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Effect of Primary Water Zinc Injection on PWSCC in Ni-Based RCS Components

Peter Andresen
GE Global Research

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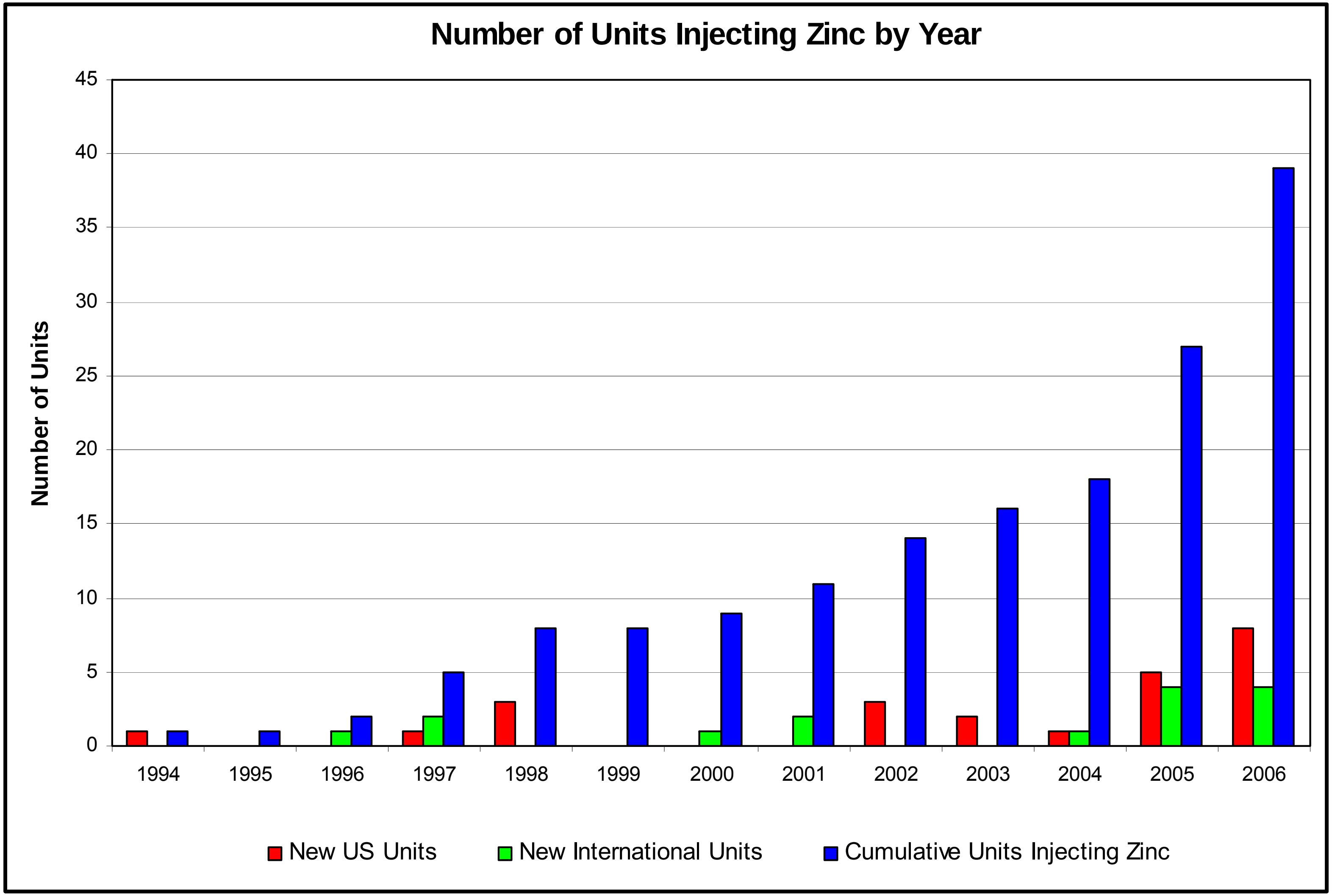
MRP/PWROG Mitigation Briefing to NRC RES

History and Status of Zinc Injection

- BWRs started adding zinc for radiation field control in 1986
- Farley 2 was the first US PWR plant to inject zinc in 1994
- By Dec 2006, 39 PWR units world-wide were injecting zinc, including 18 International units
- Of the 21 US PWRs, 5 are injecting with the prime objective of PWSCC mitigation (≥15 ppb zinc), and the remainder for radiation field control, using lower zinc injection levels
- A further 10 PWRs have indicated definite plans to implement zinc within the next year or two

Plants Injecting Zinc



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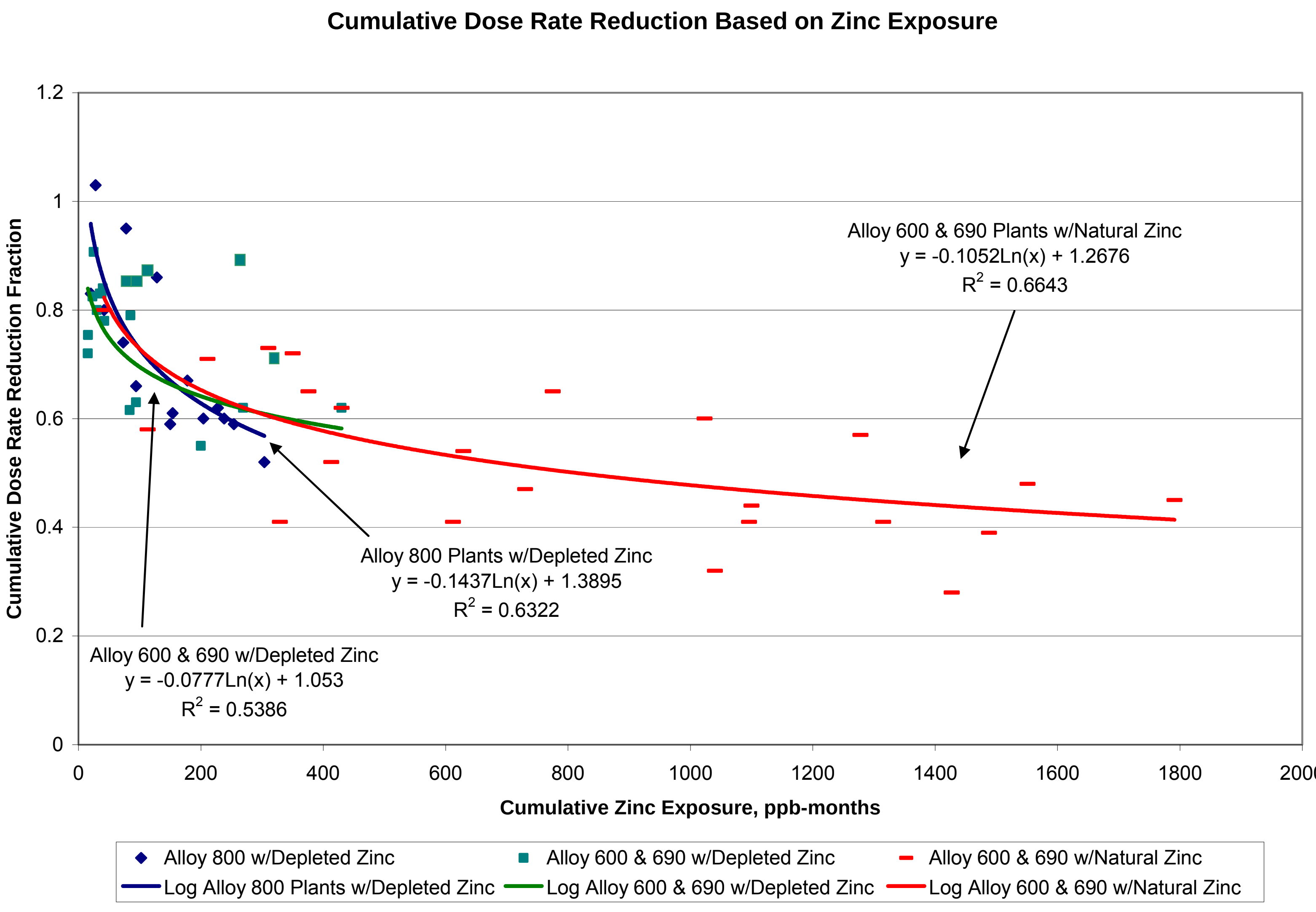
Overall Correlation of Dose Rate to Zinc Exposure Positive Benefit with Zinc



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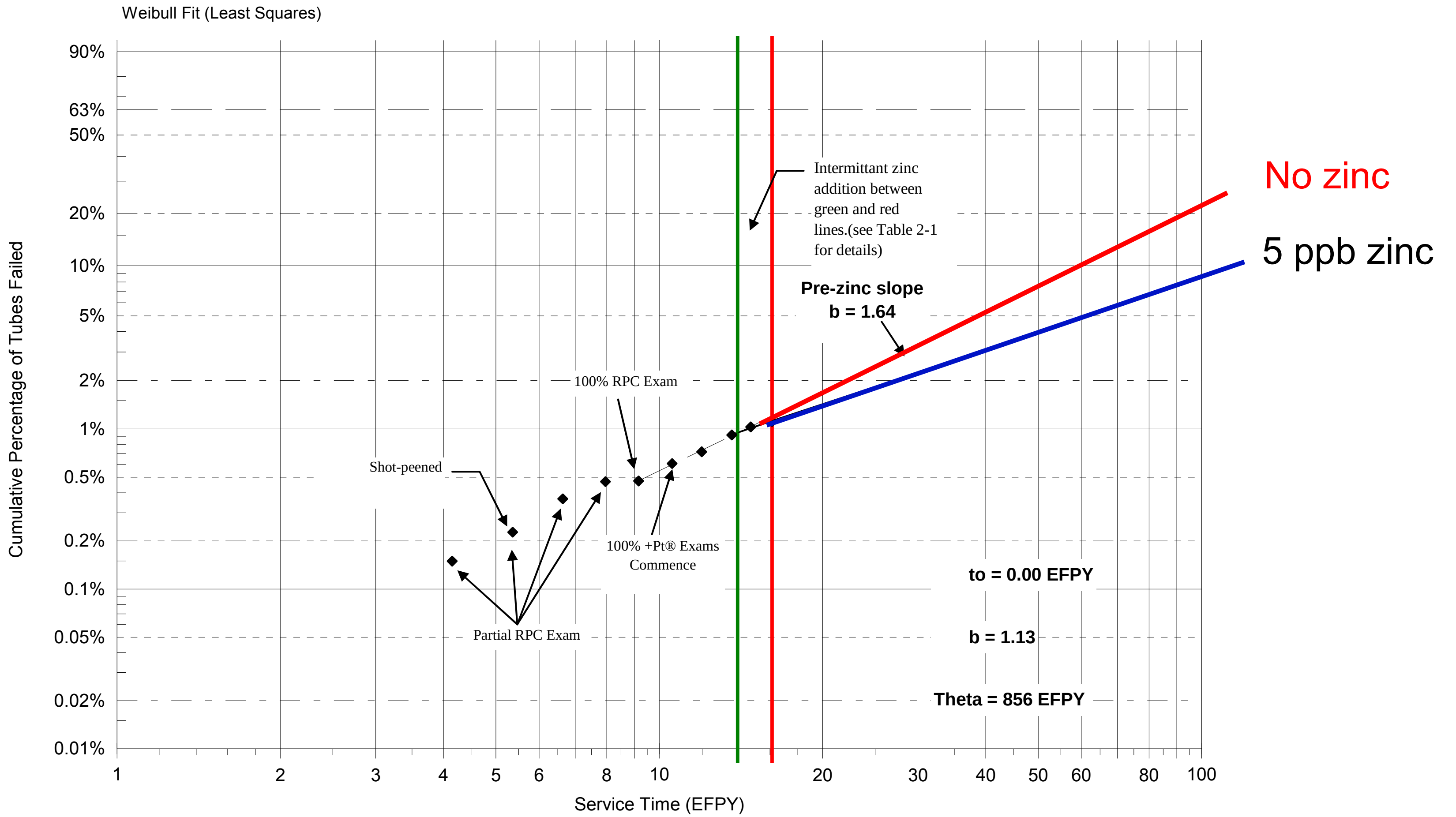
Field SG Data Evaluation: PWSCC Zn Mitigation

- Five units injecting zinc primarily for PWSCC mitigation (15-40 ppb)
  - Farley 1 and 2, Diablo Canyon 1 and 2, and Beaver Valley 1
- Steam Generator data analyzed for PWSCC indications:
  - Numbers of cumulative PWSCC indications
    - Rate of increase in PWSCC observations (2 to 10X reduction)
  - Voltage growth rate data
    - Growth rate measurements (20% to 60% reduction)
- Comparisons performed of the results for periods of operation with and without zinc
  - **Quantify the Benefit!**

Example of Smallest Zn Benefit Observed

31% Decrease in Weibull Slope

(It would take 1.9 times as long to go from 1% to 10% tubes affected)

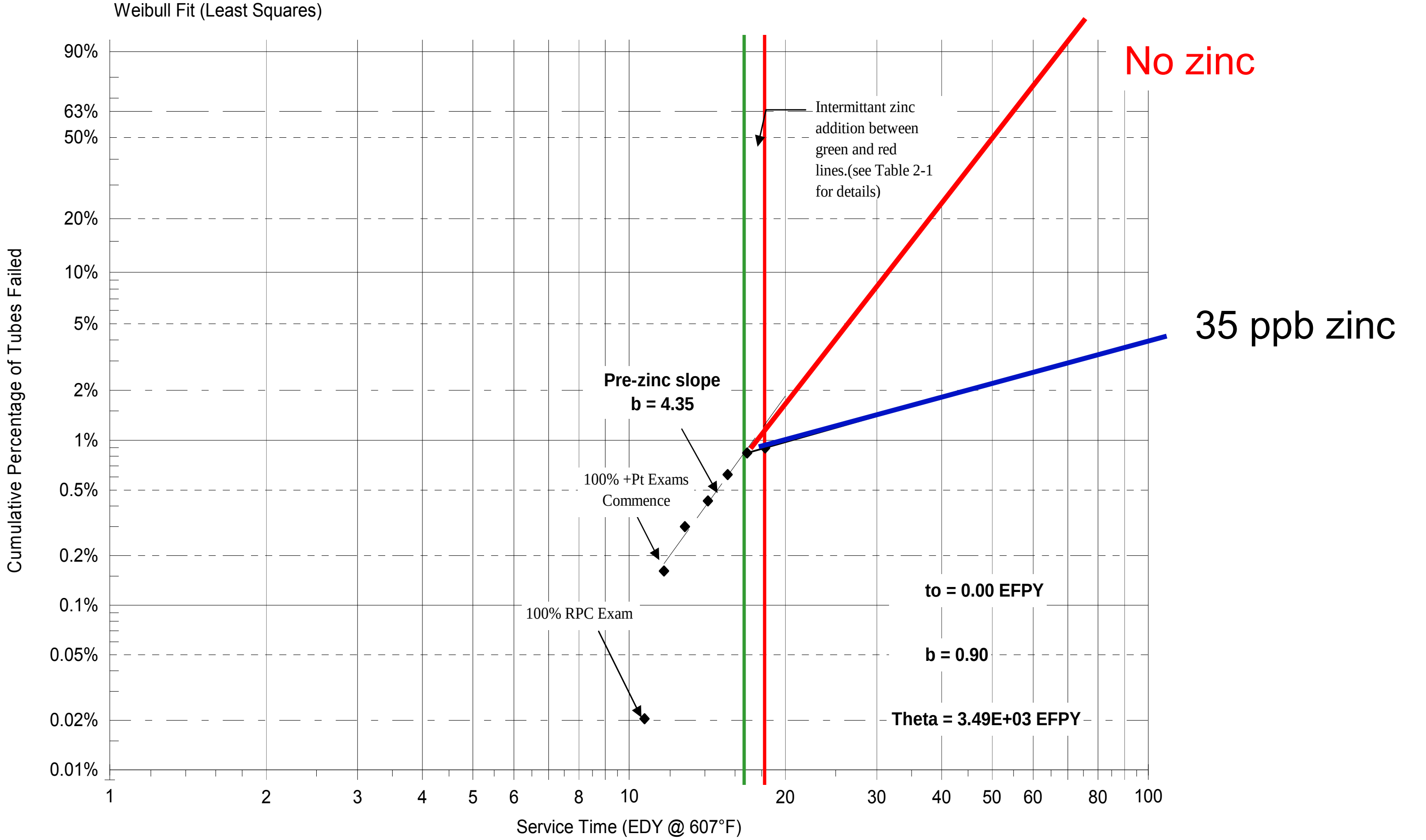


Sequoyah 2 (**5 ppb zinc**) has experienced a **31% decrease** in Weibull Slope

Example of Largest Zn Benefit Observed

79% Decrease in Weibull Slope

(It would take 9.6 times as long to go from 0.8% to 10% tubes affected)



Beaver Valley 1 (**35 ppb zinc**) has experienced a **79% decrease** in Weibull Slope

Fuel Materials Compatibility (Fuel)

Zinc, by itself, is not expected to negatively affect fuel cladding integrity.

- Early autoclave and in-reactor tests showed no impact.
- Cladding corrosion measurements have shown zinc to have little or no impact on clad performance.

- Assessments by vendors have determined that zinc does not interact with or exacerbate the degradation of leaking rod failure locations caused by other mechanisms.
- Zinc was shown to have no negative effect on other fuel component materials during early autoclave testing,
- FRP and vendors are expanding the fuel surveillance database as higher duty plants inject zinc.

Fuel Materials Compatibility (Fuel)

Experience:

- Fuel surveillances at Farley, Diablo Canyon and Palisades have shown zinc to be relatively benign at low duty units.
- In 2002, FRP sponsored detailed crud scrapes at Diablo Canyon-1 following Cycle 11 on the two highest-powered assemblies in-core for later comparison with higher duty fuels
  - Surveillance performed for background information.
- Crud scrapes and cladding corrosion measurements at Callaway (first high-duty plant to add zinc) following Cycles 13 (2004) and 14 (2005) showed no accelerated cladding corrosion.

Fuel Materials Compatibility (Fuel)

- Vandellos II (Spain) demonstration in progress. Vandellos bounds most PWRs in U.S. with respect to fuel duty.
  - Baseline oxide measurements taken during Refuel 14 (spring 2005)
  - Zinc injection commenced half-way into Cycle 15 (June 2006)
  - Refuel 15 planned May 2007 (oxide measurements & crud scrapes
  - Refuel 16 planned fall 2008 (oxide measurements & crud scrapes)
- Expansion of the database to other high-duty units is being pursued.
- FRP-sponsored autoclave experiments are underway to define the limits under which zinc can be added.
  - This includes heated single-rod tests under bounding heat flux and sub-cooled nucleate boiling conditions and includes tests at high zinc concentrations and various levels of contaminants (e.g. silica) known to negatively affect crud deposits.

Zinc Mitigation of PWSCC Initiation and Growth

The inhibitive effect of zinc on PWSCC initiation is well documented

- Decrease in SG degradation rate (indications) by 2 to 10X
- Farley 2 head experience

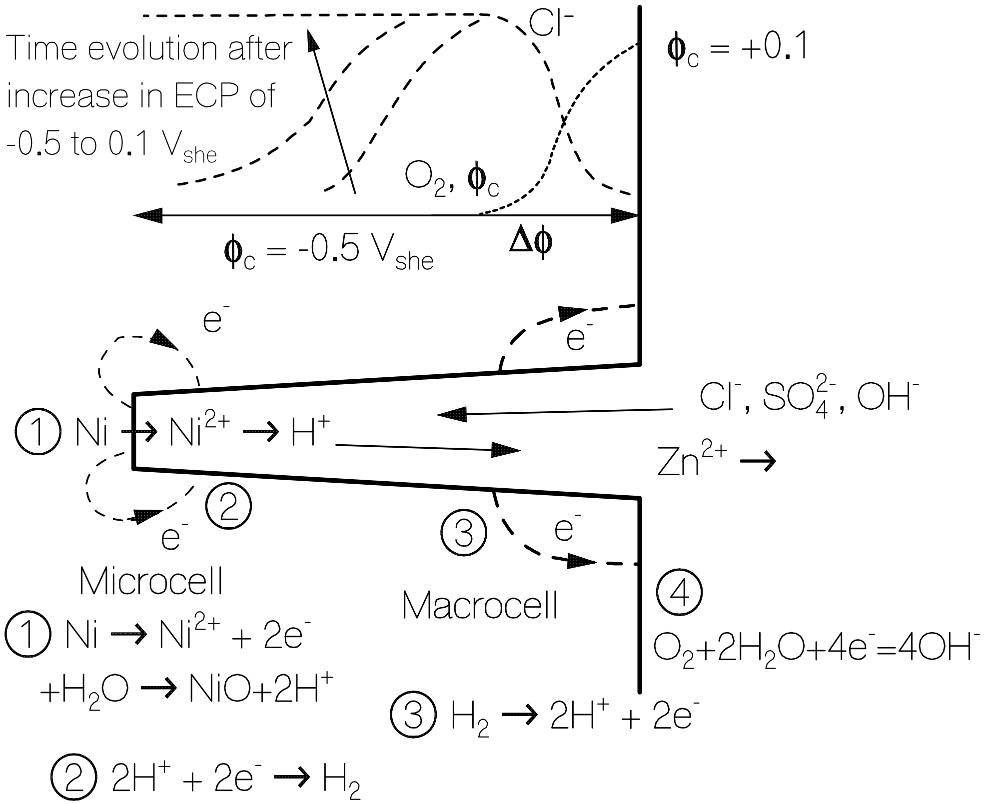
However:

- Reduced crack growth benefit of zinc shown for A600 SG tubes does not necessarily transfer to thick-wall RCS components and to A82/182 welds

Mitigation of PWSCC in RCS A600/182/82 by Zinc Injection

- MRP/PWROG objective is to supplement confirmed radiation field control benefit from zinc injection with demonstrated reduction in rate of PWSCC initiation and growth in thick-wall RCS components to:
  - Avoid or delay component repair/replacement by retarding PWSCC initiation and growth of shallow (undetected) cracks
  - Obtain inspection relief for susceptible RCS locations by demonstrating reduction in initiation and growth of existing cracks
- Parallel efforts underway by FRP and Chemistry to assure:
  - Recommended levels do not effect fuel performance and cladding integrity
  - Orderly dissemination to utilities via Zn application guidelines
- Investigating synergistic PWSCC benefit of zinc and elevated H_2

Zn: Penetration to Crack Tip



$$J_A = -D_A \Delta C_A - z\mu C_A F \Delta\phi + C_A V$$

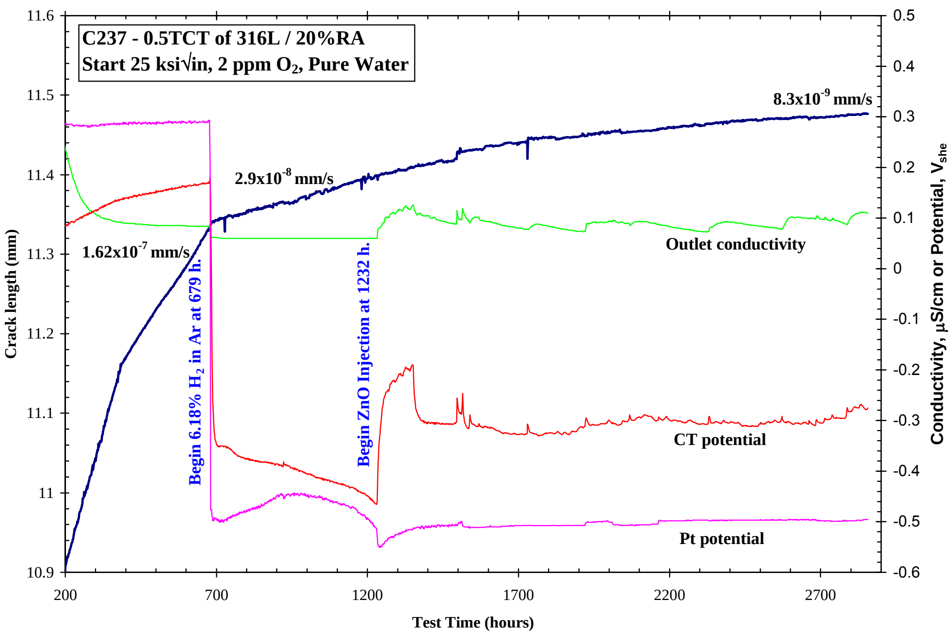
flux = diffusion + ϕ-driven + convection

Limited benefit of Zn in BWRs related to high corrosion potential, which drives Zn^{2+} from crack.

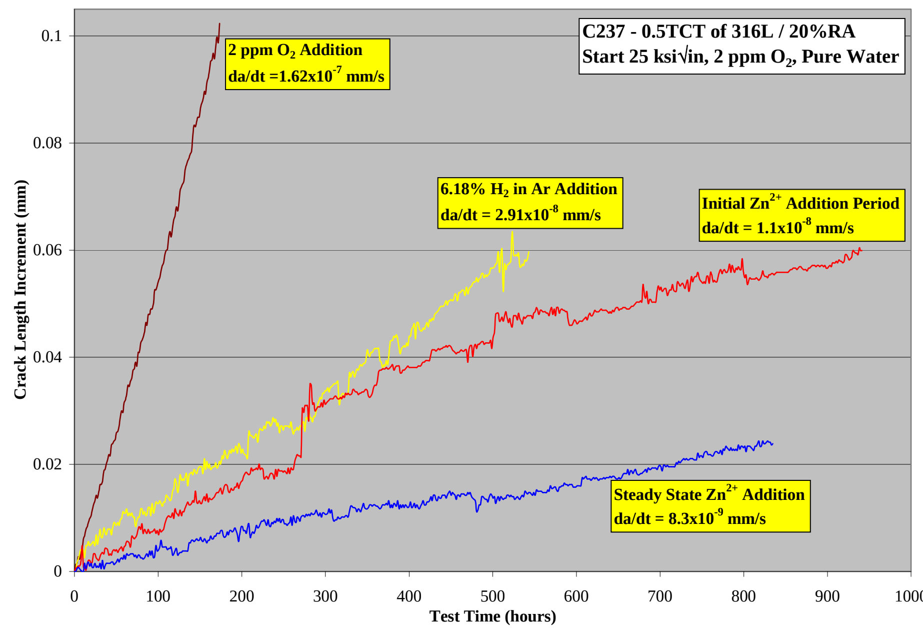
But at low potential, Zn diffuses slowly and is initially "consumed" by incorporation into crack oxides.

GE Tests on SS at 20 ppb Zn

NobleChem + 20 ppb Zn^{2+}



Longer-term Effects of Zn on SCC



Injection of Zn^{+2} at low potentials may mitigate cracking in highly irradiated materials. Zn is currently injected at 5 – 7 ppb into reactor feed water for radiation control

Effects of Zn on SCC Growth Rate

Test	Li, ppm	B, ppm	pH_{300C} (1)	Zn, ppb	Duration hours
1	2.2	600	7.2	$0 \rightarrow 30$	5000
2	2.2	600	7.2	$0 \rightarrow 10 \rightarrow 30 \rightarrow 0$	6500
3	0.3	1200	6.9	$0 \rightarrow 30 \rightarrow 0$	5000

500 hrs for SCC transitioning + 1500 hrs per test segment

Each test uses two 1TCT specimens; 325C, 30 cc/kg H_2

Spike Zn for several weeks to saturate system and crack

Testing focused on Ni-metal stability = high H_2

Testing now underway on Alloy 182 weld metal

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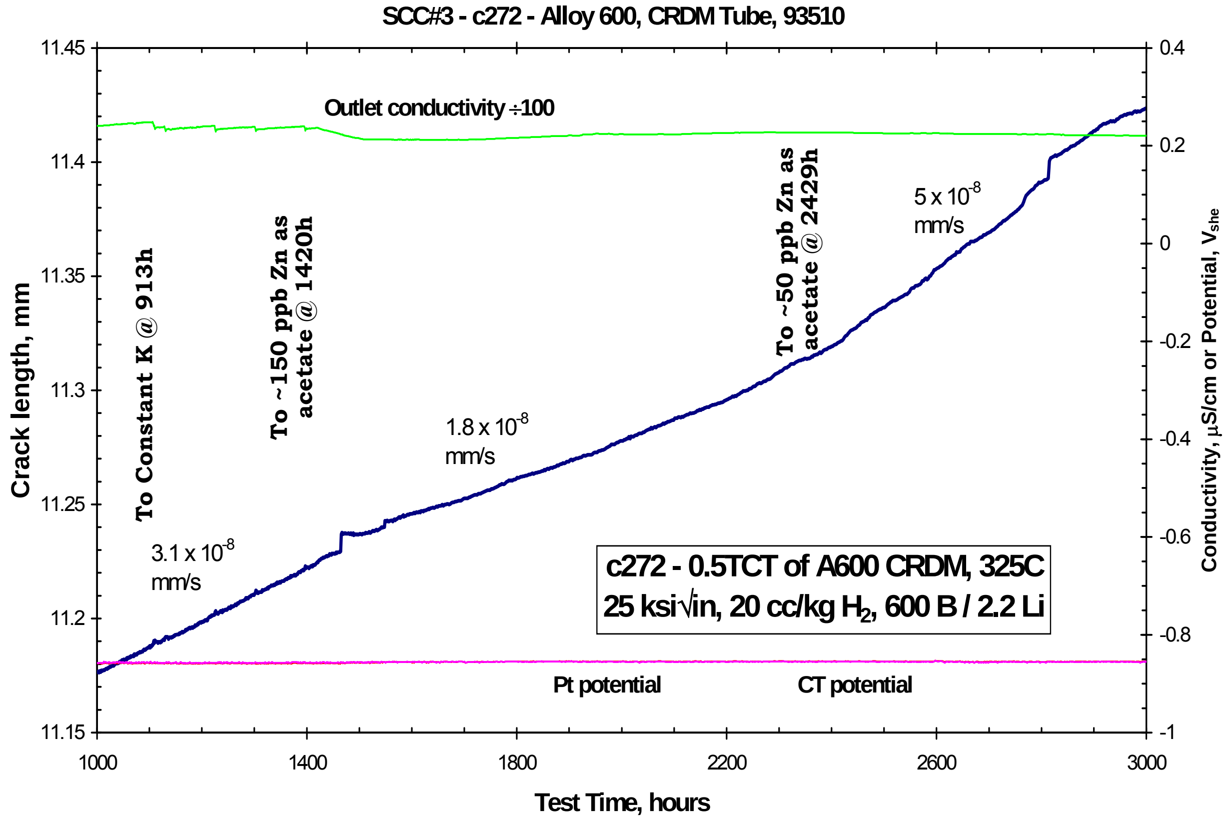
30 ppb Zn Effect

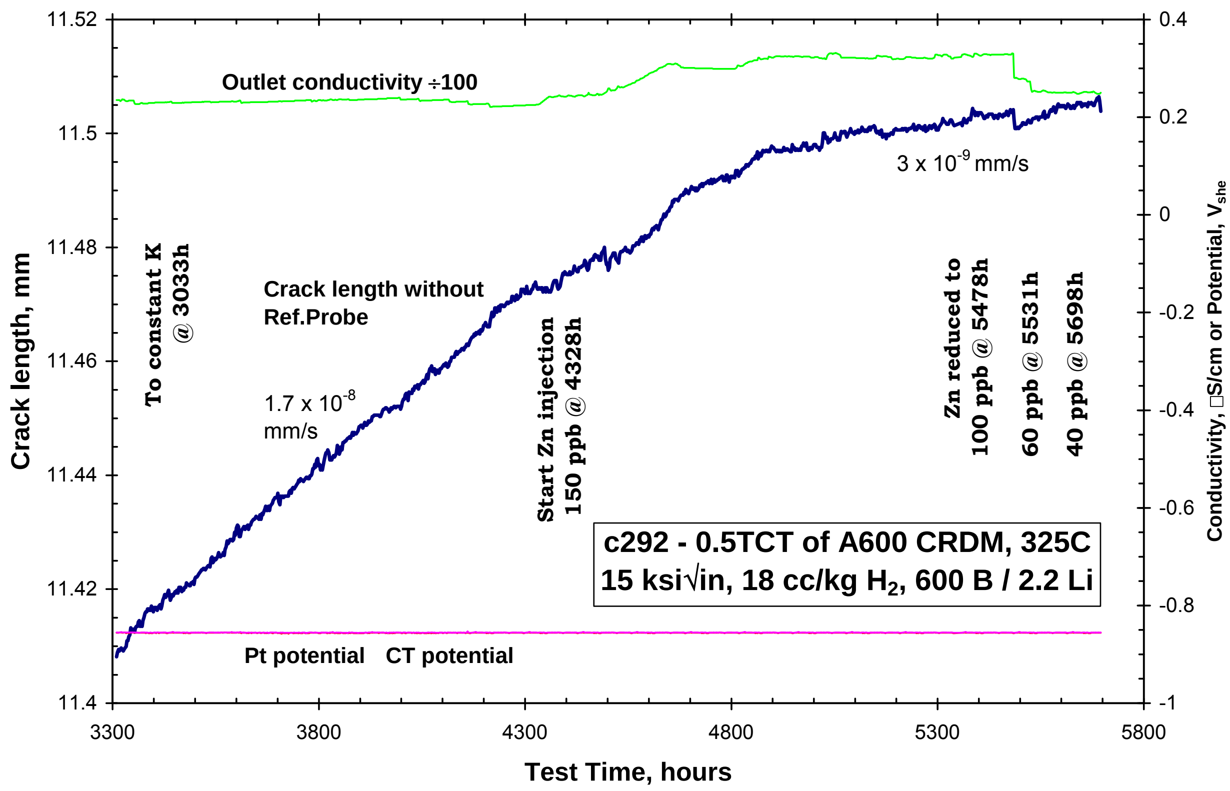
Spiked to 150 ppb Zn injected for six weeks



Specimens run at 325C, 600 B / 2.2 Li, 30 cc/kg H_2 then 150 ppb Zn injected for six weeks.

Test #2: 30 ppb Zn Effect

Spiked to 150 ppb Zn injected for six weeks



325C, 600 B / 2.2 Li, 18 cc/kg H_2

Used 15 ksi√in so growth rates are lower

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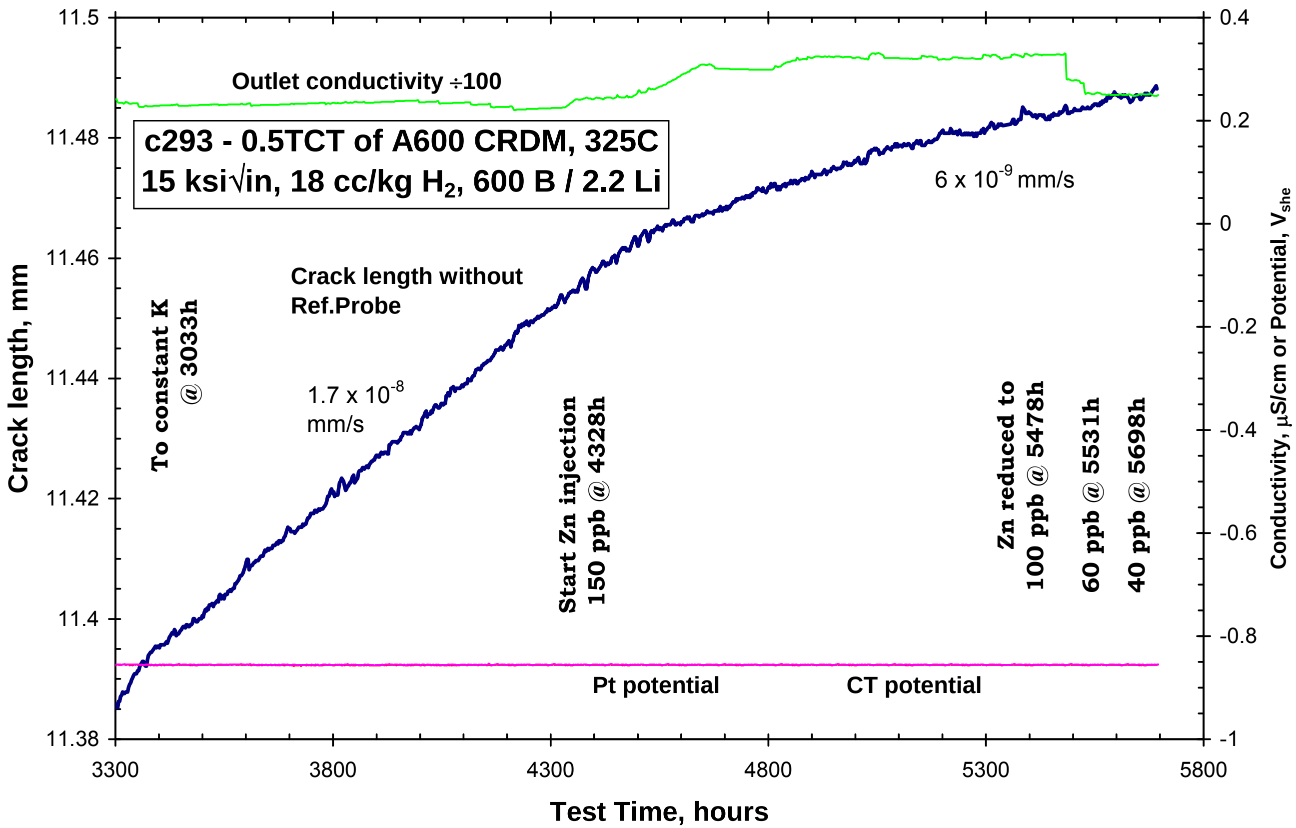

325C, 600 B / 2.2 Li, 18 cc/kg H_2

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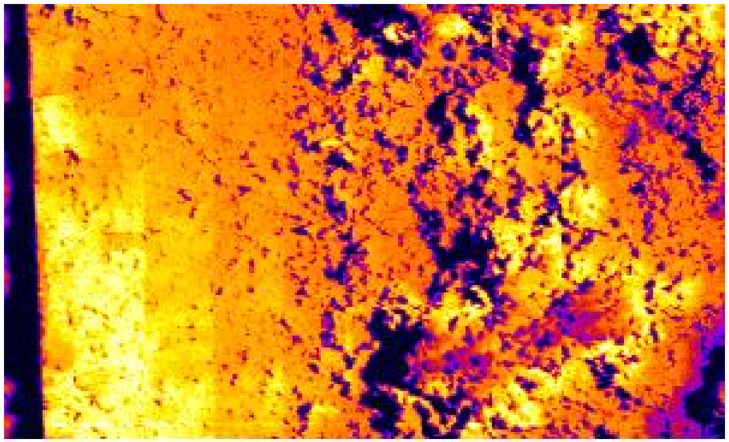
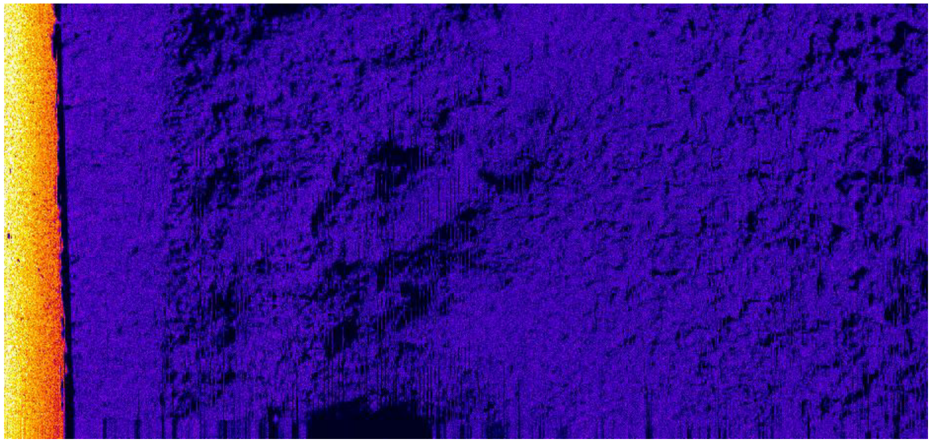
Test #1: Zn Maps in Crack

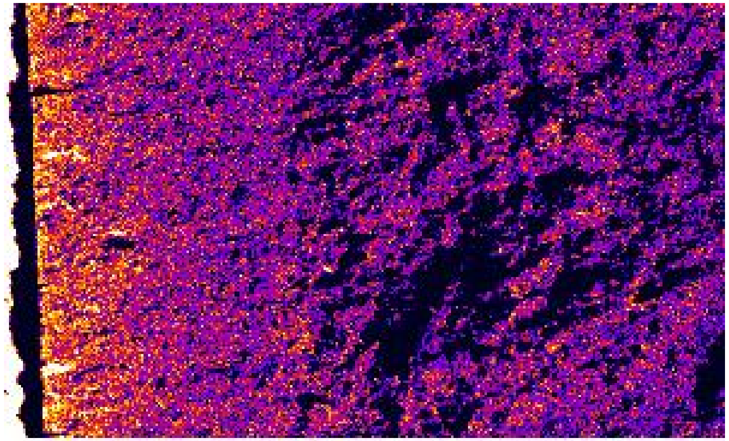
Microprobe (WDS) very roughness/orientation sensitive



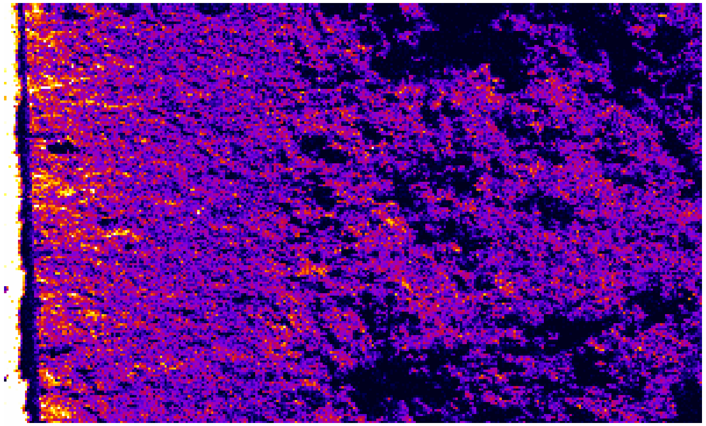
500µm
Ni fracture surface



Zn fracture surface



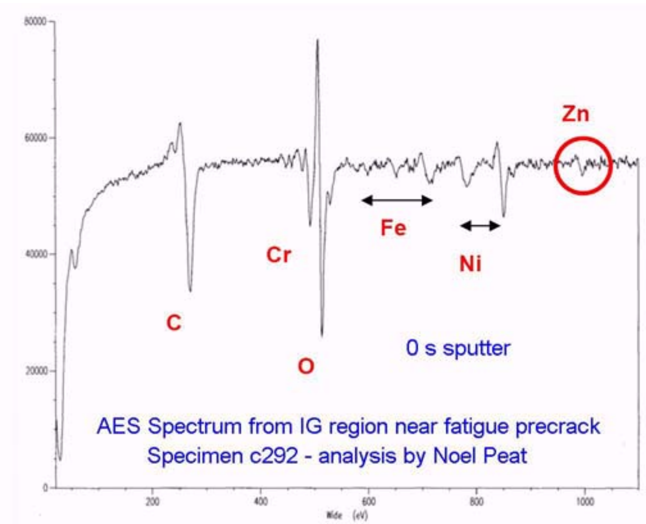
500µm
Zn fracture surface

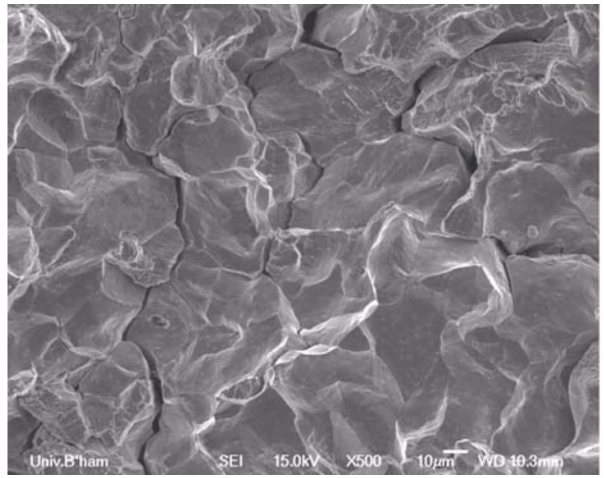


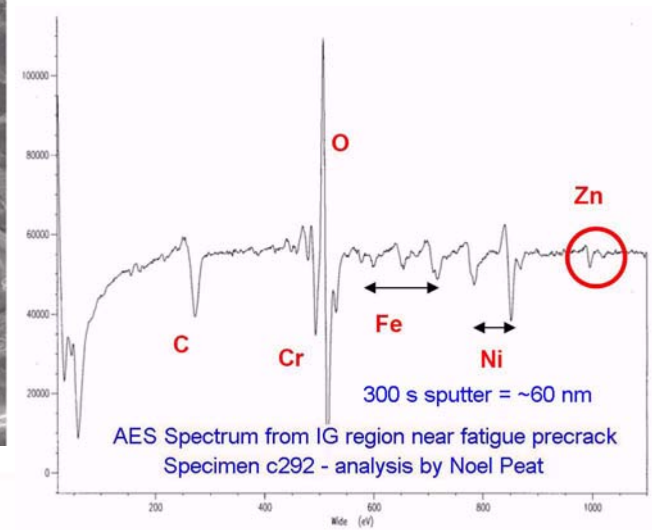
500µm
Zn-Lalpha fracture surface

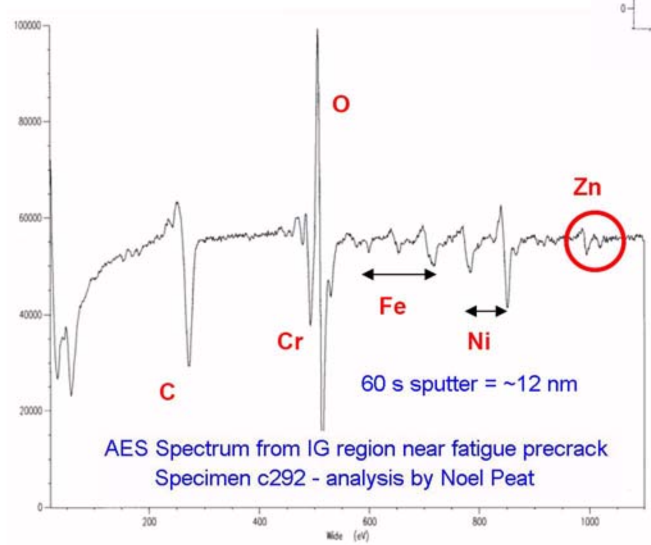
Test #2: Zn Maps in Crack

Auger Electron Spectroscopy in IG Area Near Fatigue Precrack









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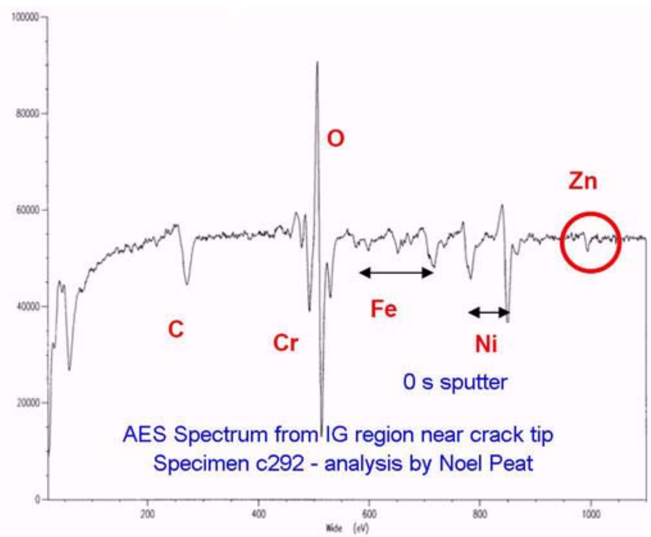
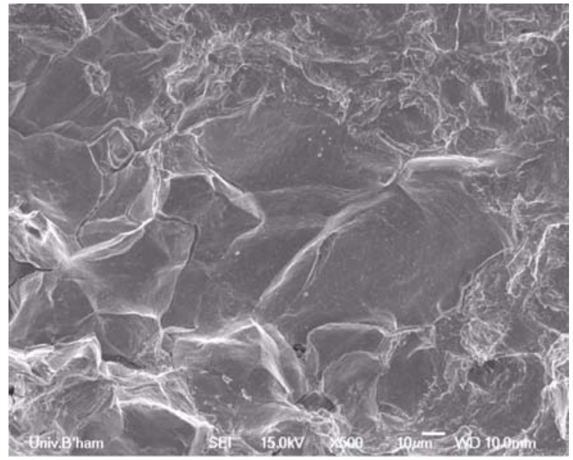
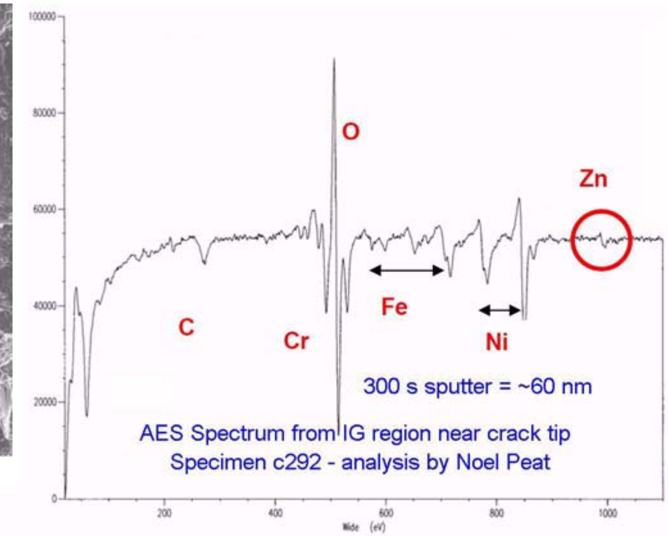
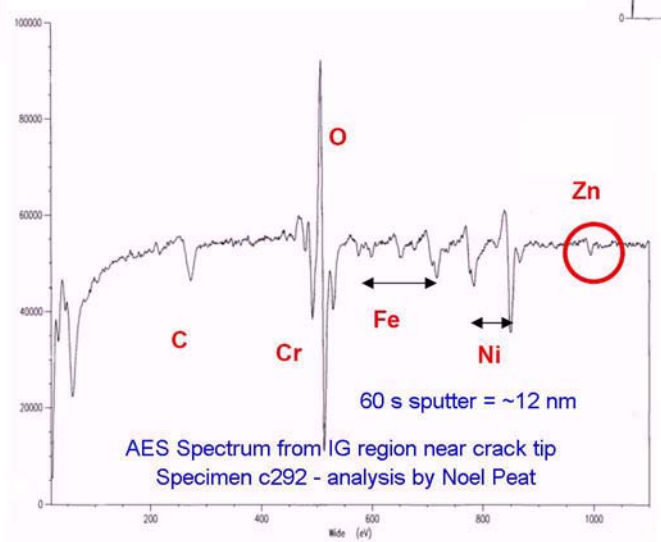
Test #2: Zn Maps in Crack

Auger Electron Spectroscopy in IG Area Near Crack Tip









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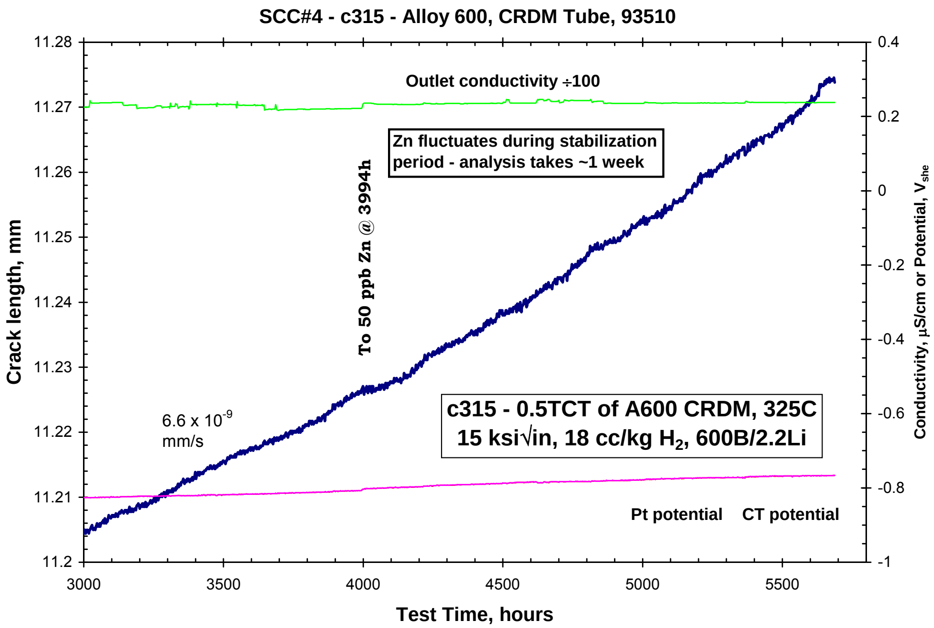
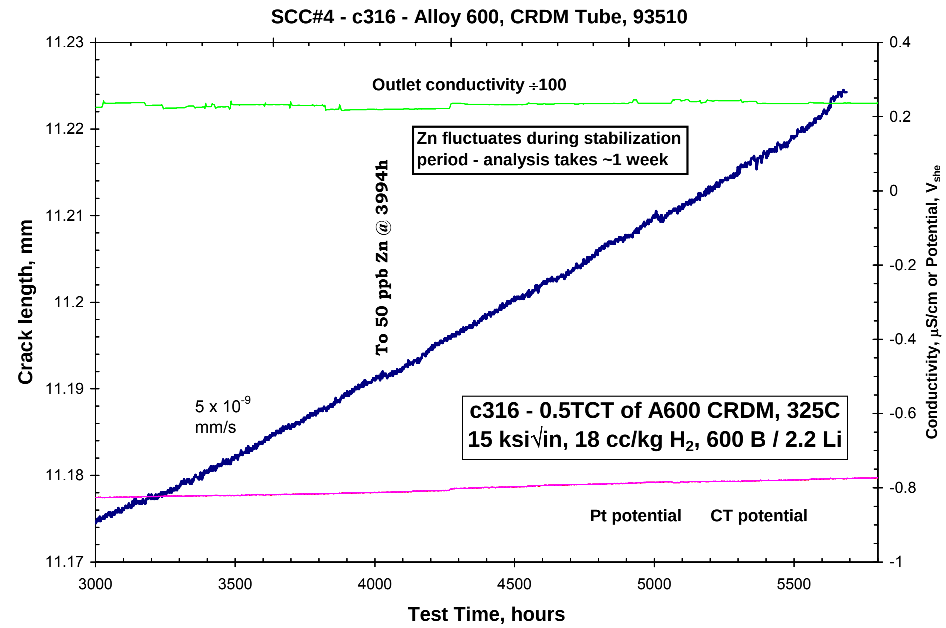
Test #3: 30 ppb Zn Effect

~50 ppb Zn for ~10 weeks – no effect observed yet





325C, 600 B / 2.2 Li, 18 cc/kg H_2

At 15 ksi√in growth rates are lower

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Conclusions on Zn Effects

Summary and Interpretation of Zn Results:

- Some benefit may occur at high Zn levels (150 ppb)
- Limited evidence of benefit at 30+ ppb Zn, 25 ksi√in
- Stronger evidence of benefit at 30+ ppb Zn, 15 ksi√in
- Follow-up, corroborative experiments essential
- Uncertain theoretical benefit of Zn in NiO structure
  – known benefit is from Zn incorporation into spinel
- Testing underway focuses on Alloy 182

A600 PWSCC Summary of Test Results and Ongoing Work

- Field and test data shows zinc inhibits PWSCC initiation in Alloy 600/82/182; recently-initiated PWROG project will provide confirmation. Task-by-task results over the next few years.
- Some initial tests indicate zinc can reduce growth rate of undetected (shallow-low stress intensity) cracks in thick A600 components, confirmatory tests underway. Results in 2008.
- A600 tests to date have not shown zinc can reduce growth rate of deep cracks in high stress areas (high stress intensity cracks). It appears that crack-tip in a fast-growing crack out-runs zinc species that deposit on crack flanks rather than on the tip. Further testing is underway. Results expected in 2008.
- Ongoing testing will address crack growth in A182 material.
- Future MRP work will include evaluation of synergistic effects of elevated hydrogen and zinc.
- SCC tests require thousand hours; results are slow to come.

Present Schedule for Deliverable on Chemical Mitigation

- Technical basis document to be provided to NRC in 2008
  - Zinc
  - Hydrogen