Early Hydrogen Water Chemistry Injection in Boiling Water Reactors

Impact on Fuel Performance and Reliability

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ABSTRACT

Early injection of hydrogen during plant startup has been proposed to further mitigate intergranular stress corrosion cracking (IGSCC) in boiling water reactors (BWRs). To assess the effectiveness of early hydrogen water chemistry (EHWC), laboratory tests were performed under simulated BWR startup conditions at 200-400°F in the absence of radiation with pre-oxidized stainless steel specimens treated with noble metals to simulate plant surfaces. The electrochemical potential (ECP) of these specimens was lowered to levels at which IGSCC mitigation is expected when the hydrogen to oxygen molar ratio is 2 or greater. The total effect of EHWC is to reduce the crack growth by ~7% during a 24-month reactor cycle.

Exelon’s Peach Bottom Unit 3, which is a Noble Metal Chemical Application (NMCA) plant, was selected as a demonstration plant. The first implementation of EHWC was performed during the fall 2011 startup. A feasibility study was performed, which supports proceeding with plans and evaluations leading to a demonstration of EHWC in Peach Bottom Unit 3.

A white paper was developed in 2010 to summarize the crack mitigation benefits expected from EHWC; to outline a process for a U.S. demonstration of EHWC; to summarize operational experience from Japanese BWRs where hydrogen has been injected during the startup; and to assess the impact of EHWC on fuel performance and reliability. In addition, a research plan was developed to confirm fuel performance in the EHWC environment. In 2011, fuel vendors (AREVA NP, Global Nuclear Fuel Americas and Westinghouse Electric Company) and the Electric Power Research Institute (EPRI) Fuel Reliability Program’s B-TAC (BWR Crud and Corrosion Technical Advisory Committee) endorsed the assessment and research plan outlined in the white paper. The Fuel Reliability Program’s B-TAC has been implementing the plan. This report includes the fuel vendor and B-TAC-endorsed version of the white paper.

Keywords

BWR fuel performance
Early hydrogen water chemistry (EHWC)
Hydrogen water chemistry (HWC)
Chemical mitigation of IGSCC
Hydrogen pickup
BWR fuel cladding corrosion

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INTRODUCTION

Early injection of hydrogen during startup has been proposed to further mitigate IGSCC (Intergranular Stress Corrosion Cracking) in BWRs (Boiling Water Reactors). To assess the effectiveness of EHWC (Early Hydrogen Water Chemistry), laboratory tests were performed under simulated BWR startup conditions at 200-400°F in the absence of radiation with pre-oxidized stainless steel specimens treated with noble metals, simulating plant surfaces. The ECP (Electrochemical Potential) of these specimens was lowered to levels at which IGSCC mitigation is expected when the hydrogen to oxygen molar ratio was 2 or greater. The total effect of EHWC is to reduce the crack growth by ~7% during a 24-month reactor cycle.

Exelon's Peach Bottom Unit 3, which is a NMCA (Noble Metal Chemical Application) plant, was selected as a demonstration plant, and the first implementation of EHWC was performed during the fall 2011 startup. A feasibility study has been performed which supports proceeding with plans and evaluations leading to a demonstration of EHWC in Peach Bottom Unit 3.

There are four primary objectives of this report: (i) to summarize the crack mitigation benefits expected from EHWC; (ii) to outline a process for a U.S. demonstration of EHWC; (iii) to summarize operational experience from Japanese BWRs where hydrogen has been injected during the startup; and (iv) to assess the impact of EHWC on fuel performance and reliability.

All U.S. BWRs currently begin injecting hydrogen between 5% and 60% power. In order to maintain hydrogen to oxygen molar ratio greater than 2, 1-1.5 ppm H_2 needs to be injected during the leak test, 75 ppb during heatup without steaming and ~40-50 ppb H_2 during heatup with steaming. In the demonstration at Peach Bottom Unit 3, hydrogen will be injected only during heatup and low power, not during the leak test. The duration of early hydrogen will be limited to less than three days.

The potential impact of EHWC injection on fuel performance has also been discussed in this document. According to our understanding:

- Starting HWC in BWRs at 5% power and above has never resulted in a fuel performance issue.
- Prototypical concentrations of hydrogen in an autoclave have never resulted in a fuel concern, even when starting with unoxidized zirconium surfaces (a zirconium surface will passivate even in hydrogen gas as long as sufficient moisture is present).
- HWC and noble metals have not resulted in a fuel performance issue except when the noble metal was applied directly to the fresh fuel cladding surface.
- There is probably some degree of noble metal deposition on fresh fuel surfaces under current conditions, which means that Pt redistribution occurs following NMCA. However, this phenomenon occurs throughout the cycle, not only during startup.
- Crud restructuring, migration, and re-deposition has been observed previously in HWC (Hydrogen Water Chemistry) and NMCA+HWC plants (due to reducing conditions in HWC and NMCA+HWC, crud is dissolved and can redeposit in different locations).

- Any oxide on the zirconium surface will be less developed when hydrogen is injected early.
- Pt is a catalyst, which splits hydrogen molecules into hydrogen atoms.
- Ni has a strong affinity to hydrogen. Like stainless steel and many other metals, a non-porous Ni deposit can serve as a hydrogen diffusion window. Therefore, Nickel metal deposition on Zr surfaces has been known to serve as a hydrogen diffusion window. A PWR (Pressurized Water Reactor) experience showed that during startup when Ni metal deposited on fresh guide tube inner surfaces with embedded foreign metallic particles from manufacturing caused accelerated hydrogen pickup.

Although possibility of having accelerated hydriding on fresh fuel cladding and significant crud restructuring due to EHWC is generally expected to be minimal, there are gaps in our understanding. There are two major concerns:

- **Accelerated hydrogen pickup:** Combined effect of fresh fuel cladding, platinum on the cladding surface (from redistribution) and dissolved hydrogen has not been directly studied. More specifically, if Pt is deposited on fresh fuel cladding without a sufficient protective oxide layer, it could act as a catalyst and cause accelerated hydrogen pickup when dissolved hydrogen exists in the coolant.
- **Crud restructuring:** Injecting hydrogen early could further impact crud restructuring during startup that would cause increased crud deposition on the fresh fuel surface. Any redistribution of Pt will be of particular interest (whether there is any measurable Pt redistribution during start-up in BWRs, with or without EHWC, is not known).

Since it is quite difficult to determine the effect of EHWC on cladding hydrogen pickup and crud restructuring, the goal is to confirm that fuel performance is still within the experience base after EHWC. Therefore, it is recommended:

- To monitor plant chemistry during cycle operation after EHWC in the startup to determine if extensive crud restructuring is occurring.
- To perform fuel surveillance at the demonstration plant (Peach Bottom 3) to ensure that hydrogen pickup is not accelerated in fresh fuel cladding and no increased crud deposition occurred on fresh fuel surface due to extensive crud restructuring. The purpose of the fuel surveillance program is not to quantify the hydrogen content or crud restructuring due to EHWC, but rather to confirm there is no adverse effect. Therefore, scope of the fuel surveillance program should include only visual inspection of once burned fuel after EHWC during startup to confirm no adverse effect of EHWC on fuel performance is observed. However, visual, eddy current liftoff, profilometry, fuel rod length and water rod length measurements should be performed on the same fuel bundle after three cycles of operation under the same environment. Three-cycle eddy current liftoff/profilometry and fuel rod length and water rod length measurements after EHWC can then be compared to the experience base, which is determined using the data collected from many plants (not only Peach Bottom) operated without EHWC (may include different water chemistries, i.e., NWC, HWC, NMCA etc.). In addition, if possible, in conjunction with other hot cell programs, take the opportunity to analyze high burnup fuel rod cladding hydrogen pickup fraction for rods that were exposed to EHWC as fresh fuel and compare this with similar data from historical fuel cladding performance that was not exposed to EHWC.

2

BENEFITS OF EHWC ON IGSCC MITIGATION

At BWRs that have implemented Hydrogen Water Chemistry (HWC) with Noble Metal Chemical Application (NMCA) or On-Line Noble Metal Chemistry (OLNC), hydrogen is injected to the feedwater to establish a molar ratio of hydrogen to oxidants as oxygen of >2 in the reactor water. Oxidants (hydrogen peroxide and oxygen) in the reactor coolant are consumed by reaction with hydrogen on noble metal treated surfaces, reducing the non-boiling surface concentration of oxidants to near zero. As a consequence, the electrochemical corrosion potential (ECP) of stainless steels and nickel-based alloys is reduced to << -230 mV(SHE), which mitigates intergranular stress corrosion cracking (IGSCC) of these materials [1].

The hydrogen injection systems are designed to be started after power has exceeded a plant-specific minimum value. In the original design, the minimum plant power ranged from 20% to 30%. Over the years, several plants have implemented design changes to start hydrogen injection at lower power levels and also to shut down hydrogen injection at lower power levels to maximize hydrogen availability and thus minimize crack growth. The power levels at which plants start and secure hydrogen injection are given in Table 2-1. The EPRI database shows 13 BWRs start hydrogen injection at ≤10% power and 4 BWRs start hydrogen injection at ≤5% power. Since the mid-1990s, Oyster Creek has been starting hydrogen injection during startup when the steam jet air ejector system is placed in service, which occurs at approximately 5% power when reactor water temperature is approximately 460°F. Additional plants are planning to inject hydrogen at lower power levels, as indicated in the comments in Table 2-1. However, for all plants, there is currently no hydrogen injection during heatup and low power operation prior to the start of the condenser steam jet air ejectors and offgas recombiners. The concentration of oxidants during these periods is initially high due to the presence of air-saturated water from the refuel outage and the generation of oxidants from core radiation.

Table 2-1
Power Levels at which Hydrogen Injection is Started and Secured

Plant	Type	Power Level for Hydrogen Injection Shutdown	Power Level for Hydrogen Injection Startup	Comments
Browns Ferry 1,2,3	NMCA+HWC	25	10	5% injection start by design, but 10% practice
Brunswick 1, 2	HWC-M	30-45%	30%	Design allows for starting at 17.3% power. In practice 2nd feed pump must be in service
Chinshan 1, 2	HWC	90%	90%	
Clinton	NMCA+HWC	18%	28%	Mod in progress to start at 5%
Columbia	NMCA+HWC	15%	5%	
Cooper	NMCA+HWC	25% (system trip)	6%	

Table 2-1 (continued)
Power Levels at which Hydrogen Injection is Started and Secured

Plant	Type	Power Level for Hydrogen Injection Shutdown	Power Level for Hydrogen Injection Startup	Comments
Dresden 2 & 3	NMCA+HWC	20%	6-7%	
Duane Arnold	NMCA+HWC	10%	20%	
Fermi 2	HWC-M	30%	30%	Usually start at 60%; usually stop 5 days prior to plant shutdown for shield block removal
FitzPatrick	NMCA+HWC	50-25%	25%	Requires offgas recombiner in service; Evaluation in progress for 5% injection start
Grand Gulf	HWC-M			
Hatch 1, 2	NMCA+HWC	30%	30%	Evaluation for injection at 7% power in progress
Hope Creek	NMCA+HWC	35%	8.5%	Changes partially complete to allow starting at ~ 5% power
Kuosheng 1, 2	HWC	85%	90%	
Laguna Verde 1, 2	NMCA+HWC	30%	30%	
LaSalle 1,2	NMCA+HWC	Scram	~4%	
Limerick 1, 2	NMCA+HWC	30%	30-40%	Requires 2nd feed pump in service for starting; pursuing mod to start at 10% power
Monticello	HWC-M	75%	70%	
Mühleberg	NMCA+HWC	100%	40%	Stop HWC ~36-48 hrs prior
Nine Mile Point 1	NMCA+HWC (OLNC)	25%	75%	
Nine Mile Point 2	NMCA+HWC (OLNC)	25%	70%	
Oyster Creek	NMCA + HWC	<5%	~5%	Hydrogen injection operated until SJAE is secured; hydrogen started when SJAE is in service
Peach Bottom 2, 3	NMCA+HWC (Unit 3 OLNC)	15-20%	~13-15%	Revised to coordinate with turbine online and offline
Perry	NMCA+HWC	20%	20%	
Pilgrim	NMCA+HWC	30-50%	30-50%	
Quad Cities 1, 2	NMCA+HWC	20%	5-10%	

Table 2-1 (continued)
Power Levels at which Hydrogen Injection is Started and Secured

Plant	**Type**	**Power Level for Hydrogen Injection Shutdown**	**Power Level for Hydrogen Injection Startup**	**Comments**
River Bend	HWC-M	30%	30%	Third feed pump start for startup
Santa Maria de Garona	HWC-M	100%	100%	
Susquehanna 1, 2	HWC-M	30-60%	50%	Usually start at 50% for dose reduction
Vermont Yankee	NMCA+HWC	30%	30%	

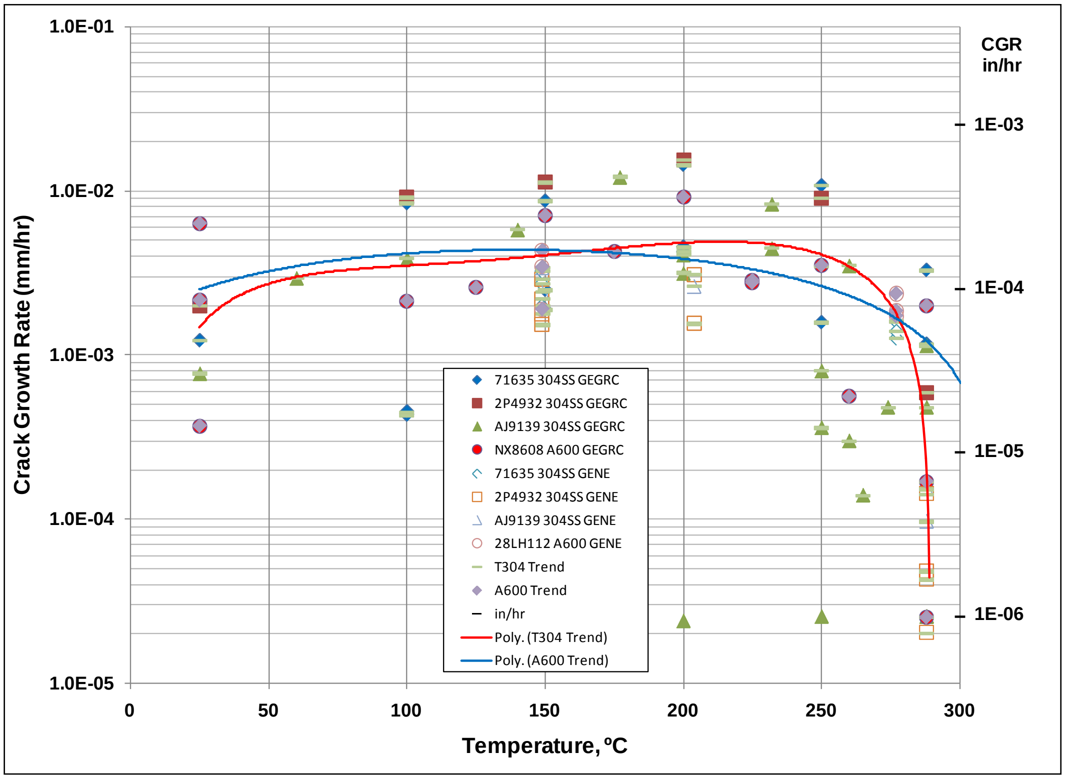

Figure 2-1
Effect of Temperature on Crack Growth Rates (200 ppb O2 ≤0.27 µS/cm)

Available data indicate that IGSCC is accelerated during BWR startups under oxidizing conditions [1]. The maximum Type 304 stainless steel crack growth rate at low conductivity is observed between 150 and 200ºC (302 and 392ºF) in oxidizing environments. Figure 2-1 shows the crack growth rates for sensitized (highly susceptible to IGSCC) stainless steel and Alloy 600 (nickel-based equivalent to stainless steel) in high purity water with 200 ppb oxygen. An extensive review of the available data on crack growth rates under oxidizing conditions and with HWC indicates that crack growth rates could be reduced by a factor of ~13.5 if ECP could be reduced to low values during heatup and startup. EHWC is being considered to reduce crack growth rates of susceptible materials during heatup and startup up to ~10% power, extending the period of IGSCC mitigation. The total effect of EHWC is to reduce the crack growth by ~7% during a 24-month reactor cycle.

Laboratory tests were performed under simulated BWR startup conditions at 200-400°F in the absence of radiation with pre-oxidized, stainless steel surfaces treated with noble metals, simulating plant surfaces. The ECP of these specimens was lowered to levels at which IGSCC mitigation is expected when the hydrogen to oxygen molar ratios was 2 or greater. No significant ECP reduction was observed for the pre-oxidized untreated stainless steel specimen that had not been treated with noble metals even at high hydrogen/oxygen molar ratios.

A feasibility study has been performed [2] which supports proceeding with plans and evaluations leading to a demonstration of EHWC at a U.S. BWR at which noble metal has been applied. Work is in progress for EHWC demonstration at Exelon’s Peach Bottom Unit 3 during fall 2011 startup.

3

PROPOSED DEMONSTRATION FOR EHWC

EHWC has the potential to be applied both during the leak test and during startup. Following assembly, a reactor vessel leak test (or a hydrostatic test if required) is conducted during which temperature may be raised above 200°F. The reactor coolant temperature is then decreased after the test, typically to <100°F. The EHWC demonstration planned for Peach Bottom 3 will not include hydrogen injection during the RPV leak or hydrostatic pressure test. However, hydrogen injection during the leak test has been considered in feasibility studies as an option for plants where the test temperature is >200°F. When the temperature is increased above 200°F, the temperature typically held for 4 to 8 hours and then lowered to typically <100°F until the plant commences heatup for startup. For future consideration, hydrogen could be injected during the RPV fill to establish a molar ratio >2 in reactor water. The hydrogen concentration would depend on the oxygen concentration of the reactor water. If the water is air saturated (~8000 ppb dissolved oxygen), between 1000 and 1500 ppb dissolved hydrogen would be required to establish a molar ratio of 2 to 3. If the water can be partially degassed to reduce the oxygen concentration, the hydrogen concentration would be reduced proportionally. The coolant temperature will be low during the test (typically <240°F).

During startup, the reactor coolant temperature is gradually increased to the normal operating temperatures of >500°F. The total time at temperatures above 200°F before feedwater hydrogen injection is started varies, but is typically 60 to 75 hours during a normal startup. Hydrogen injection is being considered for periods when the reactor coolant temperature is >200°F (93°C) and power is ≤10%, which is defined as Startup/Hot Standby in the EPRI BWR Chemistry Guidelines [1]. Hydrogen would be injected to achieve a hydrogen: oxidants molar ratio of 2:1 or greater. The phases of the EHWC process are described below and also summarized in Figure 3-1. Representative concentrations of species in reactor water are shown in the chart.

This report addresses the potential impact of EHWC on fuel. However, it is noted that the potential for early hydrogen injection to produce flammable or explosive gas mixtures in the reactor vessel and connected systems, particularly including the offgas system, is an important issue which was initially addressed in the feasibility study [2]. These issues are currently being addressed in detail as part of the development of the EHWC demonstration plan, implementing procedures and technical bases for the 10CFR50.59 safety evaluation. Since the EHWC demonstration will not include hydrogen injection during the reactor pressure vessel leak test, the maximum hydrogen concentration required in the reactor water to achieve a molar ratio >2 is estimated to be 40-50 ppb. These hydrogen concentrations are bounded by the Japanese experience with Hydrogen During Startup, as discussed below.

Startup Phase 1 – Closed System (Minor Steam Venting)

Hydrogen injection would begin upon starting the first reactor recirculation pump and securing Shutdown Cooling. Sufficient hydrogen would be added to establish a molar ratio >2 when the coolant temperature reaches 200 °F. A review of a number of plant startups indicates that the reactor water oxygen concentration decreases rapidly as the reactor coolant is heated through 200

°F. Reactor water oxygen concentrations during startup are in the range of 100 to 400 ppb at 200 °F. Assuming 400 ppb equivalent oxygen in the reactor coolant, the hydrogen concentration required for a molar ratio of 3 would be approximately 75 ppb.

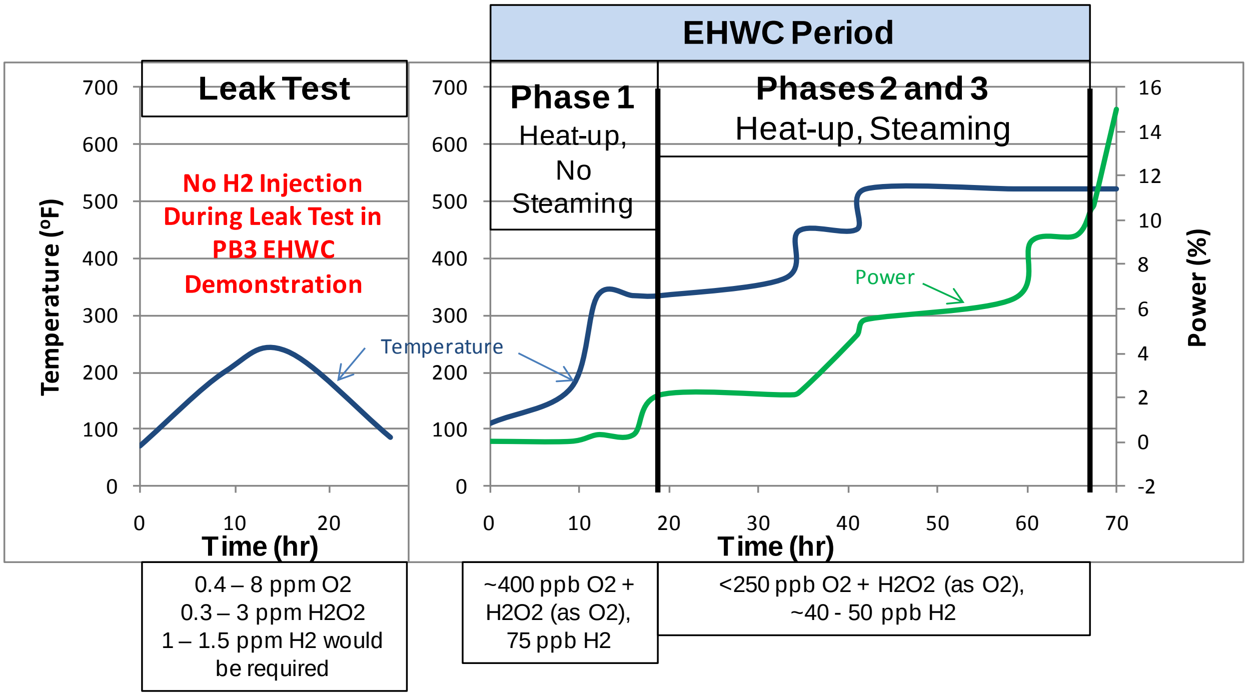

Figure 3-1
EHWC During BWR Startup

Startup Phase 2 – Open System (Significant Steam Venting)

At this point, steam flow occurs. When reactor coolant temperature increases to about 350°F, there is sufficient steam flow to open a turbine bypass valve, which releases steam containing hydrogen and oxygen to the condenser. At approximately 450 psig, the steam jet air ejectors are placed in service and the mechanical vacuum pump is secured. Reactor water oxygen concentrations during this period can range from 25 to several hundred ppb. Assuming 250 ppb, the hydrogen concentration required to establish a molar ratio of 3 would be ~50 ppb. The Peach Bottom 2 Cycle 18 startup data showed that the duration of this phase was approximately 15 hours; the duration can be shorter or longer depending on plant specific startup conditions.

Startup Phase 3 – Up To 10% Power

The hydrogen demand to maintain a hydrogen:oxidants molar ratio >2 from the point of significant steam flow through 10% power will be driven by the concentration of oxidants. A review of several plant startups indicate that the oxygen concentration can range from <20 ppb following start of the steam jet air ejectors to ~200 ppb at 10% power. The hydrogen concentration required to establish a molar ratio of 3 would be ~40 ppb. The Peach Bottom 2 Cycle 18 startup data showed that the duration of this phase was approximately 30 hours; the duration can be shorter or longer depending on plant specific startup conditions.

4

JAPANESE EXPERIENCE WITH HDS (HYDROGEN DURING STARTUP)

Hydrogen injection during heatup through the low power portions of startups is practiced in Japan. Chemistry and ECP measurements during HDS at Shimane 2 and Tokai 2 have been published [3]. Since the Japanese units had not applied noble metals, the objective of the HDS process is to reduce the oxidant concentration in reactor water to low values. As is the case with Moderate-HWC plants compared to noble metal HWC plants, significantly more hydrogen is needed to consume oxidants than to establish a molar ratio >2.

Hydrogen was injected into the reactor water cleanup (RWCU) return to the feedwater line. Published data indicate that startup oxidant levels and ECP were lowered with hydrogen injection in comparison with normal water chemistry conditions, although the decrease in oxidant concentration was not as low as anticipated at low temperatures. During the demonstration of the HDS process at the Tokai-2 unit, the hydrogen concentration in reactor water during most of the heatup was in the range of 40 to 70 ppb. A peak concentration of 160 ppb was measured at 550°F and ~3.5% power. This concentration is consistent with expectations for a Moderate-HWC plant.

Estimates have been made of the hydrogen injection requirements to establish molar ratios of 2 and 3 based on the Tokai-2 data. The maximum concentrations occur at the start of heatup, with estimated values of 60 ppb for a molar ratio of 2, and 90 ppb for a molar ratio of 3.

5

POTENTIAL IMPACT OF EHWC ON FUEL PERFORMANCE AND RELIABILITY

There are two concerns regarding the effect of EHWC on fuel performance:

- **Accelerated hydrogen pickup:** Zr-based alloys in BWRs are subject to corrosion by reactor water, and the resultant oxide formation is accompanied by the passage of hydrogen through the oxide film into the metallic phase. When the solubility for hydrogen is exceeded in the Zr alloy, the excess hydrogen precipitates as hydrides which, at sufficiently high levels, can have deleterious effects on the fracture toughness and corrosion resistance. As the hydride has a 15% higher specific volume relative to the Zr metal reacted, high hydrogen concentrations can also result in measurable dimensional changes of the components. Although it is believed that early hydrogen injection during startup (very short period of time compared to the rest of the cycle length and low coolant temperature) will not cause accelerated hydrogen pickup, there is no direct applicable data to confirm.
- **Crud restructuring:** Crud restructuring in HWC and NMCA+HWC has been observed previously without EHWC. Therefore, it is a concern that injection of hydrogen early might further increase crud restructuring during startup.

These concerns are discussed in more detail in the sections below.

Effect of Coolant Hydrogen on Zircaloy Hydriding

There are four different known hydrogen pickup mechanisms by Zirconium alloy [4]:

1. Absorption during normal corrosion process that occurs at high temperature aqueous solution. Hydrogen Pickup Fraction (HPUF) is defined as the fraction of corrosion-generated hydrogen that is adsorbed by the metal.
2. By direct reaction of a clean (no species other than Zr) surface with gaseous hydrogen.
3. By diffusion of hydrogen through a metallic bond with a dissimilar metal in which hydrogen has higher activity. (i.e., Ni window)
4. By cathodic polarization of zirconium alloys in electrolyte. (This method is usually used to charge hydrogen in Zr-based alloys in laboratory environment using different electrolytic solutions.)

It is generally believed that the hydrogen picked up by the Zr alloy is a portion of that generated by the corrosion reaction [4-6] with differences in observed pickup fractions dependent on alloy composition, heat treatment, and corrosion temperature. The hydrogen content of the aqueous media is not considered to significantly affect the hydrogen pickup fraction [5, 6]. However, with the possibility of injecting hydrogen during startup in BWRs, the effect of the coolant hydrogen on HPUF (Hydrogen Pickup Fraction) of the unoxidized Zr-alloy components need to be revisited even if the EHWC injection period during startup is limited to a few days.

Hillner [7] presented a good review of hydrogen absorption in the Zircaloys during aqueous corrosion. Figure 5-1 shows the hydrogen pickup versus hydrogen overpressure for Zircaloy-2 and Zircaloy-4 exposed for 14 days in 650°F degassed water (static autoclave, hydrogen and oxygen concentrations were not controlled during the tests). The weight gains of all the samples were in the range of 14 to 22 mg/dm^2, and there was no systematic effect of hydrogen on corrosion weight gains. The lowest hydrogen overpressure, 500 psi, is the equivalent of 9416 cc/kg, 840.8 ppm (from Himmelblau [8], 0.0531 psia/(cc STP/kg) for hydrogen at 650°F and 1 cc H_2 (STP)/kg H_2O = 0.0893 ppm H). Therefore, although this particular data showed that dissolved hydrogen concentration in the coolant might accelerate hydrogen pickup of Zircaloys (especially Zircaloy-2), the hydrogen concentration of 840 ppm further exceeds the current level of interest. Also the amount of hydrogen uptake for the 14 day test was limited (~10 ppm). For the practical purpose of injecting 45-75 ppb hydrogen in BWR reactor water during startup (0.000213-0.000355 psia at 650°F) for less than 3 days, the effect of the change on hydrogen pickup should be miniscule.

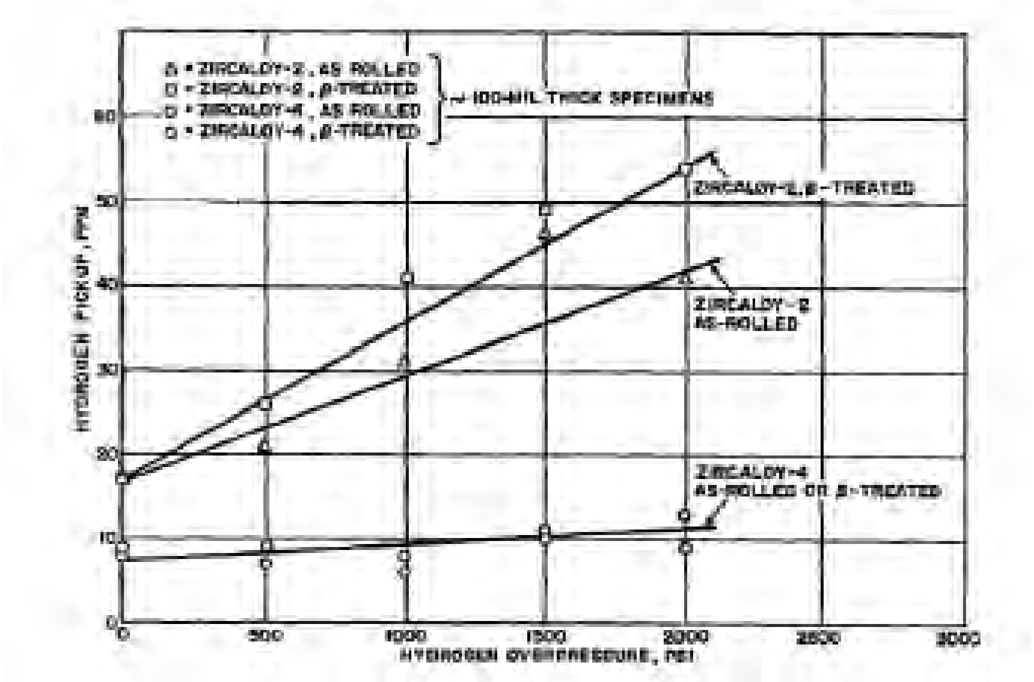

Figure 5-1
Hydrogen Pickup of Zircaloy-Type Alloys in 650°F Water as a Function of Hydrogen Overpressure. Exposure time 14 days. [7]

On the other hand, the temperature of the Hilner's test is higher than the BWR reactor water temperature during startup in EHWC (100-536 F^o). If hydrogen uptake at very high concentrations is due to simple diffusion of hydrogen atom in the coolant through fairly thin air-formed oxide on Zircaloys in the beginning of the test (it is assumed that coupon surface was not pre-oxidized and contains only air-formed oxide prior to the test), it can be expected that diffusion of hydrogen will be slower at low temperatures. Therefore, it is expected to have much less hydrogen in Zircaloy-2 when tested at 500 psi hydrogen over pressure environment at low temperature.

Similar autoclave test to Hilner's [7] test is being performed at Studsvik for FRP P-TAC (PWR Crud Corrosion Technical Advisory Committee) to determine the effect of dissolved hydrogen in the coolant on Zircaloy corrosion and hydriding under simulated PWR water chemistry environments and to determine the threshold of dissolved hydrogen concentration that would cause accelerated hydrogen pickup. Three parallel refreshed autoclave tests are being performed at Studsvik under the simulated PWR conditions (360^{o}C coolant temperature, 750 ppm boron, 2.67 ppm Li, <1 ppb O_2 and ~7.2 pH at 300^{o}C) with hydrogen concentration as the only variable at 30, 100 and 500 cc/kg (2680, 8930 and 44650 ppb at 650 ^{o}F). A few Zircaloy-2 (processed for BWR applications) cladding samples were added in the tests to evaluate if Ni containing alloys will pickup dissolved hydrogen from coolant more than non-Ni containing alloys. Oxide thickness and hydrogen content of Zircaloy-2 and Zircaloy-4 fuel cladding samples after short exposure in 30 and 500 cc/kg (2680 and 44650 ppb) are shown in Figure 5-2. Neither Zircaloy-2 nor Zircaloy-4 samples shows accelerated hydrogen pickup under simulated PWR water chemistry environment and extremely high dissolved hydrogen conditions (2680 and 44650 ppb). Although this test does not simulate the EHWC condition in BWRs, it shows that Zr-based alloys (regardless of Ni content) do not pickup dissolved hydrogen from the coolant even if there is no protective oxide layer on the surface from beginning of the tests.

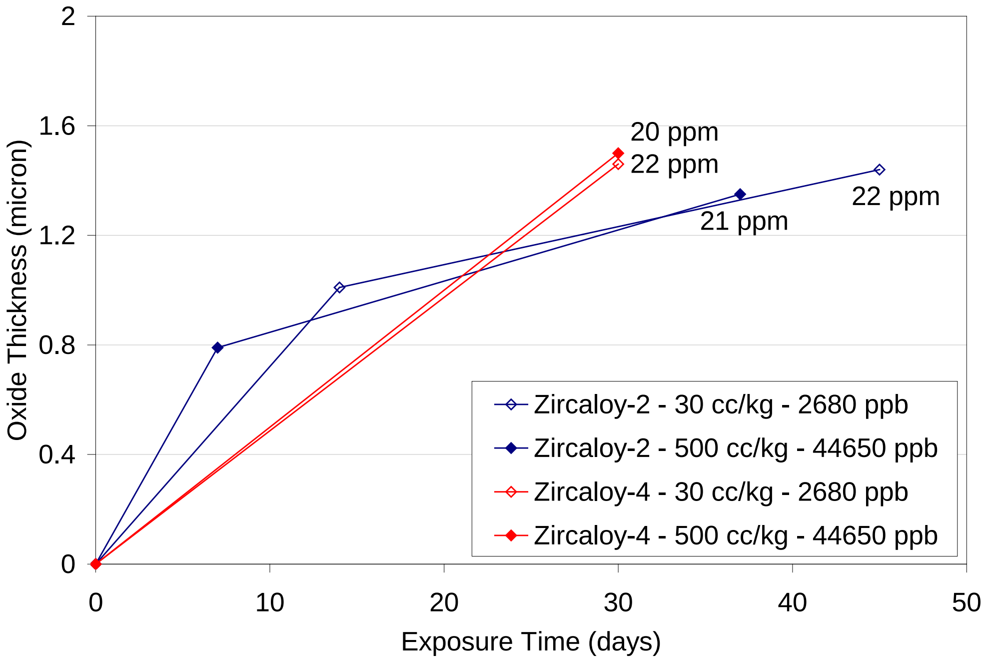

Figure 5-2
Measured oxide thickness vs. exposure time plot of Zircaloy-2 (processed for BWRs) and Zircaloy-4 (processed for PWRs) cladding samples oxidized in simulated PWR environment in 30 cc/kg and 500 cc/kg dissolved hydrogen conditions. The measured hydrogen content of the Zircaloy samples using HVE method is shown in the plot next to the data points. [9]

An in-reactor loop test in Halden reactor was performed to understand the effect of HWC on Zircaloy fuel cladding and fuel structural materials [10]. Two separate tests were designed: (1) 400 ppb H_2 was injected in mini-autoclaves to test corrosion and hydrogen pickup properties of non-heat transfer Zircaloy coupons for 100-140 EFPD at 288 ^{o}C (MAC-4C). (2) Fuel rods were tested in 350 ppb H_2 in boiling condition for 110 days at 288 ^{o}C (Test 5). Hydrogen was circulating in the loops in both tests from beginning to the end (simulates the EHWC condition). Test coupons and fuel rod cladding surfaces were in belt polish conditions with no protective oxide but only natural air-formed oxide. Table 5-1 shows the measured oxide thickness and hydrogen concentrations of various Zircaloy-2 and new alloys. According to MAC-4C test (400 ppb H_2 in coolant), all alloys show 1-2 micron oxide thickness and 15-90 ppm hydrogen in the alloys. Alloy A and B are more modern version of Zircaloy-2 used in BWRs nowadays, and their hydrogen content was reported as 20 and 50 ppm, respectively. When compared to the simulated NWC environment test (MAC-1A), measured hydrogen content of Alloys A and B are 60 and 15 ppm, respectively. Therefore, it can be concluded that no accelerated hydrogen pickup was observed due to dissolved hydrogen in the coolant (MAC-4C).

Test 5 results (fuel rod test by injection 350 ppb H_2 in coolant) are shown in Table 5-2. Zebra fuel cladding was used by welding 12 inch long various Zircaloy-2 and new alloys together. Oxide thickness and hydrogen contents of different zones were determined by metallography. The measured oxide thickness and hydrogen contents are 1-2 micron and 5-25 ppm, respectively. When Test 5 results are compared to Test 4 (simulated NWC condition in 1000 ppm O_2 and 40 ppb H_2), oxide thickness and hydrogen content of the Zebra cladding are quite similar except that oxide in Alloy B at plenum and right below plenum region in Test 4 are slightly thicker.

The fuel rod in Test 5 shows similar oxide thicknesses but much lower hydrogen content than coupons tested in MAC-4C test in simulated HWC. Although it is known that the fuel rod surface is in oxidizing condition under boiling (dissolved hydrogen in the coolant is stripped into the steam phase), it is quite difficult to conclude that higher hydrogen content in coupons in MAC-4C tests are due to dissolved hydrogen in the coolant. In fact, non-heat transfer fuel components generally show much higher hydrogen pickup than fuel cladding [11]. Therefore, it can be concluded that both the MAC and the fuel rod tests confirmed that there is no accelerated hydrogen pickup in simulated HWC environment, where hydrogen was circulating during all periods of the tests and test materials did not have any pre-oxidation.

Table 5-1
Corrosion Behavior and Hydrogen Content of MAC Tests in [10]. Only 400 ppb hydrogen was injected in MAC-4C.

	TEST ID	MAC-1A		MAC-1C		MAC-3C	
	Test Spec	250 ppb O_2/30 ppb H_2		750 ppb O_2		1300 ppb O_2	
Alloy		Oxide	Hydrogen	Oxide	Hydrogen	Oxide	Hydrogen
Zry-2	Alloy A	O	60	O	50	O	10
	Alloy B	O	15	X 20, (3)	15	X 10, 20%	5
	Alloy C	O	30	X 5, 70%	70	X10, 90%	40
	Alloy D	X 12, 40%	20	X 29, 20%	20	X 13, 90%	30
New Alloy	Alloy E	O	10	O	15	O	5
	Alloy F	O	5	O	15	O	5
	Alloy G	O	5	O	5	O	15
	Alloy I	O	40	O	60	O	10

	TEST ID	MAC-4C		MAC-4A		MAC-2C	
	Test Spec	400 ppb H_2 (HWC)		400 ppb H_2/800 ppb O_2		300 ppb N_2/750 ppb O_2	
Alloy		Oxide	Hydrogen	Oxide	Hydrogen	Oxide	Hydrogen
Zry-2	Alloy A	O	20	O	5	X 5, (1)	80
	Alloy B	O	50	O	50	X 8, 30%	70
	Alloy C	O	50	X 3, (1)	50	X 10, 30%	60
	Alloy D	Not tested	--	Not tested	--	Δ 16	30
New Alloy	Alloy E	O	15	O	5	O	70
	Alloy F	O	50	O	50	O	50
	Alloy G	O	50	O	10	O	50
	Alloy I	O	90	O	50	O	10

O : Uniform oxide (1-2 μm)

X : Nodular oxide (Max. thinkness in μm), (Coverage ratio in %, or Number of nodules)

Δ : Thick uniform oxide (Max. thickness in μm)

Table 5-2
Corrosion Behavior and Hydrogen Content of Fuel Rod Tests in [10]. 350 ppb H_2 was injected in Test 5.

Elevation (cm)	Note	Alloy ID	Test 4		Test 5		Test 6a		Test 6b	
			Uniform*	Hydro-gen	Uniform	Hydro-gen	Uniform*	Hydro-gen	Uniform*	Hydro-gen
92	plenum	B	--	--	--	--	--	--	--	--
85		B	--	--	--	--	--	--	--	--
84		B	~4(max. 7)	~15	1 – 2	19	2	19	9.7	17
73	UO_2	B	--	--	--	--	--	--	--	--
72		B	1.8	~15	0.9	~15	--	--	--	--
71		B	2(max. 3.1)	~15	--	--	--	--	--	--
66		B	--	--	1	8.9	1.1(max. 4)	34	13.7(max. 18)	~20
65		B	--	--	--	--	--	--	--	--
58		G	--	--	--	--	--	--	--	--
57		G	1.1	~10	1	~10	1.3	23	7.9	26
55		G	--	--	--	--	--	--	--	--
51		G	--	--	--	--	--	--	--	--
48		I	--	--	--	--	--	--	--	--
47		I	--	--	--	--	--	--	--	--
46		I	1 – 2	~25	--	--	--	--	--	--
41		I	--	--	1	~25	0.8	31	1.8(max. 2.5)	~45
39		I	--	--	--	--	--	--	--	--
37		I	1 – 2	~25	--	--	--	--	--	--
34		B	1.2	~10	1.1	17	2.1	23	15.7	17
32		B	--	--	--	--	--	--	--	--
30		B	--	--	--	--	--	--	--	--
22		F	--	--	--	--	--	--	--	--
18		F	1.3	~10	1	~10	1.9	23	10.3	15
16		F	--	--	--	--	--	--	--	--
13		F	--	--	--	--	--	--	--	--
9		B	--	--	--	13	--	--	--	--
4		B	--	--	1	5.13	--	--	--	--
1		B	1 – 2	~10	--	--	1.3(max. 2.5)	10	14(max. 15.5)	~15

* max. : maximum thickness of uniform oxide

The only drawback of this test is that the test temperature was 288°C, which is higher than the temperature range of the coolant under EHWC (100-536°F). If the only hydrogen pickup mechanism is the corrosion process, which is temperature controlled, then the corrosion kinetics and, therefore, the hydrogen pickup rate will be slower at low temperatures [4].

Crud Restructuring

Crud restructuring is important to consider in the context of EHWC because the restructuring process can result in the release, transport, and re-deposition of species onto fresh surfaces. Since this restructuring can occur, to varying extents, under a range of conditions, the important consideration for EHWC is whether the restructuring is more significant or whether it impacts the clad in some unique way (e.g., might lead to heavier deposition on fresh fuel cladding surfaces).

The loading, composition and morphology of the crud deposit depend on the type and concentration of the impurities and additives in the reactor water. Hematite (Fe_2O_3) is the most common deposit because of its relative abundance and low solubility (<~1 ppb) inside the oxidizing fuel channels. This deposit exists under either normal water chemistry (NWC) or hydrogen water chemistry (HWC). The deposit, in the absence of zinc or copper, is typically loose and fluffy and presents little impedance to heat flux, as water and steam can easily pass through it. Certain impurities (such as Ni, Zn, Co and Cr) can promote the formation of iron oxide spinels in the deposit making it tenacious to the fuel rod surface. Under typical conditions, the tenacious deposits accumulate more closely to the fuel rod surface underneath the loose hematite deposit, forming a double layer crud structure. In some cases with high zinc injection (>0.4 ppb), thick tenacious crud with high zinc concentration up to 40% and higher, can dominate the total deposit.

Hydrogen in the reactor water creates a reducing condition so that existing hematite (Fe_2O_3) will transform into magnetite (Fe_3O_4). During this transition, FeO (or Fe^{2+}) is formed and due to high solubility in the reactor water, it is released into to the reactor water. In the normal operating conditions, this transition happens after startup and takes about a few months. The released Fe might deposit on the fresh fuel cladding surface. On the other hand, Pt on the fuel surface is in metallic form but it stays with the crud. During crud dissolution after hydrogen injection, some of the Pt in the crud might be released into the reactor water and deposit on the fresh fuel surface as well as the released Fe. The same process might happen when hydrogen is injected early in the startup.

As temperature rises, the environmental conditions for the fuel approach to those currently experienced during startup. Crud restructuring may begin during the heatup, resulting in some crud release. However, the total quantity of crud released during the startup is not likely to increase, since there is only so much available to restructure. The period of restructuring may be extended, which would spread the release over a longer time period, lowering the coolant activity.

Ni Deposition Effect

Accelerated hydrogen pickup in Zr alloys due to Ni deposition on PWR fresh guide tube surface due to mechanical contamination by dissimilar metal particles was reported previously [12]. In Ringhals Unit 2 in 1990, two guide tubes were broken during insertion of control rods in the spent fuel pool during an outage. It was due to high hydrogen content in Zircaloy-4 guide tubes. In extreme cases, a rim of hydrides was observed in hot cell examinations in the inner surface of the guide tubes and the hydrogen content was up to 3000 ppm (average in wall thickness), which means that hydrogen pickup fraction is well above 100%. It was obvious that the hydrogen is not from the corrosion process alone. A root cause analysis revealed that stainless steel (SS) and silicon carbide (SiC) particles were embedded in the inner surface of the guide tubes as a result of grit blasting during manufacturing and those particles acted as a window for hydrogen once they were coated by metallic Ni during reactor startup. During normal PWR operation, NiO is the stable phase. However, during startup once hydrogen is injected into the reactor coolant system (RCS) at low temperature, Ni metal becomes stable for short period of time. Laboratory tests showed that once the foreign metallic particles were removed from the guide tube surface, the accelerated hydrogen pickup phenomenon is not observed even if surface contained metallic Ni from the coolant. On the other hand, if there was no metallic Ni deposition on the foreign metallic particles, accelerated hydrogen pickup phenomenon could not be reproduced in the laboratory tests [12]. As a result of the root cause analysis, grit blasting was eliminated from guide tube manufacturing process and also plants were recommended to inject hydrogen at a later stage during startup. EPRI PWR Water Chemistry Guideline recommends delaying H_2 injection to Mod 3 as an option [13].

Concern is that a similar phenomenon might happen in BWRs during EHWC if the cladding surface contains foreign metallic particles embedded on the surface and if there is enough Ni in the BWR reactor water to deposit on embedded foreign metallic particles in metallic form. If one of the factors does not exist, the phenomenon will not occur.

Since PWRs have many Inconel (Ni-based alloy) structural material components, Ni impurities in the reactor water are much higher than BWRs. The 12-month median values of the feedwater Ni in US BWRs are shown in Figure 5-3 [14]. Compared to Fe and other impurities in BWRs, the Ni concentration in the feedwater of BWRs is quite low (less than 0.16 ppb).

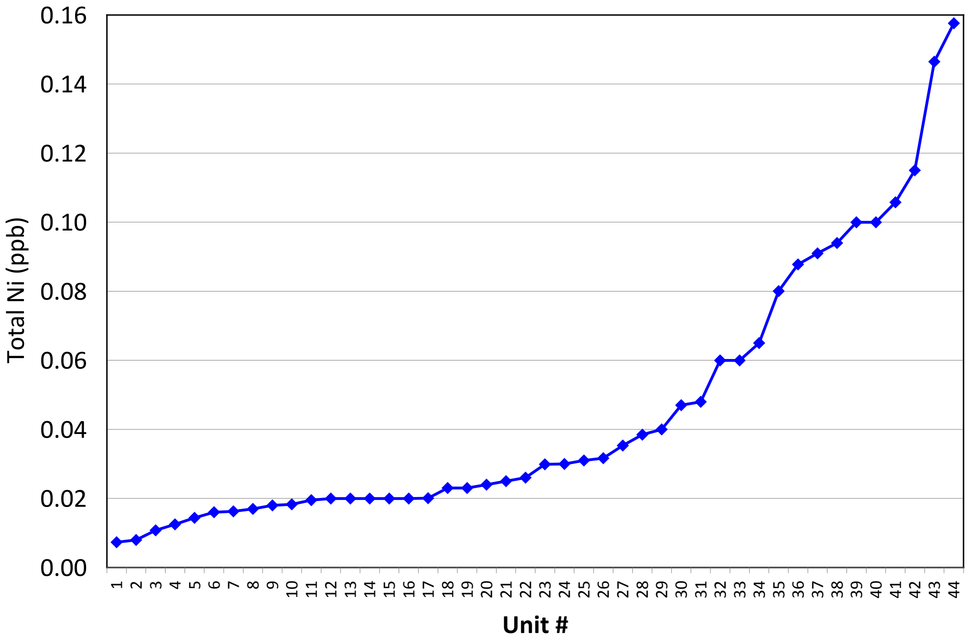

Figure 5-3
Median FW Ni concentration in the last 12 months [14]

On the other hand, this phenomenon was limited to Ringhals, and it was not observed in any other PWR even though many of those were not implementing delayed hydrogen injection during startup. Therefore, the risk to observe the same phenomenon in a BWR due to EHWC, is quite minimal.

Noble Metal Effect

As discussed further below, many BWRs in US have been operated under NMCA+HWC and OLNC+HWC conditions for many years. In both NMCA and OLNC, Pt is injected in the reactor water to coat structural material surfaces to reduce its ECP but the majority of the injected Pt+Rh or Pt deposits on the fuel surface [11]. It is known that Pt and Rh are catalysts, which splits dissolved molecular hydrogen into active H atoms. Active hydrogen atoms might pass through the thin protective oxide on the cladding, thereby leading to enhanced hydrogen pickup once Pt metal deposits on fresh fuel cladding surface in BWRs. Therefore, plants are advised by their respective fuel vendors to inject Noble Chem at least 90 days after cycle startup in order to form protective oxide on fresh fuel cladding surface. However, the concern is that even if the Noble Chem application is performed during shutdown for NMCA or 90 days into a cycle for OLNC, certain concentration of Pt and Rh might have been redistributed during startup when EHWC is injected and might deposit on fresh fuel cladding surface before cladding forms protective oxide layer (when there is only air-formed oxide). In this case, combination of dissolved hydrogen injected during startup and redistributed Pt might cause accelerated hydrogen pickup in fresh fuel cladding.

A relevant in-reactor loop test was performed in the Halden reactor to investigate the effect of Pd on fuel cladding under simulated HWC environment [15]. Two fuel rod segments, one pre-treated with a Pd solution in an out-of-pile autoclave, and another untreated in belt-polished condition were compared in a simulated BWR HWC environment in the Halden reactor. The operating temperature was 288^{o}C, and the loop exit steam quality was 30-40%. Right after rods were placed in the loop, the rods were pre-treated with flowing water in the loop containing 25 ppb Pd and 300-400 ppb O_2 at 245^{o}C for 48 hours. Then immediately 400 ppb H_2 was injected into the loop and kept constant throughout the test for 72-110 EFPD. Metallography examination of these pre-treated and un-treated rods show that the oxide thickness is less than 0.5 micron and the hydrogen content was about 10 ppm, indicating essentially no hydrogen uptake. There are two drawbacks of this test: 1) It is not representative of EHWC since hydrogen was injected 48 hours after test started. 2) Pd was used instead of Pt. However, Pd is a stronger catalyst than Pt. If Pd does not cause any accelerated hydrogen pickup in HWC condition, Pt will likely not.

Industry Experience with HWC and Noble Metals

Moderate HWC injection (<~2 ppm) started in the early 1980s in US BWRs. The HWC lead plant was Dresden Unit 2 and a fuel surveillance program, including post-irradiation examination, was performed after four 18-month cycles. The results demonstrated that HWC does not have noticeable effects on cladding corrosion and crud deposition as reported in References [11, 16]. Crud was fluffy and fell off even during bundle movement. Cladding corrosion and hydriding, with oxide thickness <25 micron (1 mil) and hydrogen <100 ppm after 4 cycles (~38 GWd/MTU), were well within the performance limits. However, the hydrogen uptake for a 4-cycle water rod was unexpectedly high, with an uptake of about 800 ppm at the upper elevations (~200 to 300 cm from the bottom end plug). Hydrogen uptake of the water rods behaved as expected after 1, 2 and 3 cycles. Although the reason of the accelerated hydrogen pickup at high burnup is not known, additional literature data indicates that it is not due to HWC as shown in Figure 5-4 below.

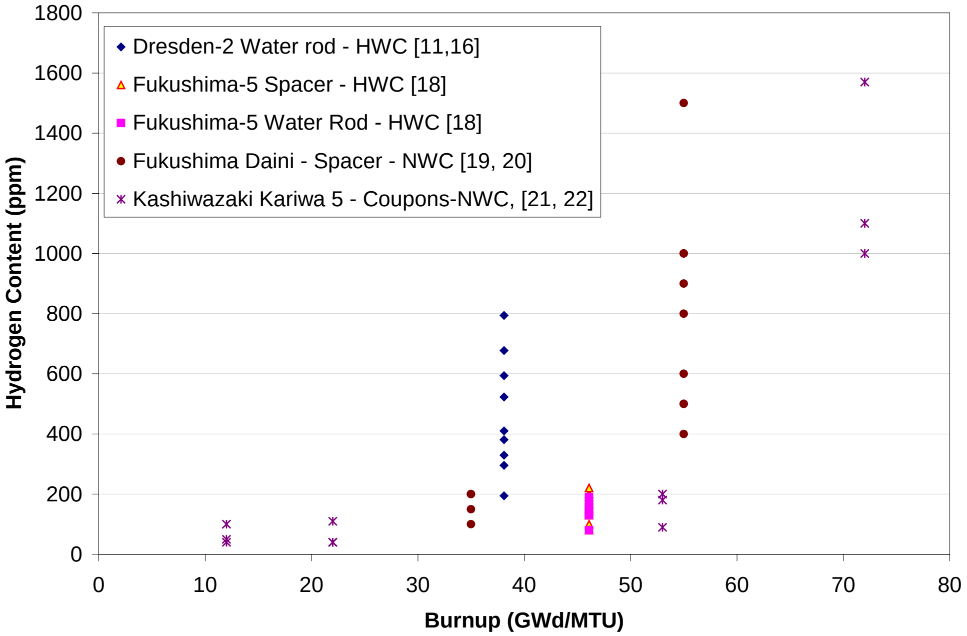

Figure 5-4
Accelerated hydrogen pickup is generally observed after 40 GWd/MTU burnup in non-heat transfer components independent of water chemistry.

Since moderate HWC is not effective in protecting many parts of core internals, starting in late 1990s, catalytic materials, namely Pt and Rh, are applied into the re-circulating lines over 48 hours while the unit is in hot shutdown mode. The noble metals are dispersed throughout the core internal systems and precipitate as nano-particles on system material surfaces, including fuel rods. Sufficient hydrogen (typically <0.25 ppm in the feed water, equivalent to <40 ppb in reactor water) is injected during operation to maintain a molar ratio of hydrogen to oxidant of >2 in bulk water downstream of the feedwater spargers. The first implementation of classical NMCA was performed in Duane Arnold, and the impact of NMCA on fuel performance was determined with fuel surveillance program for three cycles. Fuel surveillance at Duane Arnold includes visual inspection, surface liftoff measurements, crud scraping and analysis for chemical composition and surface loading as well as two hot cell examination on fuel rods (after one cycle and after three cycles of NMCA) [11,17]. After the first NMCA implementation in Duane Arnold, poolside fuel surveillance was also performed in Dresden unit 2 after one cycle of NMCA and Peach Bottom unit 2 for two cycles as well as some other poolside data from many other plants [11, 17]. The fuel surveillance results can be summarized as follows:

1. The oxide thickness and hydriding of Zircaloy-2 cladding from Duane Arnold were well within performance limits. Hot cell examination of a 3-cycle fuel rod and two 3-cycle spacers showed normal oxide (<30 micron) and hydriding (<150 ppm).
2. Two pre-treated fuel rods (fresh rods exposed to simulated NMCA environment in an out-reactor loop) from Duane Arnold showed nodular corrosion with <50 micron oxide but low hydrogen with <20 ppm after one cycle operation following NMCA.
3. Significant noble metal movement occurred during power operation at Duane Arnold. The fresh fuel, which was not exposed to NMCA during treatment, picked up some Pt

and Rh over the course of the 18-month cycle, (similar to levels found on once burned fuel that had seen the application directly).

4. High eddy current liftoffs and oxide spallation in the bottom span of high burnup fuel rods were found at the plant with highest noble metal injection (Peach Bottom 2). More generally, observations of “thick” and often spalling tenacious crud were attributed to (a) increased Zn injection by increasing the FW Zn concentration in many plants; and (b) redistribution of crud due to the reducing conditions by NMCA.

Starting in mid-2000s, an on-line application process became available (small quantities of Pt are injected to reactor coolant over 10-14 days with the plant at full power). On-line NobleChem^{TM} (OLNC) requires similar concentrations of hydrogen injection in the feedwater system (typically less then 0.25 ppm). OLNC was first implemented at KKM, a BWR4 in Europe, in 2005 and a fuel surveillance program including visual, eddy current liftoff, crud scraping and crud analysis was performed. The results show that the Pt concentration in the crud is gradually increasing, but no adverse effect has been observed based on the limited amount of data. No hot cell examination has been performed to determine oxide thickness and hydrogen content after OLNC implementation. However, there are extended programs to qualify OLNC applications by other fuel vendors by performing poolside fuel inspections and crud analysis.

Although, the experience with HWC in U.S. BWRs is quite extensive, hydrogen was injected into the system during power increase, not at startup. Timing of hydrogen in the beginning of cycles in the demonstration units for HWC, NMCA and OLNC and fuel surveillance results are summarized in Table 5-3.

Based on the information in Table 5-3, there is no fuel surveillance data that directly shows the impact of EHWC on Zircaloy fuel cladding hydrogen pickup by fresh fuel cladding and crud restructuring during startup. The earliest hydrogen injection in a US BWR was Oyster Creek at 5% power (as soon as the steam jet air ejectors are placed in service, reactor water temperature reaches approximately 460 ^{o}F), and there is no fuel surveillance data for assessing the impact.

Although two Japanese units are operated HDS (Hydrogen During Startup) for several cycles (see Section 2) and no fuel-related issues reported, no fuel surveillance or laboratory tests had been performed to assess EHWC impact on fuel performance. On the other hand, Japanese BWRs are operated in HWC environment with annual cycles, while the majority of US BWRs are operated in NMCA+HWC or OLNC+HWC environments with two year cycles. Therefore, Japanese plant experience might not be directly applicable to US plants due to the absence of noble metal.

Table 5-3
Summary of Fuel Surveillances on HWC, NMCA and OLNC

Plant	Cycles	Type	FW Hydrogen Concentration (ppm)/ NMCA & OLNC Fuel Deposition (µg/cm2)	Power Level for Hydrogen Injection During Startup	Fuel Surveillance Scope	Observations
Dresden 2	9, 10, 11, 12	HWC	1.5 ppm	25%	Poolside, crud analysis and hot cell	Normal cladding corrosion and hydriding after 3 cycle but accelerated HPU on four cycle water rods Fluffy crud on fuel surface
Duane Arnold	14, 15, 16, 17	HWC (14) NMCA (15-17)	CY14 2 ppm H_2 CY15-16, 0.28 ppm H_2, 19.7 µg/cm^2 CY17, 0.28 ppm H_2, 30 µg/cm^2	33-57%	Poolside, crud analysis and hot cell	No impact on Zircaloy hydriding Significant crud redistribution might happen during power operation High eddy current liftoff when noble metal applied on fresh fuel surface but normal hydriding High concentration of NM may also cause high eddy current liftoff May form thick tenacious crud when Zn >0.4 ppb in RW
Peach Bottom 2	13, 14	NMCA	CY13 0.15 ppm H_2 CY14 0.23 ppm H_2 61.5 µg/cm^2	~30%	Poolside and crud analysis	
Dresden 2	17	NMCA	0.27 ppm H_2, 30 µg/cm^2	7%	Poolside	
KKM	32, 33, 34	OLNC	0.18 ppm H_2, 8-10 µg/cm^2	>40%	Poolside and crud analysis	Pt content on fuel crud gradually increasing No adverse effect on Zircaloy corrosion No hot cell examination to determine hydrogen content of cladding Limited amount of data

Gaps in Our Understanding

Although the possibility of having accelerated hydriding on fresh fuel cladding and significant crud restructuring due to EHWC is quite low, there are gaps in our understanding:

- What is the combined effect of Pt on fresh cladding surface and dissolved hydrogen during startup on Zircaloy hydrogen pickup properties?
- Is there any Pt redistribution during start-up in BWRs (with EHWC or without EHWC)? If so, how much Pt is expected to deposit on the fresh fuel cladding surface?
- How much crud restructuring occurs during startup due to EHWC that would cause increased crud deposition on the fresh fuel surface?

Summary of Fuel Recommendations

Initially, plant chemistry during cycle operation after EHWC in the startup should be monitored closely to determine if extensive crud restructuring is occurring. Then a fuel surveillance program should be launched in the demonstration plant, Peach Bottom 3. The objective of the fuel surveillance program is to ensure that no accelerated hydrogen pickup is observed by fresh fuel cladding and no increased crud deposition has occurred on fresh fuel surface due to extensive crud restructuring and to make sure that fuel performance is within experience base. The purpose of the fuel surveillance program is not to address the individual gaps listed above in any detail, but rather to confirm no adverse effect is observed. Therefore, scope of the fuel surveillance program should include only visual inspection of once burned fuel after EHWC during startup to confirm no adverse effect of EHWC on fuel performance is observed. However, visual, eddy current liftoff, profilometry, fuel rod length and water rod length measurements should be performed on the same fuel bundle after three cycles of operation under the same environment. Three-cycle eddy current liftoff/profilometry, fuel rod length and water rod length measurements after EHWC will be compared to the experience base, which is determined using the data collected from many plants (not only Peach Bottom) operated without EHWC (may include different water chemistries, i.e., NWC, HWC, NMCA etc.). In addition, if possible, in conjunction with other hot cell programs, take the opportunity to analyze high burnup fuel rod cladding hydrogen pickup fraction for rods that were exposed to EHWC as fresh fuel and compare this with similar data from historical fuel cladding performance that was not exposed to EHWC.

6
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