios were considered, and the resulting increase in nickel and other corrosion product release were determined based on the zinc exposure (ppb-mo) for the scenario. Zinc injection at various zinc levels for the entire cycle was considered. An additional case was also generated assuming no zinc addition for the first portion of the cycle, followed by stepped increase in the zinc concentration. An initial zinc concentration of 5 ppb beginning 6 months into the cycle was increased to 10 ppb after three months. As expected, the first cycle of zinc addition resulted in increased CIPS risk. However, the expected increase in CIPS risk was relatively small for the scenarios considered. The BOB results are summarized in Figure 1-4.

The final case, delaying zinc addition and using a stepped concentration, was confirmed to meet the acceptable risk level criteria. This was the approach that has been used for implementing zinc addition at Callaway. Delaying zinc has the advantage of confirming, early in the cycle, that there is not a pre-existing CIPS or other anomalous condition. The stepped approach to increasing zinc ensures that the increases are done in a cautious and controlled manner, allowing for sufficient time for any unexpected behavior to become evident.

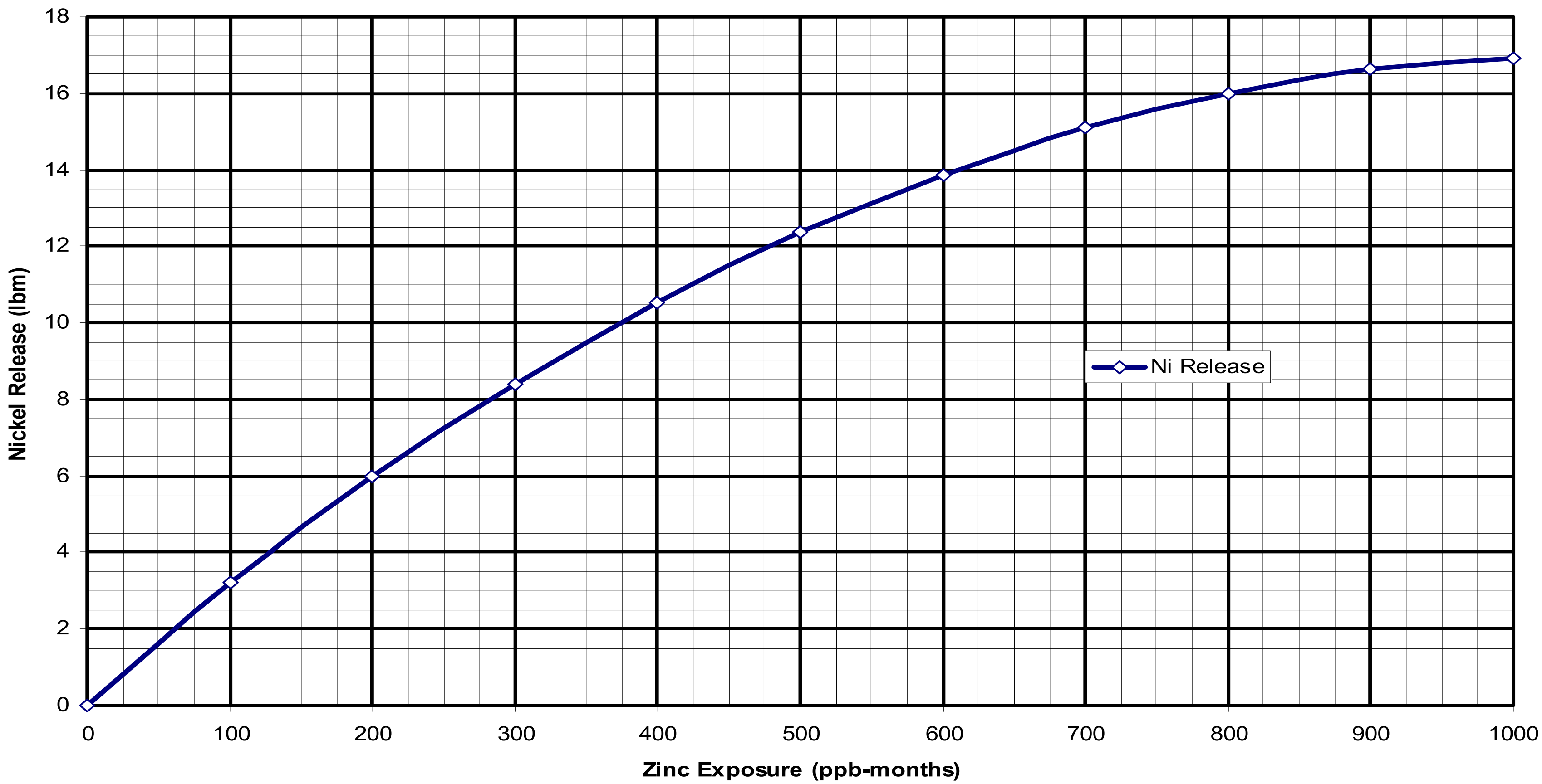

Figure 1-3
Estimated First Cycle Nickel Release versus Zinc Exposure

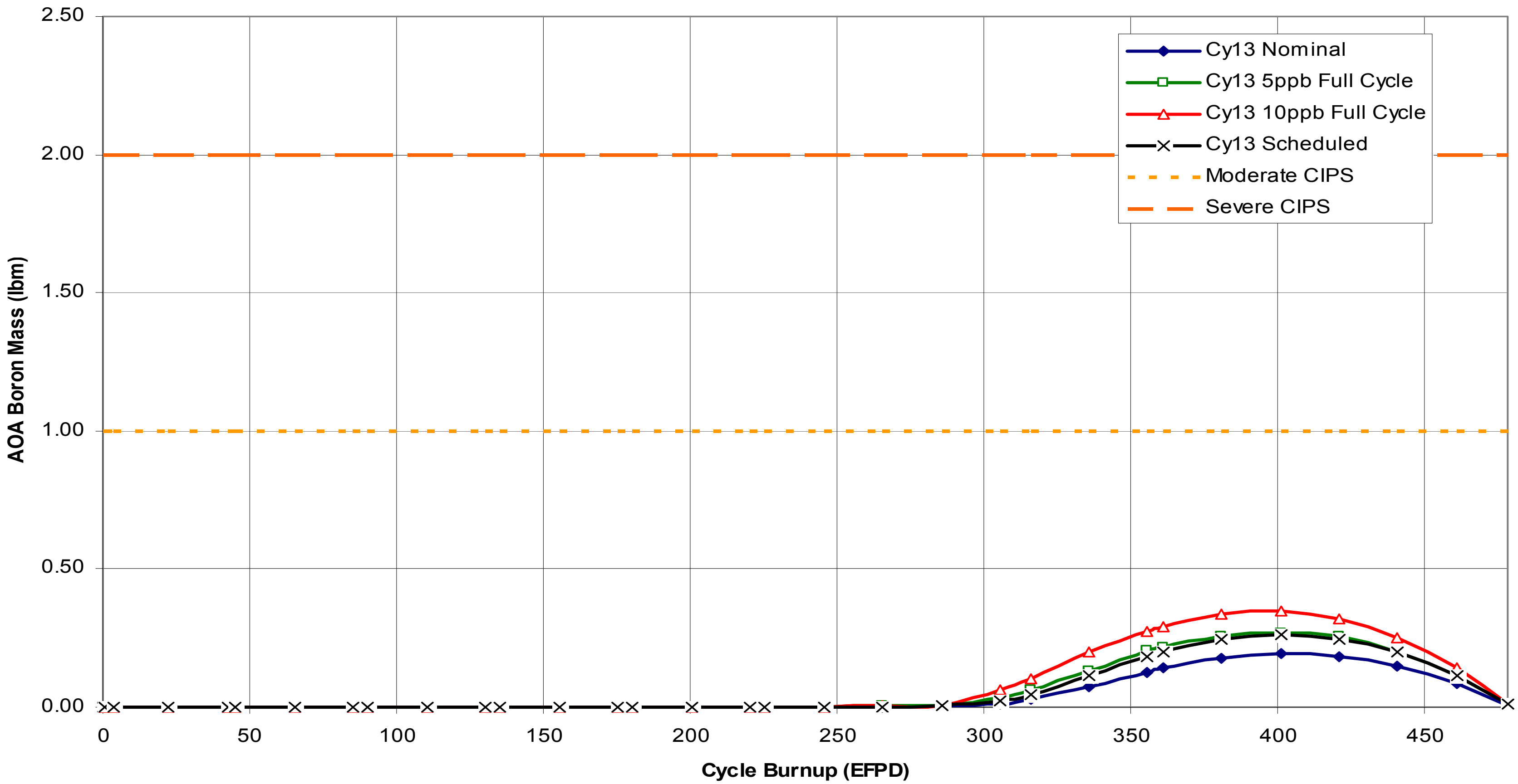

Figure 1-4
Callaway BOB Code Boron Buildup Prediction

Cladding Oxidation Evaluation

Clad oxide thickness measurements after the initial zinc addition demonstration cycle at Farley Unit 2 resulted in higher than expected oxide thicknesses. The fuel in this time-period used Westinghouse Improved Zr-4 cladding material. Eddy current measurements showed the oxide thickness to be about 10% higher than expected after about 10 months of zinc exposure based on the clad corrosion model in use at that time. A subsequent root cause evaluation of the increased cladding oxidation did not assign a significant role to the presence of zinc. However, based on the data from these fuel examinations, conservative corrosion estimates were assigned to cladding oxidation rates for units adding zinc. An increase in predicted oxide thickness of 1%/month during zinc addition was applied in the fuel rod design corrosion analysis. Even with this conservative penalty the design criteria for fuel cladding oxide thickness was met. Subsequent fuel examinations, and general usage of the advanced fuel cladding material ZIRLO™, have confirmed that any impact due to zinc addition are minimal for low-duty plants with ZIRLO™ clad. As a result of the fuel examinations, the conservative corrosion penalty is no longer applied to the low-duty Farley or Diablo Canyon units for clad corrosion analysis in zinc addition cycles.

Since Callaway is considered a high-duty plant, the concern for enhanced cladding oxidation with zinc addition still exists. Callaway has had a history of thicker crud than the lower duty zinc plants such as Farley or Diablo Canyon. Incorporation of zinc into the crud layer, or changes in the crud morphology resulting from zinc addition could enhance clad corrosion. This concern for Callaway is being addressed in a number of ways:

1. Callaway utilizes ZIRLO™ cladding material.

2. The conservative corrosion "penalty" has been applied in the fuel rod design activities and the cladding oxide thickness criterion has been confirmed.

3. Multi-cycle fuel examinations will be performed subsequent to the addition of zinc at Callaway in order to assess any impact related to zinc addition. Based on the results and conclusions of these examinations, the estimated increase in oxidation rate may be reduced or eliminated.

The detailed fuel evaluation for Callaway addressed all key fuel performance criteria. Cladding corrosion is the primary fuel performance criterion that can be impacted by zinc addition. Rod internal pressure can also be impacted by zinc addition, but only insofar as the increased cladding corrosion affects the analysis. These two criteria (cladding corrosion and rod internal pressure) have been explicitly evaluated for Callaway. The other fuel rod design criteria such as clad stress/strain, rod growth, clad fatigue, or fuel temperatures are either not significantly impacted or not impacted at all by the increase in cladding corrosion due to zinc addition.

The Callaway Cycle 13 reload core design was used as the reference core to assess the impact of zinc addition on the fuel rod design analyses for both Callaway Cycle 13 and future Callaway cores. The analyses of the fuel regions in Callaway Cycle 13, with advanced cladding materials, confirmed that all fuel performance criteria are met (with margin). The analysis conservatively assumed zinc addition in Cycle 13 for the entire 18 months of the cycle. The maximum best estimate oxide thickness calculated occurred in second cycle fuel and was less than 40 microns even with the zinc penalty applied.

While there is a potential for the use of conventional clad fuel at Callaway (via reinsertion of burned assemblies from the spent fuel pit), this usage would be limited to a single cycle. The impact of zinc addition on these assemblies (as well as all assemblies resident in the core for any future cycle) will be assessed as part of the routine fuel rod analyses performed on a cycle-specific basis.

Monitoring and Remedial Actions

While the evaluations performed confirm all criteria are met and the level of any risk is tolerable, additional operational considerations are defined in order to mitigate the consequences of any unexpected behavior. These include specifications of various coolant chemistry and core power distribution parameters to be monitored leading up to and during zinc addition at Callaway. These parameters provide indications and insight into core behavior while zinc is being added to the primary system. The frequency of measurements is such that, in the event any anomalous behavior is detected, sufficient time is available to initiate remedial actions (including potentially securing zinc addition) to avoid any worsening of the unexpected behavior. In this regard, it is noted that the time-scale for the zinc interaction processes is measured in days and weeks.

Prior to commencing zinc addition, certain preconditions must be met. Primary system nickel concentrations should be <2 ppb and silica concentrations <1 ppm. Meeting these specifications offer some margin that there is no pre-existing or potential adverse condition (e.g. elevated crud levels) and allows some additional margin for the expected increase in nickel concentration when zinc is added. Additionally, regularly scheduled core flux and power distributions are reviewed to confirm no pre-existing CIPS condition.

RCS Nickel Monitoring

During operation, monitoring the RCS nickel concentration (weekly while the targeted zinc concentration is being established and twice monthly thereafter) and regularly scheduled (monthly) core flux and power distributions will provide indication of the need for further actions. Nickel concentrations should remain below 6 ppb. If this limit is exceeded, a flux distribution measurement is taken. The flux distributions are reviewed for indications of the onset of CIPS. Further review and assessments may be necessary and result in additional actions. Such actions and assessments would be used to define the need to reduce (or suspend) the zinc concentration.

RCS Zinc Monitoring

The RCS zinc concentration is also monitored as a control parameter. Normally, the concentration would be controlled against the targets established by the CIPS analysis for a high-duty core. In the case of Callaway Cycle 13 (first cycle of zinc addition), a lower limiting value of zinc concentration has been defined in order to introduce an additional level of prudence until operational experience and fuel examination results are gained. Subsequent Callaway cycles are expected to be able to use higher levels of zinc concentration. For low-duty cores, the limit would be set no higher than that based upon a value supported by the current operational experience and/or any safety-related evaluations (currently 40 ppb).

Core Power Distribution Monitoring

Monthly core power distribution monitoring for indications of CIPS is also required. Should CIPS occur with a measured axial offset differing from predictions in excess of 3%, further reviews of plant data with the fuel vendor are required. These reviews could lead to reducing or terminating zinc addition.

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NON-FUEL EVALUATIONS

While not the focus of this document, non-fuel related evaluations performed or supporting information used in supporting the zinc injection program for Callaway Cycle 13 included the following:

- General background and historical information related to zinc addition in order to categorize Callaway relative to the existing operational experience.
- Summary of the zinc addition process in the RCS for understanding of the various mechanism's associated with zinc injection.
- Supporting laboratory or plant data related to potential impact on plant materials and components, including:
  - Alloy 600, 690,
  - Inconel X-750,
  - Type 304 and 316 steel,
  - Stellite,
  - Fuel cladding materials,
  - RCP internal components, seals and leak rate (including silicon nitride seals),
  - CVCS, CCP, RHR pump seals, boron/holdup tank systems, valve stems & seat materials.
- General summary of all key plant/utility considerations (especially those which may have cost implications).
- General zinc implementation strategy (timing and concentration).
- Projections for dose reductions under various assumptions.
- Evaluation of safety- or accident-related items as follows:
  - Boron dilution accident,
  - Technical Specification and UFSAR impacts,
  - Post-LOCA hydrogen generation,
  - Sump pH,
- Reactivity control,
- All other accidents for confirmation of no impact as a result of zinc injection.

- Safety class transition.

These evaluations were used to support the 10 CFR 50.59 assessment for zinc injection into Callaway Cycle 13. A 10 CFR 50.59 screen was the recommended conclusion.

Other plant related considerations included:

- Considerations for the use of natural or “depleted” zinc.
- Coolant activity impacts.
- Demineralizer shielding considerations.
- Primary system chemistry and sampling equipment.
- Waste considerations:
  - Effluents,
  - Resins,
  - Filters.
- Impacts on outage schedule and shutdown releases.
- Definition of when to secure zinc addition during the cycle.
- Considerations for the injection equipment and installation.
- Summary of operating experience from other PWRs injecting zinc and an assessment of applicability to Callaway.
- Overall conclusions and recommendations.

3 CONCLUSIONS

Zinc injection, in the short-term, will exacerbate the mechanisms that can result in an Axial Offset Anomaly (AOA) or Crud Induced Power Shift (CIPS). Zinc displaces nickel and other metals from existing corrosion films and the resulting increased nickel concentration in the reactor coolant may lead to increased crud deposition on the fuel. This increases the risk of AOA. If zinc is incorporated in the fuel crud and changes the crud characteristics, increased clad corrosion may result. An engineering evaluation of zinc injection for Callaway Cycle 13 has demonstrated that clad corrosion will remain acceptable. A zinc injection strategy has also been identified to minimize AOA risk.

For other high duty plants considering zinc addition, a similar risk analysis is recommended. A conservative evaluation of clad corrosion including a penalty for zinc effects on clad corrosion is recommended until examinations of fuel cladding in high-duty plants exposed to zinc demonstrate that no enhancement of clad corrosion occurs. Determination of conservative zinc injection approaches to minimize AOA risk by application of the BOB or BOA[3] codes is also recommended.

4
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