

# ZIRAT-8 SPECIAL TOPICS REPORT

## **The effects of Zn injection (PWRs and BWRs) and Noble Metal Chemistry (BWRs) on fuel performance – an update**

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## FOREWORD

The current trends to change coolant water chemistry to reduce: 1) radiation buildup and, 2) cracking tendency in reactor internals poses a growing threat to the fuel integrity as we moving into quite new water chemistry regimes where we have very little or no previous experience.

This special topic report has been prepared within the ZIRAT-8 program and reviews the most recent experience of the impact of Zn-injection (in PWRs and BWRs) and NMCA (in BWRs) on fuel integrity. The report also discusses fundamentals in crud formation related to Zn-injection and NMCA.

Different section of this report has been prepared by the following authors: Brian Cox Friedrich Garzarolli, Peter Rudling and, Al Strasser. The whole report has been reviewed by all the authors as well as by Ron Adamson.

Throughout this document, references are made to previous ZIRAT-reports, as follows:

- Special Topical Report entitled: “CORROSION OF ZIRCONIUM ALLOYS” by Ron Adamson, Brian Cox, Friedrich Garzarolli, Peter Rudling, Al Strasser, Gunnar Wikmark, 2002.
- Special Topical Report entitled: “WATER CHEMISTRY AND CRUD INFLUENCE ON CLADDING CORROSION”, by Gunnar Wikmark and, Brian Cox, 2001.
- ZIRAT-6 and –7 Annual Report, 2001 and 2002, respectively.

*Peter Rudling, Editor*

## CONTENTS

<b>1</b>	<b>INTRODUCTION</b>	<b>1-1</b>
<b>2</b>	<b>MECHANISMS (BRIAN COX)</b>	<b>2-1</b>
2.1	NMCA AND ZINC ADDITIONS TO REACTOR WATER	2-1
2.1.1	Reasons for adopting NMCA in reactor water	2-1
2.1.1.1	Why add noble metals in BWRs	2-1
2.1.1.2	Why add noble metals in PWRs	2-2
2.2	HOW SHOULD THE NOBLE METAL BE ADDED	2-6
2.3	ACTUAL AND POTENTIAL EFFECTS ON FUEL CLADDING CORROSION	2-8
2.4	REASONS FOR ADDING ZN TO REACTOR WATER	2-15
2.4.1	Why add Zn to BWR water	2-15
2.4.2	Why add Zn to PWR water	2-17
2.5	POTENTIAL EFFECTS ON CLADDING CORROSION	2-18
<b>3</b>	<b>BWR EXPERIENCE WITH NMCA AND/OR ZN-INJECTION (AL STRASSER AND PETER RUDLING)</b>	<b>3-1</b>
3.1	IMPACT OF NMCA AND ZN-INJECTION ON STAINLESS STEEL/NICKEL BASE AND ZIRCONIUM ALLOYS	3-3
3.1.1	NMCA impact	3-3
3.1.1.1	SCC Propagation and Monitoring Experience in BWRs	3-3
3.1.1.2	Effect of NMC on SCC Crack Propagation --- Experimental Work	3-4
3.1.1.3	Coatings to Inhibit Stainless Steel SCC	3-8
3.1.2	Zn-injection impact	3-8
3.2	IMPACT OF NMCA AND ZN-INJECTION ON FUEL PERFORMANCE IN COMMERCIAL REACTORS	3-9
3.2.1	Browns Ferry 2	3-17
3.2.2	CGS	3-20
3.2.3	Hatch 1 and 2	3-24
3.2.4	River Bend	3-25
3.2.4.1	River Bend-1, CY 8, 1999	3-25
3.2.4.2	River Bend Fuel Failures Cycle-11	3-27
3.2.5	Vermont Yankee	3-28
<b>4</b>	<b>PWR EXPERIENCE WITH ZN-INJECTION (TO REDUCE ACTIVITY BUILDUP AND PIPE CRACKING)</b>	<b>4-34</b>
4.1	PWR WATER CHEMISTRY RELATED FAILURES	4-34
4.2	HIGH PH OPERATION IN PWRs	4-37
4.3	PWR EXPERIENCE WITH ZN-INJECTION	4-39
4.3.1	Qualification of Zn-injection to PWR primary coolant	4-39
4.3.2	Plant Experience	4-39
4.3.3	Water chemistry changes after Zn-injection	4-42
4.3.4	Effect of Zn-injection on fuel rod behavior	4-43
<b>5</b>	<b>DISCUSSION AND SUMMARY</b>	<b>5-45</b>

<b>6</b>	<b>APPENDIX A</b>	<b>6-1</b>
6.1	OBSERVATIONS AND THEORY	6-1
6.1.1	Crud Sources	6-1
6.1.1.1	Corrosion and Corrosion Release	6-1
6.1.1.2	Materials Corroding in the LWRs	6-4
6.1.2	Chemical Composition of Corrosion Products and Fuel Crud	6-6
6.1.2.1	Spinel Structure Oxides	6-7
6.1.2.2	Solubility of Iron, Nickel, and Chromium in LWRs	6-8
6.1.3	Water Chemistry in BWRs	6-10
6.1.3.1	Non-monitored Crud Sources	6-13
6.1.4	Water Chemistry in PWRs	6-13
6.1.5	Crud Transport	6-15
6.1.5.1	The RW Concentration and Removal of Crud in the BWR	6-15
6.1.6	Fuel Crud Deposition	6-17
6.1.6.1	Boiling Impact - Experiments and Theory	6-21
6.1.6.2	A Tentative Model of the Boiling and Crud Deposits	6-24
6.1.6.3	An Important Observation of Impact of Boiling	6-26
6.1.7	Crud Deposits in LWRs	6-27
6.1.7.1	Crud Deposits in BWRs	6-27
6.1.7.1.1	BWR Crud Profiles	6-28
6.1.7.2	Crud Deposits in PWRs	6-30
6.1.7.3	Solubility of Crud	6-32
6.2	POSSIBLE IMPACT FROM CRUD	6-32
6.2.1	Local Chemistry	6-32
6.2.2	Thermal Resistance	6-33
6.2.3	Neutron Poison	6-36
6.2.3.1	Activity Dispersion in the Reactor System	6-36
6.2.3.2	Impact of Fuel Failures	6-36
6.2.4	Flow Restriction	6-37
<b>7</b>	<b>APPENDIX B - ELECTROCHEMICAL DEFINITIONS (BRIAN COX)</b>	<b>7-1</b>
<b>8</b>	<b>REFERENCES</b>	<b>8-1</b>

## 1 INTRODUCTION

The current trends to increase burn-up and local power in combination with introduction of new water chemistry regimes (BWR HWC, NMCA (noble metal addition), zinc injection, iron addition, etc.) and changes in operation (longer cycles, leading to higher boron concentration and lower/higher pH in PWRs; reoccurring system decontamination, etc.) poses a growing threat to the fuel integrity. The reason for this is not only that more chemicals are added but also that we move into quite new water chemistry regimes, in some cases also in combination, where we have no previous experience.

As from the early, 1990's there has been a trend to to tailor the water chemistry to decrease:

1. the activity build-up and/or to
2. mitigate stress corrosion cracking of the stainless steel and nickel base austenitic materials.

Hydrogen water chemistry, HWC, was first introduced in 1979, to obtain more reducing conditions in BWRs and thereby mitigating the stress corrosion cracking tendency in reactor internals. However, high radiation fields may result from the application of HWC since it is often necessary to have a rather high injection rate in order to attain the low potential of  $-230$  mV vs. SHE of the austenitic materials, intended to be protected. Noble Metal Chemical Addition, NMCA, was applied in 1996 in BWRs to enhance the efficiency of hydrogen injection and was developed to transform the austenitic stainless steel or nickel base material to have an electrochemical behaviour similar to platinum. It would then be possible to use a lower hydrogen addition level, and hence, to avoid the negative impact from the HWC application.

To improve the radiological situation in BWRs, zinc injection has been introduced. Normally, the reason for zinc injection in PWRs is dose rate decrease, but occasionally the aspect of using zinc to prevent Pressurised Water reactor Stress Corrosion Cracking, PWSCC, is considered, then a much higher zinc level in the primary water is required

The mechanisms of NMCA and Zn-injection on the decrease in cracking tendency of stainless steel material and reduction in radiation buildup as well as the potential impact of these water chemistry changes on fuel performance is treated more in section 2. Section 3 and 4 summarises the data generated in plants with NMCA and /or Zn-injection as well as plants with corrosion problems without these water chemistry modifications. Section 5 summarises the key point of this report. Appendix A – provides CRUD fundamentals and Appendix B – Electrochemical definitions

## 2 MECHANISMS (BRIAN COX)

### 2.1 NMCA AND ZINC ADDITIONS TO REACTOR WATER

#### 2.1.1 Reasons for adopting NMCA in reactor water

Many utilities are adding noble metal compounds NMCA or Zinc salts to their reactor water. Why do they do it, what are the advantages over other possible additions, and what (if any) are the disadvantages.

##### 2.1.1.1 Why add noble metals in BWRs

In BWRs the intergranular stress corrosion of recirculating piping and stainless steel reactor internals has been an ongoing problem. Stress corrosion cracking of stainless steel is basically an anodic dissolution of the metal grain boundaries if these are susceptible either because of the failure to stress relieve welds in unstabilised steel where the grain boundaries become depleted in chromium, or under irradiation where migration of chromium and other impurities away from or to the grain boundaries renders them sensitive to dissolution. This simple explanation has been cast into doubt by recent studies, Andresen, et al., 2001 and Busby and Was, 2001, showing that cracking occurs in 304SS even in the absence of Cr depletion or Si and P enrichment of the grain boundaries and is slowed (but not stopped) at corrosion potentials below  $-340\text{mV/SHE}$ . No alternative mechanisms have been offered, other than general "hand waving". In highly oxygenated BWR water the high anodic potential of the steel ( $+0.25$  to  $+0.28\text{V SHE}$ ) stimulates this crack growth process, Indig, 1989. By adding hydrogen to the reactor feed water this potential can be reduced, but it is difficult to add sufficient hydrogen to lower the electrochemical potential (ECP) of the steel to  $-0.23\text{V (SHE)}$ , at which point the intergranular SCC should cease to be possible. Reduction of the potential in the reactor core, Figure 2-1 is even more difficult than in the external piping because the oxidising radiolytic species produced there reduce the efficiency of the hydrogen in the water to reduce the ECP of the steel, and boiling carries off the dissolved hydrogen in the steam bubbles.

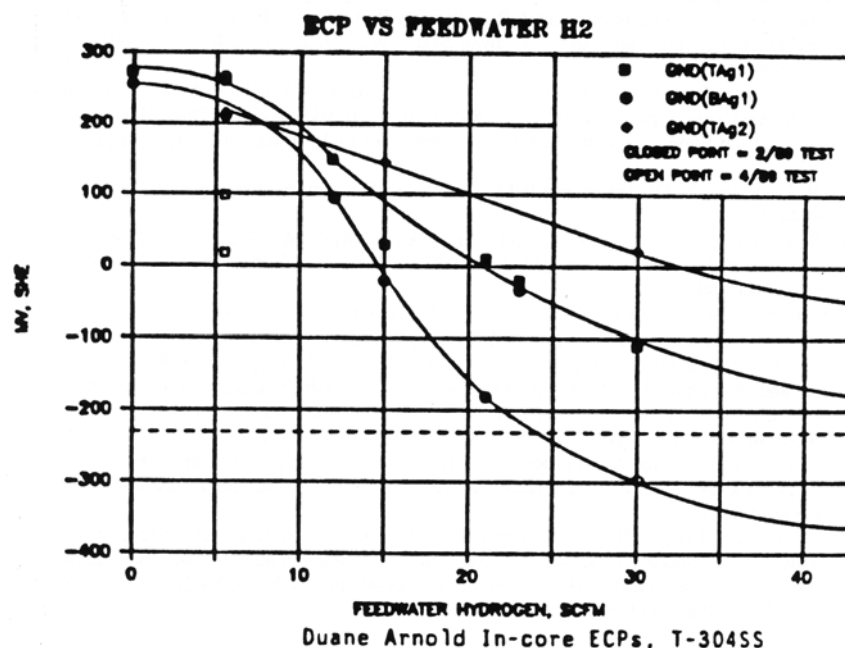


Figure 2-1: Duane Arnold In-core ECPs, T-304SS. The plot shows the ECP (mV,SHE) against the feedwater hydrogen concentration (SCFM) for two in-core silver chloride electrodes (TAg1,TAg2) for two tests (2/89test,4/89test) done 1989, Indig, 1989.

Stainless Steels are not efficient electrodes in terms of their efficiency to respond to hydrogen in the water because of the passive oxide film that covers their surfaces. By contrast the noble platinum group metals that do not form passive oxide films in high temperature water are much more efficient electrodes and easily attain the "reversible hydrogen potential" which on the Standard Hydrogen Electrodes (SHE) scale is determined by the concentration of hydrogen in the water. By depositing a thin film of a platinum group metal on the stainless steel surface it was expected that the steel would easily get below the desired  $-0.23\text{V}$  (SHE) even with a decrease in the hydrogen addition rate. The high dissolved hydrogen levels, and lack of boiling in early PWRs made such noble metal additions unnecessary.

### 2.1.1.2 Why add noble metals in PWRs

To understand this we have to look at the SCC processes in the different materials in BWRs and PWRs. In BWRs we are mainly dealing with cracking in 304 type stainless steels. In PWRs the primary cracking processes have been in Inconel 600. The main locations of this cracking have been primary water side cracking of steam generator tubes and in core the cracking of Inconel 600 nozzles in the pressurizer; control rod drive penetrations in the pressure vessel head; and instrumentation tube penetrations at the bottom of the pressure vessel. Changes to more SCC resistant nickel alloys such as Incoloy 800 or Inconel 690 are not easily done in some of these locations, so other solutions to the cracking problems have been sought.



The understanding of mechanisms of SCC in the different materials still has many uncertainties. There have been two schools of thought over many years. One sees IGSCC processes as an anodic dissolution of the grain boundaries. The other (originally applied to TGSCC) relates this to a form of hydrogen induced cracking. However, proponents of this second cracking mechanism have tried to apply hydrogen induced cracking mechanisms to IGSCC. Such attempts have been rejected for IGSCC of 304 type stainless steels, Andresen, et al., 2001. However, the answer is not so clear for nickel alloys, particularly as the cracking proceeds with high dissolved hydrogen in the water, and ECPs for the Inconel that should be cathodic enough to prevent an anodic dissolution reaction. Early studies of cracking in nickel and its alloys, Bruemmer, et al., 1981, showed that cracking was fastest at 0.0 V (SHE) or below in the region where the nickel was active because of the reduction of the passive film, Figure 2-2. They also showed the importance of the segregation of species such as P, Sb etc. to the grain boundaries, even though these did not affect the polarisation curves.

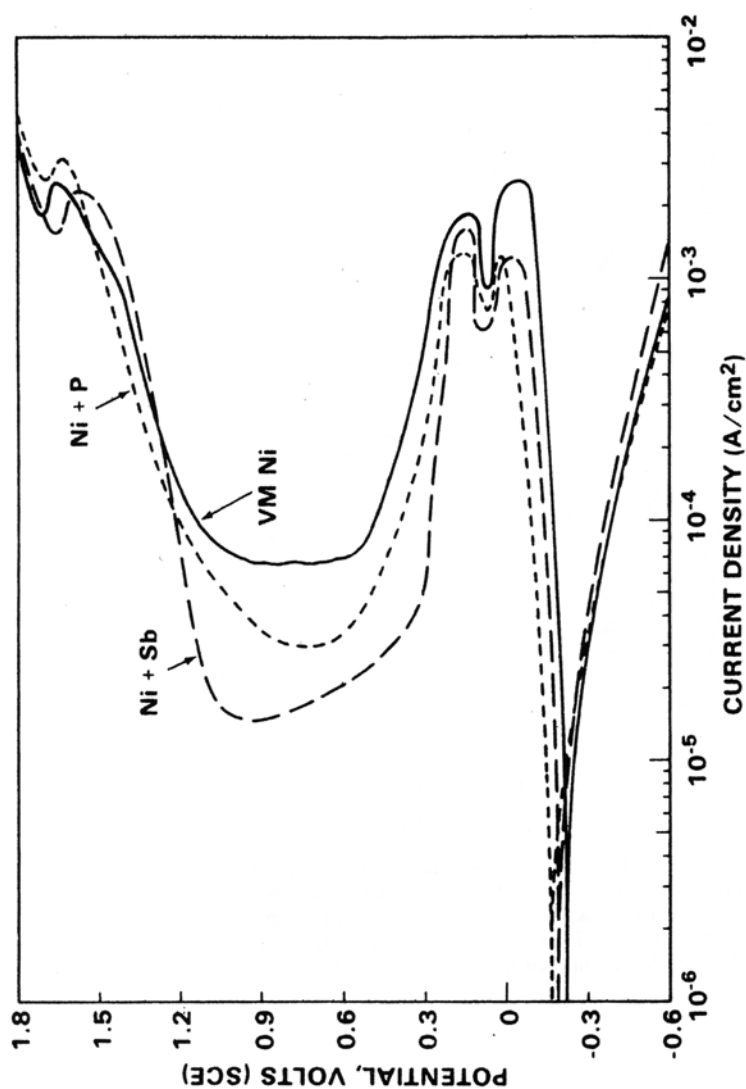


Figure 2-2: Anodic Polarisation Curves for Ni Alloys in 1N.H<sub>2</sub>SO<sub>4</sub>.

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Mitigation of the Inconel 600 cracking problems, by reducing the high dissolved hydrogen levels in the primary water, has been one solution considered by some utilities, but efforts must be made to keep the ECP out of the range where cracking is fastest, Figure 2-2. Theoretical calculations have suggested that 0.3-0.5 cc/kg, Hisamune, et al., 1998, Ishihara, et al., 1998, Garbett, et al., 1998(b), Pastina, et al., 1999, should be enough to prevent any significant formation of oxidising radicals. However, PHWR experience, where hydrogen specifications in the D2O are 3-10 cc/kg, show that one needs to keep above the 3-5 cc/kg range to eliminate all evidence of the formation of oxidising species, Elliot, 2003. This correlates well with experience in Belleville, that 3.6 cc/kg, or more was necessary, Brun, et al., 1994. At lower temperatures than normal reactor operating conditions less hydrogen may be sufficient; e.g. 0.23 ppm (2.5 cc/kg) at 200°C, Pastina, et al., 1999, but the boric acid concentration then becomes very important, Figure 2-3.

However, again recent results are casting doubt on these assumptions, Lee, et al., 2001 and Scott and Benhamou, 2001. Reducing the concentration of H<sub>2</sub> dissolved in the water may actually be counter productive if the observations that crack velocities in Alloy 600 actually increased as hydrogen levels were reduced, Lee, et al., 2001, are confirmed.

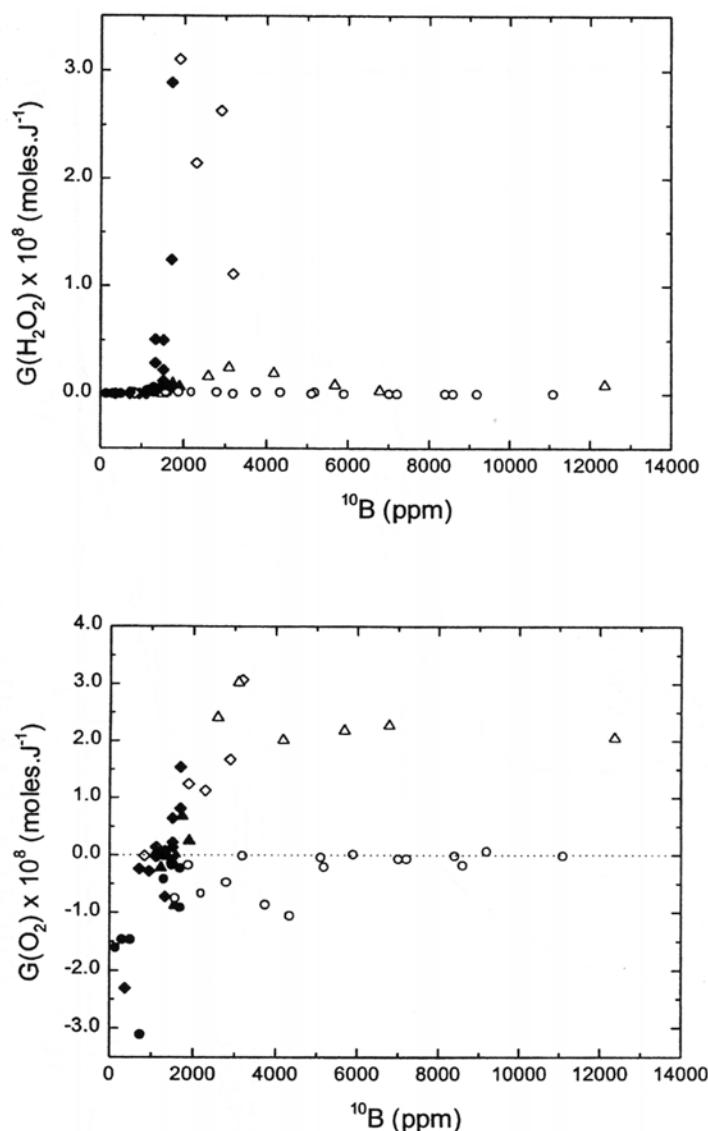


Figure 2-3: The Effect of  $^{10}\text{B}$  Concentration on the Water Radiolysis Products.

The ECP in the reactor water will increase regularly as the concentration of hydrogen is reduced, and this could have other consequences. Reducing the concentration of hydrogen in the primary coolant water (for instance) has been claimed to lower the amount of crud. Earlier views of the cracking mechanism for Inconel 600, Rebak et al., 1991 argued that it is an effect of three processes acting in combination:

- (i) Dissolution occurring preferentially at the crack tip, exposing base metal and generating hydrogen.
- (ii) Creep producing micro voids at grain boundaries, that enhance the preferential path for cracking.
- (iii) Atomic hydrogen absorption facilitates the decohesion at the grain boundaries.

No alternatives for these explanations of IGSCC of Alloy 600 have been offered. The questions that remain are, however, will reducing the hydrogen content of the coolant actually reduce the crack growth rate in Inconel 600, and can we avoid the problem area of ECP for cracking of Ni alloys which is in the range 0.0-0.15 V (SCE)). With the enhanced amounts of boiling in PWRs could enhanced crud deposition and problems such as increased frequency of Axial Offset Anomalies (AOA) incidents occur, with its possibility of through wall cladding oxidation if the AOA disappears and a local overpower situation arises in the presence of heavy crud deposits. One other consequence of increasing the ECP by lowering the hydrogen content of the water could be a reduction of the incidence of reduced nickel in the crud.

## 2.2 *HOW SHOULD THE NOBLE METAL BE ADDED*

The original idea was to coat the austenitic steel component by some suitable coating technique, such as plasma spraying, Niedrach, 1991, Kim, et al., 1992. Alloying with platinum or rhodium, Andreson, 1993 and Kim, et al., 1996 was effective, but not easily applied retrospectively. Coating retrospectively could conceivably be applied retrospectively, but not with ease. The depositing of a noble metal film from a chemical solution containing the noble metal in a suitable form appeared to be the best possible approach, Hettiarachchi, et al., 1995. However, this technique loses the advantage of the direct coating techniques by not being able to control where the noble metal ends up. This was demonstrated after the first NMCA addition to a commercial BWR, Hettiarachchi, et al., 1998. This was in Duane Arnold at the very end of cycle 14, in October 1996. Current practice is to add a mixture of  $\text{Na}_2\text{Pt}(\text{OH})_6$  and  $\text{Na}_3\text{Rh}(\text{NO}_2)_6$ , Hettiarachchi, 2003. Test coupons of 304 stainless steel picked up very little of the added noble metal (0.2mg/cm<sup>2</sup>). Most of it ended up on the fuel cladding. Although first and second cycle fuel picked up about the same amount as each other (~ 1mg/cm<sup>2</sup> Pt; ~ 2mg/cm<sup>2</sup> Rh). The third cycle fuel, with the thickest oxide film picked up the most noble metal, a peak of 5.5 mg/cm<sup>2</sup> Pt and a peak of 9.5 mg/cm<sup>2</sup> Rh at the same location, Levin, et al., 1998, about 30 in. above the lower end plug, Figure 2-4. This is the region where the thickest oxide is often formed on BWR fuel cladding, Figure 2-5. The correlation with oxide thickness made in this instance may have given erroneous lift-off numbers because of magnetic crud, Levin, et al., 1998. By the beginning of the next cycle, most of the noble metal that had been deposited on the stainless steel surfaces had migrated to the fuel cladding, so that over 90% of the total noble metal was on the fuel surfaces. If an attempt is made to do an inventory of the noble metal in the reactor, it appears that a large fraction of the total noble metal at any one time is in transit in the reactor circuit. It is assumed that much of this noble metal, which is assumed to be in a particulate form, will end up depositing in low-flow regions of the core (such as crevices), at the expense of the high flow locations. This will lead to a very uneven distribution of noble metal around the core, and could make it difficult to protect some locations against SCC.

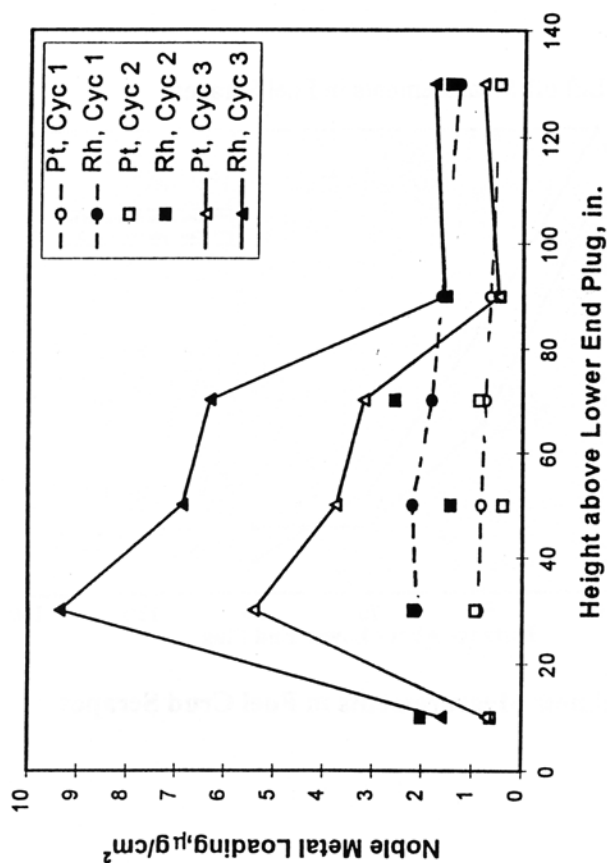


Figure 2-4: Noble Metal (Pt and Rh) Deposition Profile on Cladding in Duane Arnold.

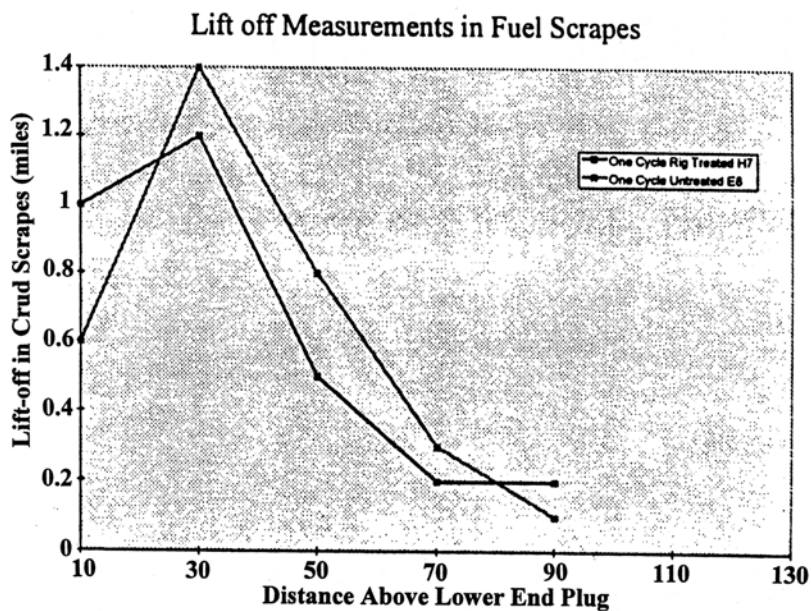


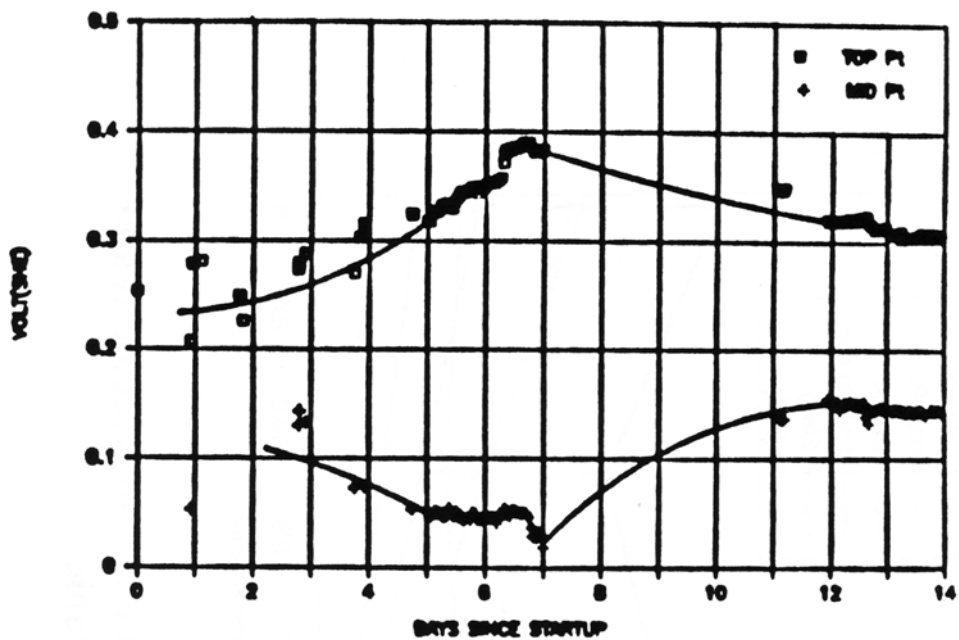
Figure 2-5: Oxide Thickness Measurements in Fuel Crud Scrapes from Duane Arnold.

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### 2.3 ACTUAL AND POTENTIAL EFFECTS ON FUEL CLADDING CORROSION

Initial experience with adding NMCA to reactor water chemistry did not give any indications of negative effects on fuel cladding corrosion. However, more recently there have been several observations of oxide spalling, which tend to suggest that increased oxide growth has occurred. Eddy current measurements suggest increased oxide thicknesses (see later), but the calibration of the eddy current signals in the presence of magnetic crud still leaves doubts about the actual oxide thickness numbers. So far none of these examples of apparently enhanced corrosion have undergone hot cell examination, although at least one hot cell examination is imminent. Until the results of these hot cell examinations are known it is impossible to say whether the oxide spallation results from thicker than expected oxide films, or earlier than expected spallation (i.e. oxide thickness normal, but spalling well below expected onset of spallation). A further possible interpretation of the reactor fuel observations could be that with NMCA an unusually hard crud layer is being formed and it is the crud rather than the oxide film that is spalling. These in-reactor observations will be discussed in more detail in the next section.

There are however good reasons to be concerned about possible effects on fuel cladding performance. In BWRs most if not all examples of uneven oxide film growth result from galvanically enhanced corrosion. Thus, "Shadow Corrosion" which is regularly observed in BWRs, but is seldom severe, arises from the close proximity (< 5mm) of the Zr alloy surface to another metal (stainless steel, Ni alloy or noble metal) which is cathodic to the Zr alloy. The enhanced conductivity under irradiation of the water, and of the normally electrically insulating oxide film on the Zr alloy allows significant galvanic currents to pass between the cathodic alloy and the Zr alloy, provided there is an electrical connection between the two somewhere in the system. The electrochemical potentials between the two metals persist in BWRs because of the generally oxidising state of the coolant, and the different efficiencies of the metals for redox reactions in oxygen containing water, Indig, 1989, Figure 2-6a and b). The amount of hydrogen added during hydrogen water chemistry in BWRs is insufficient to eliminate these galvanic potentials, particularly because of the low redox efficiencies of some of the alloys' surfaces. Noble metals are generally much more efficient than steels and nickel alloys, and so potentially could cause much larger shadow corrosion effects. These effects are not generally seen in PWRs because of the high dissolved hydrogen concentrations. However, a significant reduction in the dissolved hydrogen, coupled with excessive local boiling (even if the core as a whole remains sub-cooled) could change this.



In-reactor Core Bypass Platinum ECPs vs Day Since Reactor Startup (NWC)

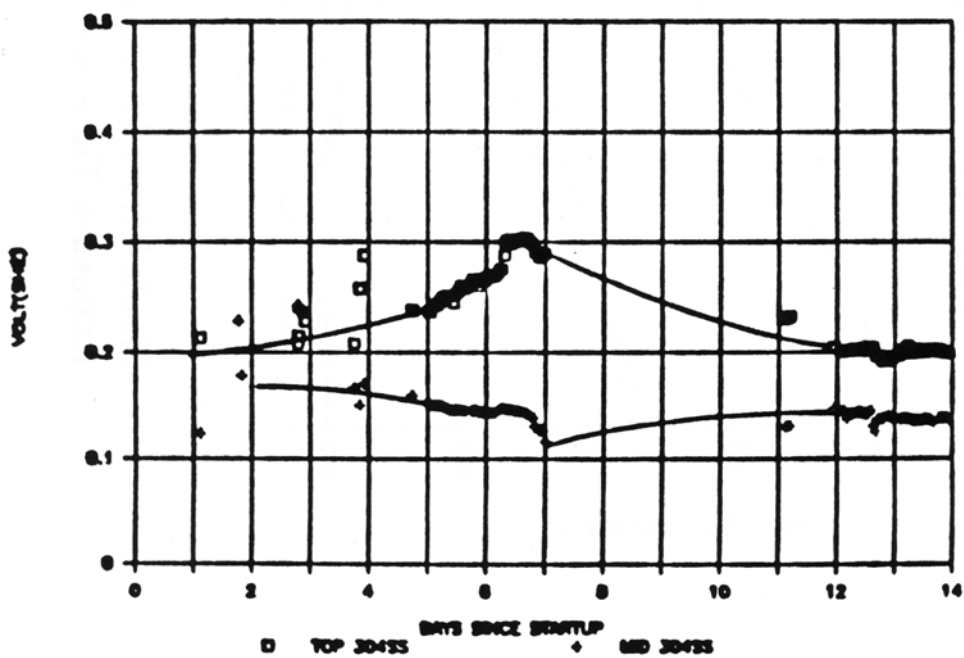


Figure 2-6: a) Pt and b) 304SS ECPs in the Core By-pass Region of Nine Mile Point-1. The plot shows ECP (V,SHE) against days since reactor startup for platinum and 304SS, Indig, 1989.

Nodular corrosion in BWRs appears to be a micro-version of shadow corrosion where the intermetallic particles are cathodic to the Zr matrix and generate enhanced oxidation around the intermetallics that develops into a heavily cracked nodule. Since galvanic effects are controlled by the cathode to anode area ratio, the size of the intermetallics becomes very critical in determining the size of the galvanic current, and hence the extent of the local (nodular) oxide growth, Cox, 2003.

So how might these two potential situations leading to enhanced corrosion appear during NMCA. The first one would require a significantly electrically connected layer of noble metal particles to develop adjacent to the Zr alloy surface. This might occur on the surface of the crud, as a layer within the crud, or at the crud Zr oxide film interface. Such a layer could act as the cathodic layer in a shadow corrosion scenario, but would need to be extensive enough to make electrical contact with the Zr alloy through some connection site such as the stainless steel bottom (or top) plate. Since the noble metal appears to be very mobile in BWR water, Figure 2-7, such a layer could arise from noble metal concentration in one region of the fuel (30in. above the lower end plug?). In general there is no excess hydrogen absorption during shadow corrosion, since the hydrogen is evolved at the cathode, and there is no metallurgical contact between cathode and anode that would allow it to diffuse into the Zr alloy. It is, therefore, evolved from the cathode into the water as dissolved hydrogen (or reacts with oxygenated species in the water).



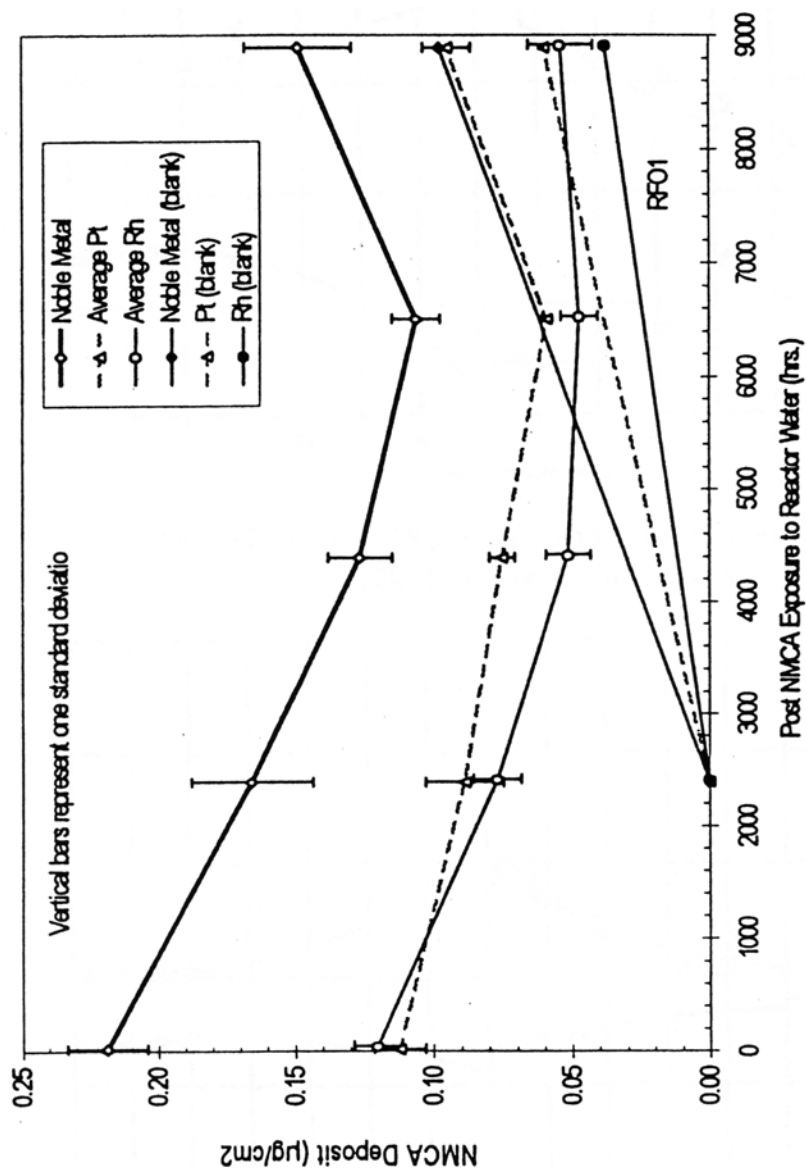


Figure 2-7: Noble Metal Loading Variation with Reactor Water Exposure Time in Duane Arnold.

The other possible scenario for NMCA effects is analogous to nodular corrosion. This would require noble metal particles to make good electrical and metallurgical contact with a clean Zr surface. The noble metal particle would then perform all the functions of a natural intermetallic particle in the alloy surface. It would be cathodic to the Zr matrix and would stimulate the formation of a "nodule" of thicker oxide around itself. In this instance, however, there would be both good electrical and mechanical contact between the noble metal particle and the Zr matrix so that it is possible that both enhanced corrosion and enhanced hydrogen pick-up would ensue. Note, however, that this is not the case for nodular corrosion in BWRs, where no enhanced hydrogen uptake is associated with severe nodular corrosion, and the excess hydrogen is apparently released as dissolved hydrogen in the water. This, suggests that a hydrogen diffusion barrier must form between the intermetallic particle and the Zr matrix that is a good electrical conductor (galvanic corrosion continues) but prevents hydrogen diffusion. This could be due to the formation of an oxide of the intermetallic metals that provide a hydrogen barrier (much as the intermetallic hydrogen storage powders become passive and do not pick up hydrogen without high temperature activation) but is electrically conducting, Hara, et al., 2003. Noble metals do not form such oxide films, which may be why the Zr/noble metal alloys tested picked up close to 100% of the corrosion hydrogen at high temperature, Cox, 1963, Figure 2-8. Unfortunately these were tested in low pressure steam rather than water, so it is not possible to tell whether they would be susceptible to both enhanced corrosion and enhanced hydrogen uptake. In his specimens with Pt rivets, Johnson, 1987, observed enhanced local corrosion around the noble metal implant, Figure 2-9 and saw both "localised corrosion and hydriding adjacent to the inserts", which suggests that hydrogen from the cathodic reaction on the platinum was entering the zirconium. Noble metal particles could only achieve this contact with the Zr matrix if they adhered strongly to the fresh cladding surface immediately upon insertion in the reactor. Even then the air formed oxide that is already present might be an adequate barrier to good metallurgical contact, although the good electrical contact would appear once irradiation started, because of the enhanced conductivity of the oxide, Shannon, 1962.

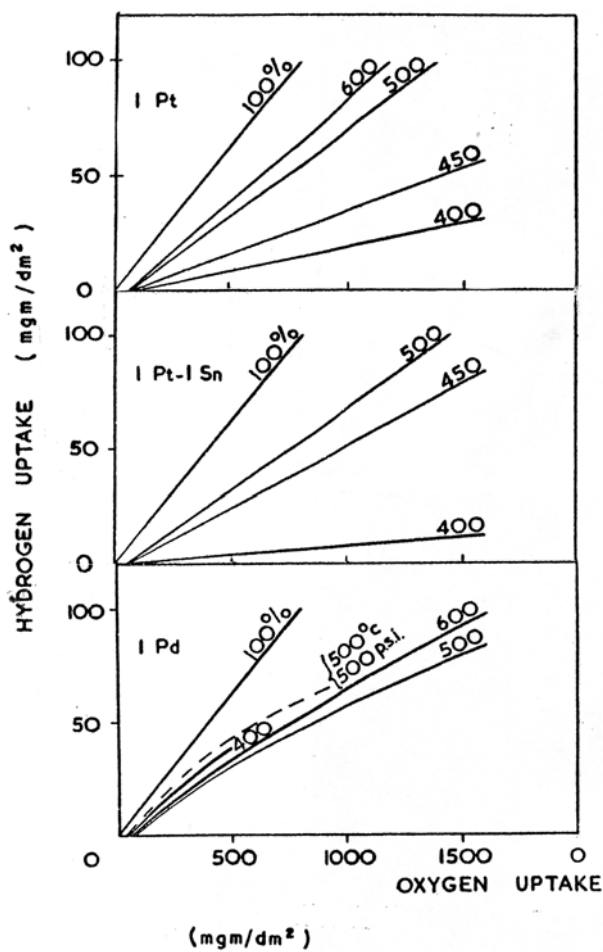


Figure 2-8: Hydrogen Uptake by Zr-1%Pt and Zr-1%Pd alloys.

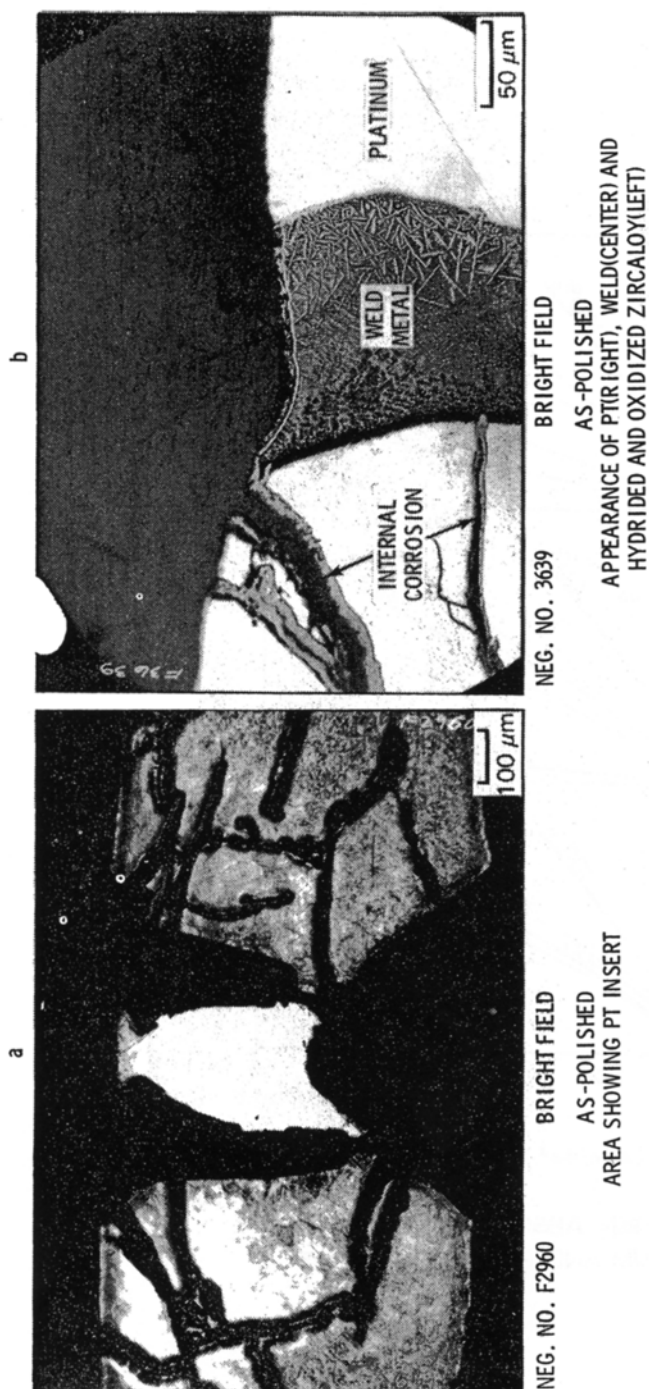


Figure 2-9: Corrosion and Hydriding Around Welded Pt Implants in Zircaloy.

#### 2.4 REASONS FOR ADDING ZN TO REACTOR WATER

Zn injection in BWRs arose from the serendipitous observation that BWRs with Admiralty Brass condensers tended to have lower pipe dose rates than those that had changed to Ti condenser tubes, or had never had brass tubes, Marble, 1986 and Niedrach and Stoddard, 1986. Laboratory tests determined that the addition of as little as 5ppb Zn to the water generated a more protective passive film on stainless steel surfaces than in its absence.

##### 2.4.1 Why add Zn to BWR water

The reduction in radiation dose rates on reactor piping was sufficient incentive in itself. However, some countervailing problems also had to be considered. The first was the enhanced  $^{65}\text{Zn}$  activity that would ensue, and the second was the potential to change the crud composition and to form hard crud layers that would return us to a CILC failure scenario.

The  $^{65}\text{Zn}$  activity increase was found to be negligible compared to the reduction in  $^{60}\text{Co}$  activity that resulted from the improved protective oxide on the stainless steel, Figure 2-10 which limited the escape of  $^{60}\text{Co}$  into the reactor water, and hence its transport to the external pipework, Niedrach and Stoddard, 1986.

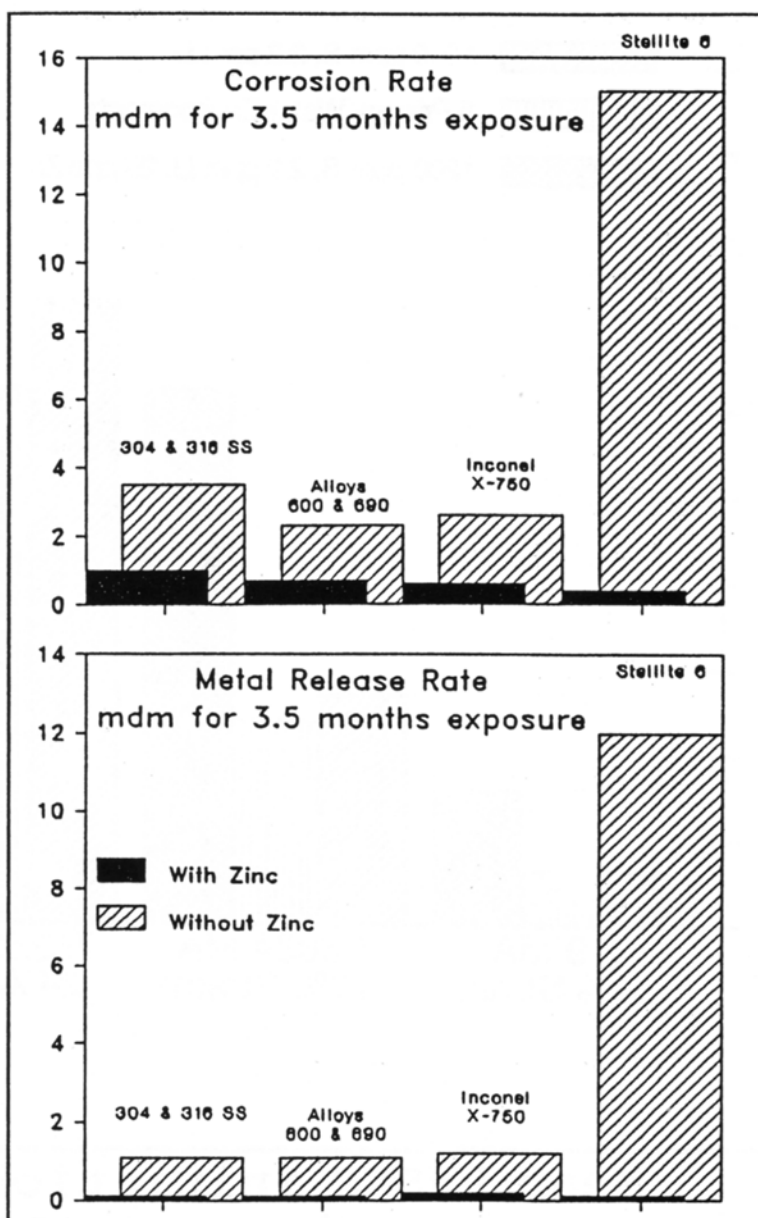


Figure 2-10: Reduced Corrosion and Metal Dissolution of S/S and Alloy 600 in PWR Water.

Studies of CILC failures strongly suggested that Cu in the crud was the primary factor, and that Zn played an insignificant part, Marble, et al., 1986. The precise effect of Zn on the passive film on stainless steel is far from clear, but nevertheless appears to be an established phenomenon.

### 2.4.2 Why add Zn to PWR water

The primary reason seems to be that if Zn additions were good for reducing radiation fields on BWR pipework, then the same had to be true for PWRs. The idea that in addition to improving the protective film on 304SS, Figure 2-10, it would also reduce Inconel 600 SCC in PWR primary coolant, Figure 2-11, seems to be based on a single piece of work, Esposito, et al., 1992. Countervailing arguments were based on the low solubility of zinc borate. Since this compound has a retrograde solubility, there was some concern that it might increase the observation of AOA in reactors using it. So far there is no evidence of this, and Zn concentrations are kept well below any possible level at which the retrograde solubility might initiate a feed back loop.

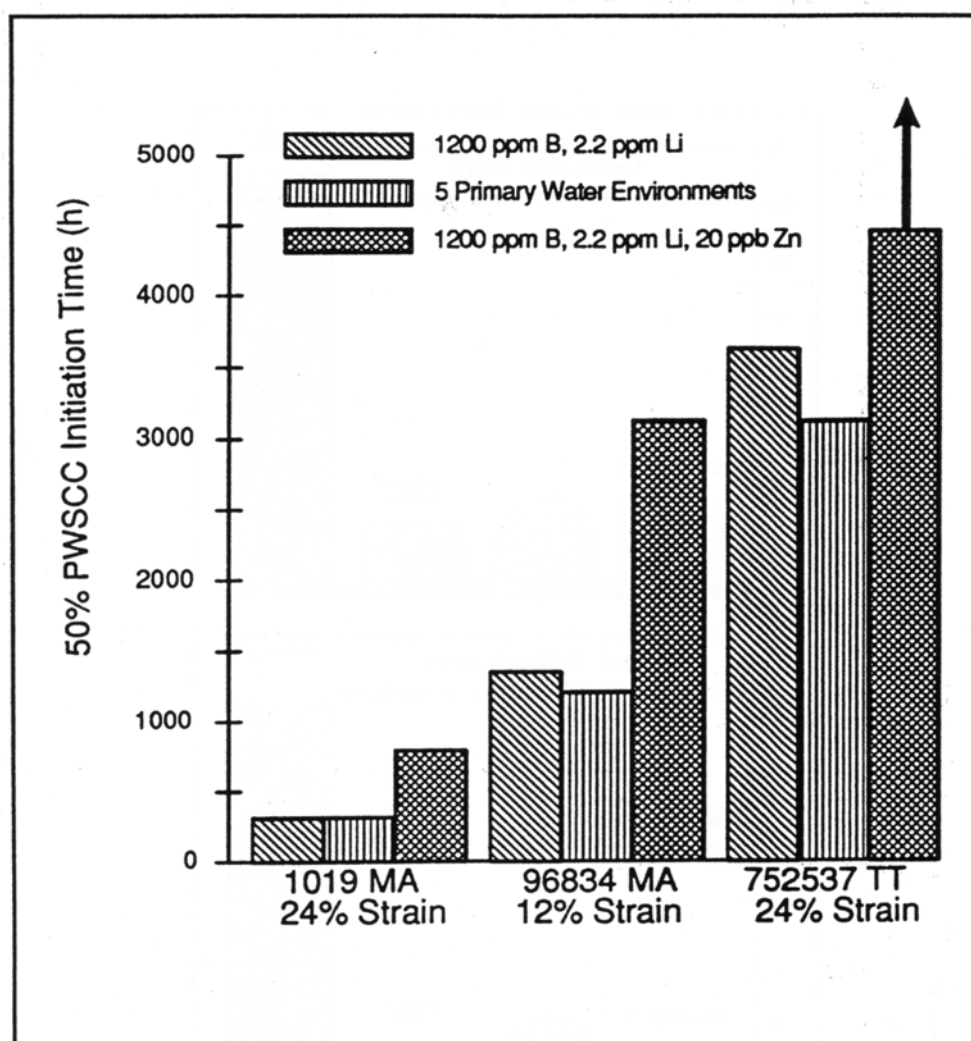


Figure 2-11: Increase in PWSCC Initiation Times with Zinc Additions.

## 2.5 *POTENTIAL EFFECTS ON CLADDING CORROSION*

No direct effects of Zinc on cladding corrosion have been reported. The deleterious effects of LiOH concentration as a result of boiling in thick oxide films on zirconium alloys, are mitigated by the presence of boric acid, Wikmark and Cox, 2001. The mechanism for this is thought to be the precipitation of a Li/Zr borate in the porous oxide which plugs the pores preventing the LiOH concentration process from developing. The low solubility of zinc borate may be an advantage here, if an even lower solubility salt occurs in the Zr/Li/Zn borate system. No studies of this system have been reported.

The only possible mechanism for deleterious effects of zinc additions on cladding corrosion would appear to be through changes in crud chemistry. If a hard crud layer was produced that allowed steam blanketing in cracks in the crud, then earlier concentration of LiOH in such cracks might lead to increased corrosion. A recent study, Kawamura, et al., 2003, examined any possible effects in an out-reactor loop that simulated BWR conditions as far as heat-flux and void fractions up to 5% were concerned. No irradiation was involved. Tests with and without 10ppb zinc showed no differences in either oxide thickness or hydrogen uptake. However, it must be remembered that phenomena like nodular corrosion and shadow corrosion cannot be induced in such a test without irradiation. However, as an initial result these tests are encouraging. In contrast, Walters, et al., 2002, using an in-reactor loop, demonstrated that corrosion product deposition on Zircaloy-4 was enhanced by Zn additions to the loop water, while deposition on other loop components was reduced. There was no heat flux on the Zircaloy specimens that would have shown whether the increased crud levels caused any enhanced corrosion by raising the clad surface temperatures. Foucault, et al., 2002, reported on a redeveloped loop that would study these effects under heat flux, but without irradiation. No results from this loop were available.



### **3 BWR EXPERIENCE WITH NMCA AND/OR ZN-INJECTION (AL STRASSER AND PETER RUDLING)**

As mentioned in section 2, NMCA are applied in BWRs to enhance the efficiency of Hydrogen Water Chemistry, HWC. The purpose of HWC is to minimise the crack growth of stress corrosion cracks in austenitic materials. However, in cases when rather high hydrogen injection rates are needed to attain a low potential of  $-230$  mV vs. SHE of the austenitic materials high radiation fields may result. Noble metal technology was developed to attain this low potential with only a slight hydrogen addition level that would not lead to this negative environmental impact.

One of the concerns with NMCA is the potential impact this water chemistry modification may have on fuel clad corrosion. It is well-known that metallic nickel plated on zircaloy may act as a hydrogen window that may increase the hydrogen pickup significantly. It is not clear today if the Pt and Rh that also plates out on the fuel cladding will also increase hydrogen pickup. Increased hydrogen pickup may at some critical hydrogen clad concentration accelerate corrosion. The results of examinations of fuel cladding operated in plants with NMCA are interpreted by GE and GNF as follows: "Data from the highest noble plant metal plant input to date shows the cladding lift off values to be within GE's experience base after NobleChem™ operation at a high exposure of up to 53 GWD/MTU". Hettiarachchi, 2003. The statement omits to say that that this plant had *higher* lift off than the experience base after 2 cycles and that other plants (with less than the highest NM input) have lift offs *higher* than the GE experience base at extended burnups. The GE author believes that the oxide measurements made during pool examinations are incorrect because they are not corrected for magnetic effects and the spalling that is observed is crud and not oxide. They have not been able to capture and analyze a piece of the spalled material and this remains a much debated issue.

GE's opinion is based partly on preliminary data of cladding samples examined in a hot cell after 3cycles (4.5 years) of operation in Duane Arnold. Cladding corrosion is reported to be  $27$   $\mu\text{m}$  max. (normal) and the crud "thicker and porous". Metallography showed "low" hydrogen levels and there was no indication of hydride concentrations by neutron radiography.

The idea about zinc injection was conceived by GE in 1983, after observing a correlation between low pipe dose rates and presence of elevated zinc (and copper) levels in the reactor water due to presence of admiral brass condensers in some older BWR plants. The laboratory experiments showed that 5 ppb zinc was providing a more protective oxide film on stainless steel than no addition. The oxide growth and incorporation of Co-60 into the oxide film on the stainless steel materials would consequently be reduced, thus decreasing radiation plant buildup. There was however also a concern related to Zn-injection, since the earlier CILC failures that haunted some BWRs in earlier days was observed in plants with elevated Cu and Zn coolant concentrations due to their brass condensers. The first test in a commercial BWR plant was performed already at the first start-up of the Hope Creek plant in 1986 with a target RW level of 7.5 ppb, Lovell, et al., 1988. The pipe dose rates were also quite low in Hope Creek after 0.8 cycles, some 2 – 3 times lower due to a much lower amount of Co-60 on the surfaces. In general, the Zn-65 did not cause problems, but high iron input and unavailability of the RWCU during the end of the first cycle lead to extreme levels of particulate crud high in Zn-65, Wood, et al., 1989. Subsequent operation with only 2 ppb zinc in the reactor water during the following cycle did not produce good activity suppression, which lead to the conclusion that the zinc level should be higher. During subsequent additions – Millstone-1 and Nine Mile Point-2 implemented zinc injection in 1987 and early 1988, respectively – care was taken to have a low iron input, i.e.  $\leq 2$  ppb in the feed water. Furthermore, the problems with Zn-65 activity also started development to inject zinc depleted in Zn-64 down to about 5% or below, DZO, hence possibly reducing the problem of Zn-65 by a factor of 10 or more, Marble and Cowan, 1991.

The experience with Zn injection alone represents 280 reactor years of experience without accelerated cladding corrosion according to GE. Duane Arnold operated with a combination of Zn injection and NMCA and the hot cell examination results indicated normal cladding corrosion as noted above. However, there does appear to be an effect on crud that had up to 25% Zn in that plant. GE believes that Zn in combination with NMCA changes the crud structure and that this type of crud has a tendency to flake off. The implication is that the “oxide” flaking observed with some NMCA treated fuel is the result of this effect.

(GE declined to comment on the effect of Zn at River Bend CY 11, since their fuel was not involved.)

### 3.1 *IMPACT OF NMCA AND ZN-INJECTION ON STAINLESS STEEL/NICKEL BASE AND ZIRCONIUM ALLOYS*

#### 3.1.1 **NMCA impact**

##### 3.1.1.1 *SCC Propagation and Monitoring Experience in BWRs*

During the verbal presentation of the paper, Hettiarachchi, 2003, the author showed data that indicated continued crack growth in stainless steel components during NMCA operation. While some of these were thought to be due to interruptions in the application of HWC, the author indicated that the crack length data measured in '94 and '96 may not be reliable due to old equipment and measurement errors (the data are "too high"), but the next set made in '02 with new equipment are reliable. *With only one reliable point on a measurement curve, however, this means that current in-plant crack length propagation data trends are not reliable.* The data shown in the verbal presentation were not reproduced in the printed paper and will not be published for another 6 months to a year.

There are several crack length inspections scheduled for '04 and '05 and GE believes that by '05 they will have reliable in-plant data on the effectiveness of the NMCA/HWC treatment on crack growth. The only plant doing inspections on a regularly scheduled basis at each refueling shutdown is KK Mühleberg; cracks in their components have been growing (based on inspections with "good" equipment) and GE does not have an explanation for it.

The paper, Hettiarachchi, 2003 also warned that some of the indirect monitoring methods of NMCA effectiveness might be misleading.

- Dissolved oxygen (DO) measurements should not be used as a replacement for ECP measurements. As examples, at zero DO in the recirculation piping of one plant the ECP was only -80 mv at 0.5 ppm H. In another US BWR4, at zero DO the ECP was +100 mv in the lower plenum at 0.8 ppm H, due to the fact that H<sub>2</sub>O<sub>2</sub> penetrates down there. The ECP measurements are plant and location specific.
- Main steam line radiation levels (MSLR) as a function of ECP vary considerably from plant to plant and should be used with caution as a measure for SCC mitigation.
- Maintaining H availability is important. If H is interrupted in an HWC environment the ECP will increase and the magnetite coating on the stainless steel will transform to hematite. When H is turned on again in a non-NMCA plant, it will take 24 hours to return to the low ECP again, because it takes time for the reverse transformation. In the presence of Pt the return to the low ECP is rapid. The reverse transformation from hematite to the spinel magnetite is accompanied by an increase in water conductivity as the result of the release of Fe<sup>2+</sup> and OH<sup>-</sup> ions.

Another paper, Yeh, et al., 2003, proposed that ECP itself can not be used as the sole indicator of SCC mitigation as discussed next under "Experimental Work".

### 3.1.1.2 Effect of NMC on SCC Crack Propagation --- Experimental Work

The effect of platinum treatment on the IGSCC of Type 304 stainless steel was evaluated by electrochemical polarization and crack growth (CGR) tests, Yeh, et al., 2003. These ex-reactor test conditions were:

- Sensitized and pre-oxidized Type 304 with and without Pt treatment,
- Loop with 288<sup>0</sup> C pure water,
- Molar ratios of H/O: 0 (with no H), 0.5 (10 ppb H) and 2.7 (50 ppb H),
- Dissolved oxygen (DO) contents of 50, 150 and 300 ppb,

The objective of the low H/O ratios and high DO levels was to simulate conditions at the reactor exit where much of the H has been removed by gas stripping and the radiolytically produced H<sub>2</sub>O<sub>2</sub> has decomposed. NMC operation is recommended at H/O levels of >2.0.

The results of the polarization tests shown in Table 3-1 indicate that the Pt treated specimens had a lower ECP at DO levels of 50 and 150 ppb, but higher at 300 ppb and that their corrosion current density was consistently higher at all DO levels. This would indicate that *the ECP should not be used as the sole indicator for evaluating the IGSCC behavior of Type 304.*

Table 3-1: Corrosion Data Obtained from CGR Tests, Yeh, et al., 2003.

Specimen	[O <sub>2</sub> ] <sub>dis</sub> (ppb)	Corrosion Potential (mV <sub>SHE</sub> )	Corrosion Current Density (μA/cm <sup>2</sup> )
P-1	50	-152	0.28
C24-1	50	-223	0.62
P-2	150	-49	0.48
C24-2	150	-148	0.89
P-3	300	57	0.63
C24-3	300	175	1.14

(P = untreated specimen, C = Pt treated specimen)

The results of the CGR tests appear inconsistent. Tests with 300 ppb DO shown in Table 3-2 indicate that at the 300 ppb DO level an H/O of 2.7 is insufficient to protect the Pt treated specimens from IGSCC, in fact the untreated specimen was unaffected! Also the reactor location where these H/O and DO combination might exist is not clear either.

Table 3-2: Results of CGR Tests, Yeh, et al., 2003.

Specimen	[O <sub>2</sub> ] <sub>dis</sub> (ppb)	[H <sub>2</sub> ] <sub>dis</sub> (ppb)	Test Duration (hours)	Crack Growth Duration (hours)	Maximum Crack Depth (hours)	Average CGR (cm/s)	True CGR (cm/s)
P-4	300	0	472	-	130	$0.8 \times 10^{-8}$	-
C12-4	300	0	472	-	900	$5.3 \times 10^{-8}$	-
C24-4	300	0	472	-	430	$2.5 \times 10^{-8}$	-
P-5	300	10	665	275	1240	$5.2 \times 10^{-8}$	$12.5 \times 10^{-8}$
C12-5	300	10	665	425	950	$4.0 \times 10^{-8}$	$6.2 \times 10^{-8}$
C24-5	300	10	665	425	890	$3.7 \times 10^{-8}$	$5.8 \times 10^{-8}$
P-6	300	50	672	-	0	0	-
C12-6	300	50	672	432	270	$1.1 \times 10^{-8}$	$1.7 \times 10^{-8}$
C24-6	300	50	672	432	1450	$6.0 \times 10^{-8}$	$9.3 \times 10^{-8}$

(P = untreated, C = Pt treated)

This particular laboratory has been reporting laboratory experiment data on the effects of noble metals for several years, much of it contradictory to GE and Japanese results on similar topics. A careful audit of the results and experimental procedures used would be needed to evaluate the validity of the results.

An excellent paper, Andresen, et al., 2003, describes the mechanistic role of corrosion potential as it influences crack chemistry and in turn the SCC growth rate. The author emphasized that crack chemistry and not high ECP controls SCC.

Characteristics of the crack chemistry indicate there is a steep gradient of oxygen that decreases rapidly from the mouth of the crack to its tip, so that presence of a catalyst at that location can be very effective as shown in Figure 3-1. Throwing power” of Pd (presumably similar to Pt and Rh) was estimated at 0.1 – 0.5 mm, the distance the catalyst can be effective.

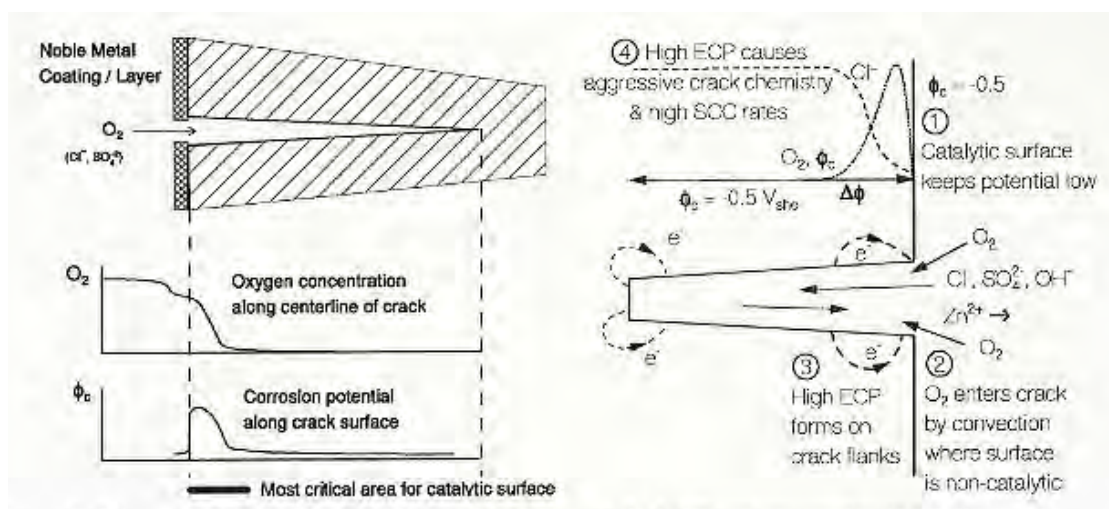


Figure 3-1: Schematic Diagrams Showing that Electrocatalysis on the Boldly Exposes Surface is not Adequate to Mitigate Crack Chemistry and SCC if Occidents can Penetrate More Deeply into Crack, Andresen, et al., 2003.

An important issue discussed was what role, if any, convection has in a crack, which in turn could result in a high corrosion potential all the way to the tip of the crack. Ion migration and ordinary diffusion appear to be controlling, rather than convection, and the corrosion profile in the crack is controlled by the oxygen diffusion into the crack and its consumption by H or catalytic processes.

The crack growth rates under various non-catalytic and catalytic conditions have been characterized as shown on Figure 3-2. The effect of NMCA is shown on Figure 3-3 where crack growth rate on a CT specimen is measured first under excess H conditions followed by application of NMCA at 4,427 hours which consumes all O present. The decreased crack growth rate shows catalytic behavior.

## **4 PWR EXPERIENCE WITH ZN-INJECTION (TO REDUCE ACTIVITY BUILDUP AND PIPE CRACKING)**

### *4.1 PWR WATER CHEMISTRY RELATED FAILURES*

Table 4-1 gives an overview on the PWR failures from the last years which probably have been caused by interaction with the primary coolant. All these failures were obviously due to excessive CRUD. The general problem for the root cause analysis is that only very little is known e.g. on water chemistry of the plants and on the detailed power distribution.

In TMI during cycle 10 (1995) nine fuel rods failed 122 days after BOC. The failures were connected with larger depositions in areas of lower flow velocity on the periphery of fuel assemblies close to the spacer. In such areas the crud deposited was thick enough to increase cladding temperatures greater than  $T_{sat}$  and to cause steam formation. The increased thermal resistance resulted in a significant rise in temperature across the crud layer. The increased temperature caused a large increase in the corrosion rate and hydrogen pickup by the cladding. The defects were probably initiated at the beginning of cycle where high soluble boron levels and a relatively low Li level existed. This condition led to a low pH at BOC (below 6.9). Such a low pH increases the general corrosion of the primary circuit materials and the loss of Ni and Fe to system, Mitchell and Thomazet, 1998.

In Seabrook during cycle 5 (1997) 5 high enriched (4.8%) fuel rods failed at burnups between 25 and 30 MWd/kgU. The failed rods, all IFBA rods with ZIRLO cladding, were internally located adjacent to thimble tubes. The rods were the highest power rods in the core ( $F_{xy} = 1.35$ ) during most of the cycle. Inspection shows clad breaches and dense and fairly adherent CRUD with some spalling in the top grid spans. Non IFBA rods exhibited CRUD as heavy as IFBA rods but experienced a different power history, Nucleonics week 5.5.97, 19.5.97, and 16.5.97.

In Palo Verde 2, in cycle 9 (2000) eleven one-cycle Zr-4 (OPTIN cladding) rods failed. Primary defect occurred in span 8-9. AOA was experienced early in cycle 9. A mid-cycle shut-down produced a reversed AOA situation, i.e. the previously low relative power in the upper core now had a significantly higher than predicted power resulting in fuel failures 3 months after the MCO. All but one rod were high-duty peripheral rods. All rods showed significant tenacious crud deposits in grid spans 7 – 9.

High CRUD deposits are generally to expect on high power rods with a high steaming rate, when the corrosion product load (Fe and Ni) is high. High corrosion product loads can occur if the pH is low or if oxygen in the SG is high, e.g. due to residue oxygen in dead ends or due to leaks. A possibility to measure the oxide content before the coolant enters the core, as it exists in the Siemens designed PWRs, would be helpful to detect any oxygen in the SG. The usual measurements of the oxygen in the cleanup system, after the coolant has passed the core and all oxygen has reacted with hydrogen by radiolysis, can not give security for a low oxygen content in the SG. Conclusions from the radioactive isotope Ar, formed in the core from Ar entering with air are also not very conclusive. Probably a corrosion potential measurement device (potential between SS and Pt) could be installed at a position before coolant enters the core. The use of excessive amounts of hydrazine during start up as used in some European PWRs could also be considered to reduce the oxygen content in the system after BOC as fast as possibly. High Ni contents may be the consequence of oxygen or of low pH values. Thus intentions exist to keep the pH not only as high as possible with 3.5 ppm LiOH but constant over the whole cycle at 7.2 to 7.4 (at operation temperature).



Table 4-1: Summary of previous PWR failures, see previous ZIRAT-reports.

Nuclear unit	Zn-injection	Corrosion effect
TMI-1, Cy 10, 1995 <sup>5</sup>	No	<p>High rod peaking factors CRUD/corrosion related failures. Nine Zr-4 Cladding fuel rods failed after 122 days of operation. All failed and degraded pins reportedly had DCP Distinctive Crud Pattern <sup>6</sup></p> <p>High peaking factors, thermal-hydraulic conditions. Calculations indicated that no boiling should have occurred on the pins with DCP, although the pins with DCP were calculated to have a slightly higher temperature. Water chemistry (low pH at BOC, pH &lt; 6.9, max LiOH 2.2 ppm). Some AOA effect was found reaching a maximum in the middle of cycle 10. The source of the crud could not be determined. The crud sampling showed that the nickel-to iron ratio was in the range 1.25 to 16.7, which was reportedly somewhat lower than in previous investigations.</p>
Seabrook, Cy 5, 1997 <sup>7</sup>	No	Five one-cycle ZIRLO rods failed. Longer cycle in transition to 24-month cycle. Possibly crud-induced overheating resulting in substantial nucleate boiling
Palo Verde 2, Cy 9, 2000 <sup>8</sup>		Eleven failed one-cycle Zr-4 (OPTIN cladding) rods. Primary defect in span 8-9, secondary hydrides in span 2-4. AOA was experienced early in cycle 9. A mid-cycle shut-down produced a reversed AOA situation, i.e. the previously low relative power in the upper core now had a significantly higher than predicted power resulting in fuel failures 3 months after the MCO. All but one were high-duty peripheral rods, and significant tenacious crud deposits were observed in grid spans 7 – 9 on all rods.

<sup>5</sup> For more details, see section 5.6.2 in ZIRAT-6 Special Topical Report, “Water Chemistry and Crud Influence on Cladding Corrosion”, by Wikmark and Cox, 2001.

<sup>6</sup> This acronym implies that the fuel inspection revealed crud deposits on the fuel rod and that the deposits were uneven in the rod circumference

<sup>7</sup> For more details, see ZIRAT-6 Special Topical Report, “Water Chemistry and Crud Influence on Cladding Corrosion”, by Wikmark and Cox, 2001.

<sup>8</sup> See section 9.2.1.1 in ZIRAT-6, Annual Report for more details.

## 5 DISCUSSION AND SUMMARY

NMCA additions are being made in 26 BWRs with the aim of improving the efficiency of stainless steels to electrochemical processes, thereby reducing the ECP of these components to a point where stress corrosion cracks fail to propagate. It remains unclear whether or not these aims are being achieved. However, at the same time concerns have been raised about whether or not fuel cladding corrosion and hydrogen uptake could be accelerated by NMCA. There are plausible mechanisms by which such accelerations could occur, and it is known that much of the noble metal that is added eventually ends up on the cladding surfaces. So far, there are no well established instances of accelerated corrosion, but there have been some worrying incidents that are presently awaiting hot-cell examination.

Suggestions that NMCA might also aid in suppressing crack growth in I-600 components in PWRs operating in the Low Hydrogen Water Chemistry regime are presently unsupported by experimental evidence. Thus, NMCA should not be pursued in PWRs unless definite evidence of a benefit is found.

Recent GE data challenges the effectiveness of NMCA to mitigate cracking in Fe and Ni alloys. This since continued crack growth in stainless steel components during NMCA operation occurred in some recent experiments. Furthermore, it was indicated that the crack length data measured in '94 and '96 may not be reliable due to old equipment and measurement errors (the data are "too high"), but the next set made in '02 with new equipment are reliable. With only one reliable point on a measurement curve, however, this means that current in-plant crack length propagation data trends are not reliable. There are several crack length inspections scheduled for '04 and '05 and GE believes that by '05 they will have reliable in-plant data on the effectiveness of the NMCA/HWC treatment on crack growth. The only plant doing inspections on a regularly scheduled basis at each refueling shutdown is KK Mühleberg; cracks in their components have been growing (based on inspections with "good" equipment) and GE does not have an explanation for it.

Apparently, indirect monitoring methods of NMCA effectiveness might be misleading.

- Dissolved oxygen (DO) measurements should not be used as a replacement for ECP measurements.
- Main steam line radiation levels (MSLR) as a function of ECP vary considerably from plant to plant and should be used with caution as a measure for SCC mitigation.

Also, ECP measurements should not be used as the sole indicator for evaluating the IGSCC behavior of Type 304 since crack chemistry and not high ECP controls SCC.

Protective inhibiting coatings (PIC – a GE acronym) are being developed as a potential alternate or additive measure to NMCA for protection of stainless steel components against SCC. The ceramic coatings are applied only locally at SCC sensitive locations and not the entire piping systems or core internals. Since NMCA is not effective above the feedwater line, this could have special application in such locations; some locations are not accessible to the coating application process so there are some limitations to system locations where they might be applied. This is clearly a developmental idea and process; there are no plant demonstrations planned at this time.

The fuel clad oxidation data up to date indicate that cladding lift off values lies within GE's experience base after NMCA operation at a high exposure of up to 53 GWD/MTU. However, plants with NMCA tends to have lift offs *higher* than the GE experience base at extended burnups. GE believes that the oxide measurements made during pool examinations are incorrect because they are not corrected for magnetic effects and the spalling that is observed is crud and not oxide. Another concern with NMCA is the potential impact this water chemistry modification may have on fuel clad hydrogen pickup fraction. Increased hydrogen pickup may at some critical hydrogen clad concentration accelerate corrosion. Up to now, very limited hot cell data exists. Preliminary data of cladding samples examined in a hot cell after 3cycles (4.5 years) of operation in Duane Arnold, showed cladding corrosion to be 27  $\mu\text{m}$  max. (normal) and the crud "thicker and porous". Metallography showed "low" hydrogen levels and there was no indication of hydride concentrations by neutron radiography. Clearly, more data are needed to assess the potential impact of NMCA on fuel clad corrosion and hydrogen pickup.

Zn additions in both BWR and PWR primary coolant reduce radiation fields, whether or not they modify crud morphology to produce hard crud layers that could trigger possible CILC-type fuel cladding failures remains unknown. However changes in crud properties with Zn additions have been observed.

Summarising the published BWR data, it appears that in all the reported cases with accelerated fuel clad corrosion (sometimes leading to fuel failures), either Zn-injection and/or NMCA has been applied, Table 3-3. However, this does not mean that these water chemistry changes always leads to corrosion acceleration. Only in US more than 30 BWR plants are applying Zn-injection and more than 25 plants have implemented NMCA while Table 5-1 only lists 9 plants with Zn-injection and/or NMCA that experienced accelerated corrosion. There are consequently a large number of plants that most likely have not experienced any corrosion acceleration. Thus, the data implies, that whether the plant is applying NMCA and/or Zn-injection or not is not enough to cause corrosion acceleration. Some other parameters must also be involved impacting the corrosion rate.

Table 5-1: Summary of recent cases when accelerated BWR corrosion have been noted.

Reactor	Year of Corrosion Assessment	NMCA, g/m <sup>2</sup>	Zn-injection	Corrosion status
KKL	1998	No	Yes	A few rods of LK 2 type failed due to ESSC
Duane Arnold	1997, 1999, 2001	Yes, 1996 and 1999	Yes	Mild increase in clad corrosion after 1 and 2 NM cycles, oxide spallation after three NM cycles
River Bend CY8	1999	No	Yes	> 12 GE11, P6, 1st cycle fuel rods failed
Peach Bottom 2	Sept. 2000	Yes, Sept. 1998	No?	Increased corrosion and spallation after 1 NM cycle
Vermont Yankee, CY22	2002	Yes, April 2001 (EOC 21)	Elevated Cu and Zn (Brass condensers)	5 GE13B, P6, 2nd cycle fuel rods failed (1 NM cycles)
River Bend CY11	2003	No	FW 0.3-1.0ppb	6, ATRIUM-10, LTP, 1st cycle fuel assemblies failed
Hatch 2	EOC16 (1NM cycle) and EOC 17 (2NM cycles, 2003)	Yes, EOC 15 (2000)	RW 5 ppb	Higher oxide thickness values than expected after 1NM and 2 NM cycles; Oxide spallation on 3xburned fuel after 2 NM cycles
CGS	EOC15	No	Yes, CY12-15	EOC 15 - Higher oxide thickness values than expected on LK 2, 2+ and 3 claddings
Browns Ferry-2	EOC12, 2003	Yes, EOC 11, 2001	Yes	63 GE13B, P6, 2nd cycle fuel assemblies failed

## 6 APPENDIX A

The information provided in the Appendix are extracted from the ZIRAT-6 Special Topical Report by Wikmark and Cox, 2001.

### 6.1 OBSERVATIONS AND THEORY

The fuel crud deposition phenomenon does include seven different steps, as follows, Berry and Diegle, 1979.

- Generation (of corrosion products)
- Release (of corrosion products, due to dissolution, erosion or scaling)
- Transport (by the coolant)
- Deposition on the fuel elements
- Release from the fuel element
- Transport by the coolant
- Deposition on, or incorporation in, system surfaces

In the following, we will discuss the various phenomena in this listing for both PWRs and BWRs.

#### 6.1.1 Crud Sources

##### 6.1.1.1 Corrosion and Corrosion Release

Corrosion is the process by which the environment will degrade a material. More specifically for metallic materials, this involves the process by which the metal is oxidised by the environment. During the metal oxidising process, oxides or salts are formed. If the formed oxides or salts have a high solubility in the corroding environment, or inferior physical forces between the corroding surface and the solid corrosion product exist, there will be a considerable corrosion release, i.e. dissipation of the formed corrosion products to the surrounding. If the solubility is low or the physical interaction force is high all or a large part of the formed corrosion products are left (or re-deposited) on the corroding metal. A special case occurs when the formed corrosion product is forming a dense and protecting layer impeding further corrosion attack. The formed corrosion film is then called a passivating film, since it hinders and in some cases almost inhibits further corrosion attack.

It should be clear when we discuss corrosion that corrosion is never controlled by thermodynamics, but always by the kinetic rate of the corrosion process. This rate is normally controlled by one or several chemical reaction rates. Any thermodynamic treatment of the corrosion behaviour will hence only give an understanding what chemical transformations are possible, and what the final, asymptotic goal will be for a certain material in a certain environment. The corrosion process will, however, in most cases never reach that goal in the lifetime of the plant. This is also what we rely on: that only a few tens of micrometers of the stainless steels or Zircaloy structural material will be consumed within 5 to 40 years in operation.

The use of virtually every material in the LWRs is based on the principle of a passive corrosion film. Hence, even such metals as zirconium alloys, which are thermodynamically very unstable, and react almost explosively with water even at room temperature, are protected from aggressive corrosion attacks by a very dense and relatively impervious film of corrosion products, IAEA TECDOC-996, 1998. This means, of course, that any chemical or physical effect on the protective film will pose a considerable potential risk for very quick corrosion attack of the material. This could threaten the structural integrity, of, for instance, Zircaloy cladding or carbon steel piping, but this is not the scope of this review, and is not further discussed, except of some special cases regarding effects on zirconium alloys.

Accelerated corrosion is, however, important in the present context since this could lead to excessive corrosion release, resulting in elevated corrosion product input to the RPV and thus threatening to deposit on the fuel in excessive amounts. It must be pointed out that increased corrosion does not necessarily lead to increased corrosion release, but is a matter of the actual materials and the environment. By this, we should also be aware that changes, even small changes, in the environment, could affect the corrosion rate and the corrosion release considerably. Temperature, pH, oxidising potential (i.e. whether excess of oxidising or reducing species are available in the environment, i.e. coolant in our case), and specific impurities are important factors in determining the corrosion rate and corrosion release.

The corrosion release could be in the form of ions dissolved, that is, the corrosion product release given by expressions like (Eq. 6-3) – (Eq 6-5), which is the actual case for iron release from magnetite films in reducing environments. In other cases, the release could be in the form of colloids or small particles, as is often the case with rust, i.e. release of oxidised iron compounds from carbon steels in more oxidising conditions. The corrosion release could also be in the form of scales, that is flakes of oxide released to the environments, as is normally the case for corrosion release from Zircalloys. In the latter case, the oxide flakes could remain as flakes, then being able to produce extreme radioactive hot-spots if released from radioactive materials. They could also in such a case form a physical hinder to flow, if the flakes stick in narrow locations. Flakes could also, at least in principle, be transported as flakes, in a new local environment become soluble, and hence release the corrosion products in a different form in the new location.

Most materials in the LWR, carbon steels (in feed water piping etc.), low-alloy steels (in turbine system piping), stainless steels (in RHR piping), nickel-base materials (Inconel, Alloy 600, etc. in in-core components and PWR steam generators), Stellite (in valves), and zirconium alloys (in fuel cladding and BWR flow channels) rely on the principle of a passivating oxide film. This is also why the water chemistry of the PWR is adjusted with lithium and hydrogen, i.e. to have the best possible passive film and lowest possible corrosion release (of the nickel base material in the steam generators). The passive films are sometimes of constant chemical composition, as for the corrosion film on zirconium alloys, IAEA TECDOC-996, 1998, or a double layer, with the inner layer being a diffusion barrier, and the outer a protection against attack of the environment on the diffusion barrier, as for stainless steels, Robertson, 1991.

The passive film is in reality always a barrier against mass transport, i.e. hinders the release of oxidised ions (for all steels and nickel base alloys) or intrusion of oxidants (for zirconium alloys). The corrosion attack and corrosion release,  $r_{corr}$ , is therefore depending on the oxide film thickness under otherwise constant conditions. This dependence is often given by the inverse square or inverse cube of time, as shown in Eq. (6-1).

$$r_{corr} = k_{corr} \cdot t^{-n} \quad n = 0.33 - 0.5 \quad (6-1)$$

A typical example is shown for Inconel in simulated BWR environment in Figure 6-1.

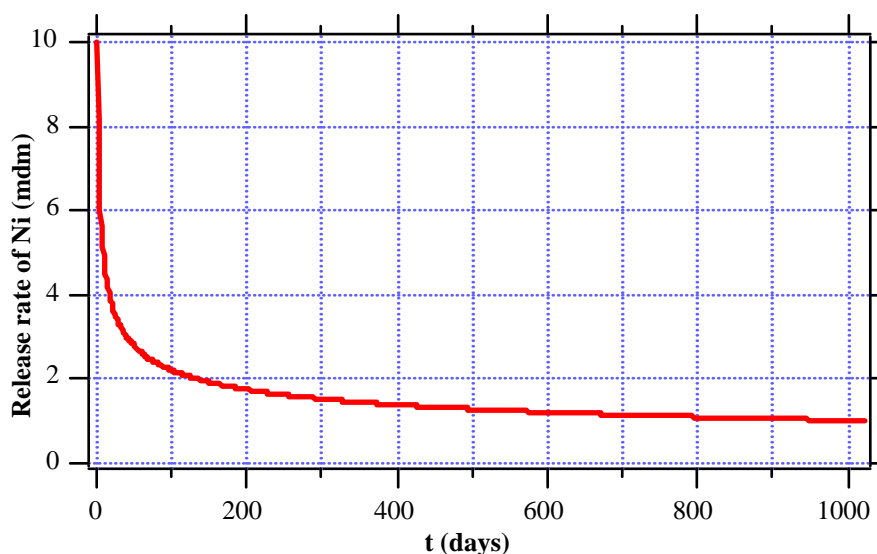


Figure 6-1: Corrosion release from Inconel X-750 in BWR environment. Data from Hemmi, et al., 1994.

## 7 APPENDIX B - ELECTROCHEMICAL DEFINITIONS (BRIAN COX)

- **ELECTROLYTE:-** A solution (usually aqueous) that contains enough charged ions to be a reasonable conductor of electricity.
- **ELECTROCHEMICAL POTENTIAL (ECP):-** The potential (in Volts) of a metal in an electrolyte measured relative to a Reference Electrode (e.g. Standard Hydrogen Electrode).
- **STANDARD HYDROGEN ELECTRODE:-** Typically a platinum wire immersed in an electrolyte through which hydrogen is bubbled at standard temperature and pressure (20°C, 1 atm.). This maintains a constant reference potential that is arbitrarily defined as zero on the electrochemical potential scale.
- **REVERSIBLE HYDROGEN POTENTIAL:-** Under other conditions of temperature and pressure a hydrogen electrode will give a non-zero potential on this scale referred to as the Reversible Hydrogen Potential for that particular temperature and pressure.
- **OPEN CIRCUIT POTENTIAL:-** the potential achieved by a metal at equilibrium following immersion in an electrolyte, when there is no externally applied current.
- **POLARISATION CURVE:-** A plot of the current versus voltage measured by slowly varying the voltage applied to a metal immersed in an electrolyte. The voltage should be varied both anodically and cathodically with respect to the open circuit potential. The shape of the curve gives an indication of when oxidation and reduction reactions occur.
- **ANODIC REACTION:-** this is a reaction in which some component of the system is oxidised by the the passage of an electric current which makes its potential positive with respect to the open circuit potential. (e.g. Zr will grow oxide films anodically).
- **CATHODIC REACTION:-** The opposite of the above, in which some component of the system is
  - reduced by the passage of a current at a negative potential.



- **GALVANIC REACTIONS:-** When two dissimilar metals are electrically connected in an electrolyte one metal will adopt a positive potential (anode) with respect to the other
  - more negative metal (cathode). A current can then pass such as to oxidise the anodic
  - metal and reduce the cathodic metal ( or reduce protons to hydrogen atoms on it). This sort of galvanic reaction is the basis of "Shadow Corrosion" in BWRs.
- **NOTE-1:-** The relatively pure water in BWRs is a poor electrolyte, but radiolysis in
  - reactor can produce enough charged species for galvanic currents to pass.
- **NOTE-2:-** In PWR coolant the high dissolved hydrogen contents cause all metals to be at the RHP. So there is no Shadow Corrosion.
- **NOTE-3:-** All normal metals are collections of small crystalline grains. The size, shape, and relative orientation of these depends on fabrication. Because of the misorientation between adjacent grains, the boundaries between them are disordered, and therefore more reactive than the grains. Impurities may also segregate in the disordered grain boundary regions

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