Overview Report on Zinc Addition in PWRs

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Overview Report on Zinc Addition in PWRs

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The report is a corporate document that should be cited in the literature in the following manner:

Laboratory studies have shown that zinc addition to PWR primary coolant can mitigate primary water stress corrosion cracking (PWSCC) of alloy 600 and reduce PWR radiation fields. This report provides an overview of the major results of zinc addition programs at Farley Units 1 and 2 and Diablo Canyon Units 1 and 2 over several cycles and summarizes the conclusions of these programs.

**Background**
EPRI and Southern Nuclear cosponsored the initial field demonstration of zinc addition at Farley Unit 2 in 1994-95. The results of this demonstration confirmed the beneficial effect of zinc in mitigating radiation fields. Because of the short duration of the initial test, additional studies were conducted at Farley Units 1 and 2 and Diablo Canyon Units 1 and 2 (operated by Pacific Gas & Electric) to evaluate the effect of zinc on radiation fields, PWSCC of alloy 600, and fuel cladding corrosion.

**Objective**
To evaluate the effect of zinc addition on primary coolant chemistry, radiochemistry, dose rates, PWSCC of alloy 600 steam generator tubing, and fuel cladding corrosion in PWRs.

**Approach**
Investigators added zinc as an aqueous solution of zinc acetate. Depending on the initial rate of injection, the first detection of zinc occurs after a 10- to 20-day injection period. PWRs have demonstrated efficient management of reactor coolant system (RCS) zinc concentrations from 5 to 40 ppb over essentially a full fuel cycle. This report compares the zinc addition experience at Farley and Diablo Canyon units. It also provides a brief review of zinc addition at one U.S. PWR (Palisades) and three German PWRs (Obrigheim, Biblis A, and Biblis B). These PWRs are using zinc at a lower concentration than Farley and Diablo Canyon for the sole purpose of radiation field (dose rate) reduction.

**Results**
The addition of zinc to the RCS in concentrations from 5 to 40 ppb increases the radiocobalt activity concentrations in the coolant. Demonstrations clearly show that zinc additions to the reactor coolant reduce dose rates and deposited radionuclide activities. At Farley Unit 2, in specific, a factor of two reduction in dose rates has been realized over the last four cycles of zinc injection, although zinc has been added for less than half of any given cycle. Shorter exposures at Diablo Canyon Units 1 and 2 have yielded qualitatively similar results. Following partial cycles (up to 10 months) of zinc injection, the release and removal of $^{58}$Co, $^{60}$Co, and nickel have shown
significant increases during subsequent refueling/maintenance shutdowns. Substantial releases of $^{65}\text{Zn}$ have also occurred in plants using natural zinc acetate.

To date, the maximum period of zinc injection in plants seeking to mitigate PWSCC of alloy 600 tubing has been limited to about 10 months. Because of inspection uncertainties from cycle to cycle, it is premature to assign a significant role to the addition of zinc in mitigating PWSCC of alloy 600 steam generator tubing. However, characterization of spinel oxide corrosion films on the inside surfaces of steam generator tubing following exposure to zinc confirms the incorporation of significant concentrations of zinc in the corrosion films. Laboratory studies have shown that when zinc is incorporated in the corrosion film it has a beneficial effect on the PWSCC resistance of alloy 600.

The addition of zinc to the RCS appears to result in the formation of a thin dark deposit on the surface of the fuel rods at the end of the cycle. This has been reported at plants in which the RCS zinc concentration was greater than about 20 ppb during the operating cycle, but has not been reported for PWRs in which the zinc concentration remained at the 5 ppb level. The results of oxide thickness measurements indicate that zinc does not have a statistically significant effect on fuel cladding corrosion.

**EPRI Perspective**

The studies reviewed here confirm that zinc addition has a beneficial effect on radiation fields, but does not have a statistically significant effect on fuel cladding corrosion. The impact of zinc addition on mitigation of PWSCC in steam generator tubes is still unclear, since the duration of zinc exposure in these studies was too short and the tube inspection uncertainties too large to discern an effect. Multiple cycle monitoring will be needed to determine whether zinc actually mitigates PWSCC of alloy 600 steam generator tubes. Previous EPRI reports on zinc addition in PWRs include TR-106357, TR-106358 Vols. 1-2, TR-107904, TR-111349, and TR-113540.

**Keywords**

PWR
Radiation chemistry
Primary coolant chemistry
Alloy 600
Zircaloy
Stress corrosion cracking
ABSTRACT

Zinc additions to the primary reactor coolant system have been performed at:

- Farley Unit 2 in Cycles 10, 12 and 13, and
- Diablo Canyon Unit 1 in Cycle 9

under the aegis of tailored collaborations between EPRI and the Southern Nuclear and Pacific Gas & Electric Companies. Comprehensive reports have been published by EPRI for each of these campaigns.

Additional zinc injection programs have been carried out at Farley Unit 1 in Cycle 16, Diablo Canyon Unit 2 in Cycle 9, and are continuing in current operating cycles at Farley Units 1 and 2 and Diablo Canyon Units 1 and 2. At each of these plants the addition of zinc, as a dilute aqueous solution of zinc acetate, has been for the purpose of mitigating stress corrosion cracking (PWSCC) of Alloy 600 components in the primary coolant system. Zinc concentrations have been in the range from 20 to 40 ppb.

The purpose of this report is to provide a single overview document that summarizes the major results of these programs. Data are reviewed for the impact of zinc additions on:

- operating cycle chemistry and radiochemistry,
- end-of-cycle dose rates and component activities,
- end-of-cycle shutdown releases of radionuclides and metallic elements,
- stress corrosion cracking of Alloy 600 steam generator heat transfer tubing,
- fuel cladding corrosion, and
- other components of the primary coolant system.

The major effect seen to date has been significant reductions in dose rates and component activities. The data are inadequate to establish an effect of zinc on Alloy 600 stress corrosion cracking. After initial concerns related to enhanced fuel corrosion, the results of the last several campaigns have shown negligible effects on fuel cladding. Based on limited inspections, no effects have been seen for either reactor coolant pumps or primary system valves.

In addition to the programs at Farley and Diablo Canyon, which have the objective of PWSCC mitigation, zinc additions are also being carried out at the Palisades PWR nuclear power plant, and at three PWRs in Germany. The objective of these latter programs is the reduction of
radiation fields; the RCS zinc concentrations are maintained at approximately 5 ppb. The available data from these programs is also reviewed in this report.
ACKNOWLEDGMENTS

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EXECUTIVE SUMMARY

Zinc additions to the reactor coolant system of PWRs have been made since June 1994. Much of this effort has been carried out under the aegis of EPRI, with tailored collaboration by the participating utilities. In addition to the U. S. plants that have been using zinc addition as a means to mitigate stress corrosion cracking of Alloy 600, one U. S. plant and three German PWRs are using zinc for the sole purpose of radiation field (dose rate) reduction.

An overall time-line for the periods of zinc addition at these plants is presented in the attached figure. Although details of the schedules are not available for the German plants, zinc additions are continuing.

For the EPRI-sponsored programs, detailed reports of the results have been published. These reports have included the results of chemistry and radiochemistry monitoring during the fuel cycles, end-of-cycle dose rate and activity measurements, shutdown chemistry and radiochemistry releases, fuel inspections, and eddy current examinations of SG heat transfer tubing. The specific objective of this report is to present a single-source summary of the results and conclusions of these programs. Where available, data are also presented for the recent programs evaluating zinc additions for dose rate reduction.

A summary of the major observations from the various examinations/evaluations performed that are summarized in this report are presented below.

Primary Coolant Chemistry

The introduction and control of zinc into the reactor coolant in PWRs is easily and efficiently accomplished. The zinc is added as an aqueous solution of zinc acetate, usually into the suction of the CVCS charging pump downstream of the VCT, avoiding the use of a high-pressure safety-related line.

Depending on the initial rate of injection, the first detection of zinc occurs after a ten to twenty-day injection period. PWRs have demonstrated efficient management of RCS zinc concentrations from 5 to 40 ppb over essentially a full fuel cycle. Analyses to determine the zinc concentration are performed by either atomic absorption or SIMA of acidified grab samples taken on approximately a once per day basis.

The net mass of zinc introduced into PWRs to date has ranged from about 1 to more than 5 kg in any given cycle. Natural zinc acetate has been used at plants with a nominal target of 20 to 40 ppb zinc, while plants using zinc in the 5 ppb range for purposes of dose rate reduction have opted to use depleted (in $^{64}$Zn) zinc acetate to avoid the production of $^{65}$Zn.
The additional zinc, and the increased radiocobalt, $^{65}$Zn, and nickel concentrations in the coolant due to the injection of zinc, do not significantly affect the performance of the CVCS demineralizer or filters.

**Primary Coolant Radiochemistry**

The addition of zinc to the RCS in concentrations from 5 to 40 ppb results in an increase in the radiocobalt activity concentrations in the coolant. The ultimate “equilibrium” activity concentrations that are attained appear to be plant-specific, and depend upon the pre-zinc values, as might be expected. The factor increase in the pre-zinc to post-zinc values does, however, appears to depend upon the average zinc concentration in the coolant.

Increases in the $^{58}$Co activity are somewhat greater than increases in the $^{60}$Co activity, suggesting that zinc may be effecting greater release of nickel than cobalt from the ex-core corrosion films.

Partitioning of the radiocobalt activity between soluble and insoluble fractions is reported to be different at the Farley and the Diablo Canyon plants. At Farley, most of the radiocobalt activity is insoluble (particulates) whereas at Diablo Canyon the obverse is true. This may be related to different sampling and analytical practices at the various plants. This is not the case for $^{65}$Zn activity, where all Westinghouse plants using natural zinc acetate report the soluble activity dominates.

For plants using natural zinc acetate, the greater the cumulative zinc exposure (the product of the time that zinc was in the RCS and the average coolant zinc concentration), the higher the RCS $^{65}$Zn “equilibrium” concentration.

**Dose Rates and Component Activities**

Clear benefits have been observed in reduced dose rates and deposited radionuclide activities as the result of zinc additions to the reactor coolant. At Farley Unit 2, a factor of two reduction in dose rates has been realized over the last four cycles of zinc injection, although zinc has been added for less than half of any given cycle. Shorter exposures at Diablo Canyon Units 1 and 2 have yielded qualitatively similar results.

While the Farley data indicate an increasing dose reduction benefit with increasing cumulative zinc exposure, comparison of the Farley and Diablo Canyon results with those from plants using lower zinc concentrations (Palisades and the German plants) suggests concentrations on the order of 5 to 10 ppb may be adequate.

Single-cycle zinc injection experience has resulted in net reductions of approximately 25% in deposited radionuclide activities. This reduction includes a net increase in deposited activity of 4 to 9% by $^{60}$Zn for plants using natural zinc acetate. The reduction would be further enhanced by the use of depleted zinc acetate.
Refueling Shutdown Chemistry and Radiochemistry

Following partial cycles (up to ten months) of zinc injection, significant increases have been observed in the release and removal of $^{58}$Co, $^{60}$Co, and nickel in subsequent refueling/maintenance shutdowns. Substantial releases of $^{65}$Zn are also observed in plants using natural zinc acetate.

The $^{58}$Co specific activity (Ci $^{58}$Co/g Ni) increases slightly after cycles with zinc injection, suggesting an increase in the core residence time for nickel.

Steam Generator Inspection Results

To date, the maximum period of zinc injection in plants seeking to mitigate PWSCC of Alloy 600 tubing has been limited to about ten months. While for individual plants some possible trend of a decrease in the tube repair rate may be inferred, it is judged premature to assign a significant role to the addition of zinc in mitigating PWSCC of Alloy 600.

Auger spectroscopic characterization of spinel oxide corrosion films on the inside surfaces of steam generator tubing following exposure to zinc confirms the incorporation of significant concentrations of zinc in the corrosion film.

Fuel Region Examinations

The addition of zinc to the reactor coolant system consistently appears to result in the formation of a thin dark deposit on the surface of the fuel rods at the end of the cycle. This has been reported at plants in which the RCS zinc concentration was greater than about 20 ppb during the operating cycle, but has not been reported for PWRs in which the zinc concentration was maintained at the 5 ppb level.

The results of crud scraping, rod brushing and eddy current lift-off remeasurements, and observations of the ease with which the black deposit is removed, suggest that this deposit is very thin (a possible exception is Diablo Canyon Unit 1) and is having no effect on the accuracy of corrosion oxide measurements.

The overall corrosion product burden does not appear to have been increased at Farley Units 1 and 2 by the presence of zinc. However, at Diablo Canyon Unit 1, after a partial cycle of zinc injection, the corrosion product deposition appeared to be substantial, approaching 25 μm or more. It is not known whether or to what extent the presence of zinc contributed to this condition.

The results of oxide thickness measurements indicate that zinc is not having a statistically significant effect on cladding corrosion.

Other Primary Components

Based on in-situ monitoring of reactor coolant pump (RCP) shaft and frame vibration, end-of-cycle inspections of RCP seal leak-off characteristics, and the examination of valve repair
records, the addition of zinc to the reactor coolant system of PWRs, at zinc concentrations up to 40 ppb, has no apparent effect on the safe and reliable operation of these primary system components.
CONTENTS

1 INTRODUCTION .................................................................................................................. 1-1
References......................................................................................................................... 1-1

2 PRIMARY COOLANT CHEMISTRY ...................................................................................... 2-1
  2.1 Introduction ................................................................................................................ 2-1
  2.2 Nominal Zinc Concentration ..................................................................................... 2-1
  2.3 Method and Location of Zinc Injection ................................................................. 2-1
  2.4 Analytical Techniques for Zinc Analyses .............................................................. 2-2
  2.5 Behavior and Control of Zinc Concentration ....................................................... 2-2
      Farley 2 Cycle 10 ................................................................................................. 2-2
      Farley 2 Cycle 11 ................................................................................................. 2-4
      Farley 2 Cycle 12 ................................................................................................. 2-4
      Farley 2 Cycle 13 ................................................................................................. 2-5
      Farley 1 Cycle 16 ................................................................................................. 2-6
      Diablo Canyon 1 Cycle 9 ...................................................................................... 2-7
      Diablo Canyon 2 Cycle 9 ...................................................................................... 2-8
  2.6 Net Zinc Added to the RCS ..................................................................................... 2-9
  2.7 Results of Other Coolant Chemical Analyses ....................................................... 2-11
  2.8 Waste Generation .................................................................................................... 2-11
      General Considerations of the Effect of Zinc on Plant Wastes ................................ 2-11
      Liquid Waste Effluents .......................................................................................... 2-12
      Resin Bed Performance ....................................................................................... 2-13
      Decontamination Factors ...................................................................................... 2-13
      Resin Bed Usage ................................................................................................... 2-14
      Filter Usage .......................................................................................................... 2-14
  2.9 Conclusions ............................................................................................................... 2-15
References......................................................................................................................... 2-16
3 PRIMARY COOLANT RADIOCHEMISTRY ................................................................. 3-1
  3.1 Introduction ........................................................................................................ 3-1
  3.2 Total Radiocobalt Activity Trends ................................................................... 3-1
    Farley 2 Cycles 8 through 13 ........................................................................... 3-1
    Farley 1 Cycles 15 and 16 ............................................................................. 3-3
    Diablo Canyon 1 Cycles 8 and 9 ................................................................. 3-4
    Diablo Canyon 2 Cycles 8 and 9 ................................................................. 3-5
  3.3 Comparison of Radiocobalt Data ................................................................... 3-5
  3.4 Total $^{65}$Zn Activity Trends ........................................................................... 3-7
    Farley 2 Cycles 10 through 13 ..................................................................... 3-7
    Other Plants .................................................................................................. 3-8
  3.5 Soluble and Insoluble Activity Trends ............................................................ 3-9
    Farley 2 Cycles 12 and 13 .......................................................................... 3-9
    Diablo Canyon 1 Cycle 9 .......................................................................... 3-11
    Diablo Canyon 2 Cycle 9 .......................................................................... 3-13
  3.6 Conclusions ..................................................................................................... 3-14
  References ........................................................................................................ 3-15

4 DOSE RATES AND COMPONENT ACTIVITIES .................................................... 4-1
  4.1 Introduction ...................................................................................................... 4-1
  4.2 Component Dose Rates .................................................................................. 4-1
    4.2.1 EPRI Standard Radiation Monitoring Program (SRMP) Locations ............ 4-1
      Farley 2 ...................................................................................................... 4-2
      Diablo Canyon 1 ...................................................................................... 4-6
      Diablo Canyon 2 ...................................................................................... 4-7
    4.2.2 Non-EPRI SRMP Locations .................................................................. 4-8
  4.3 Radionuclide Concentrations ........................................................................ 4-9
    Farley 2 ...................................................................................................... 4-9
    Diablo Canyon 1 and 2 and Comparison to Farley 2 .................................... 4-10
  4.4 Relationship Between Zinc Exposure and Dose Rate Reduction ................. 4-12
  4.5 Conclusions .................................................................................................. 4-15
  References ........................................................................................................ 4-16

5 REFUELING SHUTDOWN CHEMISTRY AND RADIOCHEMISTRY ................. 5-1
  5.1 Introduction .................................................................................................... 5-1
### 6 STEAM GENERATOR INSPECTION RESULTS

6.1 Introduction ................................................................. 6-1
6.2 Plant Operating Experience ............................................. 6-1
6.3 Inspection Results .......................................................... 6-2
   6.3.1 Farley Unit 2 .............................................................. 6-3
       Cycle 10 ........................................................................ 6-5
       Cycle 11 ........................................................................ 6-6
       Cycle 12 ........................................................................ 6-6
       Cycle 13 ........................................................................ 6-6
   6.3.2 Diablo Canyon Unit 1 .................................................. 6-7
   6.3.3 Diablo Canyon Unit 2 .................................................. 6-9
6.4 Conclusions .................................................................... 6-10
References ........................................................................ 6-10

### 7 FUEL REGION EXAMINATIONS

7.1 Introduction .................................................................. 7-1
7.2 Inspection Methods ......................................................... 7-1
7.3 Farley Unit 2 – End-of-Cycle 10 ....................................... 7-2
7.4 Farley Unit 2 – End-of-Cycle 11 ....................................... 7-5
7.5 Farley Unit 2 – End-of-Cycle 12 ....................................... 7-5
7.6 Farley Unit 2 – End-of-Cycle 13 ....................................... 7-6
7.7 Diablo Canyon Unit 1 – End-of-Cycle 9 ............................. 7-8
7.8 Diablo Canyon Unit 2 – End-of-Cycle 9 ............................. 7-10
7.9 Farley Unit 1 – End-of-Cycle 16 ....................................... 7-11
7.10 Obrigheim .................................................................... 7-12
7.11 Palisades ...................................................................... 7-13
7.12 Discussion and Conclusions ............................................. 7-13
   Visual Observations of Corrosion Deposits ......................... 7-13
   Fuel Cladding Corrosion – Oxide Thickness Measurements ..... 7-13
References ........................................................................................................................................7-16

8 OTHER PRIMARY COMPONENTS ....................................................................................................................8-1

8.1 Introduction ...................................................................................................................................................8-1

8.2 Reactor Coolant Pump Data ......................................................................................................................8-1

8.2.1 RCP Seal Data .........................................................................................................................................8-2

  Seal Data Prior to Zinc Addition ..................................................................................................................8-2
  Seal Performance after the Start of Zinc Injection ........................................................................................8-3
  Conclusions – RCP Seal Performance ........................................................................................................8-4

8.2.2 RCP Vibration Monitoring Data ...........................................................................................................8-4

  RCP Vibration Data During Cycle 10 at Farley Unit 2 ................................................................................8-5
  Conclusions - RCP Vibration Data ...............................................................................................................8-7

8.3 Reactor Coolant Valve Maintenance Data ............................................................................................8-7

8.4 Conclusions ...............................................................................................................................................8-8

Reference ......................................................................................................................................................8-8
LIST OF FIGURES

Figure 2-1 Farley 2 Cycle 10 RCS Zinc Concentration and Injection Feed Rate .......................... 2-3
Figure 2-2 Farley 2 Cycle 12 RCS Zinc Concentration and Injection Feed Rate .......................... 2-4
Figure 2-3 Farley 2 Cycle 13 RCS Zinc Concentration and Injection Feed Rate .......................... 2-5
Figure 2-4 Farley 1 Cycle 16 RCS Zinc Concentration and Injection Feed Rate .......................... 2-7
Figure 2-5 Diablo Canyon 1 Cycle 9 RCS Zinc Concentration .................................................. 2-8
Figure 2-6 Diablo Canyon 2 Cycle 9 RCS Zinc Concentration .................................................. 2-9
Figure 3-1 $^{58}$Co Activities in the Farley 2 RCS During Cycles 8 through 13 ............................... 3-2
Figure 3-2 $^{60}$Co Activities in the Farley 2 RCS During Cycles 8 through 13 ............................... 3-2
Figure 3-3 Radiocobalt Activities in the Farley 1 RCS During Cycles 15 and 16 ......................... 3-4
Figure 3-4 Radiocobalt Activities in the Diablo Canyon 1 RCS During Cycles 8 and 9 .............. 3-6
Figure 3-5 Radiocobalt Activities in the Diablo Canyon 2 RCS During Cycles 8 and 9 .......... 3-6
Figure 3-6 $^{65}$Zn Activity in the Farley 2 RCS During Cycles 10 through 13 .............................. 3-8
Figure 3-7 Soluble and Insoluble $^{65}$Zn Activity in Farley 2 Cycles 12 and 13 ......................... 3-10
Figure 3-8 Soluble and Insoluble $^{58}$Co Activity in Farley 2 Cycles 12 and 13 ......................... 3-10
Figure 3-9 Soluble and Insoluble $^{60}$Co Activity in Farley 2 Cycles 12 and 13 ......................... 3-11
Figure 3-10 Soluble and Insoluble $^{58}$Co Activity in Diablo Canyon Unit 1 Cycle 9 ............. 3-12
Figure 3-11 Soluble and Insoluble $^{60}$Co Activity in Diablo Canyon Unit 1 Cycle 9 ............. 3-12
Figure 3-12 Soluble and Insoluble $^{65}$Zn Activity in Diablo Canyon Unit 1 Cycle 9 ............. 3-13
Figure 3-13 Soluble and Insoluble $^{58}$Co Activity in Diablo Canyon Unit 2 Cycle 9 ............. 3-14
Figure 4-1 Locations of EPRI SRMP Measurement Points ....................................................... 4-2
Figure 4-2 Dose Rates at Various Locations before $H_2O_2$ Addition in Farley Unit 2 ........... 4-3
Figure 4-3 Dose Rates at Various Locations after $H_2O_2$ Addition in Farley Unit 2 ............. 4-4
Figure 4-4 Steam Generator Channel Head General Area TLD Dose Rate Trend in Farley Unit 2 after Hydrogen Peroxide Addition ................................................................. 4-5
Figure 4-5 Dose Rates at Various Locations in Diablo Canyon Unit 1 ....................................... 4-7
Figure 4-6 $^{58}$Co Concentrations at Various RCS Locations in Farley 2 ..................................... 4-10
Figure 4-7 $^{60}$Co Concentrations at Various RCS Locations in Farley 2 ................................. 4-11
Figure 4-8 Deposited Radiocobalt Activities on the Hot Leg Piping in Three Plants after One Cycle of Zinc Addition ................................................................. 4-12
Figure 4-9 Deposited Radiocobalt Activities on the Crossover Leg Piping in Three Plants after One Cycle of Zinc Addition ................................................................. 4-13
Figure 4-10 Zinc Exposure and Percent Dose Rate Reduction in All Plants .............................. 4-15
Figure 7-1 Eddy Current-Measured Lift-off Data vs. Burnup for Zircaloy 4 for Farley Unit 2 Cycles 10, 12 and 13 and Diablo Canyon Unit 1 Cycle 9 .............................................7-15

Figure 7-2 Fuel Duty Index vs. Lift-off Data: The Zircaloy 4 Database and Results for Diablo Canyon Unit 1 Cycle 9 ..............................................................7-15
# LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-1</td>
<td>Comparison of Zinc Input and Removal in Zinc Addition Plants</td>
</tr>
<tr>
<td>3-1</td>
<td>Comparison of Radiocobalt “Equilibrium” Concentrations and Factor Increase after the First Cycle of Zinc Addition</td>
</tr>
<tr>
<td>3-2</td>
<td>Comparison of $^{65}$Zn “Equilibrium” Concentrations after the First Cycle of Zinc Addition</td>
</tr>
<tr>
<td>4-1</td>
<td>Description and Rationale for Dose Rate Measurement Locations</td>
</tr>
<tr>
<td>4-2</td>
<td>Comparison of Farley 2 RCS Component Dose Rates</td>
</tr>
<tr>
<td>4-3</td>
<td>Farley 2 RCS Component Dose Rate Ratios</td>
</tr>
<tr>
<td>4-4</td>
<td>Comparison of Diablo Canyon 1 Component Dose Rates and Ratios from EOC 8 to EOC 9</td>
</tr>
<tr>
<td>4-5</td>
<td>Comparison of Diablo Canyon 2 Component Dose Rates and Ratios from EOC 8 to EOC 9</td>
</tr>
<tr>
<td>4-6</td>
<td>Summary of Zinc Exposure and Dose Rate Reduction Data after Shutdown Chemistry Evolutions</td>
</tr>
<tr>
<td>5-1</td>
<td>Summary of Zinc Injection Experience for Plants for Which Shutdown Data are Available</td>
</tr>
<tr>
<td>5-2</td>
<td>Summary of Shutdown Releases for PWRs Using Zinc Injection</td>
</tr>
<tr>
<td>5-3</td>
<td>Comparison of Radiocobalt and Nickel Releases before and after Experience with Zinc Injection</td>
</tr>
<tr>
<td>6-1</td>
<td>Summary of Zinc Injection Experience for PWSCC Mitigation</td>
</tr>
<tr>
<td>6-2</td>
<td>Plugging/Repair Actions for PWSCC within F$^{+}$1 at the Hot Leg TTS Region in Farley Unit 2</td>
</tr>
<tr>
<td>6-3</td>
<td>Inspection and Plugging for PWSCC in Diablo Canyon Unit 1</td>
</tr>
<tr>
<td>6-4</td>
<td>Inspection and Plugging for PWSCC in Diablo Canyon Unit 2</td>
</tr>
<tr>
<td>7-1</td>
<td>Oxide Measurement Results – Farley 2 EOC 9 &amp; 10</td>
</tr>
<tr>
<td>7-2</td>
<td>Oxide Measurement Results – Twice-burned Improved Zircaloy 4 in Farley 2 EOC 10</td>
</tr>
<tr>
<td>7-3</td>
<td>Oxide Measurement Results – Once-burned Improved Zircaloy 4 in Farley 2 EOC 10</td>
</tr>
<tr>
<td>7-4</td>
<td>Oxide Measurement Results – Once and Twice-burned Improved Zircaloy 4 in Farley 2 EOC 11</td>
</tr>
<tr>
<td>7-5</td>
<td>Oxide Measurement Results – Twice-burned Improved Zircaloy 4 and Once-burned ZIRLO in Farley 2 EOC 12</td>
</tr>
</tbody>
</table>
Table 7-6 Oxide Measurement Results – Improved Zircaloy 4 and ZIRLO in Farley 2 EOC 13 .......................................................................................................................... 7-8
Table 7-7 Oxide Measurement Results – Diablo Canyon 1 EOC 8 & 9......................... 7-9
Table 7-8 Oxide Measurement Results - Diablo Canyon 2 EOC 9..................................... 7-11
Table 7-9 Oxide Measurement Results - ZIRLO-Clad Rods in Farley 1 EOC 16............... 7-12
Table 8-1 Shaft and Frame Vibration Changes and Shaft Position Changes in Farley Unit 2 in Cycle 10°................................................................................................. 8-6
1 INTRODUCTION

Zinc has been added to the reactor coolant system of five U. S. and three European PWRs since the first Demonstration Program was initiated at Farley Unit 2 during Cycle 10 in 1994. The incentives for these programs have included the mitigation of primary water stress corrosion cracking (PWSCC) at Farley Units 1 and 2 and Diablo Canyon Units 1 and 2, and for the purpose of radiation field (dose rate) reduction at Palisades, Biblis Units A and B, and Obrigheim. The concentrations of zinc in the RCS have been in the range from approximately 20 to 40 ppb in the former plants, whereas in the plants looking for dose rate reductions the concentrations have generally been in the range 5 to 7 ppb.

Since the initial Demonstration Program at Farley 2, which was carried out under the dual aegis of EPRI and the Westinghouse Owners Group, the activities directed at mitigation of PWSCC have been funded by EPRI with tailored collaboration agreements with Southern Nuclear Operating Company and Pacific Gas & Electric. Detailed reports of the results of these programs have been published by EPRI (Refs. 1.1 through 1.6). The objective of this report is to present a single-source summary of the essential results and conclusions of the previous programs. There is no attempt to reproduce the detail provided in the former reports. Where they are available, published results from the Palisades and German PWRs are also presented for comparison.

The subsequent sections of this report present summaries of the following:

- Primary Coolant Chemistry
- Primary Coolant Radiochemistry
- Dose Rates and Component Activities
- Refueling Shutdown Chemistry and Radiochemistry
- Steam Generator Inspection Results
- Fuel Region Examinations
- Other Primary Components

References


Introduction


2 PRIMARY COOLANT CHEMISTRY

2.1 Introduction

Zinc as zinc acetate was injected into the primary coolant to effect the anticipated benefits of zinc addition. This section discusses zinc injection parameters such as the nominal zinc concentration range(s), the method of zinc injection, analytical techniques for analyses of zinc, the behavior and control of zinc in the coolant, and the estimated net amount of zinc injected into the reactor coolant system (RCS) for those U. S. plants currently injecting zinc. A summary of other coolant chemistry parameters that have also been monitored and the effects on demineralizer performance and waste considerations are also presented.

2.2 Nominal Zinc Concentration

Based on the results of laboratory testing published in 1994, a zinc concentration of 40 ppb was initially selected in an effort to mitigate the primary water stress corrosion cracking (PWSCC) of Alloy 600 components, primarily the steam generator tubing (Ref. 2.1). Although the testing and BWR experience indicated a potential beneficial effect of zinc addition in reducing plant dose rates, this effect was considered a secondary benefit. In November 1998, the nominal zinc concentration was reduced to 30 ppb on the basis of an evaluation of additional laboratory studies of the solubility of zinc species in water at elevated temperatures. The results were interpreted with reference to PWR coolant conditions (Ref. 2.2) and concluded that, to be conservative, the zinc concentration should be kept below 40 ppb to minimize the possibility of zinc oxide precipitation on fuel surfaces.

Subsequent to this reduction, a lower value of 15 ppb zinc was judged to be sufficient for PWSCC alleviation and dose rate reduction in plants that had replacement steam generators with Alloy 690 tubing (Ref. 2.3). At Palisades and Obrigheim, a zinc concentration of 5 ppb was used, since the interest in these plants was in dose rate reduction, and BWR experience indicated that concentration was sufficient to effect significant dose rate reduction under BWR coolant chemistry conditions (Refs. 2.4 and 2.5).

2.3 Method and Location of Zinc Injection

Initially, for the Farley 2 Cycle 10 Demonstration Program, a semi-automatic zinc injection system was designed to permit automatic batching and injection of zinc acetate solution into the
RCS (Ref. 2.6). This prototype proved to be overly complex with unacceptable reliability, and was subsequently replaced by a much simpler system that was largely manually operated. Analyses to measure and control the RCS zinc concentration relied upon grab samples. An initial concern with this approach was that this might become labor intensive but, in practice, the control of the zinc concentration did not offer any problems at Farley. A simple manual batching system that requires servicing about once per week was installed and has been used without problems at Diablo Canyon Units 1 and 2; RCS zinc analyses are also done on grab samples. The system used at Palisades has been further simplified and consists of a small electronic metering pump and a 20-liter carboy injection tank; grab samples are used to monitor the RCS zinc level.

At the Farley and Diablo Canyon plants zinc was injected into the reactor coolant system via the suction of the CVCS charging pump downstream of the VCT. A similar injection location was used at Palisades. This injection location avoids the use of a high-pressure safety-related line. At Obrigheim, injection is made into one of the reactor pressure vessel hot-leg outlet nozzles, which means that initial contact of the zinc acetate solution occurs in one of the steam generators.

2.4 Analytical Techniques for Zinc Analyses

After early attempts at Farley to perform analyses by in-line Anodic Stripping Voltammetry, a method that proved intractable for operating plant chemistry laboratories, off-line atomic absorption spectroscopy (AA) has been used to determine the RCS zinc concentration in acidified grab samples. The AA method is considered to be reliable for zinc concentrations of 10 ppb or greater. The AA analytical method has also been used at Diablo Canyon.

A SIMA graphite furnace technique (analytic sensitivity to 0.8 ppb zinc) has been used at Palisades in view of the desire to analyze and control the coolant zinc concentration to 5 ppb.

2.5 Behavior and Control of Zinc Concentration

The concentration of zinc in the coolant is basically maintained by adjusting the feed concentration and/or the feed rate. An initial zinc injection rate of about 4 g/h was selected as adequate for Farley 2 Cycle 10. This was later reduced to about 1 to 2 g/h which proved to be sufficient for controlling zinc at the nominal 40 ppb concentration. It was found that changing the feed rate rather than the feed tank concentration was a simpler means to control the zinc coolant concentration, and that responses to changes in injection parameters were relatively slow, i.e., requiring a day or so. Based on laboratory studies, the zinc concentration behaved as expected; e.g., reactor coolant temperature decreases caused an increase in the concentration in the coolant. The following sections present and discuss the zinc concentration trends in the Farley and Diablo Canyon plants.

Farley 2 Cycle 10

Figure 2-1 shows the zinc concentration trend in the coolant and the zinc injection pump feed rate during Farley 2 Cycle 10 (Ref. 2.6).
The first analysis that detected zinc in the coolant occurred eleven days after the start of injection. Inspection of the early trend of zinc concentration in the RCS indicated that the feed rate was initially sufficiently high to result in a fairly rapid increase in the zinc concentration such that the nominal upper limit was exceeded slightly. This was not a serious event, since reduction of the feed rate resulted in a prompt decrease of the RCS zinc concentration. The concentration trends showed a learning effect as the injection rate and concentration were adjusted to maintain the 40-ppb target. After several months, the target of 40 ppb was easily maintained, with the exception of periods of plant shutdown or when the coolant temperature was decreased at the end-of-cycle shutdown.

Shown on Figure 2-1 are the times when the injection system was shut down either for maintenance, during plant shutdowns, or at the EOC. The latter injection system shutdowns occurred so that the zinc concentration would not exceed 80 ppb, the upper bound limit of the Safety Evaluation. It was expected that the zinc concentration would increase as the coolant temperature decreased during the shutdowns, but the extent of the increase could not be predicted with any certainty. Thus, to be conservative, zinc injection was suspended during these periods.

It was also found during the plant shutdowns that the time to reduce the zinc concentration by one-half (84 hours) was considerably longer than the 7 hours expected for zinc removal by the CVCS system demineralizers. This indicated that zinc was being continuously released into the coolant at the lower temperature. After the coolant returned to normal operating temperature, and zinc injection was re-started, the concentration was stabilized.
Farley 2 Cycle 11

Zinc addition was suspended for Cycle 11 in order to fully assess the results of the visual observations and cladding corrosion data that were obtained following Cycle 10 (Ref. 2.7). Without continued addition of zinc to the RCS, a release of zinc from the primary system corrosion films was expected based on laboratory tests (Ref. 2.1) and the observations noted above during Cycle 10. With a single exception of a 13-ppb value measured during the startup power escalation, the zinc concentrations were below the 10 ppb detection limit throughout Cycle 11. The fact that the RCS zinc concentrations during Cycle 11 did not exceed 10 ppb indicates that zinc was released to the primary coolant at a sufficiently slow rate that the removal rate capability of the CVCS demineralizers was not exceeded. The CVCS letdown flow at Farley (130 gpm) is unusually high for a three-loop PWR.

Farley 2 Cycle 12

The zinc concentration and injection feed rate data for Farley 2 Cycle 12 are shown in Figure 2-2.

Figure 2-2
Farley 2 Cycle 12 RCS Zinc Concentration and Injection Feed Rate

Zinc addition was originally planned for about nine months during Cycle 12 (Ref. 2.8). However, for fuel-related reasons it was stopped after only three months of injection. There were several differences between Cycle 10 and Cycle 12 with respect to zinc addition: (1) depleted zinc was
used in Cycle 12, and (2) the injection concentration and flow rate were changed. Depleted zinc refers to natural zinc that has been depleted in $^{64}$Zn, the precursor isotope to $^{65}$Zn, so that the contribution of $^{65}$Zn to the plant dose rate is minimized. In Cycle 12, the injection flow rate was about one-tenth of that in Cycle 10, whereas the feed concentration was about 10 times that in Cycle 10. Thus, the net zinc mass injection rate was essentially the same in both cycles.

Figure 2-2 shows two zinc measurements above 10 ppb shortly after injection was resumed. However, subsequent analyses indicated values less than 10 ppb, and the earlier values were judged to be spurious. The appearance of zinc after nine days of injection was slightly earlier than the eleven days experienced during Cycle 10. The 40-ppb target concentration was fairly well maintained as the injection feed rate was decreased slightly with injection time during the three months of injection. After zinc injection was terminated, the zinc concentration decreased from about 38 to 20 ppb over the next five days and then decreased further to 12 ppb with an “effective half-life” of about 14 days. Similar to the Cycle 10 observations, this type of behavior indicates that zinc is being released into the RCS from the primary system surfaces. Following this period, the concentrations were in the 12 to 15 ppb range for an additional twelve days and then decreased to less than 10 ppb for the remainder of the cycle.

**Farley 2 Cycle 13**

The zinc concentration and injection feed rate for Farley 2 Cycle 13 are shown in Figure 2-3.

![Figure 2-3](image)

**Figure 2-3**

**Farley 2 Cycle 13 RCS Zinc Concentration and Injection Feed Rate**
In contrast to Cycles 10 and 12, the nominal zinc concentration for Cycle 13 was reduced to 30 ppb compared to 40 ppb in the prior cycles. Since there was a supply of depleted zinc remaining from the Cycle 12 experience, zinc injection using depleted zinc acetate was used for the first 126 days of the injection period; this was about 40% of the total zinc injection period (Ref. 2.9). Subsequently, natural zinc acetate was added for the remainder of the cycle. The typical mass injection rate was about 2 g/h. Zinc was first detected in the coolant three days after initial injection. This is shorter than the experience in Cycles 10 and 12 and may suggest that the sites for the incorporation of zinc in the corrosion product film are being saturated as zinc injection continues.

The zinc concentration in the coolant increased rapidly to about 30 ppb, in response to an initially high injection rate, and then oscillated between 20 and 42 ppb for about 40 days while the injection feed rate was adjusted to meet the target value of 30 ppb. After the first 40 days, the concentration was fairly well maintained at 30 ppb for the rest of the cycle. The variation at about 390 days was due to a reactor trip and ensuing five-day shutdown of the injection system. Note that the injection rate was decreased three times the last 100 days of injection to maintain the target concentration. This suggests that the exchange of the zinc in the coolant with that in the oxide films may be beginning to reach an equilibrium condition.

**Farley 1 Cycle 16**

The zinc concentration and injection feed rate for Farley 1 Cycle 16 are shown in Figure 2-4.

Farley 1 Cycle 16 has experienced the longest operational time with zinc addition (368 days); the longest period of zinc addition in Farley 2 was 310 days in Cycle 13. Like Farley 2 Cycle 13, the target zinc concentration was 30 ppb (Ref. 2.10). Natural zinc acetate was used as the zinc additive. Inspection of the trends in Figure 2-4 shows that with the exception of the startup period and the two plant and injection system shutdowns, the concentration was well controlled at 30 ppb.

In contrast to the Farley 2 experience, zinc was not detected in the RCS until 23 days after initial injection. The zinc injection rate was about the same for the two plants, i.e., about 2 g/h. The longer time to observe zinc in the coolant may reflect a thicker surface corrosion film in Farley 1 at the time of injection compared to that in Farley 2 since injection was not started in Farley 1 until Cycle 16, compared to Cycle 10 in Farley 2.
Farley 1 Cycle 16 Zinc Concentration & Injection Feed Rate vs. Time

Figure 2-4
Farley 1 Cycle 16 RCS Zinc Concentration and Injection Feed Rate

**Diablo Canyon 1 Cycle 9**

Figure 2-5 shows the zinc concentration trend for Diablo Canyon 1 during Cycle 9.

Details of the charging pump flow rates were not available for Diablo Canyon 1 and are thus not shown on Figure 2-5. In general, a flow rate of 1 gph was used with an injection feed concentration of 600 ppm zinc, thus giving a nominal zinc mass injection rate of about 2 g/h; similar to that at the Farley plants (Ref. 2.11). A measurable zinc concentration was first observed nine days after zinc injection was initiated, again similar to the experience in Farley 2 Cycle 10. Several activities affecting the zinc concentration are noted on the figure. These include a decrease in concentration when the injection pump was out of service and increases in concentration when the power (temperature) was reduced or the plant was shut down.
The 275 ppb peak concentration reached during the plant shutdown was considerably greater than the 70 ppb observed at Farley 2 during a shutdown. This may reflect the CVCS purification flow rate of the Diablo Canyon plants (75 gpm) compared to the greater rate in the Farley plants (130 gpm). Note also that the target concentration was reduced to 30 ppb 540 days into the cycle. This was done for the reason noted previously for Farley 2 Cycle 13. The reduction in the concentration to 10 ppb starting at 580 days was intended to minimize the generation of $^{65}$Zn during the latter part of the cycle.

**Diablo Canyon 2 Cycle 9**

The zinc concentration trend in Diablo Canyon 2 Cycle 9 is shown in Figure 2-6.
The trends in Diablo Canyon 2 Cycle 9 are similar to those in other plants/cycles of zinc addition (Ref. 2.12). Namely, an initial start-up period (about 40 days) of varying zinc concentrations as the system is being conditioned, and personnel are learning the mechanics of the injection system. At Diablo Canyon Unit 2, the target concentration was 30 ppb. Zinc was first detected in the coolant six days after the start of injection, slightly less than the nine days in Diablo Canyon 1. Similar to Unit 1, the zinc concentration was reduced to 15 ppb and then allowed to decrease even further the latter part of the cycle in an attempt to minimize the generation of $^{65}\text{Zn}$.

2.6 Net Zinc Added to the RCS

The net amount of zinc in the RCS for the Farley and Diablo Canyon plants was estimated from the difference between the amount injected and the amount removed by the letdown system. The mass of zinc injected into the RCS was calculated using the injection flow rate, the time of injection and the concentration in the feed tank. The amount removed by the letdown system was calculated using the letdown flow rate, the concentration of zinc in the RCS, and assuming 100% removal of the zinc by the system demineralizers. The time that the zinc injection system was out of service was accounted for in the calculations. Table 2-1 shows the results of the calculations for the two plant sites and the estimated inventory of zinc remaining in the RCS. The zinc exposure time was taken as the time from initial zinc injection to the end of the cycle, or in the case of Farley 2 Cycle 12, the time at which the concentration became less than 10 ppb.
### Table 2-1
Comparison of Zinc Input and Removal in Zinc Addition Plants

<table>
<thead>
<tr>
<th>Plant/Cycle</th>
<th>Zinc Exposure Time, Days</th>
<th>Zinc Inj. Time, Days</th>
<th>Zinc Injected, kg</th>
<th>Zinc Removed, kg</th>
<th>Net Zinc into the RCS, kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Farley 2/10</td>
<td>271</td>
<td>239</td>
<td>10.89</td>
<td>7.06</td>
<td>3.83</td>
</tr>
<tr>
<td>Farley 2/12</td>
<td>116</td>
<td>90</td>
<td>4.06*</td>
<td>3.03</td>
<td>1.03</td>
</tr>
<tr>
<td>Farley 2/13</td>
<td>310</td>
<td>276</td>
<td>8.10**</td>
<td>6.61</td>
<td>1.49</td>
</tr>
<tr>
<td>Farley 1/16</td>
<td>368</td>
<td>338</td>
<td>12.87</td>
<td>7.12</td>
<td>5.75</td>
</tr>
<tr>
<td>Diablo Canyon 1/9</td>
<td>227</td>
<td>180</td>
<td>5.85</td>
<td>3.05</td>
<td>2.80</td>
</tr>
<tr>
<td>Diablo Canyon 2/9</td>
<td>192</td>
<td>156</td>
<td>3.48</td>
<td>1.62</td>
<td>1.86</td>
</tr>
<tr>
<td>Palisades/14</td>
<td>193</td>
<td>180</td>
<td>0.86*</td>
<td>0.14</td>
<td>0.72</td>
</tr>
</tbody>
</table>

* - Depleted zinc  
** - Approximately 45% was depleted zinc.

The data in Table 2-1 show that the net zinc added to the RCS is not necessarily directly related to the amount injected, due to the varying amount removed; e.g., compare the net zinc in the RCS for Cycles 10 and 13 at Farley 2.

An estimate was made of the expected zinc surface concentration on the ex-core (steam generator tubing) surfaces in Farley 2 Cycle 10 and Diablo Canyon 2 Cycle 9. Table 2-1 shows that the net zinc input in Farley 2 was about 40% greater than that in Diablo Canyon 1. Recognizing the larger ex-core surface area in the four-loop Diablo Canyon 1 plant suggests that the zinc concentration in the ex-core surface corrosion films in Diablo Canyon 1 is estimated to be just over one-half that at Farley 2. The estimated surface concentrations are based on the assumption that the distribution of zinc is proportional to the ex-core surface areas, since at Farley 2 only on the order of 2 to 3% zinc had been found in the fuel surface corrosion product deposits (Ref. 2.6).

The zinc concentration in the oxide film on a Farley 2 Cycle 10 SG tube was determined by sputtering Auger emission spectroscopic analysis to be in the range of 15 to 20 at. % at the surface, decreasing to less than 0.5 at. % through the first 100 nm of the film thickness (Ref. 2.6). For a tube removed from Diablo Canyon Unit 1 at the EOC 9 outage, the zinc concentration was about 6 at. % at the surface and also decreased rapidly through the first 100 nm of the film thickness (Ref. 2.11). These results are generally consistent with expectations noted above based on the zinc input calculations.
2.7 Results of Other Coolant Chemical Analyses

Initial testing of zinc addition was with “typical” coolant chemistry conditions, i.e., boron, lithium, hydrogen, temperature and pressure, so no effect was expected with respect to these parameters. However, these normal chemistry parameters, along with others such as silica and suspended solids, were monitored in the Farley and Diablo Canyon plants and the trends evaluated. Nothing unusual was noted relative to the values before and after zinc addition.

Because of a concern for a potential impact of zinc addition on Axial Offset Anomaly (AOA), coolant chemistry samples during Farley 2 Cycle 13 and Farley 1 Cycle 16 were analyzed weekly to determine concentrations of soluble nickel in the coolant. If two consecutive analyses indicated soluble nickel concentrations greater than 6 ppb, additional actions and analyses were required to better quantify whether or not the risk of AOA had increased, and whether it was necessary to suspend zinc injection (Ref. 2.13). The samples were first obtained by filtering 0.1 liter of the coolant through a 0.45 µm filter paper, acidifying the filtrate, and analyzing for soluble nickel using a graphite furnace atomic absorption technique. Later samples (starting in about January 2000) were not filtered; the full sample was acidified to dissolve the insolubles and then analysis was performed. These latter results thus represent the total nickel concentration in the coolant.

The results of the chemical analyses for Farley 2 Cycle 13, which were all taken using the soluble technique, indicated that, with the exception of five isolated analyses, the nickel concentrations were all below the limits of detection (<1 ppb) for essentially the entire cycle. There was no apparent change in the concentration during the ten months of zinc injection with the exceptions noted, during which the nickel never exceeded 2.4 ppb. Since these variations were minor, it is concluded that there is no significant effect of zinc addition on the concentration of soluble nickel.

The results of the Farley 1 Cycle 16 analyses taken using the soluble technique showed essentially the same pattern as in Unit 2 Cycle 13, namely the nickel concentrations were all below 1 ppb with the exception of two values of 2.0 and 1.5 ppb (Ref. 2.10). However, after the total nickel concentration was determined, all the values were reported above 1 ppb and varied from 1.1 to 2.5 ppb for the last two months of the cycle. This suggests that the total nickel concentration may have been greater than 1 ppb in prior samples or that it may have increased the last two months of the cycle. Nonetheless, since no values approached the 6-ppb limit, no action relative to modification of zinc injection was needed.

2.8 Waste Generation

General Considerations of the Effect of Zinc on Plant Wastes

Changes in the RCS concentrations can impact the plant solid wastes and, in particular, the spent resin activities and loading arising from the increased amounts of radiocobalts and nickel in the coolant due to the exchange with zinc. Also, with the addition of natural zinc (approximately 48.6 a/o $^{64}$Zn) to the primary coolant, the radioactive zinc isotope, $^{65}$Zn, is formed by the $^{64}$Zn (n,γ) $^{65}$Zn reaction.
The radiocobalt activities on the resin beds that process the primary coolant, particularly the CVCS demineralizer mixed bed, increase as the RCS activity concentration increases and result in higher specific activities of the spent resin. In addition, the \(^{65}\text{Zn}\) in the coolant increases the resin bed activity. A conservative estimate of the effect of these increases on the demineralizer dose rate was made for both the Farley and Diablo Canyon plants (Refs. 2.13 through 2.15). It was found that although an increase in the demineralizer design basis dose rate could be expected, the increase should have no effect on the occupational exposure received by plant personnel, since the radiation fields will build up slowly and are monitored by Health Physics personnel. It is also noted that the radiocobalt activity inventories in the coolant and resins are expected to decrease in subsequent cycles after the initial conditioning of the primary system deposits. Thus, it is expected that the inventory of radiocobalts to be packaged, shipped, and sent for ultimate disposal will be less for plants that continue to use zinc after the initial conditioning period than is the current experience. This conditioning period is expected to extend over several cycles of zinc addition.

Zinc injection has a potential impact on plant waste generation in the following areas:

- liquid waste effluents
- spent resins and filters

The impacts associated with each of these areas are discussed in the following sections.

Most of the relevant experience is referred to efforts and data from the early Farley 2 and later Diablo Canyon 1 operations and analyses.

**Liquid Waste Effluents**

Since the addition of zinc constitutes a net input of water to the RCS, a comparable removal of primary coolant is required to compensate for the added zinc solution.

The injected zinc acetate solution contains no boron; therefore, it has a diluting effect on the RCS boron concentration. Moreover, the RCS boron concentration is regularly reduced throughout the cycle to compensate for core burnup, even if the plant is operated without zinc addition. With injection concentrations in the range of 200 - 600 ppm zinc at a nominal injection flow rate of 1 gph, the effect on RCS boron concentration is small compared to that associated with burnup and normal plant boron dilution operations (Ref. 2.11).

Note that if the plant boron recycle system is utilized, the additional letdown volume required to compensate for that associated with zinc addition does not impact the activity in the liquid waste effluents since the water is recycled for use as makeup to the RCS. Further, if the RCS leakage is equal to or greater than the zinc injection rate, there should be virtually no impact on plant systems and liquid effluents. If the RCS letdown fluid is not processed in the boron recycle system and recycled for use, the water is eventually discharged from the plant in liquid waste discharges. Experience at Farley Unit 2 during the Cycle 10 Zinc Addition Demonstration program, where the letdown fluid was discharged via a waste holdup tank, indicates that the plant waste processing load was increased by approximately 20% during the time that zinc was
being injected (Ref. 2.6). However, even at this increased load, the available processing capacity of 35 gpm exceeded the total wastewater-processing load by a factor of 23.

Adequate margins were also observed at Diablo Canyon Unit 1, where the zinc injection pump flow rate of 1 gallon per hour was small compared to the processing capacity of the waste systems. No adverse effect was noted on the liquid radwaste system capabilities during operation and shutdown associated with the zinc addition cycle. The performance of key components of the system, including a layered carbon pre-filter bed, a zeolite bed and a cation bed, was not challenged (Ref. 2.11).

**Resin Bed Performance**

An evaluation of the potential effects of zinc additions to the RCS on the performance of the CVCS demineralizer beds at Farley Unit 2 and Diablo Canyon Unit 1 was done prior to the initiation of zinc addition (Refs. 2.14 and 2.15). These evaluations were done to address concerns associated with the overall efficiency of the resin beds with zinc addition, and to determine whether or not the added presence of zinc would necessitate premature change-out.

Zinc forms the divalent cation $\text{Zn}^{2+}$ when dissolved in primary coolant containing boric acid and does not form complex ions except in highly acidic or alkaline solutions. The zinc cation is readily removed from solution by strong acid ion exchange resins such as those used in the CVCS demineralizers. In common with the ions of such corrosion products as cobalt, nickel and iron, zinc will be exchanged for hydrogen ions from the nuclear grade strong acid resin in the cation bed and the shutdown mixed bed, and for $^7\text{Li}$ ions from the nuclear grade strong acid resin in the mixed bed.

The selectivity of a typical mixed bed resin for the zinc cation vis-à-vis the lithium cation was evaluated to determine whether or not the presence of zinc would have an adverse affect on resin performance. The results of these evaluations indicated that the selectivity values of the mixed bed resins are essentially the same for all of the divalent transition metal cations of interest. Hence, the zinc cations will be strongly adsorbed in the same exchange zone in the demineralizer bed as the alkaline earth cations such as $\text{Ca}^{2+}$ and $\text{Mg}^{2+}$, and the divalent cations of the transition metal radioisotopes, such as $^{58}\text{Co}$, $^{60}\text{Co}$, $^{54}\text{Mn}$ and $^{51}\text{Cr}$. Therefore, it was concluded that the decontamination factors (DFs), i.e., the ratio of the activity concentration upstream of the demineralizer to that downstream, for the multivalent cations should not be adversely affected by the presence of zinc, provided that the added burden does not exhaust the demineralizer bed.

**Decontamination Factors**

Decontamination factors (DFs) across the mixed bed demineralizer were calculated from the concentration of radionuclides upstream and downstream of the demineralizer in Farley 2 and Diablo Canyon 1. In Farley 2, data were obtained for the radiocobalts and for $^{65}\text{Zn}$; in Diablo Canyon 1, only $^{58}\text{Co}$ data were taken. The results in both plants showed no effect of zinc addition on the DFs of the demineralizer (Refs. 2.6 and 2.11). Thus, it is concluded that zinc addition, at least for up to 9 months and 40 ppb zinc concentration, has no effect on the demineralizer DF.
Resin Bed Usage

An estimate was also made of the potential effect of zinc on the CVCS resin bed usage rate at Farley 2 and Diablo Canyon 1 (Refs. 2.14 and 2.15). The mixed beds that are in service during power operation are normally loaded with 30 ft$^3$ (850 liters) of mixed bed resins. For Farley 2 it was estimated that the bed would remove 9.2 kg of zinc per year at a letdown flow rate of 120 gpm and for Diablo Canyon 1 the estimated value was 6.1 kg per year at a letdown flow rate of 80 gpm. For both estimates a zinc concentration of 40 ppb in the reactor coolant was assumed.

For a divalent ion with the atomic weight of zinc, 9.2 kg of zinc is equivalent to 280 g-equivalents of zinc per year and 6.1 kg of zinc is equivalent to 187 g-equivalents of zinc per year. The mixed bed operating capacity is rated at 0.5 g-equivalents per liter; thus, zinc may use up to 19.8 ft$^3$ in Farley 2 and 13.2 ft$^3$ in Diablo Canyon 1 of resin per year. At these rates, it was estimated that the resin bed capacity should easily accommodate the nominal 18-month fuel cycle at Farley 2 and the nominal 21-month fuel cycle at Diablo Canyon 1.

The actual resin bed usage in both Farley 2 and Diablo Canyon 1 was consistent with the calculations noted above. In both plants, a single mixed bed served for the entire cycle of zinc injection. Since zinc was injected for only 58% of the cycle in Farley 2 and 37% of the cycle in Diablo Canyon 1, these results are not unexpected. Based on the above zinc removal estimates, the mixed resin beds would not have been exhausted even if they had been operated for the full nominal fuel cycle length.

Filter Usage

A detailed assessment of filter usage was made for Diablo Canyon 1 Cycle 9 with zinc addition. During this cycle, the plant operated with 0.2 µm absolute letdown filters located downstream of the mixed bed demineralizers. There were no “pre-filters” in the letdown line upstream of the demineralizers. Normally, there are no letdown filter changes during plant operation. Pump seal water filters are also 0.2 µm absolute and are normally only changed out for ALARA reasons; that is, to reduce background radiation fields when service work is required in the area.

Several months prior to the scheduled refueling shutdown at the end of Cycle 9 (i.e., in November of 1998), a letdown filter was changed out in order to obtain sample material for establishing waste stream scaling factors. Subsequent to this change-out, the letdown filter was changed during the unscheduled shutdown that occurred in December 1998, based on high radiation levels. The measured dose rates were approximately 150 R/hr outside the filter housing, which is approximately 2 to 3 times that previously experienced.

During the Cycle 9 refueling outage, the letdown demineralizer bed was out of service and two letdown filters were changed out at dose rate readings of 1000 and 100 R/hr. After the bed was re-aligned, the filter vessel radiation field initially dropped from 200 to 150 R/hr and then began to increase; the filter was eventually changed out at a reading of 250 R/hr. In addition, six letdown filters were changed out during the remainder of the outage with dose rate readings of less than 25 R/hr and a startup filter was changed out during hydrazine addition with a dose rate reading of 30 R/hr.
A total of ten letdown filters were consumed during the Cycle 9 zinc addition cycle at Diablo Canyon 1. This filter consumption is basically the same as that noted during the Farley 2 Cycle 10 experience, in which four filters were changed out during the operating cycle and five were changed out during the refueling outage. However, the reason for filter change-out at Farley was generally based on differential pressure (DP) considerations, rather than dose rate limits.

In both plants, data for the filter change-out history for prior cycles was not recovered. Thus, a direct comparison between conditions when zinc was added vis-à-vis when it was not added could not be made. In any event, since most plants have been decreasing the pore size of the RCS filters, a meaningful comparison would probably not have been possible. Based on the lack of significant comments from plant waste system personnel, it is concluded that zinc addition, at least for the first injection cycles at Farley 2 and Diablo Canyon 1, did not result in any extreme effects with respect to RCS filter consumption.

### 2.9 Conclusions

Based on experience in the Farley Units 1 and 2 and Diablo Canyon Units 1 and 2 plants, the controlled addition of zinc to the reactor coolant has been demonstrated to be a fairly simple and inexpensive process. These plants, as well as those at Palisades and Obrigheim, have had no difficulties associated with the injection and control of RCS zinc concentrations from 5 to 40 ppb.

Monitoring of the RCS zinc concentration can be achieved by AA or SIMA analysis of acidified grab samples. A sampling frequency of once per day is adequate.

The net mass of zinc introduced into PWRs to date has ranged from about 1 to more than 5 kg in any given cycle. Natural zinc acetate has been used at plants with a nominal target of 20 to 40 ppb, while plants using zinc in the 5 ppb range for purposes of dose rate control have opted to use depleted (in $^{64}$Zn) zinc acetate to avoid the production of $^{65}$Zn.

After about a 40 day break-in period, the concentration of zinc in the reactor coolant can be easily maintained at concentrations varying from 5 to 40 ppb by adjusting either the injection rate or the concentration of the injection stream. The effect of the additional zinc and the increased radiocobalt, $^{65}$Zn, and nickel in the coolant due to the injection of zinc, does not significantly affect the performance of the CVCS demineralizer or filters.

These conclusions are based on approximately ten months of zinc injection. It will be interesting to see whether operations at longer time periods will result in the same conclusions.
References


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2.3 Letter, T. M. Wallace (Westinghouse) to D. N. Morey (SNOC), Subject: “Zinc Concentration in the RCS Following Steam Generator Replacement,” ALA-00-032 dated March 3, 2000.

2.4 Zinc Addition at the Palisades PWR to Reduce Shutdown Dose Rates, EPRI, Palo Alto, CA and Consumers Energy, Covert, MI: 2000. 1000190.


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2.10 E-mail, Dennis Rickertsen (SNOC) to Carl Bergmann (Westinghouse), Subject: “Zinc Data,” March 8, 2000.


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3 PRIMARY COOLANT RADIOCHEMISTRY

3.1 Introduction

Based on testing at the Halden reactor, an increase was expected in the radiocobalt activities in the coolant after initiation of zinc injection (Ref. 3.1). The general trends for the radiocobalts in a typical fuel cycle are similar. Upon startup, the activities decrease quickly and then exhibit a gradual continuing decrease during the cycle. Near the end of the cycle the activities increase, giving an overall U-bend shape (Ref. 3.2). It was uncertain what the effect of zinc addition would be on the radiocobalt activity and, in addition, an increase in the $^{65}$Zn concentration was expected due to the use of natural zinc acetate.

As a result of these considerations, primary coolant activity concentrations were monitored for the radiocobalts and $^{65}$Zn during the cycles of zinc addition in the Farley and Diablo Canyon plants. The concentrations were determined in two ways, to assess the effect of zinc on the total coolant activity, and also to determine the activity attributable separately to the soluble and insoluble portions. The activity in the soluble and insoluble fractions was determined by filtration of the sample through a 0.45 µm filter paper and counting both the filtrate and the filter paper activity, usually after a several day decay period.

3.2 Total Radiocobalt Activity Trends

Farley 2 Cycles 8 through 13

The total activity concentration trends of $^{58}$Co and $^{60}$Co during Cycles 8 through 13 are presented in Figures 3-1 and 3-2, respectively (Ref. 3.3). Cycles 8 and 9 data are included to illustrate the activity trends for the two operating cycles before zinc addition was initiated in Cycle 10. Zinc was added to the RCS during Cycle 10 for about nine months, discontinued during Cycle 11, added for three months during Cycle 12, and for ten months in Cycle 13. Therefore, the data trends reflect the radiochemical behavior during operating cycles with varying periods with and without zinc addition.
Figure 3-1
$^{58}$Co Activities in the Farley 2 RCS During Cycles 8 through 13

Figure 3-2
$^{60}$Co Activities in the Farley 2 RCS During Cycles 8 through 13
The $^{58}$Co trend shows a clear effect of zinc addition starting in Cycle 10 in that the activity concentration increased from approximately $10^{-4}$ µCi/ml to an “equilibrium” concentration (the activity concentration when the rate of increase becomes very low) of about $3 \times 10^{-3}$ µCi/ml near the end of the cycle. (The peaks in the last few months are attributed to plant shutdowns rather than to a true increase.) Recovery to pre-zinc levels did not occur in Cycle 11 while zinc injection was suspended, although some recovery was noted at the beginning of Cycle 12.

After zinc was injected during Cycle 12, a similar increase in the $^{58}$Co concentration was noted except that the increase continued after zinc injection was discontinued. Considering a final activity concentration of about $10^{-2}$ µCi/ml during the last month of operation, the value reached was about three times that attained during the last month of Cycle 10, and about a factor of 50 higher than nominal values for cycles prior to zinc addition. During Cycle 13, the $^{58}$Co activity concentration started slightly higher than at the start of Cycle 12 and then increased by a factor of 10 to about $1 \times 10^{-2}$ µCi/ml after zinc addition was resumed; this was essentially the same concentration reached during Cycle 12. Subsequently, the concentration decreased to an “equilibrium” concentration of about $4 \times 10^{-3}$ µCi/ml at the EOC. This decrease suggests that the exchange of zinc with nickel (and $^{58}$Co) in the plant corrosion product oxides may have reached an equilibrium condition.

The $^{60}$Co activity trend is somewhat different from the $^{58}$Co trend in that the concentration initially declined in Cycle 11 and then leveled off in Cycle 12 at a value about equal to the pre-zinc concentrations. The $^{60}$Co activity concentration in Cycle 12 increased after zinc injection was re-initiated and, similar to the $^{58}$Co activity, continued to increase even after termination of zinc addition. However, it increased only to about the levels found near the EOC 10, i.e., $10^{-4}$ µCi/ml. Considering a base pre-zinc value of $1 \times 10^{-5}$ µCi/ml, the $^{60}$Co activity increase attributable to zinc was by a factor of about ten, or somewhat less than that seen for $^{58}$Co. During Cycle 13, the $^{60}$Co activity concentration initially decreased as was seen during Cycle 12, and then increased after the resumption of zinc addition by a factor of about five to $1.5 \times 10^{-4}$ µCi/ml. Similar to $^{58}$Co, the concentration then decreased somewhat to $1.0 \times 10^{-4}$ µCi/ml. This decrease again, as for $^{58}$Co, suggests that the exchange of zinc with cobalt (and $^{60}$Co) in the ex-core oxide films may have reached an equilibrium condition.

The fact that the increases in $^{60}$Co activity concentration after zinc addition are somewhat lower than the $^{58}$Co increases suggests that zinc addition effects a relatively greater release of nickel than cobalt from the ex-core corrosion films.

**Farley 1 Cycles 15 and 16**

The total activity concentration trends of $^{58}$Co and $^{60}$Co during Cycles 15 and 16 for Farley 1 are presented in Figure 3-3 (Ref. 3.4). Cycle 15 data is shown to better define the trend without zinc addition. The trends of the radiocobalts in Farley 1 are similar to those in Farley 2 Cycle 10 after
Figure 3-3
Radiocobalt Activities in the Farley 1 RCS During Cycles 15 and 16

initial zinc addition; namely, a gradual increase after the initiation of zinc injection to the end of
the cycle (EOC). Note that the increase in activities normally seen at the EOC did not occur. The
$^{58}$Co concentration increased by about a factor of 16 (from $2.5 \times 10^{-4}$ to $4.0 \times 10^{-3}$ µCi/ml) and the
$^{60}$Co concentration increased by about a factor of 8 (from $3.0 \times 10^{-5}$ to $2.5 \times 10^{-4}$ µCi/ml) after
zinc addition. The $^{60}$Co increase is the same as that observed in Farley 2 Cycle 10, whereas the
$^{58}$Co increase is about half the Farley 2 Cycle 10 increase.

**Diablo Canyon 1 Cycles 8 and 9**

The total activity concentrations of $^{58}$Co and $^{60}$Co during Cycles 8 and 9 for Diablo Canyon 1 are
presented in Figure 3-4 (Ref. 3.2). Cycle 8 data is shown to provide pre-zinc baseline trends.
Inspection of the trends after zinc addition shows an abrupt increase in the radiocobalt
concentrations with the addition of zinc, a slight increase to near the EOC, and then another
significant increase during the last 40 days of the cycle. The effect of a plant shutdown which
occurred about six weeks before the EOC is also evident.

Even though the radiocobalt trend in the plant after zinc addition is different from that in the
Farley plants, the factor increases in the radiocobalt activities, about 20 for $^{58}$Co and about 11 for
$^{60}$Co, are similar to those observed for Farley 2 Cycle 10.
Diablo Canyon 2 Cycles 8 and 9

The total activity concentrations of $^{58}$Co and $^{60}$Co for Cycles 8 and 9 for Diablo Canyon 2 are presented in Figure 3-5 (Ref. 3.5). Cycle 8 data is shown to provide pre-zinc baseline trends. Inspection of the data after zinc addition shows an initial trend similar to that seen at Unit 1, namely, an abrupt increase in the radiocobalt concentrations immediately after the addition of zinc. Subsequently, however, in contrast to Unit 1, the concentrations decrease slightly rather than increase, and then increase considerably towards the EOC. The increases in the radiocobalt activities, by about a factor of 14 for $^{58}$Co and a factor of about 3 for $^{60}$Co, are somewhat lower than those seen in Unit 1 and in both of the Farley plants.

Table 3-1
Comparison of Radiocobalt “Equilibrium” Concentrations and Factor Increase after the First Cycle of Zinc Addition

<table>
<thead>
<tr>
<th>Plant/Cycle</th>
<th>Avg. Zinc Conc., ppb</th>
<th>“Equilib.” Conc., µCi/ml</th>
<th>Factor Increase</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$^{58}$Co</td>
<td>$^{60}$Co</td>
</tr>
<tr>
<td>Farley 1/16</td>
<td>29</td>
<td>$4.0 \times 10^3$</td>
<td>$2.5 \times 10^3$</td>
</tr>
<tr>
<td>Farley 2/10</td>
<td>35</td>
<td>$2.5 \times 10^3$</td>
<td>$1.5 \times 10^3$</td>
</tr>
<tr>
<td>Dia. Canyon 1/9</td>
<td>31</td>
<td>$6.0 \times 10^3$</td>
<td>$5.0 \times 10^3$</td>
</tr>
<tr>
<td>Dia. Canyon 2/9</td>
<td>21</td>
<td>$4.2 \times 10^3$</td>
<td>$1.9 \times 10^3$</td>
</tr>
</tbody>
</table>

3.3 Comparison of Radiocobalt Data

A comparison of the radiocobalt trends during the cycles of zinc injection was made to discern patterns among them. Two parameters were reviewed: the “equilibrium” activity concentration reached during the cycle and the factor increase in the radiocobalt activity concentration during the cycle after the addition of zinc. The average zinc concentration weighted by time was taken as a measure of the effect of zinc on the radiocobalt trends. Table 3-1 presents the data.

Table 3-1 indicates there is no apparent relationship between the average zinc concentration and the absolute “equilibrium” coolant concentration of either radiocobalt isotope. However, there appears to be a direct relationship between the average zinc concentration and the factor increase in the $^{58}$Co concentration. With the exception of Farley 2, a similar relationship also exists between the average zinc concentration and the factor increase in the $^{60}$Co concentration. Because of these relationships a plant operating with a higher zinc coolant concentration would have relatively more activity removed via the CVCS demineralizer during the cycle.
Figure 3-4
Radiocobalt Activities in the Diablo Canyon 1 RCS During Cycles 8 and 9

Figure 3-5
Radiocobalt Activities in the Diablo Canyon 2 RCS During Cycles 8 and 9
Increases in the total radiocobalt activities were also reported in the Palisades and German plants after zinc addition. In Palisades, an increase by about a factor of 30 was noted in the $^{58}$Co concentration (from $1 \times 10^{-3}$ to $3 \times 10^{-2}$ µCi/ml) and a factor of 50 increase occurred in the $^{60}$Co concentration (from $3 \times 10^{-3}$ to $1.5 \times 10^{-2}$ µCi/ml) (Ref. 3.6). Note that the final radiocobalt concentrations in Palisades are on the order of ten times those in the Westinghouse plants. In the Biblis B plant, increases in the total radiocobalt activities by a factor of ten were noted after the addition of zinc to the coolant (Ref. 3.7). In the Obrigheim plant, increases by a factor of ten in the soluble fraction of the coolant and a factor of two in the insoluble portion of the coolant were noted after the start of zinc addition (Ref. 3.8).

It is interesting to note that even though the target concentration of zinc in the Palisades and German plants is only 5 ppb, the increases in the radiocobalt activities are similar to those seen in the Farley and Diablo Canyon plants at a much higher zinc concentration. Note that this is in conflict with the results suggested by Table 3-1. However, design and operational differences between the two groups of plants may also play a role in these trends. For example, it was found that the radiocobalt concentrations in Obrigheim increased further after the zinc concentration was increased from 5 to 10 ppb (Ref. 3.9).

### 3.4 Total $^{65}$Zn Activity Trends

#### Farley 2 Cycles 10 through 13

Figure 3-6 illustrates the variation in the total RCS $^{65}$Zn concentration with operating time for Farley 2 from Cycles 10 through 13. Shortly after the addition of zinc, the $^{65}$Zn activity rapidly increased. It then continued to increase to an “equilibrium” concentration of about $4 \times 10^{-3}$ µCi/ml. The decrease in the activity noted during Cycle 11 while zinc addition was suspended continued during Cycle 12 to a nominal “equilibrium” value of about $5 \times 10^{-6}$ µCi/ml. After zinc addition was resumed, the $^{65}$Zn activity concentration immediately increased by a factor of 40 to $2 \times 10^{-4}$ µCi/ml and subsequently gradually decreased to approximately $6 \times 10^{-5}$ µCi/ml. Although natural zinc was used for the Cycle 10 addition, depleted zinc was used in Cycle 12. Since the amount of the parent isotope for $^{65}$Zn, i.e., $^{64}$Zn, is reduced by a factor of about 50 in depleted zinc, the increase observed in the $^{65}$Zn activity in Cycle 12 indicated that some of the depleted zinc had exchanged with the natural zinc and $^{65}$Zn activity in surface deposits. The fact that the $^{65}$Zn concentration generally declined during the 3-month period of zinc injection also suggests that the natural zinc was being replaced by the depleted zinc.

During Cycle 13, depleted zinc acetate was used for about the first half of the zinc addition period and natural zinc for the latter half. During the initial months of Cycle 13, the $^{65}$Zn concentration oscillated around $4 \times 10^{-3}$ µCi/ml until the resumption of zinc addition. Similar to Cycle 12, the $^{65}$Zn concentration quickly increased after the resumption of zinc addition although by not as great a factor, i.e., by a factor of about 13 compared to a factor of 40 in Cycle 12. The effect of continuing to use depleted zinc for four months is seen in that the concentration remained at about $5 \times 10^{-4}$ µCi/ml for that time period. After the changeover to natural zinc, the concentration increased to an “equilibrium” of about $2 \times 10^{-3}$ µCi/ml, about half the “equilibrium” concentration of $4 \times 10^{-3}$ µCi/ml reached at the EOC 10, reflecting the combined use of natural and depleted zinc during Cycle 13.
Primary Coolant Radiochemistry

Other Plants

The $^{65}$Zn concentration trends in Farley 1 and in the Diablo Canyon plants during their first cycles of operation with zinc addition were similar to those observed in Farley 2 Cycle 10. Since all of the plants used natural zinc acetate, a buildup of $^{65}$Zn occurred in the RCS. Table 3-2 lists the “equilibrium” concentration reached in the RCS after varying months of operation and several factors that may be related to the concentration.

![Graph: $^{65}$Zn Activity in the Farley 2 RCS During Cycles 10 through 13](image)

Table 3-2
Comparison of $^{65}$Zn “Equilibrium” Concentrations after the First Cycle of Zinc Addition

<table>
<thead>
<tr>
<th>Plant/Cycle</th>
<th>Zn Injection Time, mos.</th>
<th>Avg. Zinc Conc., ppb</th>
<th>Zn Exposure, ppb-mos</th>
<th>$^{65}$Zn “Equil”. Conc., $\mu$Ci/ml</th>
</tr>
</thead>
<tbody>
<tr>
<td>Farley 1/16</td>
<td>12.1</td>
<td>29</td>
<td>350</td>
<td>$4.8 \times 10^{-3}$</td>
</tr>
<tr>
<td>Farley 2/10</td>
<td>8.9</td>
<td>35</td>
<td>310</td>
<td>$4.0 \times 10^{-3}$</td>
</tr>
<tr>
<td>Dia. Canyon 1/9</td>
<td>7.5</td>
<td>31</td>
<td>235</td>
<td>$4.0 \times 10^{-3}$</td>
</tr>
<tr>
<td>Dia. Canyon 2/9</td>
<td>6.3</td>
<td>21</td>
<td>130</td>
<td>$1.4 \times 10^{-3}$</td>
</tr>
</tbody>
</table>
Although the relationship is not perfect, the data in Table 3-2 indicate that the greater the zinc exposure, the higher the RCS $^{65}\text{Zn}$ “equilibrium” concentration. Zinc exposure is the product of the zinc injection time in months and the average coolant zinc concentration.

### 3.5 Soluble and Insoluble Activity Trends

Most of the soluble and insoluble activity data presented in this section were collected from the Farley 2 and Diablo Canyon 1 plants as part of the EPRI-sponsored zinc addition programs. Data from other plants are noted as available.

#### Farley 2 Cycles 12 and 13

The distribution of activities in the insoluble and soluble portions of the reactor coolant for $^{65}\text{Zn}$ and the radiocobalts for Cycles 12 and 13 are shown in Figures 3-7 through 3-9. [“Less than” values are not shown on the figures. Most of the “less than” values were in the $^{60}\text{Co}$ and $^{65}\text{Zn}$ insoluble concentrations.] Inspection of these data suggests:

- After zinc addition, the soluble $^{65}\text{Zn}$ activity became measurable and equal to or greater than the insoluble activity. This had also been noted during Cycle 10 after zinc addition. The distribution did not change after zinc addition was terminated during Cycle 12, indicating a residual effect of zinc. However, during Cycle 13 the difference between the insoluble and soluble portions was greater than in Cycle 12, indicating the enhanced effect of the zinc addition. The predominance of the $^{65}\text{Zn}$ activity in the soluble portion of the coolant had also been observed in Diablo Canyon 1 after zinc addition (Ref. 3.2).

- For $^{58}\text{Co}$, most of the activity is in the insoluble form in both Cycles 12 and 13, before and after zinc addition. This was also observed in Cycle 10 after zinc addition. Note, however, that for a time after the initiation of zinc addition, the soluble activity approached that of the insolubles, suggesting an initial effect of zinc exchanging with the more soluble form of nickel in the corrosion film. Subsequently, the insoluble activity continued to increase whereas the soluble activity tended to level off. The predominance of the insoluble $^{58}\text{Co}$ activity in the coolant was the opposite of that observed in Diablo Canyon 1 after zinc addition (Ref. 3.2). In the Palisades plant, the soluble and insoluble $^{58}\text{Co}$ activities were evenly distributed at the beginning of the cycle and trended toward a larger contribution by the insolubles at the end of the cycle after the addition of zinc (Ref. 3.6).

- Due to the relatively few samples in which soluble $^{60}\text{Co}$ activity was detected, the trend is difficult to assess. However, it appears that the insoluble and soluble trends are similar to those for $^{58}\text{Co}$, except that the differences between the two are not as great.
Figure 3-7
Soluble and Insoluble $^{65}$Zn Activity in Farley 2 Cycles 12 and 13

Figure 3-8
Soluble and Insoluble $^{58}$Co Activity in Farley 2 Cycles 12 and 13
Figures 3-10 and 3-11 show the $^{58}$Co and $^{60}$Co activities, respectively, in the insoluble and soluble portions of the coolant during Cycle 9. Note that, with the exception of the last several weeks, most of the activity for the radiocobalts is in the soluble portion. Also, whereas the soluble concentrations for these isotopes remain fairly steady after the initial rise, the insoluble concentrations exhibit an increasing trend throughout the period of zinc injection. The effect of a plant shutdown that occurred in mid-December 1998 (at approximately 563 days) can also be seen.

The radiocobalt trends in Figures 3-10 and 3-11 indicate:

- The activity concentrations of the radiocobalts in solution increased rapidly after zinc addition and then remained nearly constant up to about the time the pH reached 7.4 (at approximately 505 days). These trends suggest an initial rapid exchange of zinc with the nickel and cobalt in the ex-core surface oxide films. After that period, they increased further and peaked during an unscheduled plant shutdown. Subsequently, the radiocobalt concentrations decreased ($^{58}$Co) or leveled off ($^{60}$Co).

- The activity concentrations of the insoluble radiocobalts also increased rapidly after zinc addition but not to the same extent as the solubles. They then remained relatively unchanged until the pH reached 7.4, at which time they began to increase. [An increase in the insoluble activity could be due to several factors: an actual increase in the RCS insoluble concentration, an increase in the specific activity of the insoluble material, and/or a combination of these factors.]
Figure 3-10
Soluble and Insoluble $^{58}$Co Activity in Diablo Canyon Unit 1 Cycle 9

Figure 3-11
Soluble and Insoluble $^{60}$Co Activity in Diablo Canyon Unit 1 Cycle 9
• At 563 days, the insoluble activity concentrations increased abruptly with the plant cold shutdown in response to the temperature decrease and associated crud release. After recovery from the shutdown the concentration increased through the remainder of the cycle. Calculations indicate that there may have been an increase in the pH at the letdown sampling point near the end of the cycle. This may have skewed the results for the particulate analyses in this period (Ref. 3.10).

The $^{65}$Zn activity, Figure 3-12, is predominantly in the soluble portion of the coolant; this is true throughout the cycle and is in agreement with the observations at Farley 2. The $^{65}$Zn activity exhibits a steadily increasing trend with only a relatively short time (from approximately 480 to 540 days) at near-steady concentrations.

**Diablo Canyon 2 Cycle 9**

The soluble and insoluble $^{58}$Co activity concentrations are shown in Figure 3-13. Comparison of the data with that for Unit 1 (Figure 3-10) indicates similar trends, with an almost immediate increase in the soluble activity and a gradual increase in the insoluble activity after the start of zinc injection. Similarly, near the end of the cycle, the insoluble activity is greater than the soluble activity. Unit 2 did not experience a shutdown near the end of the cycle, as had occurred at Unit 1. The abrupt increase in the Insoluble activity at approximately 525 days may be related to the increase in pH at the letdown sampling point, as noted previously for Unit 1.

![Graph showing Zn-65 activity](image-url)
3.6 Conclusions

The addition of zinc to the RCS in concentrations of 15 to 40 ppb results in an increase in the radiocobalt activity concentrations in the coolant. In some Westinghouse-designed plants the increase is almost immediate after the initiation of zinc injection (Diablo Canyon 1 and 2) whereas in others the increase is more gradual (Farley 1 and 2). The ultimate “equilibrium” activity concentrations that are attained appear to be plant-specific, and depend upon the pre-zinc values, as might be expected. The factor increase in the pre-zinc to post-zinc values, however, appears to have a direct dependence upon the average zinc concentration in the coolant.

Even though the nominal concentration of zinc in the Palisades and German plants is only 5 ppb, the increases in the radiocobalt activities are similar to those seen in the Westinghouse-designed plants at a much higher zinc concentration. Design and operational differences between the two groups of plants may play a role in these trends. For example, it was found that the radiocobalt concentrations in Obrigheim increased further after the zinc concentration was increased from 5 to 10 ppb.

The fact that the increases in the $^{58}$Co activity concentration after zinc addition are somewhat greater than the increases in the $^{60}$Co activity suggests that zinc addition effects a relatively greater release of nickel than cobalt from the ex-core corrosion films.

It appears that zinc in the RCS and in the corrosion films may reach an equilibrium after several cycles of zinc addition. This is inferred from the experience in the Farley 2 plant, where the
“equilibrium” radiocobalt concentrations at the end of Cycle 13 were lower than those at the end of prior cycles with zinc addition.

Although the relationship is not totally consistent, the data indicate that the greater the zinc exposure (the product of the zinc injection time and the average coolant zinc concentration), the higher the RCS $^{65}$Zn “equilibrium” concentration.

Trends in the behavior of the various radioisotopes with respect to partitioning between the soluble and insoluble activities appear to be inconclusive. In all Westinghouse plants using natural zinc acetate the soluble $^{65}$Zn activity became measurable and equal to or greater than the insoluble activity. However, in the Farley plants most of the radiocobalt activity is in the insoluble form, whereas in the Diablo Canyon plants the opposite is true. In the Palisades plant, the $^{58}$Co insoluble and soluble activities were evenly distributed at the beginning of the cycle, and trended toward a larger contribution by the insolubles at the end of the zinc addition cycle. It seems likely that at least part of these differences is associated with the sampling and analytical practices at the various plants.

**References**

3.1 In-reactor PWR Corrosion Test with Zinc at Halden, Institutt for Energiteknikk, Halden, Norway, Status Report, September 1993.


3.4 E-mail, Dennis Rickertsen (SNOC) to Carl Bergmann (Westinghouse), Subject: “Zinc Data,” March 8, 2000.

3.5 E-mail, Fidel Guerra (PG&E) to Carl Bergmann, Subject: “Diablo Canyon Unit #2 Zinc and Co Data,” March 2, 2000.


Primary Coolant Radiochemistry


DOSE RATES AND COMPONENT ACTIVITIES

4.1 Introduction

Dose rate and radionuclide concentration measurements of the reactor coolant system (RCS) components were made in the Farley and Diablo Canyon plants as baseline measurements for comparison to those after the addition of zinc to the primary coolant. In Farley 2, these measurements were repeated following cycles with varying intervals of zinc addition. In the other plants, dose rate and sometimes radionuclide concentration measurements of the RCS components were subsequently performed at the end of one cycle of zinc addition. These data were used to estimate the effects on dose rates and nuclide concentrations due to operation with and without additions of natural and depleted zinc to the primary coolant (Refs. 4.1 and 4.2).

This section presents and evaluates the results of the dose rate and radionuclide measurements performed. Reference to similar data from the Palisades and German plants that have added zinc to the RCS is made as appropriate.

4.2 Component Dose Rates

4.2.1 EPRI Standard Radiation Monitoring Program (SRMP) Locations

Dose rate measurements were made at the EPRI Standard Radiation Monitoring Program (SRMP) locations shown in Figure 4-1. Measurements on the reactor coolant loop piping and steam generator tubing were generally made twice during each refueling outage, i.e., prior to and following hydrogen peroxide addition. In addition, dose rate measurements were made of the steam generator channel head general area following hydrogen peroxide addition using survey instruments and, in Farley 2, also by thermoluminescent detectors (TLDs). A description and rationale for the locations chosen as representative of the dose rate trends is given in Table 4-1.

Specific plant results are discussed below.
Dose Rates and Component Activities

Figure 4-1
Locations of EPRI SRMP Measurement Points

Table 4-1
Description and Rationale for Dose Rate Measurement Locations

<table>
<thead>
<tr>
<th>EPRI SRMP Point No.</th>
<th>Description</th>
<th>Rationale</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 &amp; 10</td>
<td>Middle of SG channel head</td>
<td>Historical survey point</td>
</tr>
<tr>
<td>HL1, CL1, C1-C5</td>
<td>RCS piping</td>
<td>Represents stainless steel piping</td>
</tr>
<tr>
<td>S1 &amp; S2</td>
<td>Exterior of SG tube bundle</td>
<td>Represents Alloy 600 tubing</td>
</tr>
</tbody>
</table>

Farley 2

Figures 4-2 and 4-3 show the dose rate trends for Farley 2 Cycles 9 through 13 on the RCS piping and outside the SG tube bundle before and after peroxide additions during the shutdown. Noted on the figures are the periods of zinc injection during the cycle. The piping data reported is the average of points C1-C5, HL1 and CL1 and represent the overall trend of the crossover, hot leg and cold leg piping. This is in contrast to prior reports, in which data from only the
crossover piping point C5 was used to represent the piping (Refs. 4.3 through 4.5). The use of all the piping data reduces the effect of variations at individual points.

The SG tubing dose rates after peroxide additions decreased during the experience with zinc addition.

Overall, the dose rates at the locations measured decreased by a factor of two over the period of zinc injection, Cycles 10 through 13, compared to the dose rates at the end of pre-zinc Cycle 9.

Dose rate trends at the EPRI-SRMP locations given in Table 4-1 were used to evaluate changes from the Farley 2 EOC 9 through the EOC 13 outages. Table 4-2 summarizes the average dose rates at these locations before and after peroxide addition. Note that measurements can not be taken in the channel head before peroxide addition.

Table 4-3 summarizes the dose rate ratios for the three locations at the end of the five cycles; in each case, the ratios are relative to the pre-zinc addition Cycle 9 values. The results show that the average dose rates are lower by an average of 12% after hydrogen peroxide addition compared to the pre-peroxide dose rates. This indicates removal of the out-of-core activity during the shutdown process. This value is greater than the corresponding value of about 5% found in plants that do not use zinc addition (Ref. 4.6) and suggests that zinc has affected the corrosion film activity such that it is more easily removed after hydrogen peroxide addition.
**Figure 4-3**
**Dose Rates at Various Locations after H$_2$O$_2$ Addition in Farley Unit 2**

**Table 4-2**
**Comparison of Farley 2 RCS Component Dose Rates**

<table>
<thead>
<tr>
<th>Location</th>
<th>Average Dose Rate (1)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>EOC 9</td>
</tr>
<tr>
<td><strong>Pre-Peroxide Addition</strong></td>
<td></td>
</tr>
<tr>
<td>SG Tubing [S1 &amp; S2]</td>
<td>14.3</td>
</tr>
<tr>
<td>Piping Avg. [HL1, CL1, C1-C5]</td>
<td>132.0</td>
</tr>
<tr>
<td><strong>Post-Peroxide Addition</strong></td>
<td></td>
</tr>
<tr>
<td>SG Channel Head [2 &amp; 10] (2)</td>
<td>9.06</td>
</tr>
<tr>
<td>SG Tubing [S1 &amp; S2]</td>
<td>18.7</td>
</tr>
<tr>
<td>Piping Avg. [HL1, CL1, C1-C5]</td>
<td>117.3</td>
</tr>
</tbody>
</table>

(1) Values at locations 2 & 10 in R/h; others in mR/h
(2) Measured by TLD; all others by survey meter
Figure 4-4
Steam Generator Channel Head General Area TLD Dose Rate Trend in Farley Unit 2 after Hydrogen Peroxide Addition

Table 4-3
Farley 2 RCS Component Dose Rate Ratios

<table>
<thead>
<tr>
<th>Location</th>
<th>EOC 10/9</th>
<th>EOC 11/9</th>
<th>EOC 12/9</th>
<th>EOC13/9</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Pre-Peroxide Addition</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SG Tubing [S1 &amp; S2]</td>
<td>0.93</td>
<td>0.92</td>
<td>0.97</td>
<td>0.55</td>
</tr>
<tr>
<td>Piping Avg. [HL1, CL1, C1-C5]</td>
<td>0.70</td>
<td>0.74</td>
<td>0.65</td>
<td>0.61</td>
</tr>
<tr>
<td>Average</td>
<td>0.82</td>
<td>0.83</td>
<td>0.81</td>
<td>0.58</td>
</tr>
<tr>
<td><strong>Post-Peroxide Addition</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SG Ch. Head [2 &amp; 10]</td>
<td>0.77</td>
<td>0.82</td>
<td>0.70</td>
<td>0.50</td>
</tr>
<tr>
<td>SG Tubing [S1 &amp; S2]</td>
<td>0.75</td>
<td>0.67</td>
<td>0.55</td>
<td>0.50</td>
</tr>
<tr>
<td>Piping Avg. [HL1, CL1, C1-C5]</td>
<td>0.67</td>
<td>0.71</td>
<td>0.62</td>
<td>0.41</td>
</tr>
<tr>
<td>Average</td>
<td>0.73</td>
<td>0.73</td>
<td>0.62</td>
<td>0.47</td>
</tr>
</tbody>
</table>
Dose Rates and Component Activities

Diablo Canyon 1

Figure 4-5 shows the dose rate trends in Diablo Canyon 1 up through Cycle 9 (the cycle with zinc addition) at the three SRMP locations usually taken to characterize plant dose rates. The instances when the crossover leg piping and tubing dose rates were taken before peroxide are indicated.

Inspection of the data in Figure 4-5 shows a gradual increase in the steam generator channel head dose rate up to the EOC 6 outage, an increase after Cycle 7, followed by decreases at the EOC 8 and EOC 9 outages. The increase after Cycle 7 has been attributed to a cold shutdown that occurred approximately four weeks prior to the end-of-cycle shutdown (Ref. 4.7). The trend for the SG tube bundle exterior also shows a gradual increase up to EOC 8 although the data are more variable; note the decrease in the EOC 7 and EOC 9 outages. The trend at the crossover leg piping is not consistent with the other two locations, with a decreasing trend over the first five cycles followed by a continuously increasing trend to the EOC 8 and a decrease at the EOC 9. The trends for all locations from the EOC 8 to the EOC 9 are consistent, i.e., decreases were observed at all locations after the cycle with zinc addition.

A comparison of the dose rate data at the three locations compared in Farley 2 for the EOC 8 (pre-zinc) and EOC 9 (post-zinc) outages is shown in Table 4-4.

The data in Table 4-4 indicate that zinc addition along with other operations during Unit 1 Cycle 9 resulted in an average reduction of 17% (1 - 0.83) in the component dose rates compared to those at the EOC 8. They also indicate that shutdown chemistry practices, with perhaps an added zinc contribution, during the EOC 9 outage resulted in an additional 12% reduction (0.83 - 0.71) in component dose rates. This shutdown chemistry reduction is the same as that noted for the average in Farley 2.

The Cycle 8 to Cycle 9 decrease in the channel head dose rates measured at points 2 and 10 was 13% after peroxide addition. This suggests that either the peroxide effect, the zinc addition effect, and/or the operational effect is different for the channel head. A similar difference was not noted in Farley 2 after most of the cycles with zinc addition.
Table 4-4
Comparison of Diablo Canyon 1 Component Dose Rates and Ratios from EOC 8 to EOC 9

<table>
<thead>
<tr>
<th>Location (1) (SRMP Point)</th>
<th>EOC 8 Before Peroxide</th>
<th>EOC 8 After Peroxide</th>
<th>EOC 9 Before Peroxide</th>
<th>EOC 9 After Peroxide</th>
<th>EOC 9/8 Before Peroxide</th>
<th>EOC 9/8 After Peroxide</th>
</tr>
</thead>
<tbody>
<tr>
<td>SG Ch. Head (2 &amp; 10)</td>
<td>14.4</td>
<td>12.6</td>
<td></td>
<td></td>
<td>0.87</td>
<td></td>
</tr>
<tr>
<td>SG Tubing (S1 &amp; S2)</td>
<td>54.4</td>
<td>54.4</td>
<td>51.9</td>
<td>42.8</td>
<td>0.95</td>
<td>0.79</td>
</tr>
<tr>
<td>Piping Avg. (HL1, CL1, C1-C5)</td>
<td>143.5</td>
<td>155.7</td>
<td>100</td>
<td>73.2</td>
<td>0.70</td>
<td>0.47</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.83</td>
<td>0.71</td>
</tr>
</tbody>
</table>

(1) Values at 2 & 10 in R/h; others in mR/h

Diablo Canyon 2

Only the dose rate data from the cycle before and after zinc addition (Cycle 9) were analyzed for Diablo Canyon 2 (Ref. 4.8). The results for the locations of interest are given in Table 4-5.
Table 4-5
Comparison of Diablo Canyon 2 Component Dose Rates and Ratios from EOC 8 to EOC 9

<table>
<thead>
<tr>
<th>Location (1) (SRMP Point)</th>
<th>EOC 8 Before Peroxide</th>
<th>EOC 8 After Peroxide</th>
<th>EOC 9 Before Peroxide</th>
<th>EOC 9 After Peroxide</th>
<th>EOC 9/8 Before Peroxide</th>
<th>EOC 9/8 After Peroxide</th>
</tr>
</thead>
<tbody>
<tr>
<td>SG Ch. Head (2 &amp; 10)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>10.5</td>
<td>6.0</td>
<td>0.57</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SG Tubing (S1 &amp; S2)</td>
<td>19.2</td>
<td>15.9</td>
<td>18.6</td>
<td>13.4</td>
<td>0.97</td>
<td>0.84</td>
</tr>
<tr>
<td>Piping Avg. (HL1, CL1, C1-C5)</td>
<td>74.8</td>
<td>54.1</td>
<td>49.3</td>
<td>40.2</td>
<td>0.66</td>
<td>0.74</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.81</td>
<td>0.72</td>
</tr>
</tbody>
</table>

(1) Values at 2 & 10 in R/h; others in mR/h

The data in Table 4-5 indicate that zinc addition or other operations during Unit 2 Cycle 9 resulted in an average reduction of 19% (1 - 0.81) in the component dose rates compared to those at the EOC 8. They also indicate that shutdown chemistry practices and zinc additions during the EOC 9 outage resulted in an additional 9% reduction (0.81 - 0.72). These results are nearly identical to those observed in Unit 1 after zinc addition.

4.2.2 Non-EPRI SRMP Locations

The dose rates at certain non-SRMP locations in Diablo Canyon 1 increased after the initial cycle with zinc addition (Ref. 4.2). These locations included the residual heat removal system (RHRS), the reactor vessel head area, and the letdown line. An evaluation of the increases concluded that increased radiocobalt particulate concentrations in the coolant, which started in a cold shutdown that occurred six weeks before the EOC and continued into the EOC, resulted in increased deposition of activity in the RHRS. The average RHRS dose rate increased about 175 mR/h during the cold shutdown and about 50 mR/h during the EOC shutdown. The increase in the vessel head area was also judged to be due to the increased amount of coolant particulates being attracted to the magnetic jacks in the CRDMs. The increase in the letdown line has been noted in other plants without zinc addition and has been attributed to increases in the particulates in the coolant possibly due to a higher pH at the temperature of the heat exchanger (Ref. 4.9).

With respect to the RHRS dose rate behavior, it is noted that increases have been observed in other plants without zinc addition during and after the shutdown process (Refs. 4.10 and 4.11). The increase occurs after the RHRS is put into service and is attributed to deposition and/or removal of the nuclides in the coolant on the system walls during the shutdown process.

Due to the unexpected increase in dose rates in the RHRS system observed in Diablo Canyon 1, limited additional dose rate measurements were taken at two locations on the RHRS in Farley 2 at the EOC 13. Evaluation of the results of the measurements showed that the dose rates had increased by about 40 mR/h at the locations measured after shutdown. This value is within the range observed in the Callaway and Catawba 1 plants (Refs. 4.10 and 4.11) and slightly lower.
than the 50 mR/h noted in Diablo Canyon 1. Thus it was concluded that zinc addition did not contribute significantly to the RHRS dose rate changes observed in Diablo Canyon 1 during the EOC 9 shutdown.

Also, because of the observations in Diablo Canyon 1, changes were made to the operational and shutdown process in Diablo Canyon 2, which had initiated zinc addition in Cycle 9 (Ref. 4.12). The changes were effective in that no unusual dose rate increases were noted on the residual heat removal system (RHRS), the reactor vessel head area, or the letdown line at the end of the cycle with zinc addition.

4.3 Radionuclide Concentrations

Radionuclide concentrations on plant components at or near standard EPRI locations were measured by gamma ray spectrometry in Farley 2 and Diablo Canyon 1 prior to and after cycles of zinc injection. The gamma spectrometry measurements were made using a planar high purity germanium detector, a collimated shield, a multi-channel analyzer, and shielded TLDs, generally in accordance with the procedures given in Reference 4.13. Measurements are always taken after hydrogen peroxide addition and well after the shutdown chemistry process has ended.

**Farley 2**

Figures 4-6 and 4-7 show the average radiocobalt surface activity concentrations on the components measured in Farley 2 for Cycles 9 through 12. [Similar measurements were not made at EOC 13 in Farley 2.] Inspection of the data trends leads to the following observations and conclusions:

- The average $^{58}$Co concentration on the crossover leg and the hot leg piping exhibited a generally decreasing trend over these four cycles, with the exception of a slight increase after Cycle 11 when zinc was not added. Very little change was noted for the cold leg piping (note the inexplicably low EOC 11 value) while the SG tubing values showed a slight decrease after the Cycle 10 period of zinc injection followed by a small increase for both Cycles 11 and 12.
- The average $^{60}$Co concentration on the hot leg, cold leg, and crossover piping exhibited an overall decreasing trend over the four cycles (again the cold leg value at the EOC 11 is low). Very little change was noted in the SG tubing values except for a slight increase at the EOC 12.
- The crossover piping (colder leg) concentrations are about a factor of two greater than those on the hot leg. This is typical of observations in other plants.

The overall trends of the activity concentrations indicate that, similar to the plant dose rates, zinc addition results in a decrease in deposited activity concentrations on plant components. The effect is greater on the stainless steel piping components compared to that on Alloy 600 SG tubing, perhaps suggesting a different effect of zinc on the two types of materials.

The gamma spectrometry data was also used to determine the amount and percent contribution of $^{65}$Zn to the total component dose rate. It was found that the contribution varied from 0 to about
Dose Rates and Component Activities

7% depending upon the amount of zinc added and whether or not depleted zinc was used (see Table 4-6). These dose rate contributions are an indication of what further reductions in dose rates might be achieved if depleted zinc acetate (i.e., isotopically depleted in $^{64}$Zn, the precursor of $^{65}$Zn) was to be used in lieu of natural zinc.

**Figure 4-6**

$^{58}$Co Concentrations at Various RCS Locations in Farley 2

**Diablo Canyon 1 and 2 and Comparison to Farley 2**

Radionuclide measurements were made in Diablo Canyon Units 1 and 2 on the piping hot leg and crossover leg at the EOC 8 and EOC 9 to define the effect of a cycle of zinc addition (Refs. 4.2 and 4.14). The results are compared in Figures 4-8 and 4-9 to those observed in Farley 2 after its first cycle of zinc addition. Inspection of the data leads to the following observations:

- Similar to Farley 2 the concentrations on the crossover piping (colder leg) is about a factor of two greater than those on the hot leg. A similar difference was also noted in the Obrigheim plant (Ref. 4.15)
• Both radiocobalt activities on the hot and crossover legs decreased during the cycle with zinc addition, with the $^{60}$Co concentration decreasing more markedly.

• Decreases in plant dose rates for Farley 2 and Diablo Canyon Units 1 and 2 can be seen by inspection of the after-peroxide dose rate data in Tables 4-2 through 4-5.

![60 Cobalt Concentrations Measured at Various Primary System Locations](image)

Figure 4-7
$^{60}$Co Concentrations at Various RCS Locations in Farley 2

Analyses of the gamma spectrometry data showed that in Diablo Canyon 1 the percent contribution of $^{65}$Zn to the dose rate was about 8% on the crossover piping and about 10% outside the steam generator tube bundle. [These data are not presented here; see Table 4-6 for a summary.] In Diablo Canyon 2, the $^{65}$Zn contribution outside of the piping was about 4%. These values compare to $^{65}$Zn contributions of some 7% and 6%, respectively, found in Farley 2 after the first cycle of zinc addition. The lower percent contribution in Diablo Canyon Unit 2 reflects the lower amount of zinc injected during the cycle.
Deposited Activity Concentration Changes in Farley 2, and Diablo Canyon 1 & 2 After One Cycle of Zinc Addition

Figure 4-8
Deposited Radiocobalt Activities on the Hot Leg Piping in Three Plants after One Cycle of Zinc Addition

4.4 Relationship Between Zinc Exposure and Dose Rate Reduction

Dose rate and other data are available from three Westinghouse-designed nuclear plants (Farley 2, and Diablo Canyon 1 & 2), one Siemens-designed plant (Biblis B, Ref. 4.16), and one Combustion Engineering-designed plant (Palisades, Ref. 4.17) that have performed zinc addition. Since the data from Biblis B (presumably) and Palisades were taken after peroxide addition, only these results were compared. Because the time of zinc injection and the zinc coolant concentrations varied for the plants and cycles, the relationship between the amount of RCS zinc exposure for a cycle and the change in dose rate observed from the beginning to the end of that cycle was evaluated.
Zinc exposure is defined as the product of the average zinc concentration during the cycle and the time that zinc was in the RCS. The time of exposure was assumed equal to the time from initial zinc injection to the end of the cycle. Even though zinc injection may have been stopped some time during the cycle or near the end of the cycle, zinc is still in the RCS and thus the system is being exposed to zinc. A measure of this effect is essentially taken into account in using the average zinc concentration during the cycle.

The dose rate reduction for each cycle was calculated using the same points as described above for the three Westinghouse plants; the dose reduction data for the other two plants are based on similar measurement locations. A summary of the dose reduction and zinc exposure data is given in Table 4-6 along with notes regarding the type of zinc acetate added and the percent dose rate due to $^{65}\text{Zn}$.

The data in Table 4-6 indicate an increasing relationship between zinc exposure and dose rate reduction in the Farley 2 plant. However, it should be noted that, based on evaluations using the Westinghouse activity transport code (CORA), it is possible to argue that the reduction at the EOC 10 may be in large measure to operational coolant chemistry and design changes that occurred starting in Cycle 8. These changes included operating with a modified coolant
chemistry and changeover from Alloy 718 to Zircaloy fuel grid straps. Hence, the percent reduction reflects combined zinc addition and operational effects. The effect of these changes may continue for several cycles, but it is judged that their incremental effect is minimal by the EOC 13. Thus, the increasing dose rate reduction effect seen at EOC 13 can be interpreted as the result of zinc injection.

The Farley 2 Cycle 13 experience indicates that a single-cycle zinc exposure of 300 ppb-mo. resulted in dose rate reductions of about 25%.

Operating practices and design changes also occurred in both of the Diablo Canyon plants. However, they occurred during the second and third cycles. By the EOC 9, it is judged that their effects should not represent a significant factor in cycle-to-cycle changes. The data in Table 4-6 indicates that a lower zinc exposure, i.e., 130 to 235 ppb-mo. achieved a dose rate reduction similar to that observed in Farley 2. This may indicate a saturation effect of the exchange of zinc with the radiocobalts in the ex-core corrosion films, and suggests that a lower zinc concentration may be adequate in effecting the dose rate reduction benefit. However, this difference may also be influenced by design differences between the Farley 2 and Diablo Canyon plants. Note also that most of the Farley 2 and Diablo Canyon plant experience has been with natural zinc. Use of depleted zinc would further increase the benefit.

| Table 4-6 |

<table>
<thead>
<tr>
<th>Plant/Cycle</th>
<th>Zinc Added</th>
<th>Approx. Zn Conc., ppb</th>
<th>Zinc Exposure Time, mo</th>
<th>Zinc Exposure, ppb-mo</th>
<th>Percent Reduct.</th>
<th>% Dose Rate due to $^{65}$Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biblis B/17</td>
<td>Depleted</td>
<td>5</td>
<td>10.9</td>
<td>35</td>
<td>15.7</td>
<td>--*</td>
</tr>
<tr>
<td>Diablo Can. 1/9</td>
<td>Natural</td>
<td>40-30</td>
<td>7.5</td>
<td>235</td>
<td>29</td>
<td>9</td>
</tr>
<tr>
<td>Diablo Can. 2/9</td>
<td>Natural</td>
<td>30-15</td>
<td>6.3</td>
<td>130</td>
<td>28</td>
<td>4</td>
</tr>
<tr>
<td>Farley 2/10</td>
<td>Natural</td>
<td>40</td>
<td>8.9</td>
<td>310</td>
<td>27</td>
<td>6.6</td>
</tr>
<tr>
<td>Farley 2/11</td>
<td>Resid. Natur.</td>
<td>5-0</td>
<td>7.6**</td>
<td>40</td>
<td>0</td>
<td>1.3</td>
</tr>
<tr>
<td>Farley 2/12</td>
<td>Depleted</td>
<td>40</td>
<td>3.8</td>
<td>140</td>
<td>15</td>
<td>0</td>
</tr>
<tr>
<td>Farley 2/13</td>
<td>45% Depl. 55% Natural</td>
<td>30</td>
<td>10.2</td>
<td>300</td>
<td>24</td>
<td>--*</td>
</tr>
<tr>
<td>Palisades</td>
<td>Depleted</td>
<td>5</td>
<td>6.3</td>
<td>30</td>
<td>18</td>
<td>--*</td>
</tr>
</tbody>
</table>

* Gamma spectrometry results for $^{65}$Zn contribution not performed or available.
** Zn not injected; injection time equivalent to time when $^{65}$Zn concentration in coolant reached equilibrium.
The data from the Biblis B and Palisades plants also suggests that significant dose rate reductions can be realized with still smaller zinc exposures than in the Farley 2 and Diablo Canyon plants. The relationship between dose rate reduction and zinc exposure using the data from all the plants is presented in Figure 4-10. The trend line is a logarithmic fit to the data and indicates that, in general, the greater the zinc exposure, the greater the dose rate reduction. It is noted that the relationships do not take into account any effect of design and operating differences between (and among) the Westinghouse and non-Westinghouse plants.

The above observations are based on maximum zinc injection times of 10 to 11 months and a limited data base. Data from longer operating/zinc injection cycles are of obvious interest.

### 4.5 Conclusions

The following observations and conclusions result from a review and evaluation of dose rates and radionuclide activities deposited on RCS components from the Farley, Diablo Canyon, and other plants that have added zinc to the primary coolant.

- Dose rates at EPRI SRMP locations in Farley 2 decreased by about a factor of two from the EOC 9 through the EOC 13, thus suggesting a dose rate benefit of zinc addition, even when done intermittently or for part of a fuel cycle. The changes by cycle indicated an increasing dose reduction benefit with a longer cumulative zinc exposure.
• The experience in Farley Unit 2 indicates that an approximate 25% reduction may be realized for a single-cycle cumulative zinc exposure on the order of 300 ppb-mo. The experience in the Diablo Canyon units, however, indicates that a comparable benefit may be attainable with zinc exposures on the order of 130 to 235 ppb-mo. This difference may be related to plant design or operational differences.

• Zinc addition data from the Biblis B and Palisades plants also suggest that significant dose rate reductions can be attained with smaller zinc exposures than in the Farley 2 and Diablo Canyon plants; these cumulative zinc exposures were as little as 35 ppb-mo. Again, however, it is noted that these observations do not take into account any effect of design or operating differences between the Westinghouse and non-Westinghouse plants.

• With the exception of the experience in Diablo Canyon 1, the dose rates at non-SRMP locations have not exhibited an unusual increase during zinc addition. The increases observed in Diablo Canyon 1 at EOC 9 are attributed primarily to increases in the insoluble radiocobalt activity concentrations that occurred six weeks before the EOC 9 after an unplanned cold shutdown.

• Single-cycle zinc injection experience has resulted in net reductions of approximately 25% in deposited radionuclide activities. This reduction includes a net increase in deposited activity of 4 to 9% by $^{65}$Zn for plants using natural zinc acetate. The reduction would be further enhanced by the use of depleted zinc acetate.

• Average dose rate ratios from cycle-to-cycle in the Farley 2 and Diablo Canyon plants show a reduction of dose rates by an average of 12% after hydrogen peroxide addition compared to the pre-peroxide values. This indicates removal of the out-of-core activity during the shutdown process. This value is greater than the corresponding value of about 5% found in plants that do not use zinc addition and suggests that zinc has affected the corrosion film activity such that it is more easily removed after hydrogen peroxide addition.

• Gamma spectrometry results show that the radiocobalt concentrations in ex-core component deposits decrease after one cycle of zinc addition. The $^{58}$Co concentrations decrease more than the $^{60}$Co concentrations indicating a greater effect of zinc on nickel compared to the effect on cobalt. The decreases are consistent with the dose rate changes observed for the plant components.

References

4.1 Evaluation of Zinc Addition in Cycle 13 at Farley Unit 2, EPRI, Palo Alto, CA: 2000. 1000251


4.8 FAXes, H. Fong to C. A. Bergmann, “Reactor coolant loop and SG channel head surveys,” dated October 21, 1999 and November 24, 1999.

4.9 Kozin, D. (Commonwealth Edison), private communication, April 1999.


5
REFUELING SHUTDOWN CHEMISTRY AND RADIOCHEMISTRY

5.1 Introduction

The addition of zinc to the reactor coolant system affects the release of nickel, iron and cobalt from the corrosion films on primary system surfaces. The primary mechanism for this is the incorporation of zinc into the lattice of the spinel oxide corrosion film where, because of its preferred energy, it displaces the other divalent cations from tetrahedral sites (Refs. 5.1 and 5.2).

There are two major manifestations of this effect: the increase in the concentration of nickel and the radiocobalt ($^{58}\text{Co}$, $^{60}\text{Co}$) activity concentrations during the operating/injection period, and an increase in the amounts of these species released and removed from the RCS at the subsequent end-of-cycle shutdowns. The former issue has been summarized in Sections 2 and 3. This section presents a summary of the shutdown experiences at those plants for which data are available.

5.2 Plant Operating Experience

A summary of the plant operating experience with zinc for those plants for which shutdown data are available is presented in Table 5-1. Note the significant variation in the calculated ppb-mo. of zinc injected in these plants. The value for Palisades is particularly low in view of the low concentration of zinc that is being used.

Details of the shutdown varied somewhat from plant to plant and outage to outage. The variations generally reflected differences in the amount of time spent in one or more phases of the shutdown, rather than in any significant difference in the shutdown program. Plants generally follow the procedures defined in the EPRI guidelines (Ref. 5.3).

All of the plants represented in Table 5-1 follow a modified chemistry regimen. At the end of the fuel cycle, the pH is generally in the range from 7.2 to 7.4, boron is in the 10 – 50 ppm range, and the lithium concentration is approximately 1 ppm. As the reactor coolant temperature is decreased, the coolant is borated (to about 2000 ppm) with further reduction of lithium.
Table 5-1
Summary of Zinc Injection Experience for Plants for Which Shutdown Data are Available

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Farley 2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>12-14-93</td>
<td>3-11-95</td>
</tr>
<tr>
<td>11</td>
<td>4-26-95</td>
<td>10-12-96</td>
</tr>
<tr>
<td>12</td>
<td>12-18-96</td>
<td>3-28-98</td>
</tr>
<tr>
<td>13</td>
<td>5-18-98</td>
<td>10-16-99</td>
</tr>
<tr>
<td>Farley 1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>12-28-98</td>
<td>3-4-00</td>
</tr>
<tr>
<td>Diablo Canyon 1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>6-2-97</td>
<td>2-7-99</td>
</tr>
<tr>
<td>Diablo Canyon 2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>3-28-98</td>
<td>9-26-99</td>
</tr>
<tr>
<td>Palisades</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* - Net days, allowing for shutdown or maintenance of the injection system.

As this process continues, the coolant pH falls below the neutral pH and acid-reducing conditions are attained. This is generally within the first 6 to 10 hours after shutdown has begun. Significant release and removal of radiocobalt activity concentrations and nickel (by reduction of non-stoichiometric nickel ferrite) begin with the attainment of acid-reducing chemistry, and continue for approximately an additional 25 to 30 hours, depending on the letdown flow rate of the CVCS purification system. At this time the reactor coolant temperature is in the range 175 - 180°F.

Mechanical degassing of the system is used to reduce the hydrogen concentration from about 15 – 20 cm³/kg H₂O immediately before shutdown to about 6 to 7 cm³/kg H₂O through the acid-reducing phase. This includes the period following collapse of the pressurizer bubble when a short-time increase in hydrogen concentration occurs. The acid-reducing phase is completed by the initiation of chemical degassing by the first additions of hydrogen peroxide, generally about 35 to 40 hours into the shutdown. [At Palisades chemical degassing, per se, was not performed, but the first addition of hydrogen peroxide was made 35 hours after shutdown and further reduced the hydrogen concentration.]
Further additions of hydrogen peroxide create an acid-oxidizing coolant chemistry. The acid-oxidizing coolant chemistry induces a prompt increase in the dissolution rate and removal of large quantities of radiocobalt activity, particularly that of $^{58}\text{Co}$. In the Farley and Diablo Canyon plants the increase in $^{58}\text{Co}$ activity at this point is typically by a factor of 6 to 8 over that achieved in the acid-reducing phase.

Over the next 15 to 20 hours, dissolution of the nickel and radiocobalt activities continues with subsequent removal by the CVCS letdown system. The shutdown continues until the end-point limit of 0.05 $\mu\text{Ci/cm}^3$ is attained. This end-point limit is for the sum of all isotopes decaying by the emission of hard gammas, and includes $^{58}\text{Co}, ^{60}\text{Co}, ^{54}\text{Mn}, ^{134}\text{Cs}, ^{137}\text{Cs}$ and, for plants using natural zinc, $^{65}\text{Zn}$. For the plants listed in Table 5-1, the end-point limit was attained in post-shutdown times of approximately 100 to 160 hours. [Exceptions were Farley 2 EOC 10 which was extended to about 260 hours because of late releases of activity, and Farley 2 EOC 11 which was extended to 183 hours because of repairs required by a valve in the RHR system.]

Zinc addition had no significant effect on shutdown chemistry evolutions, based on the chemistry and radiochemistry parameters normally measured during refueling shutdowns. As expected, significant $^{65}\text{Zn}$ was observed in the coolant during the shutdown process, particularly in the plants using natural zinc acetate. However, in contrast to the radiocobalts, the $^{65}\text{Zn}$ concentration did not increase significantly after the addition of hydrogen peroxide. This behavior was expected based on early laboratory studies.

### 5.3 Specific Plant Shutdown Data

The data of specific interest from the shutdowns includes the total release and removal of $^{58}\text{Co}$, $^{60}\text{Co}$, $^{65}\text{Zn}$ and nickel. The release of nickel is enhanced by the reaction of zinc with the ex-core corrosion films. This has the effect of increasing both the RCS nickel concentrations and the activity concentration of $^{58}\text{Co}$ due to in-core neutron reactions with nickel. A major incentive for zinc addition is the reduction of the long-half life $^{60}\text{Co}$ isotope. This is believed to be the combined result of displacement and removal of cobalt from ex-core surfaces, and in situ decay of $^{58}\text{Co}$ that is more deeply embedded in the corrosion films. Ultimately both of these effects should reduce the source term and provide the basis for reduction of long-term radiation fields. As long as PWRs use natural zinc, the contribution of $^{65}\text{Zn}$ to radiation fields has to be weighed in the overall benefits analysis; hence the interest in the amount of this isotope removed at shutdown.

Table 5-2 presents a summary of the available results for the shutdown releases at the PWRs that are adding zinc. Also shown is the net amount of zinc added to the various plants for each period of zinc injection. Data for shutdowns prior to the period of zinc injection are provided for comparison. For Farley 1, data for the cycle prior to zinc injection (Cycle 15) were not judged to be meaningful in view of the fact that a mid-cycle shutdown had occurred. The values shown for the specific activity (Ci $^{58}\text{Co}/g$ Ni) are averaged over the full shutdown. These data have been compiled from available reports or by courtesy of the utility (Refs. 5.4 through 5.12).
5.4 Discussion

The data in Table 5-2 shows that the general trend with the addition of zinc is an increase in the amounts of radiocobalt activity and nickel that are released during shutdown. The absolute values released, however, vary from plant to plant. The individuality of plants is evident by comparing Farley 1 Cycle 16 $^{58}$Co and nickel data with that for Farley 2. The average $^{58}$Co and nickel values released in both Diablo Canyon units are significantly greater than for the Farley plants, reflecting at least in part the larger RCS area of the four-loop Diablo Canyon units. The $^{60}$Co release is not consistent in this regard.

The Palisades results for $^{58}$Co and $^{60}$Co are lower than those for Westinghouse plants, although the nickel values are in the same range.

Table 5-3 shows the percentage change in the shutdown releases before and following the period of zinc injection. The percentage increase in the amount of $^{58}$Co activity released is approximately the same in the Diablo Canyon and Farley plants, whereas the change in $^{60}$Co is much greater in the Diablo Canyon units. The change in the nickel released in the Farley 2 and the Diablo Canyon plants averages about 30%. Note that the nickel released at Farley 1 appeared to decrease after zinc injection.

The Palisades results after zinc injection generally show the same trends as the Westinghouse plants.

The $^{65}$Zn activity released and removed during the shutdowns is directly related to the use of natural zinc, although it seems to be disproportionately high for Cycle 9 at Diablo Canyon Unit 1. The low values for Farley 2 Cycle 12 and Palisades Cycle 14 reflect the use of depleted zinc acetate. Farley 2 Cycle 13 data also shows the effect of using depleted zinc acetate for approximately the first half of the injection period.

The high $^{58}$Co specific activity – in the range from about 0.69 to 0.83 Ci $^{58}$Co/g Ni for most plants after injecting zinc – suggest relatively high core residence times for nickel. Note also that the specific activity values in most cases increased slightly after the cycles with zinc addition, suggesting a modest increase in the nickel residence times. The specific activity value for Palisades is lower after zinc injection than for the Westinghouse plants, although it increased compared to the pre-zinc injection values.
### Table 5-2
Summary of Shutdown Releases for PWRs Using Zinc Injection

<table>
<thead>
<tr>
<th>Cycle No.</th>
<th>Net Zn Added, kg</th>
<th>Shutdown Releases</th>
<th>Spec. Activity, Ci/Co/g Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$^{60}$Co, Ci</td>
<td>$^{60}$Co, Ci</td>
</tr>
<tr>
<td>Farley 2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>---</td>
<td>1692</td>
<td>43.9</td>
</tr>
<tr>
<td>9</td>
<td>---</td>
<td>611</td>
<td>24.9</td>
</tr>
<tr>
<td>10</td>
<td>3.83</td>
<td>2153</td>
<td>62.5</td>
</tr>
<tr>
<td>11</td>
<td>None</td>
<td>2084</td>
<td>38.7</td>
</tr>
<tr>
<td>12</td>
<td>1.03</td>
<td>2324</td>
<td>56.2</td>
</tr>
<tr>
<td>13</td>
<td>1.49</td>
<td>2047</td>
<td>64.4</td>
</tr>
<tr>
<td>Farley 1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>---</td>
<td>930</td>
<td>---</td>
</tr>
<tr>
<td>14</td>
<td>---</td>
<td>1082</td>
<td>41.1</td>
</tr>
<tr>
<td>16</td>
<td>5.75</td>
<td>1349</td>
<td>58.4</td>
</tr>
<tr>
<td>Diablo Canyon 1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>---</td>
<td>1586</td>
<td>30</td>
</tr>
<tr>
<td>7</td>
<td>---</td>
<td>3083</td>
<td>38</td>
</tr>
<tr>
<td>8</td>
<td>---</td>
<td>3069</td>
<td>43.0</td>
</tr>
<tr>
<td>9</td>
<td>2.80</td>
<td>3858</td>
<td>112.6</td>
</tr>
<tr>
<td>Diablo Canyon 2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>---</td>
<td>2613</td>
<td>20.2</td>
</tr>
<tr>
<td>8</td>
<td>---</td>
<td>2220</td>
<td>14.5</td>
</tr>
<tr>
<td>9</td>
<td>1.86</td>
<td>3610</td>
<td>40.3</td>
</tr>
<tr>
<td>Palisades*</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>---</td>
<td>550</td>
<td>10</td>
</tr>
<tr>
<td>13</td>
<td>---</td>
<td>504</td>
<td>8</td>
</tr>
<tr>
<td>14</td>
<td>0.72</td>
<td>1030</td>
<td>27</td>
</tr>
</tbody>
</table>

* – The EOC 13 and EOC 14 data include releases that occurred in mid-cycle shutdowns
Table 5-3
Comparison of Radiocobalt and Nickel Releases before and after Experience with Zinc Injection

<table>
<thead>
<tr>
<th>Plant</th>
<th>Release</th>
<th>Avg. Pre-Zinc</th>
<th>Avg. Post-Zinc</th>
<th>% Increase</th>
</tr>
</thead>
<tbody>
<tr>
<td>Farley 2</td>
<td>$^{58}$Co</td>
<td>1151 Ci</td>
<td>2152 Ci</td>
<td>87%</td>
</tr>
<tr>
<td></td>
<td>$^{60}$Co</td>
<td>34.4 Ci</td>
<td>55.4 Ci</td>
<td>61%</td>
</tr>
<tr>
<td></td>
<td>Ni</td>
<td>2041 g</td>
<td>3010 g</td>
<td>47%</td>
</tr>
<tr>
<td>Farley 1</td>
<td>$^{58}$Co</td>
<td>1006 Ci</td>
<td>1349 Ci</td>
<td>34%</td>
</tr>
<tr>
<td></td>
<td>$^{60}$Co</td>
<td>41.1 Ci</td>
<td>58.4 Ci</td>
<td>42%</td>
</tr>
<tr>
<td></td>
<td>Ni</td>
<td>2307 g</td>
<td>1898 g</td>
<td>- 18%</td>
</tr>
<tr>
<td>D. Canyon 1</td>
<td>$^{58}$Co</td>
<td>2579 Ci</td>
<td>3858 Ci</td>
<td>50%</td>
</tr>
<tr>
<td></td>
<td>$^{60}$Co</td>
<td>37.0 Ci</td>
<td>112.6 Ci</td>
<td>204%</td>
</tr>
<tr>
<td></td>
<td>Ni</td>
<td>3634 g</td>
<td>4662 g</td>
<td>28%</td>
</tr>
<tr>
<td>D. Canyon 2</td>
<td>$^{58}$Co</td>
<td>2417 Ci</td>
<td>3610 Ci</td>
<td>49%</td>
</tr>
<tr>
<td></td>
<td>$^{60}$Co</td>
<td>17.4 Ci</td>
<td>40.3 Ci</td>
<td>132%</td>
</tr>
<tr>
<td></td>
<td>Ni</td>
<td>4170 g</td>
<td>4930 g</td>
<td>18%</td>
</tr>
<tr>
<td>Palisades</td>
<td>$^{58}$Co</td>
<td>527 Ci</td>
<td>1030 Ci</td>
<td>95%</td>
</tr>
<tr>
<td></td>
<td>$^{60}$Co</td>
<td>9 Ci</td>
<td>27 Ci</td>
<td>200%</td>
</tr>
<tr>
<td></td>
<td>Ni</td>
<td>3233 g</td>
<td>3607 g</td>
<td>12%</td>
</tr>
</tbody>
</table>

5.5 Conclusions

Following partial cycles of zinc addition, significant increases have been observed in the release and removal of $^{58}$Co, $^{60}$Co and nickel in subsequent refueling/maintenance shutdowns. Substantial releases of $^{65}$Zn are also observed in those plants using natural zinc additions. From the limited experience, the use of depleted zinc has the obvious effect of significantly reducing $^{65}$Zn release but, not surprisingly, has no discernible effect on release of the other major species. The $^{58}$Co specific activity increased slightly after the cycles with zinc addition, suggesting an increase in the core residence time for nickel.

It will be interesting to follow future end-of-cycle shutdowns as PWRs move to full-cycle periods of zinc injection. As the large-scale release and removal of these species continues, a decreasing trend should ultimately be observed since the source of the releases is finite. Once the
ex-core corrosion films have been “fully conditioned”, the release of nickel and cobalt should reach a dynamic balance that should result in lower releases than those seen to date.

References


5.9 Diablo Canyon Unit 2, End-of-Cycles 8 and 9 Shutdown Data, provided by G. Palino, NWT Corp., August 2000.


5.11 Email, D. Rickertsen (SNOC) to C. A. Bergmann, Subject: “Data for Farley 1 Cycles 14 and 15,” August 8, 2000.

5.12 Email, D. Rickertsen (SNOC) to C. A. Bergmann, Subject: “Data for Farley 1 End-of-Cycle 16 Shutdown,” April 13, 2000.
STEAM GENERATOR INSPECTION RESULTS

6.1 Introduction

The addition of zinc to the reactor coolant system as a means to mitigate PWSCC has been performed at four U.S. pressurized water reactors (PWRs): Farley Units 1 and 2, and Diablo Canyon Units 1 and 2. Based on the results of the earliest corrosion testing (Ref. 6.1), the maximum benefit in resistance to PWSCC was realized at the highest concentrations of zinc in the RCS. Thus, the earliest efforts – e.g., the Cycle 10 Demonstration Program at Farley Unit 2 – emphasized a concentration of 40 ppb zinc. This was subsequently reduced to 20-30 ppb because of concerns related to precipitation of zinc oxide, although such precipitation has never been observed.

The experience accrued at those plants that were attempting to address PWSCC is summarized in this section. While other Alloy 600 components may be expected to derive some benefit from the presence of zinc, the only component that is easily or routinely monitored is the steam generator heat transfer tube bundle. The results presented here are limited to eddy current inspections of the Alloy 600 tubing.

6.2 Plant Operating Experience

A summary of the plant operating experience for those plants that have added zinc as a means to address PWSCC is provided in Table 6-1.

Farley 2 Cycle 11 is included since eddy current inspections were performed at the end of that cycle although zinc additions had not been made. The extent of PWSCC of the Alloy 600 MA tubing in these plants varies considerably, but was recognized in each case to represent a threat to the long-term operational reliability. At Farley Unit 2, significant plugging and sleeving had been done for PWSCC in the roll expansion transitions at the top of the tubesheet. At Farley Unit 1 and at both Diablo Canyon units, the tube-to-tubesheet expansions were effected by explosive (WEXTEX) expansion rather than by mechanical rolling. The WEXTEX process results in lower residual stresses than rolling; as a result the extent of PWSCC in the expansion transitions is less. However, these latter plants have experienced some denting at the tube-tube support plate intersections, with subsequent eddy current indications of PWSCC.
### Table 6-1

**Summary of Zinc Injection Experience for PWSCC Mitigation**

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Farley 2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>12-14-93</td>
<td>3-11-95</td>
</tr>
<tr>
<td>11</td>
<td>4-26-95</td>
<td>10-12-96</td>
</tr>
<tr>
<td>12</td>
<td>12-18-96</td>
<td>3-28-98</td>
</tr>
<tr>
<td>13</td>
<td>5-18-98</td>
<td>10-16-99</td>
</tr>
<tr>
<td>Diablo Canyon 1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>6-2-97</td>
<td>2-7-99</td>
</tr>
<tr>
<td>Diablo Canyon 2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>3-28-98</td>
<td>9-26-99</td>
</tr>
</tbody>
</table>

* - these are the net days, allowing for shutdowns, etc.

Data for Farley Unit 1 Cycle 16 are not presented here, despite the fact that that cycle is the longest single-cycle experience with zinc addition for PWSCC mitigation. At the end of Cycle 16 the steam generators were replaced; hence, no eddy current inspections of the tube bundle were performed. Following steam generator replacement, zinc additions were resumed at the lower nominal concentration of 15 ppb. Addition at this level is being continued in order to provide some measure of mitigation of PWSCC of such components as control rod drive mechanism head penetration adapters, and to maintain the benefits of dose rate reduction.

At the time of this report [November 2000], zinc addition programs for PWSCC mitigation are in place at Farley Unit 1 Cycle 17, Farley Unit 2 Cycle 14, Diablo Canyon Unit 1 Cycle 10, and Diablo Canyon Unit 2 Cycle 10.

### 6.3 Inspection Results

The inspection results for each of the plants of interest are summarized below. These are reduced summaries from previously published assessments for Farley 2 (Refs. 6.2 through 6.5) and Diablo Canyon Unit 1 (Ref. 6.6); for Diablo Canyon Unit 2, the data have been provided by Pacific Gas & Electric (Ref. 6.7).
6.3.1 Farley Unit 2

Farley Unit 2 is a three-loop PWR, equipped with Westinghouse Series 51 steam generators (SGs) with full-depth mechanically-rolled tube-to-tubesheet joints. All heat transfer tubing is mill annealed Alloy 600 (A600 MA) manufactured by Westinghouse at the Blairsville Specialty Metals Plant.

Zinc was first introduced into the primary reactor coolant system during mid-Cycle 10. The zinc injections were discontinued for Cycle 11 and resumed in approximately mid-Cycle 12. Zinc additions during Cycle 12 were continued for approximately 3 months before being discontinued for fuel clad oxide film and gap closure issues not related to the zinc program. During Cycle 13, zinc was injected into the reactor coolant system from December 1998 to October 1999, when injection was terminated for the end-of-Cycle 13 shutdown. Unlike the previous experience in Cycles 10 and 12, when the nominal concentration was 40 ppb, the concentration was maintained in the 30 ppb range for Cycle 13.

Eddy current data from steam generator tube inspections are available for each outage. Caution is advised when comparing data among the outages because of the number of variables, both in terms of the eddy current probes and the inspection scopes/procedures used, for the various outages over this period. Table 6-2 summarizes the eddy current data for the number of tubes that were repaired (plugged or sleeved) due to reported PWSCC in the hot leg tube ends near the top-of-the-tubesheet (TTS) for all three steam generators.

Farley Unit 2 went critical in May 1981. The first instance of eddy current indications interpreted as PWSCC at the TTS occurred at the EOC 4 (May 1986) inspection after approximately 4 effective full power years (EFPY). The EOC 4 outage included only a partial inspection of the tube bundle with RPC probes to confirm the bobbin coil indications.

For both the EOC 5 and EOC 6 inspection campaigns, a limited inspection of the tube bundle was again performed with RPC eddy current probes, primarily as a means to verify bobbin coil indications. However, a new variable was introduced in the EOC 5 outage in that a modified plugging criterion, F*, was used. This plugging criterion is based primarily on whether or not the degradation occurs within a distance (F*) below the TTS (or below the bottom of the roll transition). Tubes with indications below this elevation do not have to be plugged and may remain in service. For each of the outages following Cycles 5 through 11, the F* distance was 1.72 inches.

Another factor that may affect the results is that the hot leg tube ends in all three SGs were shot peened at the end-of-Cycle 5 in the region at the top of the tubesheet to inhibit the initiation and propagation of PWSCC. Hence, the observable decrease (by a factor of 2) in the number of newly repairable tubes in Cycle 6 may be at least partially explained by the shot peening operation.
Steam Generator Inspection Results

Table 6-2
Plugging/Repair Actions for PWSCC within F* at the Hot Leg TTS Region in Farley Unit 2

<table>
<thead>
<tr>
<th>Outage</th>
<th>Reevaluated No. of Rep’d Tubes</th>
<th>Cumul. No. of Rep’d Tubes</th>
<th>Comments on Inspection Data and Significant Plant or Operation Modifications</th>
</tr>
</thead>
<tbody>
<tr>
<td>2R4 (5/86)</td>
<td>39</td>
<td>39</td>
<td>Partial inspection of bundle with RPC to validate bobbin calls. F* not used in this inspection.</td>
</tr>
<tr>
<td>2R5 (11/87)</td>
<td>31</td>
<td>70</td>
<td>Partial inspection of bundle with RPC to validate bobbin calls. F* = 1.72 inches. HL shot peening this outage.</td>
</tr>
<tr>
<td>2R6 (4/89)</td>
<td>15</td>
<td>85</td>
<td>Partial inspection of bundle with RPC to validate bobbin calls. F* = 1.72 inches.</td>
</tr>
<tr>
<td>2R7 (9/90)</td>
<td>305</td>
<td>390</td>
<td>100% inspection of HL side of bundle using RPC probes. F* = 1.72 inches.</td>
</tr>
<tr>
<td>2R8 (4/92)</td>
<td>61</td>
<td>451</td>
<td>100% inspection of HL side of bundle using RPC probes. F* = 1.72 inches.</td>
</tr>
<tr>
<td>2R9 (10/93)</td>
<td>77</td>
<td>528</td>
<td>100% inspection of HL side of bundle using RPC probes. F* = 1.72 inches.</td>
</tr>
<tr>
<td>2R10 (4/95)</td>
<td>151</td>
<td>679</td>
<td>100% inspection of HL side of bundle using RPC probes. F* = 1.72 inches. Zn injected last 9 months of Cycle 10.</td>
</tr>
<tr>
<td>2R11 (11/96)</td>
<td>424</td>
<td>1103</td>
<td>100% inspection of HL side of bundle using + Point probes. F* = 1.72 inches. Zn additions suspended in Cycle 11.</td>
</tr>
<tr>
<td>2R12 (4/98)</td>
<td>63</td>
<td>1166</td>
<td>100% inspection of hot leg side of bundle using + Point probes. F* = 1.94 inches. Zn injected months 9 - 12 of Cycle 12.</td>
</tr>
<tr>
<td>2R13 (10/99)</td>
<td>90</td>
<td>1256</td>
<td>100% inspection of hot leg side of bundle using + Point probes. F* = 1.94 inches. Zn injected last 10 months of Cycle 13.</td>
</tr>
</tbody>
</table>

1 F* is a modified plugging criterion based primarily on whether or not the degradation occurs within a distance (F*) below the TTS or below the bottom of the roll transition.

2 Reevaluation of field eddy current data resulted in revisions to the originally reported data. The reevaluated data used the criteria described in Ref. 6.3.
Beginning with the EOC 7 outage, the scope of the eddy current inspection was increased to 100% of the hot leg roll transitions, and the reliance on bobbin coils was replaced by the use of rotating pancake coil (RPC) probes which are more sensitive to degradation in the roll-expanded region. Consequently, an abrupt increase (often described as an “inspection transient”) was observed in the number of repairable tubes due to the presence of PWSCC; such an increase is seen in the data for EOC 7 in Table 6-2.

The inspection results for the EOC 8 through EOC 10 outages exhibit a gradually increasing trend, although the numbers for EOC 8 were substantially lower than had been reported for the inspection transient at EOC 7. During Cycle 10, zinc addition to the RCS was started approximately mid-cycle and was continued for the remaining nine months of the cycle. The use of zinc is expected to ultimately reduce the number of tubes with first indications of PWSCC; however, no such effect was seen in Cycle 10, where the number of tubes requiring repair increased by a factor of nearly two.

During Cycle 11, zinc addition was suspended. At the end of Cycle 11, the SG inspection program was performed using Plus-Point (+ Point) probes. Plus-Point eddy current probes have a lower detection threshold for tube degradation than RPC probes. The effect of this change is seen in Table 6-2 where the number of tubes with first indications of PWSCC increased by a factor of nearly three in the EOC 11 outage.

In Cycle 12, a total of sixty-three tubes were repaired for PWSCC. This represented a substantial decrease from the plugging at the previous outage where Plus-Point probes had been used for the first time. For this outage the F* distance was changed to 1.94 inches.

During Cycle 13, zinc injection was performed for approximately the final ten months of the cycle. The 100% hot leg tube end inspections were again performed with Plus-Point probes and the F* distance remained 1.94 inches. A total of ninety tubes were repaired for PWSCC indications at hot leg TTS locations (eighty-four were interpreted as axial in orientation and six were judged to represent circumferential degradation). This is not significantly different from the EOC 12 plugging (sixty-three tubes) and again represents a substantial decrease from the EOC 11 plugging. The number of repaired tubes at the latter two outages are similar to the number of tubes repaired at EOC 8 and EOC 9 after the previous “inspection transient” of EOC 7. In this regard, the slight increase in EOC 13 plugging compared to the EOC 12 plugging parallels the trend observed previously where gradually increased plugging followed the EOC 7 inspection (see the data for outages following Cycles 8 through 10 in Table 6-2).

With respect to the influence of zinc on PWSCC of steam generator tubing, the following is a summary of the Farley 2 experience to date:

Cycle 10

- Zinc was injected for the last nine months; the estimated net accumulation in the RCS was 3.83 kg Zn.
Steam Generator Inspection Results

- At EOC 10, the number of tubes repaired for PWSCC increased by a factor of nearly two relative to the EOC 9 outage.
- A steam generator tube pull (Ref. 6.2) confirmed efficient incorporation of zinc into ex-core corrosion films, as had been seen in laboratory tests (Ref. 6.8).

Cycle 11
- Zinc addition was suspended pending root cause evaluation of fuel cladding oxidation seen at EOC 10.
- A large increase (by a factor of 2.8 relative to EOC 10) was seen in the number of tubes repaired for PWSCC. Much of this increase is judged to be attributable to an inspection transient due to the first-time use of Plus-Point eddy current probes.
- A steam generator tube pull indicated residual zinc remained in corrosion films (but less than was found at EOC 10).

Cycle 12
- Zinc was added to the RCS for 3 months in the middle of the cycle; the estimated net mass of zinc added this cycle was 1.03 kg.
- The number of tubes repaired for PWSCC decreased by a factor of 7 relative to EOC 11 (424 to sixty-three).

Cycle 13
- Zinc was added to the RCS for the last 10 months of the cycle; the estimated net mass of zinc added during this cycle was 1.49 kg.
- The number of tubes repaired for PWSCC increased from sixty-three at the end of Cycle 12 to ninety at the end of Cycle 13.

There may be a general trend in this data when viewed over the period from the outages following Cycle 7 through the EOC 13 outage. At the EOC 7 and EOC 11 outages large increases occurred in the numbers of tubes repaired for PWSCC; each of these are believed to reflect the first-time use of more sensitive inspection probes (RPC at EOC 7 and Plus-Point at EOC 11). Following these abrupt increases, the numbers of tubes repaired decreased significantly in the subsequent outage and then slowly increased over the next several outages.

Trying to decipher a potential role of zinc on the degradation observed is not possible from the data available. It must be concluded that the experience with zinc at Farley Unit 2 has not been sufficient to provide unambiguous results from the SG eddy current inspection data. While the several observations that zinc is being incorporated into the ex-core corrosion films are encouraging, more definitive evidence of a positive effect will require additional experience. Future cycles, including the current Cycle 14 operations, are expected to provide for longer periods of zinc injection, ultimately approaching full fuel cycles. Perhaps when such experience
is accrued it will be possible to reach definitive conclusions about the role of zinc in mitigating PWSCC.

### 6.3.2 Diablo Canyon Unit 1

Diablo Canyon Unit 1 is a four-loop PWR, equipped with Westinghouse Series 51 steam generators (SGs) in which the tube-to-tubesheet crevice closure was effected by explosive expansion (WEXTEX process). The tubing in SGs 1 and 2 was manufactured at the Westinghouse Blairsville Specialty Metals Plant, whereas the tubing in SGs 3 and 4 was manufactured by Huntington Alloys, a Division of INCO Alloys International.

Denting of the tubes at tube-tube support plate intersections was detected after the first several cycles, but is believed to be no longer active. However, based on experience at plants with similar SGs, PWSCC as the result of the ID surface dent-induced strain is a potential degradation mode and, in fact, has been detected in the last several outages.

A summary of the inspection practices and the plugging required for PWSCC is presented in Table 6-3. Zinc was added to the RCS for only the last approximate 7 calendar months of Cycle 9, Table 6-1. After an initial period of injection at an RCS zinc concentration of 40 ppb, the nominal concentration was reduced to 30 ppb approximately half-way through the zinc injection period.

<table>
<thead>
<tr>
<th>Outage - EOC</th>
<th>EFPY</th>
<th>EC Scope</th>
<th>TTS Plugging for PWSCC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>At TTS</td>
<td>At TSPs</td>
</tr>
<tr>
<td>EOC 1 thru 3</td>
<td>---</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Mar 1991 - 4</td>
<td>4.49</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Sep 1992 - 5</td>
<td>5.86</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Apr 1994 - 6</td>
<td>7.14</td>
<td>2</td>
<td>31</td>
</tr>
<tr>
<td>Nov 1995 - 7</td>
<td>8.46</td>
<td>5</td>
<td>77</td>
</tr>
<tr>
<td>Apr 1997 - 8</td>
<td>9.75</td>
<td>8</td>
<td>133</td>
</tr>
<tr>
<td>Feb 1999 - 9</td>
<td>11.40</td>
<td>2</td>
<td>27</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0</td>
<td>5</td>
</tr>
<tr>
<td>Totals</td>
<td></td>
<td>17</td>
<td>263</td>
</tr>
</tbody>
</table>
Steam Generator Inspection Results

For the first several outages the inspections of the WEXTEX-expansion region consisted of limited bobbin (or 8 x 1) eddy current probe inspections. For outages EOC 4 through EOC 6 rotating pancake coil (RPC) probes were used to inspect about 20% of the hot leg tube ends at each outage. Beginning with the end-of-Cycle 6 (EOC 6) outage, with the detection of PWSCC at dented tube-tube support plate intersections, the locations with the largest dent voltage signals were also inspected. For the EOC 7 (November 1995) through EOC 9 (February 1999) outages the inspections were performed with Plus-Point eddy current probes. In the EOC7 outage, tube-TSP intersections with dent signals greater than 2 volts were inspected; in the EOC 8 and EOC 9 outages, tube-TSP intersections with dent signals less than 2 volts were also inspected. For the most recent outage (EOC 9, February 1999) the WEXTEX expansion regions were inspected in 100% of the hot leg tube ends. The Rows 1 and 2 U-bend tubes have been inspected at each outage; Plus-Point probes are also being used for these inspections.

Data in Table 6-3 does not include tubes that were exempted from plugging on the basis of modified plugging criteria. For EOC 9, degradation within the tubesheet or at/near the WEXTEX expansion transition was evaluated according to the W* criterion. By this criterion, if the degradation is axial in orientation, and located completely within the region between the top of the tubesheet (or below the bottom of the WEXTEX transition, whichever is lower) and the depth W*, the tube may remain in service; for Diablo Canyon the value of W* is 5.32 or 7.12 inches, depending on the specific location of the tube in the bundle. [There are additional factors involved in the W* plugging criterion; they are not important to the present discussion and are not reproduced here.] All tubes with circumferential degradation in the W* region must be plugged. There are no limits on the length, depth or orientation of degradation below the W* depth. For the EOC 9 outage, nine tubes with axial indications in the W* region were left in service.

Also, by applying a “depth sizing” correlation developed under contract by Westinghouse, Diablo Canyon was able to leave in service 44 tubes that would have required plugging for PWSCC at dented tube-tube support plate intersections. This correlation was established deterministically by relating the phase angles measured by Plus-Point eddy current probes to corrosion crack depths determined by destructive examination of laboratory-prepared corrosion mockups. Without this correlation, a total of 71 tubes would have been plugged for PWSCC at dented tube-TSP intersections.

The degradation reported at/near the WEXTEX transitions is low for steam generators that have operated for more than 11 efpys. Clearly, the degradation at the dented tube-tube support plate intersections represents the area of greatest concern, although the most recent inspection suggests the number of tubes with first indications of degradation may be decreasing. The apparently persistent degradation of Rows 1 and 2 U-bends after thermal stress relief is unusual; the reasons for this are not apparent despite careful reevaluations of the eddy current records.

Note that the general resistance of the tube bundle to PWSCC at the TTS WEXTEX expansion locations appears to be quite good. For example, contrast the Table 6-3 data with that for the full-depth rolled tubing at Farley Unit 2, Table 6-2. A total of only 17 WEXTEX-expanded tubes (of more than 13,000) have required plugging for corrosion degradation through the first 9 cycles of operation.

6-8
The addition of zinc for less than half of a fuel cycle was judged not likely to result in an observable effect on PWSCC degradation. Although the EOC 9 plugging totals, Table 6-3, are somewhat lower than those experienced at other recent inspections, the overall data base and plant experience with zinc addition are too limited to support an interpretation that zinc was responsible for the decrease. However, it is reasonable to expect that the benefits in reduced initiation of PWSCC observed in the laboratory will ultimately be realized in an operating PWR. This may prove to be especially important for the higher dented tube-tube support plate (lower temperature) locations.

### 6.3.3 Diablo Canyon Unit 2

Diablo Canyon Unit 2 is an identical plant to Unit 1. Tubing in the Series 51 SGs was also WEXTEX-expanded into the tubesheets. Denting at the tube-tube support plate intersections is significantly less than at Unit 1, with a corresponding decrease in the number of tubes that have been plugged for eddy current indications of degradation.

A summary of the inspection practices and the plugging required for PWSCC is presented in Table 6-4. Zinc was added to the RCS for only the last approximate 6 calendar months of Cycle 9, Table 6-1. The nominal RCS zinc concentration was initially 30 ppb but was subsequently reduced to approximately 15 ppb because of concerns related to increased concentration of $^{65}$Zn at shutdown.

The inspection and plugging history at Diablo Canyon Unit 2 is generally comparable to that of Unit 1; cf., Tables 6-3 and 6-4. The same plugging criteria apply to both units at all locations. Note that relatively more tubes have been unplugged and returned to service at Unit 2. Also, most of the eddy current indications at the TSP intersections at Unit 2 are limited to the lowest span – i.e., the TSP where the temperature is highest.

#### Table 6-4

<table>
<thead>
<tr>
<th>Outage - EOC</th>
<th>EFPY</th>
<th>TTS EC Scope</th>
<th>Plugging for PWSCC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>At TTS</td>
<td>At TSPs</td>
</tr>
<tr>
<td>EOC 1 thru 3</td>
<td>---</td>
<td>~ 25% Bobbin</td>
<td>0</td>
</tr>
<tr>
<td>Sep 1991 - 4</td>
<td>4.43</td>
<td>20% RPC</td>
<td>0</td>
</tr>
<tr>
<td>Apr 1993 - 5</td>
<td>5.74</td>
<td>41% RPC</td>
<td>25</td>
</tr>
<tr>
<td>Oct 1994 - 6</td>
<td>7.08</td>
<td>30% RPC</td>
<td>12</td>
</tr>
<tr>
<td>May 1996 - 7</td>
<td>8.41</td>
<td>56% + Point</td>
<td>42</td>
</tr>
<tr>
<td>Mar 1998 - 8</td>
<td>10.03</td>
<td>100% + Point</td>
<td>30</td>
</tr>
<tr>
<td>Oct 1999 - 9</td>
<td>11.49</td>
<td>100% + Point</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Unplugged</td>
<td>-43</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Net Tubes Plugged</td>
<td>72</td>
</tr>
</tbody>
</table>
Steam Generator Inspection Results

The number of tubes with new indications, both at the top of the tubesheet and at the TSP elevations, decreased in the EOC 9 outage. As discussed above for Unit 1, however, it would be premature to conclude this is a consequence of zinc addition in Cycle 9.

6.4 Conclusions

To date, the longest period of injection of zinc has been approximately ten months, or less than one-half of a fuel cycle, in plants that have operated for as long as 18 years. For individual plants, it may be possible to point out signs that the plugging trend for PWSCC is decreasing. However, in view of the fact that inspection equipment and plugging criteria have changed substantially over this period, it would be premature to assign any significant role to the addition of zinc. Final judgment regarding such an effect must necessarily wait for data following multiple full cycles of zinc addition.

References


6.7 Personal communication, John Arhar, Pacific Gas & Electric, July 2000.

7
FUEL REGION EXAMINATIONS

7.1 Introduction

It was recognized at the inception of the zinc addition program that it was necessary to monitor for potential effects on fuel cladding corrosion. Hence, at both Farley 2 for the Cycle 10 Demonstration Program, and at Diablo Canyon Unit 1, prior to the addition of zinc in Cycle 9, extensive pre-zinc cladding corrosion measurements were made to provide a direct baseline to understand post-zinc measurements.

In addition, at Farley Unit 2 Cycle 10 scraping and analysis of fuel cladding corrosion product deposits was performed to assess the effect(s) of zinc addition on the composition of the deposit.

A complication to these efforts was the fact that, over the period from late 1994 through 1999, the fuel rod cladding evolved from Standard Zircaloy 4 to Improved (low-Sn) Zircaloy 4 to ZIRLO™. Also, changes in core design occur continually; these have the effect of confounding efforts to compare directly the results of successive inspections. The formation and evolution of oxide corrosion films on zirconium-based fuel cladding is strongly dependent on the fuel burnup history, specific fuel rod temperatures, etc., not merely the total burnup. Thus, identical fuel that has experienced successive two-cycle burnups of 30 and 20 GWd/MTU may experience significantly different corrosion than fuel exposed three consecutive cycles at burnups of 22, 18 and 10 GWd/MTU.

Plants and cycles for which fuel inspection results are available include Farley Unit 2 Cycles 9 through 13, Farley Unit 1 Cycle 16, Diablo Canyon Unit 1 Cycles 8 and 9, and Diablo Canyon Unit 2 Cycle 9. These are presented and discussed in the approximate chronological order in which the inspections occurred. Brief comments are also offered to summarize the reports of inspections at Obrigheim and Palisades.

The inspection results presented here are summaries of the detailed data that can be found in the respective formal reports.

7.2 Inspection Methods

The most common inspections performed are visual, to notice and document any unusual appearance of the cladding surface or distribution of corrosion product deposits, and measurement of the oxide corrosion film thickness by a nondestructive (eddy current) technique. The oxide measurement technique consists of passing a probe over the surface of the fuel rods and collecting and processing the signal. [Several different probes have been used to collect the
data presented here; they are considered equivalent in range and accuracy.] The probes are calibrated against Zircaloy 4 or ZIRLO™ standards for which the oxide film thickness is known, and are rechecked in the field at the beginning and end of each inspection shift.

7.3 Farley Unit 2 – End-of-Cycle 10

At the end-of-Cycle 10 refueling outage, visual inspection of the fuel assemblies indicated the presence of a uniform-appearing black deposit over the full height of the assemblies (Ref. 7.1). Subsequent measurements of the rods after crud scraping indicated the black film was extremely thin, generally less than 0.5 µm even in the hottest (upper) spans.

The results of the oxide thickness measurements that were made on fuel assemblies common to both Cycles 9 and 10 are summarized in Table 7-1. [These are only part of the data collected at EOC 10; other data are discussed below.] The values shown are the average of the maximum values measured for all rods in the assembly identified; unless otherwise specified this is true for all maximum oxide values reported in this section. Note that for assembly Y47 the average maximum value is greater than 100 µm. This is greater than the expected value, but was judged to be of less importance than other results, discussed below, because it was for Standard Zircaloy 4 and the fuel was to be permanently discharged from the core.

### Table 7-1
Oxide Measurement Results – Farley 2 EOC 9 & 10

<table>
<thead>
<tr>
<th>Fuel Assembly</th>
<th>End of Cycle 9</th>
<th>End of Cycle 10</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Rods</td>
<td>Avg. Max., µm</td>
</tr>
<tr>
<td>Standard Zircaloy 4 Cladding (no. of cycles in parentheses)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Y40</td>
<td>6</td>
<td>15 (2)</td>
</tr>
<tr>
<td>Y47</td>
<td>8</td>
<td>38 (2)</td>
</tr>
<tr>
<td>W10</td>
<td>6</td>
<td>39 (2)</td>
</tr>
<tr>
<td>W50</td>
<td>7</td>
<td>38 (2)</td>
</tr>
<tr>
<td>R48</td>
<td>6</td>
<td>34 (2)</td>
</tr>
<tr>
<td>Improved Zircaloy 4 Cladding (no. of cycles in parentheses)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2L02</td>
<td>6</td>
<td>15 (1)</td>
</tr>
<tr>
<td>2L26</td>
<td>6</td>
<td>15 (1)</td>
</tr>
<tr>
<td>2L33</td>
<td>6</td>
<td>12 (1)</td>
</tr>
<tr>
<td>2L51</td>
<td>6</td>
<td>15 (1)</td>
</tr>
<tr>
<td>Y04</td>
<td>6</td>
<td>38 (2)</td>
</tr>
<tr>
<td>Y09</td>
<td>6</td>
<td>29 (2)</td>
</tr>
<tr>
<td>Y10</td>
<td>6</td>
<td>33 (2)</td>
</tr>
</tbody>
</table>
Table 7-2 presents results for all measurements made for twice-burned assemblies for which the fuel rods were clad with Improved Zircaloy 4. Table 7-3 presents similar data for the Improved Zircaloy 4-clad once-burned fuel assemblies; several of these were also measured at the end of the subsequent fuel cycle (EOC 11).

### Table 7-2
Oxide Measurement Results – Twice-burned Improved Zircaloy 4 in Farley 2 EOC 10

<table>
<thead>
<tr>
<th>Assembly</th>
<th>Rods</th>
<th>Avg. Max., µm</th>
<th>GWD/MTU</th>
<th>Assembly</th>
<th>Rods</th>
<th>Avg. Max., µm</th>
<th>GWD/MTU</th>
</tr>
</thead>
<tbody>
<tr>
<td>2L01</td>
<td>4</td>
<td>40</td>
<td>38.6</td>
<td>2L37</td>
<td>4</td>
<td>44</td>
<td>40.9</td>
</tr>
<tr>
<td>2L02*</td>
<td>6</td>
<td>54</td>
<td>40.0</td>
<td>2L39</td>
<td>4</td>
<td>39</td>
<td>38.2</td>
</tr>
<tr>
<td>2L03</td>
<td>4</td>
<td>39</td>
<td>39.1</td>
<td>2L40</td>
<td>4</td>
<td>46</td>
<td>41.5</td>
</tr>
<tr>
<td>2L04</td>
<td>4</td>
<td>34</td>
<td>38.7</td>
<td>2L43</td>
<td>4</td>
<td>41</td>
<td>41.5</td>
</tr>
<tr>
<td>2L05</td>
<td>4</td>
<td>34</td>
<td>38.8</td>
<td>2L44</td>
<td>6</td>
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<td>2L06</td>
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<td>39.8</td>
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<td>2L07</td>
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<td>43</td>
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<td>4</td>
<td>45</td>
<td>40.2</td>
<td>2L49</td>
<td>4</td>
<td>30</td>
<td>35.4</td>
</tr>
<tr>
<td>2L26*</td>
<td>6</td>
<td>42</td>
<td>41.6</td>
<td>2L50</td>
<td>4</td>
<td>39</td>
<td>39.9</td>
</tr>
<tr>
<td>2L28</td>
<td>6</td>
<td>44</td>
<td>41.7</td>
<td>2L51*</td>
<td>6</td>
<td>47</td>
<td>41.9</td>
</tr>
<tr>
<td>2L30/1</td>
<td>4</td>
<td>27</td>
<td>35.6</td>
<td>2L52</td>
<td>4</td>
<td>40</td>
<td>42.1</td>
</tr>
<tr>
<td>2L30/2</td>
<td>4</td>
<td>25</td>
<td>29.7</td>
<td>2L53</td>
<td>4</td>
<td>38</td>
<td>39.9</td>
</tr>
<tr>
<td>2L31</td>
<td>4</td>
<td>26</td>
<td>35.6</td>
<td>2L54</td>
<td>4</td>
<td>50</td>
<td>42.0</td>
</tr>
<tr>
<td>2L33/1*</td>
<td>4</td>
<td>29</td>
<td>38.2</td>
<td>2L55</td>
<td>4</td>
<td>41</td>
<td>41.6</td>
</tr>
<tr>
<td>2L33/2</td>
<td>4</td>
<td>14</td>
<td>20.8</td>
<td>2L56</td>
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<td>44</td>
<td>41.8</td>
</tr>
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<td>2L36</td>
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<td>36</td>
<td>38.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* - these assemblies were also measured at EOC 9 after one cycle; see Table 7-1.
The combined results of the visual inspections and the fact that the oxide thickness data were higher than expected based on EOC 9 results, led to a decision to withhold all twice-burned assemblies from Cycle 11 operation. Thus none of the fuel assemblies for which data are shown in Table 7-2 were returned to service.

In addition, pending the results of a Root Cause evaluation, a decision was made to suspend further injection of zinc. A Root Cause Evaluation Team was formed under the aegis of Southern Nuclear in an effort to determine the cause(s) for the unusual visual appearance of the fuel assemblies and the apparently high corrosion results for the twice-burned Improved Zircaloy 4 cladding. In addition to participation by Southern Nuclear, Westinghouse and EPRI, independent consultants were charged with the task of conducting the Root Cause evaluation. The results of this evaluation were published in October 1996 (Ref. 7.2). The consensus of the Root Cause team was that:

- Zinc addition had no more than a small detrimental effect on cladding corrosion.
- Differences between the observed and expected cladding corrosion during Cycle 10 were caused primarily by variations in the fuel duty and the inherent variability in corrosion of the Zircaloy 4 fuel cladding.

A separate evaluation of the Farley 2 EOC 10 results was performed by the Electric Power Research Institute (Ref. 7.3). This evaluation considered cladding oxide corrosion data from the shutdowns following Farley 2 Cycles 9 and 10, and Farley 1 Cycle 13. The results from Farley 1 Table 7-3

<table>
<thead>
<tr>
<th>Assembly</th>
<th>Rods</th>
<th>Avg. Max., µm</th>
<th>GWd/MTU</th>
<th>Assembly</th>
<th>Rods</th>
<th>Avg. Max., µm</th>
<th>GWd/MTU</th>
</tr>
</thead>
<tbody>
<tr>
<td>2M09</td>
<td>4</td>
<td>18</td>
<td>24.7</td>
<td>2M49/1</td>
<td>4</td>
<td>21</td>
<td>23.8</td>
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<tr>
<td>2M13</td>
<td>4</td>
<td>18</td>
<td>24.5</td>
<td>2M49/2</td>
<td>4</td>
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<td>12.3</td>
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<tr>
<td>2M24</td>
<td>4</td>
<td>19</td>
<td>24.5</td>
<td>2M55/1</td>
<td>4</td>
<td>11</td>
<td>12.4</td>
</tr>
<tr>
<td>2M29</td>
<td>4</td>
<td>19</td>
<td>24.5</td>
<td>2M55/2</td>
<td>4</td>
<td>21</td>
<td>22.8</td>
</tr>
<tr>
<td>2M46/2</td>
<td>4</td>
<td>23</td>
<td>23.6</td>
<td>2M56*</td>
<td>6</td>
<td>23</td>
<td>23.1</td>
</tr>
<tr>
<td>2M46/2</td>
<td>4</td>
<td>11</td>
<td>12.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* these assemblies were also measured at EOC 11 after a cycle in which zinc addition was suspended; see Table 7-4.
EOC 13 had also been noted to be higher than expected based on previous experience. The EPRI analysis was performed using the EPRI PWR Fuel Cladding Corrosion (PFCC) model (Refs. 7.4 and 7.5). The conclusion of the EPRI report was consistent with that of the Root Cause report but offered the further caution that care should be exercised in subsequent operating cycles if the fuel duty continued to be increased.

The results of the analysis of crud scrapings indicated that the concentration of zinc in the corrosion deposits on the fuel cladding varied from 2.4 to 3.6% (Ref. 7.1)

7.4 Farley Unit 2 – End-of-Cycle 11

Visual inspections following Cycle 11 indicated that the surfaces of the fuel rods were brighter in appearance compared to the EOC 10 inspections, with little evidence of corrosion product deposits (Ref. 7.6).

Although zinc injection was suspended in Cycle 11, measurements of the fuel cladding oxide thickness were made for once-burned and a limited number of twice-burned fuel assemblies. The once-burned 2N assemblies had not been exposed to zinc, whereas the twice-burned 2M assemblies had experienced a half-cycle of zinc injection preceding the Cycle 11 zinc-free exposure. The data are summarized in Table 7-4.

These results were generally comparable to those seen for both once-burned (Table 7-3) and twice-burned (Table 7-2) assemblies after Cycle 10. Corrosion deposit removal and remeasurement of the oxide thickness was not performed during the EOC 11 outage.

Fuel assemblies 2N41 and 2N52 were lead-test-assemblies (LTAs) in which the corner positions were rods clad with Improved Zircaloy 4, and the central three rods on each face were ZIRLO-clad. Unfortunately, oxide thickness measurements are not available for the ZIRLO-clad rods at EOC 11. Following Cycle 12 (next section), measurements were made for both the Improved Zircaloy 4-clad and the ZIRLO-clad rods in the LTAs.

7.5 Farley Unit 2 – End-of-Cycle 12

Zinc was injected for only three months near the middle of Cycle 12. The injection was discontinued for reasons not related to the zinc injection program. Visual examinations revealed that the fuel assemblies were again covered with a thin, dark coating (Ref. 7.7). A number of rods were brushed with a Scotch-brite pad to determine whether or not the deposit was influencing the accuracy of the oxide thickness measurements. Differences between the pre-brushed and post-brushed values were in the 0 to 2 µm range.
Table 7-4
Oxide Measurement Results – Once and Twice-burned Improved Zircaloy 4 in Farley 2 EOC 11

<table>
<thead>
<tr>
<th>Assembly</th>
<th>Rods</th>
<th>Avg. Max., µm</th>
<th>GWd/MTU</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Improved Zircaloy 4 Cladding (no. of cycles in parentheses)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2N32</td>
<td>6 (1)</td>
<td>12</td>
<td>26.3</td>
</tr>
<tr>
<td>2N41/1*</td>
<td>2 (1)</td>
<td>14</td>
<td>25.8</td>
</tr>
<tr>
<td>2N41/2*</td>
<td>2 (1)</td>
<td>10</td>
<td>23.5</td>
</tr>
<tr>
<td>2N41/4*</td>
<td>2 (1)</td>
<td>9</td>
<td>23.5</td>
</tr>
<tr>
<td>2N52/2*</td>
<td>2 (1)</td>
<td>15</td>
<td>24.2</td>
</tr>
<tr>
<td>2N52/3*</td>
<td>2 (1)</td>
<td>19</td>
<td>25.8</td>
</tr>
<tr>
<td>2N52/4*</td>
<td>2 (1)</td>
<td>10</td>
<td>23.5</td>
</tr>
<tr>
<td>2N05</td>
<td>6 (1)</td>
<td>14</td>
<td>25.6</td>
</tr>
<tr>
<td>2M15**</td>
<td>6 (2)</td>
<td>34</td>
<td>44.7</td>
</tr>
<tr>
<td>2M19**</td>
<td>6 (2)</td>
<td>30</td>
<td>43.8</td>
</tr>
<tr>
<td>2M52**</td>
<td>6 (2)</td>
<td>42</td>
<td>44.5</td>
</tr>
<tr>
<td>2M56</td>
<td>6 (2)</td>
<td>35</td>
<td>44.7</td>
</tr>
</tbody>
</table>

* also measured at EOC 12; see Table 7-5.
** previously measured at EOC 10; see Table 7-3.

Results of the oxide measurements are presented in Table 7-5. Note that the oxide corrosion thickness for the Improved Zircaloy 4 cladding on the LTA rods (assemblies 2N41 and 2N52) is generally in the range from 60 to 80 µm after burnups of approximately 45 GWd/MTU, whereas for the ZIRLO-clad rods in the same fuel assemblies the oxide thickness ranges from 32 to 40 µm.

### 7.6 Farley Unit 2 – End-of-Cycle 13

Visual inspection of the fuel assemblies once again indicated that the rods were coated with an apparently very thin semi-reflective coating (Ref. 7.8). This coating was quite thin – it was often removed by the action of the guide rollers on the eddy current probe-carrying fixture – and had no appreciable effect on the oxide thickness measurements.
Table 7-5
Oxide Measurement Results – Twice-burned Improved Zircaloy 4 and Once-burned ZIRLO in Farley 2 EOC 12

<table>
<thead>
<tr>
<th>Assembly</th>
<th>Rods</th>
<th>Avg. Max., µm</th>
<th>GWd/MTU</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Twicenburned Assemblies; Improved Zircaloy 4 Cladding</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2N35/1</td>
<td>4</td>
<td>35</td>
<td>37.7</td>
</tr>
<tr>
<td>2N35/4</td>
<td>4</td>
<td>89</td>
<td>45.5</td>
</tr>
<tr>
<td>2N38/1*</td>
<td>4</td>
<td>29</td>
<td>35.7</td>
</tr>
<tr>
<td>2N38/4*</td>
<td>4</td>
<td>34</td>
<td>37.7</td>
</tr>
<tr>
<td>2N41/1**</td>
<td>2</td>
<td>70</td>
<td>46.7</td>
</tr>
<tr>
<td>2N41/2**</td>
<td>2</td>
<td>66</td>
<td>44.8</td>
</tr>
<tr>
<td>2N41/4**</td>
<td>2</td>
<td>60</td>
<td>44.5</td>
</tr>
<tr>
<td>2N52/2**</td>
<td>2</td>
<td>53</td>
<td>44.5</td>
</tr>
<tr>
<td>2N52/3**</td>
<td>2</td>
<td>92</td>
<td>46.7</td>
</tr>
<tr>
<td>2N52/4**</td>
<td>2</td>
<td>84</td>
<td>44.8</td>
</tr>
<tr>
<td>Twicenburned Assemblies; ZIRLO Cladding</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2N41/1</td>
<td>3</td>
<td>38</td>
<td>46.8</td>
</tr>
<tr>
<td>2N41/2</td>
<td>3</td>
<td>33</td>
<td>44.9</td>
</tr>
<tr>
<td>2N41/4</td>
<td>3</td>
<td>35</td>
<td>44.6</td>
</tr>
<tr>
<td>2N52/2</td>
<td>3</td>
<td>32</td>
<td>44.6</td>
</tr>
<tr>
<td>2N52/3</td>
<td>3</td>
<td>38</td>
<td>46.8</td>
</tr>
<tr>
<td>2N52/4</td>
<td>3</td>
<td>40</td>
<td>46.9</td>
</tr>
<tr>
<td>Once-burned Assemblies; ZIRLO Cladding</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2P08</td>
<td>8</td>
<td>7.5</td>
<td>21.4</td>
</tr>
<tr>
<td>2P29</td>
<td>8</td>
<td>12</td>
<td>24.3</td>
</tr>
<tr>
<td>2P31</td>
<td>8</td>
<td>13</td>
<td>24.3</td>
</tr>
<tr>
<td>2P32</td>
<td>8</td>
<td>14</td>
<td>24.3</td>
</tr>
<tr>
<td>2P63</td>
<td>8</td>
<td>16</td>
<td>24.3</td>
</tr>
</tbody>
</table>

* also measured at EOC 13; see Table 7-6.
** also measured at EOC 11; see Table 7-4.
Fuel Region Examinations

Table 7-6
Oxide Measurement Results – Improved Zircaloy 4 and ZIRLO in Farley 2
EOC 13

<table>
<thead>
<tr>
<th>Assembly</th>
<th>Rods</th>
<th>Avg. Max., µm</th>
<th>GWd/MTU</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thrice-burned Assemblies; Improved Zircaloy 4 Cladding</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2N38/1*</td>
<td>4</td>
<td>55</td>
<td>47.4</td>
</tr>
<tr>
<td>2N38/4*</td>
<td>4</td>
<td>56</td>
<td>46.1</td>
</tr>
<tr>
<td>ZIRLO Cladding (no. of cycles in parentheses)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2R52</td>
<td>8 (1)</td>
<td>10</td>
<td>26.1</td>
</tr>
<tr>
<td>2R60</td>
<td>8 (1)</td>
<td>11</td>
<td>26.4</td>
</tr>
<tr>
<td>2P08*</td>
<td>8 (2)</td>
<td>20</td>
<td>41.2</td>
</tr>
<tr>
<td>2P29*</td>
<td>8 (2)</td>
<td>27</td>
<td>44.2</td>
</tr>
<tr>
<td>2P31*</td>
<td>8 (2)</td>
<td>32</td>
<td>45.9</td>
</tr>
<tr>
<td>2P32*</td>
<td>8 (2)</td>
<td>34</td>
<td>45.9</td>
</tr>
<tr>
<td>2P63*</td>
<td>8 (2)</td>
<td>32</td>
<td>45.7</td>
</tr>
</tbody>
</table>

* previously measured at EOC 12; see Table 7-5.

The oxide thickness results collected at EOC 13 are summarized in Table 7-6. Note that, for the twice-burned 2P fuel assemblies, for burnups in the 41 to 46 GWd/MTU range the oxide thickness on the ZIRLO-clad rods are on the order of 20 to 34 µm. None of the oxide thickness values measured at this outage, for Improved Zircaloy 4 or ZIRLO, challenged the upper bound estimates established for this cycle.

7.7 Diablo Canyon Unit 1 – End-of-Cycle 9

This was the first cycle of zinc injection at Diablo Canyon Unit 1 (Ref. 7.9). To provide a baseline against which to interpret the end-of-Cycle 9 results, measurements were made of the thickness of the oxide corrosion layer on a number of rods at the end-of-Cycle 8 outage. These rods, all clad with Improved Zircaloy 4, were remeasured at the EOC 9 outage. Cycle 9 was the first extensive use of ZIRLO-clad fuel rods at Diablo Canyon Unit 1; the oxide thickness on a number of these rods was also measured. The results are presented in Table 7-7.
Table 7-7
Oxide Measurement Results – Diablo Canyon 1 EOC 8 & 9

<table>
<thead>
<tr>
<th>Fuel Assembly</th>
<th>End of Cycle 8 (pre-Zinc)</th>
<th>End of Cycle 9 (Zinc added)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Rods</td>
<td>Avg. Max., µm</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Improved Zircaloy 4 Cladding (no. of cycles in parentheses)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AA04</td>
<td>6</td>
<td>15 (1)</td>
</tr>
<tr>
<td>AA06</td>
<td>6</td>
<td>15 (1)</td>
</tr>
<tr>
<td>AA11</td>
<td>6</td>
<td>15 (1)</td>
</tr>
<tr>
<td>AA28</td>
<td>6</td>
<td>15 (1)</td>
</tr>
<tr>
<td>AA32</td>
<td>6</td>
<td>15 (1)</td>
</tr>
<tr>
<td>AA38</td>
<td>6</td>
<td>17 (1)</td>
</tr>
<tr>
<td>AA59</td>
<td>6</td>
<td>20 (1)</td>
</tr>
<tr>
<td>AA63</td>
<td>6</td>
<td>20 (1)</td>
</tr>
<tr>
<td>AA64/1</td>
<td>4</td>
<td>19 (1)</td>
</tr>
<tr>
<td>AA64/3</td>
<td>4</td>
<td>18 (1)</td>
</tr>
<tr>
<td>AA82</td>
<td>6</td>
<td>16 (1)</td>
</tr>
<tr>
<td>K10</td>
<td>6</td>
<td>24 (2)</td>
</tr>
<tr>
<td>K30/1</td>
<td>4</td>
<td>28 (2)</td>
</tr>
<tr>
<td>K30/4</td>
<td>4</td>
<td>28 (2)</td>
</tr>
<tr>
<td>ZIRLO Cladding (all once-burned)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BB16</td>
<td></td>
<td>19</td>
</tr>
<tr>
<td>BB33</td>
<td></td>
<td>19</td>
</tr>
<tr>
<td>BB36</td>
<td></td>
<td>19</td>
</tr>
<tr>
<td>BB37</td>
<td></td>
<td>19</td>
</tr>
<tr>
<td>BB86</td>
<td></td>
<td>19</td>
</tr>
<tr>
<td>BB87</td>
<td></td>
<td>19</td>
</tr>
</tbody>
</table>
The results from the EOC 8 measurements were generally consistent with predictions based on previous experience with Improved Zircaloy 4 cladding. The results for the EOC 9 measurements, for both the Zircaloy 4-clad and the ZIRLO-clad rods, exceeded the best-estimate values but most were below the 95% upper bound values predicted by the design-basis corrosion model (Ref. 7.10). In particular, the measured values for all rods in assembly AA59 were in the range 100-120 μm, and several of the rods in assembly AA38 also exceeded 100 μm, whereas the 95% upper bound prediction for these rods was approximately 80 μm.

In order to determine whether or not the presence of corrosion product deposits had introduced an error in the oxide thickness results, six rods in fuel assembly AA59 (Improved Zircaloy 4) and six rods in fuel assembly BB37 were surface-brushed with a Scotch-brite pad and remeasured with the EC lift-off probe. The post-cleaning measured values for fuel assembly AA59 decreased on average by 25 μm to a final average value of 88 μm. A significant decrease was also observed in the results for the ZIRLO-clad rods in fuel assembly BB37.

These results indicated that the corrosion product burden on the Diablo Canyon 1 fuel was significantly greater than had been seen in previous inspections at Diablo Canyon and also greater than that found at Farley Unit 2 where deposits on the order of a few μm had been found.

## 7.8 Diablo Canyon Unit 2 – End-of-Cycle 9

Fuel rod cladding oxide thickness measurements were made on 30 rods that were clad with Improved Zircaloy-4, and 52 rods that were clad with ZIRLO. A summary of the results of these measurements is presented in Table 7-8 (Ref. 7.11).

The visual appearance of these rods was typical of those following periods of zinc injection, i.e., a darker-than-normal gray surface.

Because of the higher-than-anticipated values seen at Diablo Canyon Unit 1 after Cycle 9, the Unit 2 EOC 9 results were compared to the upper bound-calculated values. (The upper bound-calculated values shown in Table 7-8 are computed from the cladding database and represent the “Predicted Oxide + 2σ” values.) As the data in Table 7-8 show, all measurements were well below the upper bound values.

Note the high burnups for twice-burned fuel; most of the ZIRLO-clad rods were in fuel assemblies with average burnups over 55 GWd/MTU. Fuel rod cleaning (brushing) and remeasurement of the oxide thickness was not performed. Hence, possible contributions to the measured values by corrosion product deposits could not be determined.
Table 7-8
Oxide Measurement Results - Diablo Canyon 2 EOC 9

<table>
<thead>
<tr>
<th>Fuel Assembly</th>
<th>No. Cycles</th>
<th>No. Rods</th>
<th>EOC 9 Burnup, GWd/MTU</th>
<th>Upper Bound Calculated, µm</th>
<th>Average Max. Measured Oxide, µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Improved Zircaloy-4 Cladding</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>V26</td>
<td>2</td>
<td>6</td>
<td>44.8</td>
<td>68</td>
<td>60&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>V08</td>
<td>3</td>
<td>6</td>
<td>42.7</td>
<td>58</td>
<td>45</td>
</tr>
<tr>
<td>V21</td>
<td>3</td>
<td>6</td>
<td>41.6</td>
<td>64</td>
<td>40</td>
</tr>
<tr>
<td>V71H</td>
<td>3</td>
<td>6</td>
<td>47.7</td>
<td>68</td>
<td>53&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>V88H</td>
<td>3</td>
<td>6</td>
<td>47.7</td>
<td>68</td>
<td>49</td>
</tr>
<tr>
<td>ZIRLO Cladding</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>W04</td>
<td>2</td>
<td>13</td>
<td>52.5</td>
<td>37-45</td>
<td>24</td>
</tr>
<tr>
<td>W69H</td>
<td>2</td>
<td>3</td>
<td>51.2</td>
<td>44</td>
<td>19</td>
</tr>
<tr>
<td>W87H</td>
<td>2</td>
<td>6</td>
<td>56.3</td>
<td>46</td>
<td>23</td>
</tr>
<tr>
<td>W94H</td>
<td>2</td>
<td>6</td>
<td>55.9</td>
<td>46</td>
<td>22</td>
</tr>
<tr>
<td>W96H</td>
<td>2</td>
<td>9</td>
<td>55.7</td>
<td>46</td>
<td>20</td>
</tr>
<tr>
<td>W41</td>
<td>2</td>
<td>6</td>
<td>55.4</td>
<td>46</td>
<td>35</td>
</tr>
<tr>
<td>W52</td>
<td>2</td>
<td>9</td>
<td>51.5</td>
<td>38-40</td>
<td>34</td>
</tr>
</tbody>
</table>

(a) Includes values for two rods with spalled oxide
(b) Does not include a value for a single rod with spalled oxide

7.9 Farley Unit 1 – End-of-Cycle 16

Following Cycle 16, the first cycle of zinc injection at Unit 1, visual inspection of the fuel assemblies indicated the presence of a dark-colored deposit. Passage by the eddy current probe locally removed much of the deposit, suggesting it was quite thin and not tenacious. There was no evidence of incipient spallation on any of the assemblies that were inspected (Ref. 7.12).

Oxide thickness measurements were made on a total of six once-burned and eighteen twice-burned ZIRLO-clad fuel rods. The results of these measurements are presented in Table 7-9.

The value for the average maximum oxide measurement on rods in assembly 2G55 was exaggerated by one or two high measurements (42 and 50 µm). There is no obvious explanation for these values. In addition, in order to establish whether or not the presence of corrosion
product deposits was influencing the measurements, six rods on the Zircaloy 4-clad twice-burned assembly 2G61 were brushed and the oxide measurements were repeated. The remeasured values were within 1 to 2 \( \mu \text{m} \) of the pre-brushed values; hence, as at Farley Unit 2, the measured values are not significantly affected by the presence of corrosion product deposits.

The upper bound calculated values shown in Table 7-9 are those computed from the cladding database and represent the “Predicted Oxide + 2\( \sigma \)” values. Note that none of the measured values challenge these upper bound estimates.

<table>
<thead>
<tr>
<th>Fuel Assembly</th>
<th>No. Cycles</th>
<th>No. Rods</th>
<th>EOC 16 Burnup, GWd/MTU</th>
<th>Upper Bound Calculated, ( \mu \text{m} )</th>
<th>Average Max. Measured Oxide, ( \mu \text{m} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2H44</td>
<td>1</td>
<td>6</td>
<td>22.4</td>
<td>32</td>
<td>14</td>
</tr>
<tr>
<td>2G17</td>
<td>2</td>
<td>6</td>
<td>42.6</td>
<td>79</td>
<td>24</td>
</tr>
<tr>
<td>2G55</td>
<td>2</td>
<td>6</td>
<td>45.6</td>
<td>79</td>
<td>37</td>
</tr>
<tr>
<td>2G61</td>
<td>2</td>
<td>6</td>
<td>45.6</td>
<td>79</td>
<td>23</td>
</tr>
<tr>
<td>2G61(^{a})</td>
<td>2</td>
<td>6</td>
<td>45.6</td>
<td>79</td>
<td>22</td>
</tr>
</tbody>
</table>

(a) these are results after rods were brushed and remeasured

Note that the ZIRLO data from Farley 1 Cycle 16 in Table 7-9 show excellent agreement with ZIRLO data for Farley 2 Cycle 13, Table 7-6.

### 7.10 Obrigheim

Both before and following the first period of zinc injection, a series of measurements were made of the fuel cladding oxide thickness. Measurements were made for fuel rods with burnups up to 48 GWd/MTU and included both uranium and mixed oxide (MOX) fuel assemblies (Ref. 7.13).

The measured results were compared to those derived from theoretical predictions provided by the Siemens COMO code. Analysis of the measured data did not indicate an influence of zinc injection on oxidation of the fuel rod cladding.

Analysis of crud scrapings taken after the first six months of zinc injection indicated a zinc concentration less than 2.5%. This is much lower than the zinc concentration determined from experiments in the Halden test reactor for fuel cladding previously irradiated in Obrigheim, and is similar to that reported for crud removed from Farley Unit 2 fuel at EOC 10 (Ref. 7.1).
7.11 Palisades

Results from fuel region inspections at Palisades following Cycle 14 are limited. The results of oxide measurements for an unspecified number of fuel rods were described as “consistent with previous cycles; there was no evidence of accelerated fuel corrosion” (Ref. 7.14).

7.12 Discussion and Conclusions

**Visual Observations of Corrosion Deposits**

The addition of zinc to the reactor coolant system consistently appears to result in the formation of a thin dark deposit on the surface of the fuel rods at the end of the cycle. This has been reported at plants in which the RCS zinc concentration was greater than about 20 ppb during the operating cycle, but has not been reported for PWRs in which the zinc concentration was maintained at the 5 ppb level.

The results of crud scraping, rod brushing and eddy current lift-off remeasurements, and observations of the ease with which the black deposit is removed (e.g., by the eddy current probe carriage rollers), suggest that this deposit is very thin (see below regarding possible exception at Diablo Canyon Unit 1) and is having no effect on the accuracy of corrosion oxide measurements.

The overall corrosion product burden does not appear to have been increased at Farley Units 1 and 2 by the presence of zinc. However, at Diablo Canyon Unit 1, after a partial cycle of zinc injection, the corrosion product deposition appeared to be substantial, approaching 25 µm or more. It is unclear to what extent zinc was responsible for this, but the results suggest that it will be prudent to continue to monitor the effects of zinc injection on the volume and distribution of corrosion products, particularly for plants pursuing an aggressive fuel cycle.

**Fuel Cladding Corrosion – Oxide Thickness Measurements**

The results of oxide thickness measurements indicate that zinc is not having a statistically significant effect on cladding corrosion. The results of the eddy current lift-off measurements as a function of burnup are summarized in Figure 7-1 for Cycles 10, 12 and 13 at Farley Unit 2 and Cycle 9 at Diablo Canyon Unit 1. [The data for fuel assembly AA59/Face 2 at Diablo Canyon Unit 1 Cycle 9 have been adjusted to reflect the post-brushing values.] Only data for Improved (low-tin) Zircaloy 4 are shown; data for ZIRLO are consistently lower. Also note that the data plotted are the maximum values for each rod rather than the average maximum values for the fuel assemblies, as are provided in the preceding tables.

The data generally exhibit the same trends in behavior, with increased scatter in the data for burnups greater than about 45 GWD/MTU. However, comparison of oxide data versus burnup does not properly account for fuel duty, and hence is not a consistently reliable indicator of corrosion. For example, it does not readily account for the power in adjacent or facing rods. [At Diablo Canyon, the Face 2 rods in assembly AA59 were directly across from high power feed]
Fuel Region Examinations

fuel rods. This is believed to be partially responsible for the greater-than-expected corrosion values.]

In analyzing the Diablo Canyon 1 Cycle 9 results, as well as the results of other recent oxide measurement campaigns, a parameter referred to as the “Fuel Duty Index” (FDI) has been developed as a means to better represent the corrosion data (Ref. 7.15). The FDI is calculated from a knowledge of the cladding surface temperature (which can in turn be calculated from other design and operating data) and the operating time. While still in the early stages of its general use, this parameter shows significant promise as a means to simplify evaluation of corrosion data.

A plot of the Fuel Duty Index vs. eddy current-measured oxide thickness for Zircaloy 4 fuel cladding is presented in Figure 7-2. A best-fit line is shown for both the overall Zircaloy 4 database and the results from the Diablo Canyon Cycle 9 measurements. Most of the difference between the overall database and the Diablo Canyon results is judged to be due to the presence of substantial corrosion product deposition on the Diablo Canyon cladding. The results in Figure 7-2, combined with the results of the pre- and post-brushing measurements, support the conclusion that the data are within the general experience for this alloy and that zinc has not had a significant effect on corrosion of the fuel cladding.

The relatively greater amount of corrosion product deposition seen on the fuel assemblies at Diablo Canyon Unit 1 at EOC 9 and the large effect of brush-cleaning on the lift-off data suggest that corrosion product deposition was greater than normal at that plant. Similar data are not available from the companion plant Diablo Canyon Unit 2 after zinc injection.

Although it is not clear that the presence of zinc contributed in a significant way to this deposition it is known that zinc additions, as the result of their interaction with the ex-core corrosion films, result in the release of relatively large amounts of nickel. The nickel may then add to the general corrosion product burden in the RCS. It is prudent that the RCS be sampled regularly for nickel concentration and that measurements of the core axial power distribution be made on a regular basis to ensure the absence of axial offset anomaly.
Figure 7-1
Eddy Current-Measured Lift-off Data vs. Burnup for Zircaloy 4 for Farley Unit 2 Cycles 10, 12 and 13 and Diablo Canyon Unit 1 Cycle 9

Figure 7-2
Fuel Duty Index vs. Lift-off Data: The Zircaloy 4 Database and Results for Diablo Canyon Unit 1 Cycle 9
Fuel Region Examinations

References


8
OTHER PRIMARY COMPONENTS

8.1 Introduction

There have been no reports of any effects of zinc on pumps, valves or other components in boiling water reactors (BWRs) due to the addition of zinc. However, BWRs operate at a zinc concentration level of 5-10 ppb, whereas the nominal RCS concentration of zinc in PWRs was intended to be in the range 30 to 40 ppb. Thus, at the inception of the Demonstration Program conducted in Cycle 10 at Farley Unit 2, a number of questions were posed about the potential impact of additions of zinc to the RCS on such components as the reactor coolant pumps (RCP) and primary system valves.

It is essential that the integrity of the reactor coolant pump and seals be maintained at all times. Hence, a decision was made to assess the potential impact of zinc on RCP performance during the Cycle 10 injection period. In addition to the in situ RCP monitoring during the cycle and comparison with pre-zinc RCP performance, a review was made of the frequency and extent of maintenance activity for reactor coolant system valves in order to discern any potential effect of zinc.

The results of these evaluations are summarized in this section. More detailed presentation and discussion of these data are presented in Ref. 8.1. This is the only PWR experience for which data are available.

8.2 Reactor Coolant Pump Data

Farley Unit 2 utilizes Model 93A reactor coolant pumps. In order to determine possible effects of the addition of zinc on the RCP seals, baseline operational data, taken at normal plant operating temperature and pressure conditions, was recorded and evaluated in terms of seal/pump operation. This baseline data was taken at the end of Cycle 9, prior to the introduction of zinc into the system, and also during Cycle 10, before and during the period of zinc addition to the RCS. These data were provided by the site to Westinghouse and included: No. 1 seal leak-off flow, No. 1 seal leak-off temperature, volume control tank (VCT) temperature, seal injection flow, and RCP bearing temperature.

In addition to the seal performance, in-situ probes also monitor RCP shaft and frame vibrations during operation. These data are also summarized in this section.
8.2.1 RCP Seal Data

The addition of zinc, as zinc acetate, was initiated in mid-June 1994 and was concluded in March 1995. Performance of the RCP seals was monitored by following the No. 1 seal leak-off flow. Data were provided by the plant for the time period from March 3, 1994 through March 7, 1995. This included baseline data for the pre-zinc portion of Cycle 10 as well as data for the period of zinc injection.

The data are provided separately in the following subsections for the period prior to zinc injection and for the period of operation with zinc additions to the RCS.

Seal Data Prior to Zinc Addition

During the Cycle 9 refueling outage at Farley Unit 2 (September 1993), the RCP seals in pumps A and B were inspected. For RCP-A, the seals were reassembled with a new No. 1 ring and runner and new No. 1 and No. 2 seal insert components. The No. 1 seals in RCP-B were rebuilt with new O-rings and reused, and the No. 1 and No. 2 seal insert components were replaced. Based on Westinghouse field maintenance records, RCP-C had been inspected in March 1992. At that time the No. 1 seals were reused and the No. 1 seal insert was replaced.

Operational data was provided for the Farley Unit 2 RCPs (RCP-A, RCP-B and RCP-C). The data used to evaluate seal performance are the No. 1 seal leak-off flow, No. 1 seal leak-off temperature, VCT temperature, seal injection flow, and RCP bearing temperature. The No. 1 seal leak-off values were recorded for approximately 14 weeks during Cycle 10 operations; i.e., from March 3 to June 10, 1994. Data was not provided for each consecutive day throughout the time period.

The No. 1 seal, which is a film-riding hydrostatic seal, is the primary RCP controlled leakage seal. The integrity of this seal, in most cases, dictates whether continuous pump operation can be maintained. The primary operational characteristic used to determine how the seal is performing is the seal leak rate. This leak rate is generally a function of temperature and pressure in conjunction with the seal ring and the tapered configuration of the runner faceplate-sealing surface. A high (increasing leak-off flow) or low (decreasing leak-off flow) leakage trend will indicate a possible No. 1 seal operational problem.

The No. 2 seal operation is not normally monitored for leakage rate. The No. 2 seal standpipes are instrumented/monitored, via high and low fluid level standpipe alarms. No. 2 seal performance problems are indicated when the standpipe alarm set points are violated. Since Westinghouse was not notified of high or low No. 2 seal standpipe alarms, it was assumed that the No. 2 seals in all three RCPs operated within acceptable limits. As with the No. 2 seal, the No. 3 seal performance is not continuously monitored.

A review of the No. 1 seal leak-off stability/trend indicated that all RCPs operated within the normal instruction book operating limits (0.8 to 6.0 gpm). The leak-off flow rates ranged from 1.0 to 2.7 gpm, on the low end of normal, and exhibited slight variability.
The No. 1 seal leak-off temperature is measured at the outlet of the No. 1 seal. This temperature is a function of the seal water injection temperature and flow as well as the heat input into the fluid as it moves up the RCP shaft and through the No. 1 seal. The normal No. 1 seal operating temperature range, as noted in the RCP instruction book, is between 100°F and 170°F. The water temperature in the volume control tank (the source of the RCP seal injection water) was reported as approximately 95°F. The No. 1 seal leak-off temperatures were within instruction book limits: RCPs A and C were operating at approximately 150 - 155°F, and RCP B was operating at a slightly higher temperature of approximately 165°F.

Instruction book values specify a minimum RCP seal injection flow of 6 gpm with typical injection flows in the range 8 to 13 gpm. The RCP seal injection flow rates were approximately 7 gpm. The RCP B flow rate was slightly lower than that of the other two pumps during the early phase of the monitoring period. This may explain why the No. 1 seal leak-off temperature for this pump was higher than that of the other pumps. A lower injection flow results in a smaller volume of water exposed to the shaft and seals. The heat generated through operation (fluid friction) is input into this smaller volume of water and results in a higher fluid temperature.

The RCP bearing temperatures for each pump provide a good estimation of the temperature of the seal injection water at the inlet to the No. 1 seal. The recorded bearing temperatures for each RCP were well below the maximum recommended bearing operating temperature (225°F).

Based on the baseline data for the RCP seals, the following conclusions were indicated:

- The performance of the RCP seals in each of the pumps was acceptable.
- The No. 1 seal leak rates, for all three RCPs, exhibited some variability, but were within the acceptable seal leak-off flow range.

Seal Performance after the Start of Zinc Injection

Operational data were provided for the RCPs for Cycle 10 during zinc injection. The primary data used to evaluate seal performance were the No. 1 seal leak-off flow, the No. 1 seal leak-off temperature and the bearing water temperature. For each day, data was recorded and printed in 5-minute intervals during the early morning (ending approximately 0500 hours) and early afternoon (ending approximately 1700 hours).

The No. 1 seal leak-off flow was the primary performance characteristic used to evaluate seal performance. As has been stated previously, continuous pump operation is directly linked to the reliability and performance of this seal. The Cycle 10 seal leak-off flow data for all three RCPs were reviewed. As was observed for the pre-zinc period, the performance of the No. 1 seal leak rates showed day-to-day variations of up to 0.5 gpm. This was true for all three RCPs.

Seal leak-off temperature and bearing temperature were also considered for the period of zinc addition. The baseline temperatures for the No. 1 seal leak-off and RCP bearing were consistent for all three pumps. Reactor coolant pumps A and C had baseline No. 1 seal leak-off...
temperatures in the mid-150°F range while the baseline leak-off temperature for RCP B was in the mid-160°F range. Baseline bearing temperatures, for all three pumps, were within the 130° - 140°F temperature range. All temperature data are within allowable instruction book limits and essentially identical to the pre-zinc values.

Conclusions – RCP Seal Performance

Based on the available data, the following conclusions were indicated.

• The No. 1 seal performance of each of the Farley Unit 2 RCPs changed slightly during Cycle 10. This change was manifested by a slightly decreasing trend in No. 1 seal leak-off flows beginning in late October 1994. Each of the RCPs had approached or were approaching the lower recommended No. 1 seal leak rate (0.8 gpm).

• For each of the three reactor coolant pumps, the RCP bearing temperature and the No. 1 seal leak-off temperature showed a slight decreasing trend beginning in the same approximate time period. This temperature decrease appeared to correlate with the decrease in leak rates and therefore was judged to be the major contributor to the decrease observed in the No. 1 seal leak rates.

• Each of the three RCPs exhibited larger-than-typical day-to-day variability in leakage rates. This variability was observed to be as much as 0.6 gpm. The reason for this variability is not easily determined; however, it may have been related to operator judgment when reading the flow instrumentation or to the accuracy of the flow instrumentation itself.

Although it was believed that the decreased seal leak-off rates were related to the decrease in temperature, a number of recommendations were made. These included: continued monitoring of the No. 1 seal leak rates for all three pumps to ensure that they are operating within acceptable limits; the No. 2 seal leakage was to be checked and recorded for each RCP as a means to evaluate future No. 1 seal leak rate trends; and the No. 1 seal flow instrumentation was to be checked to verify functionality.

Subsequent to the Cycle 10 experience, there have been no further reports of unusual or unacceptable RCP seal leak-off characteristics.

8.2.2 RCP Vibration Monitoring Data

RCP vibration data were monitored to determine if the addition of zinc to the injection water (and, hence, the pump bearing film water) changes the dynamic and static characteristics of the bearing film or the bearing surfaces themselves. Since pump vibration is affected by changes in bearing temperatures and injection flow rates, the vibration trend data exhibit long-term trends which cannot be separated directly from those associated with normal wear of the motor oil-lubricated bearings and by normal wear of the pump bearing.

The RCP vibration data are obtained from two pump shaft probes, 90° apart, mounted under the pump coupling, viewing the stainless steel shaft immediately under the coupling. In addition, two velocity probes, also 90° apart, are mounted on the motor stand at the lower motor bracket/motor
stand joint. The angular orientation of the probes, based on prior information from RCP vibration studies at the Farley 2 site, is as follows.

<table>
<thead>
<tr>
<th>Probe Description</th>
<th>Orientation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shaft - vertical</td>
<td>In line with the discharge nozzle</td>
</tr>
<tr>
<td>Shaft - horizontal</td>
<td>90° left of the discharge nozzle</td>
</tr>
<tr>
<td>Frame - vertical</td>
<td>In line with the discharge nozzle</td>
</tr>
<tr>
<td>Frame - horizontal</td>
<td>90° left of the discharge nozzle</td>
</tr>
</tbody>
</table>

Thus it is possible to monitor both the shaft and frame vibration during pump operations.

**RCP Vibration Data During Cycle 10 at Farley Unit 2**

Vibration data were provided by the site for Cycle 10 for the time period from December 13, 1993 to February 14, 1995. The range of dates over which the vibration data was acquired bounds both the pre- and post-zinc addition time frames since zinc addition began on June 12, 1994.

Gradual changes in pump vibration and position data are not unusual. These may arise from normal wear of the bearings, and may also include an environmental contribution—e.g., seasonal temperature variations and their effects on bearing and seal temperatures, injection flow rates, etc.

The data were analyzed by displaying running speed frequency trends in polar plots. It is easiest to discern trending from this type of plot. [The polar plots are not presented here; only the results and conclusions are judged necessary to this summary. Greater detail is provided in Ref. 8.1.]

Historically, first level alert and shutdown limits have been defined for both the shaft vibration limit and the frame vibration limit. For shaft vibration the first level alert is 15 mils and the shutdown limit is 20 mils, measured at the between-bearing location of the pump shaft vibration probes. For the frame vibration, the first level alert limit is 3 mils, peak-to-peak, composite, and the shutdown limit is 5 mils, peak-to-peak, composite.

An additional value that can be discerned from the polar plots is the change in shaft position—i.e., movement of the shaft axis. There is no first level alert limit or shutdown limit for this factor, but when changes are observed it is prudent to try to determine their source.

A summary of the changes in the RCP shaft and frame vibration, and the shaft position data, is presented in Table 8-1. Close review of the raw data did not suggest a seasonally repetitive cycle. The trends in shaft vibration and frame vibration appeared to be greater for RCP A than for RCP B or RCP C, whereas the changes in shaft position were greatest on RCP B. These trends suggested changes might have occurred within the pumps.
Table 8-1
Shaft and Frame Vibration Changes and Shaft Position Changes in Farley Unit 2 in Cycle 10*

<table>
<thead>
<tr>
<th>RCP</th>
<th>Shaft Vibration Change, mils</th>
<th>Frame Vibration Change, mils</th>
<th>Shaft Position Change, mils</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>2.4</td>
<td>1.1</td>
<td>9.1</td>
</tr>
<tr>
<td>B</td>
<td>1.3</td>
<td>0.5</td>
<td>10.2</td>
</tr>
<tr>
<td>C</td>
<td>1.4</td>
<td>0.4</td>
<td>7.3</td>
</tr>
</tbody>
</table>

* No attempt has been made to segregate pre- and post-zinc addition changes that occurred during Cycle 10. An inspection of the data available suggests the trends were relatively "smooth" through the full fuel cycle.

Note that the data summarized in Table 8-1 did not approach the first alert levels for either the shaft vibration (15 mils, peak-to-peak) or the frame vibration (3 mils, peak-to-peak). Hence, the major observed change was in the shaft position. Interpretation of the available data suggested that the shaft position was moving toward the monitoring probes and toward the pump discharge. This trend can be conservatively interpreted as indicating a change within the rotor/bearing system due to changes in the stiffness of the static bearings.

In addition to changes in the pump performance due to seasonal variations or bearing wear, there are a number of other possible contributors to the trends observed. These include:

1. Gradual changes in the vibration monitoring system transducer calibration curves.
2. Gradual changes in the static (DC) voltages applied to the transducers (this will affect the static voltage output of the shaft probes).

Either of these factors will have a direct and easily discerned influence on shaft position measurements, revealed by trending changes in probe static voltage outputs. However, the influence on vibration trends is less significant since slope changes in the calibration curves lag the directly-measured voltage changes. Hence, the shaft position changes will appear exaggerated relative to the vibration changes; this appeared to be the case during Cycle 10, and lessened the significance of the conclusion that the pump water bearing stiffness had actually changed.

In order to examine the possibility that changes in the vibration monitoring system are gradual and continuous, i.e., a function of the age of the components, the shaft position data for each of the RCPs were replotted for the period beginning immediately after the zinc addition was begun. When this was done (plots not shown here), there was nothing in the visual comparison of the graphs which uniquely distinguish the post-zinc addition time frame responses from those of the pre-zinc addition time period.
Conclusions - RCP Vibration Data

The final determination of whether or not the presence of zinc is influencing pump bearing performance must, necessarily, be an engineering judgment based on both the available data and experience. This includes consideration of the combined limitations of the data acquisition system and the degree to which pump vibration and shaft position changes arising from other variables can be independently quantified. It was judged that the changes observed in the Farley 2 RCPs were most likely the result of naturally occurring changes within the pump/motor assembly and from changes in the vibration monitoring system. These changes, therefore, would have been evident irrespective of the presence of zinc in the RCS.

Although continued only on a level consistent with normal monitoring of RCP performance for subsequent operations at Farley 2 and other plants using zinc, there have been no reported incidents of changes in any characteristic of RCP performance.

8.3 Reactor Coolant Valve Maintenance Data

Although the chemical environment is considered secondary compared to mechanical loads with respect to effects on wear, one of the items to be assessed in the zinc addition demonstration program was whether or not zinc in the reactor coolant affects the wear of high cobalt (Stellite) or other hardfacing materials. It was judged that a qualitative approach to such an assessment could be made by defining the baseline frequency of valve repair prior to zinc addition, and to monitor any change in the frequency of repair after operation with zinc.

The repair histories of reactor coolant system valves requiring attention at the end of Cycle 10 were retrieved from plant data available in the Nuclear Plant Reliability Data System (NPRDS) and reviewed for evidence of wear of the valve parts. The results were compared with those available through Cycle 9, i.e., prior to zinc injection. This review indicated that the frequency of repair for all primary system valves at Farley Unit 2 was 2.2 per year, and the frequency of repair for only the CVCS valves was 1.6 per year.

At the end of Cycle 10, only valve Q2E21V115C was found to require repair for wear. This valve is a check valve in the CVCS Loop C RCP seal injection line and failed inspection due to debris on the valve seat. The corrective action taken was to clean the valve body and disc, and to lap the seat area. As the result of this action, the average frequency of valve repair in the CVCS system following zinc injection was about 0.7 per year.

Thus, based on the above frequencies for the overall and specific valve maintenance relative to evidence of wear of valve parts, it is concluded that the frequency of repair did not increase after zinc addition. This result, in view of the relatively low concentration of zinc in the reactor coolant, is not unexpected, and is consistent with experience in BWRs and subsequent experience at other PWRs.
Other Primary Components

8.4 Conclusions

The addition of zinc to the reactor coolant system of PWRs, at zinc concentrations up to 40 ppb, has no apparent effect on the safe and reliable operation of such primary system components as the reactor coolant pumps and valves.

Reference

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