

## **Non-Proprietary Version**

# **Materials Reliability Program Effect of Zinc Addition on Mitigation of Primary Water Stress Corrosion Cracking of Alloy 600 (MRP-78)**

1003522

Final Report, October 2002

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# PRODUCT DESCRIPTION

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EPRI and Southern Nuclear cosponsored an initial field demonstration of zinc addition at Farley Unit 2 in 1994-95. The results of that demonstration and other laboratory studies have been increasingly complemented by experience in operating pressurized water reactors (PWRs). These studies confirm the beneficial effects of zinc in mitigating radiation fields, with positive results observed in both domestic and German PWRs. A more elusive issue has been the effectiveness of zinc in mitigating primary water stress corrosion cracking (PWSCC). Although laboratory testing has indicated the benefits of zinc for mitigation of crack initiation in alloy 600, data supporting a beneficial effect on crack propagation are less certain. An assessment of field experience has shown that the duration of zinc exposure has been too short and tube inspection uncertainties too large to discern an effect. Additional data on laboratory and field experience with zinc addition has become available since EPRI's February 2001 overview report (1001020), leading the industry to request an update on the effect of zinc addition on PWSCC. This report provides a summary of the available literature and operating plant experience related to crack initiation and propagation.

## Results & Findings

Essentially without exception, the results of laboratory testing indicate the beneficial effect of zinc addition in mitigating PWSCC initiation in alloy 600, with this benefit proportional to the zinc concentration. However, data for a beneficial effect on crack propagation are less certain, requiring additional laboratory work in carefully selected environments to resolve this issue. The only substantial operating plant data to date are those from Diablo Canyon Units 1 and 2, where zinc has been injected for portions of three consecutive fuel cycles in each plant. Since zinc injection was introduced there, significant reductions in the initiation and propagation of cracks at top of the tubesheet (TTS) and tube to tube support plate (TSP) locations have been observed during outages. However, attributing these effects solely to zinc injection is complicated by concurrent changes in eddy-current inspection equipment as well as scope and plugging criteria over this same period. Thus, careful monitoring of future steam generator inspection results at all locations of known PWSCC should continue, and voltage-based eddy-current data should be subjected to detailed analysis in order to quantitatively determine potential trends in signal/flaw growth with time.

## Challenges & Objectives

PWSCC has been and is now a very significant issue for PWR operators, affecting the operation and reliability of major components in the primary system, eventually leading to very costly replacement of such components. Based on laboratory data, zinc injection appears to be a viable chemistry approach to mitigating PWSCC initiation and potentially propagation. Field data are

consistent with a zinc benefit, but changing steam generator inspection practices make it difficult to ascertain a direct link. Nonetheless, reassessment of laboratory and field data support continued use and evaluation of zinc addition as a means to mitigate PWSCC. Evaluation of data from plants continuing to inject zinc in the primary system is essential to determining a direct correlation between zinc and PWSCC mitigation in the field.

### **Applications, Values & Use**

More PWRs are implementing or are seriously considering implementing zinc injection, primarily for dose rate control at the 5 to 10 ppb level, which has proven very effective at operating plants. As the industry gains more experience with zinc injection, EPRI anticipates that PWRs will consider increasing zinc concentrations to levels shown to be beneficial for PWSCC mitigation based on laboratory studies. Continued evaluation of field data at plants operating with zinc concentrations above 10 ppb will be very important in assessing the potential benefit of zinc with respect to PWSCC mitigation. This information can then be used by utilities to support application of increased zinc concentrations in order to reduce PWSCC susceptibility.

### **EPRI Perspective**

This project incorporated additional laboratory and plant experience since February 2001 to reassess the effect of zinc addition on PWSCC of alloy 600. Laboratory data indicate a significant benefit of zinc addition with respect to crack initiation, with less certain results for crack propagation. Although firm conclusions about the field benefit of zinc addition on PWSCC of alloy 600 could not be drawn, it is important to continue careful monitoring of future Diablo Canyon steam generator inspection results at all locations of known PWSCC in order to determine the benefits of zinc addition. The recommendations in this report provide additional support to assess the effect of zinc addition on PWSCC mitigation.

### **Approach**

The objective of the present evaluation was to perform a thorough review of the literature, and to consider the expanding operating plant experience in order to develop a coherent understanding of the role of zinc with regard to PWSCC of nickel-base alloys. A brief review of the mechanism by which zinc interacts with corrosion films on nickel-based alloys provided a basis for review of the literature and field data. Investigators also reviewed available literature concerning zinc and PWSCC, including continuing efforts in Japan along with additional field experience in operating PWRs.

### **Keywords**

PWR

Alloy 600

Primary Water Stress Corrosion Cracking (PWSCC)

Zinc

# ABSTRACT

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Addition of zinc to the reactor coolant system of PWRs has been used since mid-1994 as a means to effect radiation dose rate reductions and as an approach to mitigate the occurrence or severity of primary water stress corrosion cracking (PWSCC) of Alloy 600. The basis for this activity was the experience with zinc additions in BWRs, complemented by laboratory experiments in simulated PWR environments carried out under the aegis of the Westinghouse Owners Group and EPRI.

The effectiveness of zinc in contributing to reduced radiation fields in PWRs is now well established, with positive results observed in both domestic and German PWRs. A more elusive issue has been the effectiveness of zinc in the mitigation of PWSCC. The objective of the present evaluation was to perform a thorough review of the literature, and to consider the expanding operating plant experience, in order to develop a coherent understanding of the role of zinc with regard to PWSCC of nickel-base alloys.

A brief review of the mechanism by which zinc interacts with corrosion films on nickel-base alloys is followed by a review of the available literature dealing with zinc and PWSCC. This review considers both research in the open literature and the results of continuing efforts in Japan that have been made available to EPRI. Finally, the limited experience in operating PWRs is reviewed.

The results of this review lead to the following conclusions:

- The mechanism by which zinc affects the corrosion of austenitic nickel-base alloys is by incorporation of zinc into the spinel oxide corrosion films.
- Reduction of general corrosion leads to reduced metal release rates and an associated dose rate reduction in operating steam generators by modifying the corrosion source term.
- Nearly without exception, the results of laboratory testing indicate a benefit of zinc injection in mitigating the initiation of PWSCC in Alloy 600. Early laboratory data suggest this benefit may vary with the concentration of zinc in the RCS.
- Data for a beneficial effect on crack propagation are mixed. The laboratory data vary from a substantial reduction in crack growth rates to no effect. Interpretations of these differences based on the nature of the crack tip oxides do not agree.
- The only substantial operating plant data are those from Diablo Canyon Units 1 and 2, where zinc has been injected for portions of three fuel cycles in each plant. Significant reductions in the initiation and propagation of cracks at TTS and tube-TSP locations have been observed in outages since zinc injection was adopted. Attributing these effects solely to the addition of

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zinc is complicated by the fact that concurrent changes have occurred in eddy current inspection equipment and scope, and in the plugging criteria, over this same period.

A number of recommendations related to additional crack propagation testing and closer follow and assessment of operating plant experience are also provided.

## **ACKNOWLEDGMENTS**

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# 1 INTRODUCTION

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The addition of zinc to the reactor coolant system (RCS) has been pursued in domestic PWRs since mid-1994, at which time the initial injection began at Farley Unit 2 during Cycle 10. Since that time, zinc injection has been performed at Farley Unit 1, Diablo Canyon Units 1 and 2, Palisades and Sequoyah Unit 1 in the U.S. and in the foreign PWRs Obrigheim, Biblis A, Biblis B and Angra 2. The incentives for these programs have included efforts to mitigate primary water stress corrosion cracking (PWSCC) of Alloy 600 components at Farley Units 1 and 2 and Diablo Canyon Units 1 and 2, and radiation field (dose rate) reduction at all plants. The concentrations of zinc in the RCS have been in the range from approximately 20 to 40 ppb in the former plants, whereas in plants focused only on dose rate reductions the concentrations have generally been in the range 5 to 7 ppb.

Following the initial qualification efforts, performed under the aegis of the Westinghouse Owners Group and EPRI, the majority of the programs directed at mitigation of PWSCC in operating PWRs were funded by EPRI with tailored collaboration agreements with Southern Nuclear Operating Company and Pacific Gas & Electric. Detailed reports of these programs have been published by EPRI (Refs. 1.1– 1.7).

It is essentially universally accepted that zinc is very effective in mitigating the extent and consequences of general corrosion of both austenitic stainless steels and nickel-base alloys in primary water. This appears to be the result of substantial restructuring of the corrosion films that form on these materials in high temperature primary coolant. Clear benefits have been observed in reduced dose rates and deposited radionuclide activities. For example, single-cycle zinc injection has resulted in net reductions of approximately 25% in deposited radionuclide activities (Ref. 1.7). The technical issues and overall experience associated with zinc injection in PWRs have been extensively summarized in presentations at a number of International forums; interested readers are referred to the proceedings (see, e.g., papers in Refs. 1.8 – 1.10).

What is less clear, however, is the effectiveness of zinc in mitigating the occurrence of PWSCC. The results of the laboratory testing database developed to support the initial application of zinc to PWRs showed a clear benefit with respect to crack initiation in highly strained reverse U-bends, and also suggested a reduction in crack propagation rates (Ref. 1.11). More recent published research appears to support the crack initiation benefit, but are mixed with regard to crack propagation, with some data suggesting a benefit and other data indicating zinc has no effect on crack propagation rates.

The objective of the present evaluation was to perform a thorough review of the literature, and also to consider the expanding operating plant experience, in order to try to develop a coherent

understanding of the potential role of zinc with regard to PWSCC of nickel-base alloys. The results of that review are presented in this document.

In view of the importance of the nature of the corrosion films that develop on the ex-core surfaces, with particular emphasis on the austenitic nickel-base alloys such as Alloy 600, a brief discussion is presented of the way in which zinc is believed to interact with them. This is followed by a review and discussion of the relevant literature and plant experience. The overall results of this review and analysis are provided in the final section. Issues attendant to the reduction of general corrosion and dose rates are mentioned only insofar as they may be related to the specific research being considered.

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# 2

## INTERACTION OF ZINC WITH CORROSION FILMS ON NICKEL-BASE ALLOYS

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The long-term exposure of austenitic nickel-base alloys in primary water leads to the development of a two-layer oxide corrosion film. The inner layer that forms on alloys such as Alloy 600 and Alloy 690 is a chromite spinel of the form  $(\text{Fe, Ni, Co, ..})\text{Cr}_2\text{O}_4$ , in which the Cr and Fe levels are enriched relative to their concentrations in the base metal. This layer is formed by corrosion of the alloy at the metal-oxide interface. After several thousand hours of exposure at about 600°F, this layer is typically on the order of 200 to 400 nm thick.

The outer layer consists of an irregular layer of particles that is best described as solution-grown or hydrothermally deposited. These particles range in size from about 0.5 to 2  $\mu\text{m}$ . This solution-grown film forms at the oxide-solution interface and, for Alloys 600 and 690, is typically on the order of the particle size. The composition is controlled by corrosion product release from the underlying alloy as well as the species in (super)saturation in the fluid boundary layer adjacent to the corroding alloy (Ref. 2.1), and typically consists of ferrites such as  $\text{NiFe}_2\text{O}_4$  or  $\text{CoFe}_2\text{O}_4$ , which have an inverse spinel structure.

### Spinel Oxides

The oxide corrosion films mentioned above consist of either "normal" or "inverse" spinels. The normal spinel crystal structure is cubic with a unit cell consisting of 56 atoms; the chemical formula, however, is written in terms of one octant of the unit cell, as,



where A and B represent metallic cations. In the case of normal spinels, the A atoms are in tetrahedral sites and the B atoms are in octahedral sites of the complex cubic lattice. In inverse spinels, described by,



one-half of the B atoms are in the tetrahedral sites and the A atoms and the remaining half of the B atoms are in the octahedral sites.

The distribution of the A and B atoms among the tetrahedral and octahedral sites, and whether a specific spinel is normal or inverse, depends on the energy of the structure that results from the combined effects of crystal field terms (inhomogeneous electric field effect), Madelung (electrostatic) energy terms, and short-range energy terms.

Owing to the commercial importance of ferrimagnetic spinels, a great deal of research was performed in the 1950s to characterize these materials. Notable early efforts by Gorter (Ref. 2.2) and McClure (Ref. 2.3) laid the foundation for our current understanding of the distribution of transition metal cations in spinels. McClure introduced the concept of a "site preference energy", to permit prediction of whether a specific cation would locate preferentially in the tetrahedral or in the octahedral sites; this was based primarily on crystal field theory.

Miller (Ref. 2.4) extended the site preference energy concept to include Madelung and short-range energy terms. Table 2-1 presents a partial list of the octahedral site preference energies for various transition metal ions in spinel lattices. The higher the value the greater the preference for a given ion to be located in an octahedral site; negative values indicate a preference for a tetrahedral site. Hence,  $\text{Cr}^{3+}$  and  $\text{Ni}^{2+}$  prefer the octahedral sites, whereas  $\text{Fe}^{3+}$  and  $\text{Zn}^{2+}$  prefer the tetrahedral sites. Divalent zinc, in fact, exhibits a stronger preference for the tetrahedral sites than essentially any other cation.

In general, all chromite spinels - i.e.,  $\text{MCr}_2\text{O}_4$  - are normal spinels, with trivalent chromium in the octahedral sites and divalent M cations in the tetrahedral sites. Ferrites - such as  $\text{NiFe}_2\text{O}_4$ ,  $\text{CoFe}_2\text{O}_4$ , etc. - nearly always have the inverse spinel structure ( $\text{ZnFe}_2\text{O}_4$  is a notable exception) with  $\text{Fe}^{3+}$  distributed evenly between the tetrahedral and octahedral sites and divalent Co or Ni cations in the remaining octahedral sites.

**Table 2-1**  
**Octahedral Site Preference Energies of Transition**  
**Metal Ions in Normal Spinel Lattices**

Ion	Octohadral Site Preference Energy, kcal/g atomic wt.	Preferred Site Occupancy
$\text{Cr}^{3+}$	16.6	Octahedral - strong
$\text{Fe}^{3+}$	- 13.3	Tetrahedral
$\text{Fe}^{2+}$	- 9.9	Tetrahedral
$\text{Co}^{2+}$	- 10.5	Tetrahedral
$\text{Ni}^{2+}$	9.0	Octahedral
$\text{Zn}^{2+}$	- 31.6	Tetrahedral - v. strong

Although Co is usually a minor constituent in these films (it is present only as an impurity in the alloys), its incorporation into the oxides provides the opportunity for  $^{60}\text{Co}$ , formed by activation in the core of  $^{59}\text{Co}$  released by corrosion of these alloys and other primary side materials such as Stellites, to deposit and become incorporated into the corrosion films. This leads to an increase in the  $^{60}\text{Co}$  activity of the primary loop, with associated costs in personnel radiation exposure.

Because of its higher site preference energy in the normal spinel oxides, the addition of zinc to the primary coolant leads to exchange reactions whereby zinc displaces Co, Ni, and other cations into the coolant stream where they can be removed by the cleanup systems. This principle has been used quite effectively for nearly fifteen years by operators of boiling water reactors (BWRs) to reduce primary system radiation buildup (Refs. 2.5 and 2.6).

In the case of stainless steel, the situation is much the same as for the nickel base alloys except that the relative thickness and composition of the chromite and ferrite layers are slightly different. The basic reactions, however, are the same. Lister (Ref. 2.1) has published an excellent discussion of activity transport and corrosion processes in PWRs, with particular emphasis on stainless steels and the potential role of zinc.

Data are not presented here, but the research on inverse spinels indicates that there is no such favorable site preference for divalent zinc in that structure. This is consistent with analyses of the distribution of zinc in corrosion films that indicate essentially all zinc is associated with the inner chromite film.

### **Field and Laboratory Experience with Zinc**

Examination by Auger electron spectroscopy of the surfaces of Alloy 600 and stainless steel that has been exposed to simulated primary water containing zinc clearly indicates efficient incorporation of zinc into the oxide corrosion films. At regions nearest the surface, the zinc concentrations suggest a large fraction of the tetrahedral sites are occupied by zinc (Ref. 2.7).

Zinc concentrations at the surface range from 16% to greater than 32%. Both the concentration at the surface and the depth to which zinc has penetrated appear to correlate with the total exposure times rather than with the concentration of zinc in the coolant, although the specific tests referred to here involved exposures on the order of 2000 hours with zinc concentrations up to greater than 100 ppb.

Auger examination of a tube pulled from Farley Unit 2 at the end of Cycle 10 (Ref. 2.8), following approximately nine months of zinc addition to the primary coolant at a concentration of approximately 40 ppb, gave results very similar to those seen in laboratory research. Zinc concentrations at the surface were as high as 25%, although the depth of penetration was less than that found in the laboratory specimens.

An interesting additional observation that has been reported by essentially all studies of the effects of zinc on nickel-base alloys and stainless steels is that the outer hydrothermally deposited layer becomes much thinner or less dense, and the inner chromite layer is also thinner than that found after exposures in non-zinc containing primary coolant. The former observation suggests that, given sufficient time, the amount of corrosion product being released into the coolant decreases and the balance between release and removal by the cleanup system reflects the decrease in the source term. The thinner chromite layer, which forms by corrosion at the

metal-oxide interface, probably indicates a change in ionic diffusion rates through the spinel due to restructuring by zinc incorporation.

Detailed knowledge of the precise mechanism notwithstanding, it is clear that the field experience is consistent with expectations based on laboratory tests and rational interpretation of the phenomena. Zinc effects significant releases of iron, nickel and cobalt from the tetrahedral sites. Almost immediately upon the introduction of zinc the RCS concentrations of, in particular, nickel and its daughter isotope  $^{58}\text{Co}$  increase significantly and generally remain high throughout the period of zinc injection. In time, ultimate exhaustion of the source term for these releases should lead to stable concentrations, reflecting their removal by the cleanup system demineralizers.

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# 3

## REVIEW OF EXPERIENCE WITH RESPECT TO ZINC AND PWSCC

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### 3.1 Introduction

The available literature reporting studies of the effects of zinc on PWSCC was reviewed. Attention was given to data for both initiation and propagation, with special focus on the latter aspect. In addition to published papers in the open literature, this review also included reports of Japanese laboratory research made available by EPRI. While much of this latter research has also found its way into various conference proceedings, certain aspects of the relevant test programs are better understood from the more detailed laboratory reports.

Limited results available from field surveillance and inspection programs were also consulted, and are remarked upon.

The literature surveys are presented in approximate chronological order in the following paragraphs. The exception to this is the summary of several laboratory tests in environments more appropriate to BWRs; these are presented last. The results are discussed collectively in a later sub-section

### 3.2 Literature – Laboratory Test Results

*An Engineering Assessment of Zinc Addition to PWR Primary Coolant (1994); Ref. 3.1*

#### Information Contained in this Section is Proprietary

*Loop Experiments with Zinc Additions to Primary Water Coolant (1996); Ref. 3.2*

#### Information Contained in this Section is Proprietary

*G. P. Airey et al., Water Chemistry of Nuclear Reactor Systems, 7, BNES (1996); Ref. 3.5*

This paper reported the results of the first phase of a two-phase evaluation of the effect of zinc on the SCC of Alloy 600 (a few tests were also performed on Alloy 690 but SCC was not observed

under any test condition). The test program included reverse U-bends, compact wedge open bolt-loaded (WOL) specimens prepared from archived CRDM nozzle material and Alloy 600 plate material, and bent beam specimens loaded to 6 and 12% strains. The WOL specimens were loaded to a stress intensity of 40 MPa√m.

**Table 3-1  
Results of Stress Corrosion Crack Propagation Tests on Alloy 600 CRDM Nozzle Materials**

Specimen No.	Stress Intensity, MPa√m	Water Chemistry	SCC Crack Length, μm	Avg. CGR, μm/h
20-11	26.2	No Zn	205	0.089
20-9	26.5	Zn	0	
43-10	26.0	No Zn	65	0.028
43-13	26.2	No Zn	35	0.015
43-8	26.3	Zn	0	
43-12	26.1	Zn	0	
20-8	35.4	No Zn	305	0.133
20-6	34.6	Zn	0	
20-10	37.5	Zn	0	
43-9	35.5	No Zn	64	0.028
43-11	35.5	No Zn	67	0.029
43-5	35.2	Zn	0	
43-6	35.4	Zn	0	

The test environment consisted of simulated primary water containing 1200 ppm B, 2.2 ppm Li and 25 – 50 cm<sup>3</sup> H<sub>2</sub>/kg H<sub>2</sub>O at 350°C. The zinc concentration was set at 40 ppb, added to the water as zinc acetate. The autoclaves were operated on a once-through basis with continuous additions of zinc. Exposures continued for a cumulative total of 7500 hours. Duplicate sets of specimens were exposed as controls under the same conditions but without zinc. Crack propagation was determined as a function of time by periodically removing one of the replicate specimens, breaking it under tension and measuring the crack growth.

Through the first phase, the results were reported as indicating no apparent benefits in crack initiation (RUB and bent beam tests) or crack propagation tests (WOL specimens). The authors

noted that film characterization studies of the specimens indicated the corrosion films formed on the specimens exposed to zinc were thinner than those exposed in PWR water alone. Because of some concern that the stress intensities were sufficiently high to blur any zinc effect, a decision was taken to perform additional tests. These were reported in the following paper.

***M. G. Angell et al., Proceedings, Ninth International Symposium on Environmental Degradation of Materials in Nuclear Power Systems - Water Reactors, TMS (1999); Ref. 3.6.***

In the Phase 2 evaluations which extended the work reported in Ref. 3.5, bolt-loaded WOL specimens of the same heat of CRDM material and the Alloy 600 plate were tested at stress intensities of 25 and 40 MPa $\sqrt{m}$ . Repeat tests were also performed using the RUB and bent beam specimens of the same materials used in Phase 1. These exposures were carried out for an additional 7500 hours, the only test difference was the use of 1800 ppm B and 3.5 ppm Li to simulate an 18-month rather than a 12-month fuel cycle as simulated previously.

The authors concluded from the RUB and bent beam tests that zinc was effective in mitigating, but not precluding, the initiation of PWSCC. However, once again no benefit was observed with respect to crack propagation in the WOL specimens. Crack growth rates were essentially the same for specimens in environments with and without zinc. The authors noted that detailed chemical analysis of the crack tips of the fractured WOL specimens did not identify zinc.

***D. S. Morton et al., Proceedings, Eighth International Symposium on Environmental Degradation of Materials in Nuclear Power Systems - Water Reactors, ANS (1997); Ref. 3.7.***

Stress corrosion crack growth rates were measured using compact tension specimens of Alloy 600, EN82H weld metal and Alloy X-750 in deaerated hydrogenated water over the temperature range 316 to 360°C. Crack extension was monitored *in situ* using DC electrical potential drop measurements.

Restricting this summary to only the Alloy 600 (differences for the other materials were only qualitative), the tests were conducted using stress intensities of 22 to 27 MPa $\sqrt{m}$  at 316 or 338°C. Identical specimens were tested in water containing from 22 to 108 ppb zinc and 40 cm<sup>3</sup> H<sub>2</sub>/kg H<sub>2</sub>O, and the same environment without zinc. Zinc was introduced by flowing the autoclave coolant through a ballast tank that contained sintered zinc oxide. Neither boron nor lithium were added to the test environment.

The crack propagation rates ranged from 0.042 to 0.497  $\mu\text{m}/\text{h}$  and were unchanged whether or not zinc was present. Auger electron spectroscopy (AES) and analytical electron microscopy examinations were performed on the surfaces and within the crack tips of the post-test fractured specimens. Zinc was found to be incorporated into the chromite spinel films on the free surfaces but not on the crack tip surfaces. Within the cracks, only a cubic nickel oxide was identified; the authors concluded there is no basis to expect zinc to be efficiently incorporated into such a compound and, hence, zinc offers no benefit with respect to crack propagation.

***H. Kawamura et al., Paper 141, CORROSION 98, NACE; Ref. 3.8.***

Tests were performed on mill annealed Alloy 600 tubing and plate material in order to assess the potential effectiveness of zinc in enhancing the resistance to PWSCC. Slow strain rate tests (SSRT) of the tubing material were performed at 360°C in a simulated primary water environment containing 50 ppm B, 2.2 ppm Li, 25 cm<sup>3</sup> H<sub>2</sub>/kg H<sub>2</sub>O and 10 ppb zinc. The plate material was tested in the same test environment as double cantilevered beam (DCB) specimens, wedge loaded to stress intensities that varied from less than 10 to greater than 70 MPa√m.

In order to simulate in-service material surface conditions, most of the specimens were exposed in the 50 ppm B, 2.2 ppm Li, 25 cm<sup>3</sup> H<sub>2</sub>/kg H<sub>2</sub>O environment for times up to 4000 hours to "prefilm" the surface prior to testing in the zinc-containing environment. The subsequent test results showed very little difference between prefilmed and non-prefilmed specimens.

Following slow strain rate testing, the fracture surfaces were examined by SEM to determine the relative contribution of SCC to the fracture process. The PWSCC "fracture ratios" were found to be decreased by half, from 20 to 30% without zinc addition to 10 to 15% for the SSRT tests performed in the 10 ppb Zn environment.

The extent of crack propagation was determined by periodic removal and fracturing of the DCB specimens and measurement of the crack advance. The results of these measurements are presented in Figure 3-1. The crack propagation rates are seen to be lower by an order of magnitude for the tests performed in the zinc-containing environment. Note that the crack growth rates are generally quite low for all data presented. This suggests that the authors may have included the incubation times before crack extension began in calculating the average crack growth rates. In view of the fact that the tests were conducted for 5000 hours, and the data exhibit excellent consistency, it could be argued that the effects seen are real and indicate of a zinc benefit.

The authors report that they found the chromite spinel in the crack tip surfaces. This is in direct disagreement with the report by Morton et al. (Ref. 3.7) where only cubic NiO was found. The reason for this difference is not obvious.

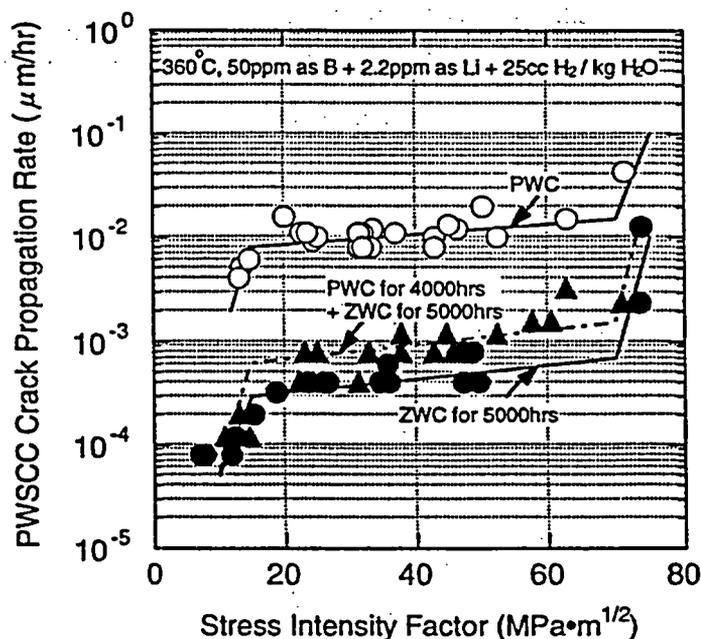


Figure 3-1  
Crack Growth Rate Test Results for Alloy 600. [PWC = Primary Water Chemistry; ZWC = PWC with Zinc] (Ref. 3.8)

**Material Integrity Test Results on Verification Test of Coolant Chemistry Control Technology, Nuclear Power Engineering Corporation (1999 through 2002); Refs. 3.9 – 3.12.**

### Information Contained in this Section is Proprietary

***P. L. Andresen and T. P. Diaz, Paper 184, CORROSION 93, NACE; Ref. 3.15.***

Tests were performed on sensitized Alloy 600 specimens in a 288°C environment [normal water chemistry (NWC) with 200 ppb oxygen] containing 10 ppb zinc, added as zinc oxide. The water also contained 0.3  $\mu\text{M}$  H<sub>2</sub>SO<sub>4</sub> (28.8 ppb sulfate) which has been found to be useful in encouraging more reproducible crack growth rates than are seen in high purity (BWR) water. The test specimens were 25 mm compact tension (CT) specimens loaded to a stress intensity of 33  $\text{MPa}\sqrt{\text{m}}$ . Crack growth was actively monitored during the tests by a reverse dc potential drop technique.

For tests for comparable times in otherwise equivalent environments, the presence of zinc lowered the crack growth rates by a factor of about 2 in sensitized Alloy 600; greater reduction in crack growth rates were reported for Type 304 stainless steel and Alloy 182 weld metal in these same environments.

***P. L. Andresen and T. M. Angeliu, Paper 409, CORROSION 95, NACE; Ref. 3.16.***

This work was also done in a 288°C NWC BWR water chemistry environment containing 200 ppb oxygen and 0.3 μM H<sub>2</sub>SO<sub>4</sub> (28.8 ppb sulfate). Sensitized Alloy 600 1T-CT specimens were exposed in water containing from 5 to as high as 100 ppb zinc (added as ZnO). On-line crack growth monitoring was done by reverse dc potential drop.

Zinc additions were consistently beneficial in reducing crack growth rates (CGRs). The efficiency of this effect was seen to vary considerably depending on several test variables. The largest reductions in CGR were observed for the highest zinc concentrations, at the lower range of corrosion potentials (ca. – 50 to + 50 mV<sub>she</sub>), and for tests in which the crack growth rates were relatively low.

The authors rationalize this behavior by pointing out that, at the higher corrosion potentials, e.g., in the + 150 to + 200 mV<sub>she</sub> range, the higher potential gradient reduces the Zn<sup>2+</sup> concentration in the crack tip by driving anions into the crack and cations (Zn<sup>2+</sup>) out of the crack, and the higher crack growth rates at the higher corrosion potential appear to afford Zn with less opportunity to have an effect on the growth rate.

While the authors do not specifically comment on the nature of the crack tip oxides, this is a similar argument to that offered by Morton et al. (Ref. 3.7) in that, if Zn<sup>2+</sup> is unable to reside at the crack tips – i.e., to encourage the formation of the stable spinel-type oxide – it may be reasonable that Zn would have little effect on crack growth. It also suggests, however, that at low corrosion potentials, such as are commonly seen in PWR primary environments, it may be reasonable to expect a beneficial effect of zinc with respect to PWSCC crack growth. That Morton et al. did not see a benefit, remains a point of contrast between these data sets.

### **3.3 Field Experience with Zinc Injection and PWSCC**

#### **Information Contained in this Section is Proprietary**

#### ***Diablo Canyon Units 1 and 2***

#### **Information Contained in this Section is Proprietary**

**Information Contained in this Section is Proprietary**

**Table 3-2**  
**Corrosion Release Data**

**Table 3-3**  
**Alloy 600 MA SSRT Test Matrix [Tests at 370°C; 0.5 μm/min strain rate]**

**Table 3-4**  
**Numbers of Alloy 600 Specimens Used in Constant Load and Constant Strain Tests in the NUPEC Large Test Loops**

**Table 3-5**  
**Summary of RUB Test Results for Alloy 600**

(a)

(b)

**Figure 3-2**  
**(a) Plugging for PWSCC at Diablo Canyon Unit 1 at TTS locations; (b) Plugging for PWSCC at Diablo Canyon Unit 1 at TSP locations**

**Information Contained in this Section is Proprietary**

(c)

**Figure 3-2 (continued)**  
**(c) Number of New Indications at TSP Locations at Diablo Canyon Unit 1**

**Information Contained in this Section is Proprietary**

(a)

**Figure 3-3**  
**(a) Plugging for PWSCC at Diablo Canyon Unit 2 at TTS locations**

**Information Contained in this Section is Proprietary**

(b)

**Information Contained in this Section is Proprietary**

(c)

Figure 3-3 (continued)

(b) Plugging for PWSCC at Diablo Canyon Unit 2 at TSP locations; (c) Number of New Indications at TSP Locations at Diablo Canyon Unit 2

## **Information Contained in this Section is Proprietary**

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- 3.17 *Overview Report on Zinc Addition in PWRs*, EPRI, Palo Alto, CA: 2001. 1001020.

# **4**

## **DISCUSSION OF ZINC AND ALLOY 600 EXPERIENCE**

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### **4.1 Laboratory Results**

**Information Contained in this Section is Proprietary**

### **4.2 Field Experience**

**Information Contained in this Section is Proprietary**

## References

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**Table 4-1**  
**Summary of Crack Propagation Data for Alloy 600 in Zn-containing Environments**

**Information Contained in this Section is Proprietary**



# 5

## CONCLUSIONS AND RECOMMENDATIONS

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### 5.1 Conclusions

Based on the review of the laboratory and operating plant experience with zinc injection to PWRs, the following conclusions are offered.

- The mechanism by which zinc affects the corrosion of austenitic nickel-base alloys is by incorporation of zinc into the spinel oxide corrosion films. The work by Lister and others (Refs. 5.1 through 5.4) appears to provide a rational explanation of this effect.
- Reduction of general corrosion leads to reduced metal release rates and an associated dose rate reduction in operating steam generators by modifying the corrosion source term.
- Essentially without exception, the results of laboratory testing indicate a benefit of zinc injection in mitigating the initiation of PWSCC in Alloy 600. Early laboratory data suggest this benefit may vary with the concentration of zinc in the RCS.
- Data for a beneficial effect on crack propagation are mixed. The laboratory data vary from a substantial reduction in crack growth rates (Ref. 5.5 through 5.7) to no effect (Refs. 5.8 – 5.9). Interpretations based on the nature of the crack tip oxides do not agree (Refs. 5.7 – 5.8).
- The only substantial operating plant data are those from Diablo Canyon Units 1 and 2, where zinc has been injected for portions of three fuel cycles in each plant. Significant reductions in the initiation and propagation of cracks at TTS and tube-TSP locations have been observed in outages since zinc injection was adopted. Attributing these effects solely to the addition of zinc is complicated by the fact that concurrent changes have occurred in eddy current inspection equipment and scope, and in the plugging criteria, over this same period.

### 5.2 Recommendations

- Consideration should be given to resolving the crack propagation issue by careful laboratory experiments using active CGR monitoring in carefully selected environments. These experiments should involve a limited number of material conditions (material history and configuration). The primary variables should be the concentration of zinc in the autoclave environment, and the stress intensity. The stress intensity should be varied to allow examination of the potential benefit over a range of crack propagation rates.

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*Conclusions and Recommendations*

- The voltage-based eddy current data collected by PG&E for the Diablo Canyon plants at degraded tube-TSP intersections should be subjected to detailed analysis in order to quantitatively determine trends in signal/ flaw growth with time.

Careful monitoring of future Diablo Canyon inspection results at all locations of known PWSCC should be continued.

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